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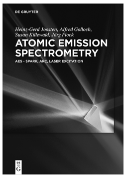

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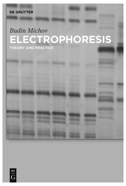

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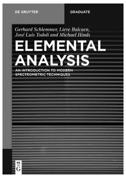

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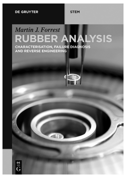

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Authors
Prof. Ajay Kumar Goswami
132/5 Subhash Nagar
Udaipur 313001
Rajasthan
India
Email: akumargoswami56@gmail.com

Dr. Shilpa Agarwal
Lachoo Memorial College of Science and Technology
Shastri Nagarr
Jodhpur 342001
Rajasthan
India
Email: shilpu08@gmail.com

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Dedicated to
Ehimay and Erisha
Prof A K Goswami

Preface

This book is truly a summary of my experience as an analytical chemist. In the initial years of my career as a research student and young teacher, there was always a dilemma over choosing methods for determination of copper and iron using any technique such as polarography, spectrophotometry or other such methods. Transition metals have been my area of research, and synthesis of still better analytical reagents to determine these metals was a true fascination and challenge to our team. Reviews are the best help to a researcher to get a state-of-the-art knowledge of the field and a specific area one is interested to pursue. Our voluminous reviews published every 2–3 years helped others to explore the status of analytical reagents available for the spectrophotometric determination of Cu, Fe, V, Cr, Zr, Pb, Co, Cd and so on, and the idea of writing this book was conceived during all these years of work. A complete collection of spectrophotometric methods and analytical reagents used during the last 10–15 years for so many metals is an arduous task, yet to begin with this book is the first step in the journey. We wish to initiate at least with two most important metals, and I hope the step becomes fruitful. The book has been planned in 2016 but it took us 3 years to finally sculpt it to the present shape. As an author, we are vulnerable to a number of shortcomings which are absolutely and without reason ours, and we would welcome suggestions and improvement for future editions.

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Introduction

Spectrophotometric determination of transition metals using chromomeric reagents is a time-tested and basic analytical method since a very long time. The beauty of this technique is in its sensitivity, selectivity and not the least economy. The branch of analytical chemistry has evolved leaps and bounds for better methods, yet the spectrophotometric methods have not lost their place, as these methods offer simplicity with accuracy and so are relevant even today. Organic reagents, on the other hand, are still the basis to determine chemical reactions, and new developments preclude a knowledge of the underlying chemical processes. The challenge to an analytical chemist today is in fact very complex and there is no single approach offering the best solution. However, for most of them, selection of a suitable reagent and reaction conditions makes the task simple. The organic reagents serve to simplify inorganic analysis. These reagents can serve as better indicators, masking agents and primary standards and have an advantage of both sensitivity and selectivity. Even they are better for extraction spectrophotometry, compared to aqueous solution-based methods. In earlier days, only inorganic reagents were available for analytical chemists. Robert Boyle first reported the use of organic reagents in inorganic analysis on systems such as vegetables. They were mostly vegetable extracts, for example, litmus. Spot test for iron on papyrus soaked with oak berry extract was described by Pelny in the first century AD. However, the foundation of study of reactivity of organic reagents with transition metal ions was stimulated with the advent of complex formation by Werner.

There is a vast growth in the quantitative techniques for determination of transition metals due to research in coordination chemistry. Therefore, a large number of new analytical reagents have been used as spectrophotometric reagents. Application of metal-based compounds and complexes in biological systems or medicinal use has further advanced the growth of organic reagents. Specificity and selectivity are two challenges for the applicability of any analytical organic reagent. The area of metal complex synthesis and application has simplified this approach. Reaction conditions for the formation of a metal complex such as pH, solubility, stability or even interference by other constituents or ions describe how any reagent can be useful for that particular metal. This makes the method simpler to handle. The research efforts by Robert Boyle, discovery of 1-nitroso-2-naphthol as a precipitant for cobalt by Llinski in 1884 and dimethylglyoxime as a specific reagent for nickel by Chugaev in 1905, as well as the development of coordination theory by Alfred-Werner in the 1890s were in true sense milestones that laid scientific foundation for organic analytical reagents. Thanks to all those pioneering scientists that today the branch has established itself as one of the most applied sciences. It can be summarized that development of organic reagents today is based on the understanding of parameters like specific atomic

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grouping, chromospheres, number and size of rings, resonance, acidity and basically, steric effects and none the less stability constants. Development of spot test by Fritz Feigle can be cited as a true example of application of theoretical principles in the development of practical tools in laboratory. G. Shwarzenbach in 1946 introduced EDTA, which was the product of such research and it is still the most versatile and common reagent for metal ions in general and copper in particular.

On the other hand, application of UV and visible molecular absorption measurement is widely used for both identification and determination of organic and inorganic species. This method is most widely used of all the quantitative analytical techniques in chemical, pharmaceutical, industrial, forensic, environmental and clinical laboratories worldwide.

Basics of quantitative analysis by absorption measurements – spectrophotometry

Ultraviolet and visible spectrophotometry is one of the most useful techniques available to analytical chemists for quantitative analysis. The technique has a number of advantages in terms of its wide applicability to both inorganic and organic systems, with detection limits of 10^{-4} to 10^{-5} M or even lower with certain modifications, moderate-to-high selectivity with good accuracy and most importantly its convenient data acquisition. A number of papers are available on the scope of spectrophotometric methods. Readers may find many textbooks in detail for scope and methods.

Inorganic species due to their characteristic absorptions in UV and visible radiation regions can be determined directly using spectrophotometry. As we know many transition ions exhibit color in their solutions, they can be suitably determined. Further, a number of species like nitrate, nitrite, chromate and so on show characteristic absorption bands and thus can be determined by spectrophotometry. However, area concerning application of analytical organic reagents is more importantly focused on the application of other nonabsorbing species which selectively yield products that absorb strongly in the UV or visible region.

If the color-forming reaction can be forced to completion yielding a stable colored product, then such a reagent can be used for the quantitative analysis. In case of a limited product, the absorbance can be used to determine analyte by the concentration–absorbance relationship. A number of color-forming reagents are in frequent use for the determination of transition elements. This is possible as the molar absorptivity of the colored reaction product is much more in magnitude compared to the species before reaction. In the last section of the chapter, a list of common organic reagents used in the last 20 years or so is given to inform readers which reagent can be the choice of his/her selection for copper or iron.

Spectrophotometry – procedural details

Development of conditions leading to a reproducible relationship between absorbance and concentration of analyte is the first step in any spectrophotometric analytical method. In general, the relationship between absorbance and analyte concentration should be linear. Various steps involved in spectrophotometric determination are briefly described in the preceding sections.

Selection of wavelength

To obtain highest sensitivity, the absorbance measurement is commonly made at a wavelength which corresponds to an absorption maximum. This is due to the reason that change in absorbance per unit of concentration is greatest at this point. Further, absorbance is almost constant at this wavelength, following Beer's law. At absorption maxima, another advantage is that small uncertainties arising from wavelength setting at varying wavelengths are minimal at this point.

Factors that influence absorbance

To avoid effects of factors influencing spectrum, the following variables have to be taken care of:

(i) Nature of solvent
(ii) pH of the solution
(iii) Temperature
(iv) High electrolyte concentration
(v) Presence of interfering species

The effect of these parameters is a prerequisite to be known and the conditions of analysis must be selected so that the absorbance is not influenced by variation of even small magnitude of these uncontrolled factors. Not to mention, an accurate analysis using spectrophotometry warrants the use of good quality matched cells also.

Determination of relationship between absorbance and concentration

In the spectrophotometric determination, the absorbance–concentration relationship is of utmost importance. The method of external standards is one of the most common methods to establish this relationship. After deciding or optimizing different conditions described earlier (factors affecting spectrum), a calibration curve is prepared from a series of standard solutions that includes the concentration range expected for the analyte. It is also extremely important to check the validity of Beer's law for a number of repeated observation and not assuming the Beer's law adherence for such calibration. By obtaining this calibration, an analyte is determined.

A detailed scheme of experimental strategy can be seen in any standard textbook of analytical chemistry.

Importance of copper and its determination: copper is an essential trace element in humans and other animals as well as plants. Its use dates back to 8000 BC in the recorded history.

Copper is a naturally occurring nonferrous metal with high electrical and thermal conductivity. Although it is produced for the basic purpose of electrical application, it is also extremely useful in building construction, transport equipment or industrial machinery to name a few. It is not only industrially important but is also an extremely vital element for human health. It is known as an essential trace element which is responsible for a number of biological functions in our body. It is absorbed through our diet and is converted to the usable form after combining with certain proteins resulting in enzymes. These enzymes assist in many physiological functions of our body. It is also used as a medicinal compound which further signifies its importance. The above description explains why determination of copper in a variety of samples such as industrial, environmental, nutritional or medicinal has gained importance in recent times.

Importance of iron and its determination: Apart from its bulk application in equipment to construction it is a critical mineral required for growth of all cells. It is essential for delivering oxygen to the body using hemoglobin. It is also useful in DNA synthesis and electron transport. So there is an important role of iron in our industry and health. For detailed uses of iron, reader can refer to any standard book of bio-inorganic chemistry. This is important to highlight the significance of iron in diverse samples, owing to its all round utility.

This book is divided into two sections describing reagents and methods for copper and iron, respectively. It comprises sections of each part on the basis of chelating groups and in particular donor atoms. The methods reported are explained, and the working conditions are described so that any researcher writing to use the particular method gets information to directly use it.

The method has been described as precise and in a technical way that is possible. Yet to save space, there may be some more details which may have been included but could not be mentioned less. It does not overlook any basic description and would make all methods comprehensive and usable.

Spectrophotometric determination of copper: *Section A* deals with reagents and spectrophotometric methods for determination of copper. The reagents are classified on the basis of their donor groups and methods appropriately described, since most of the methods chronologically collected from older to recent details have been described in brief including experimental details. Nevertheless, they are condensed yet any worker may get a guideline and may require to refer to the cited work if need be. *Section B* describes details of reagents and methods of iron. However, the one-stop solution for any reader interested in copper or iron determination is the main objective of the monograph. Tables 1 and 2 describe the reagents for copper and iron.

Table 1: List of spectrophotometric reagents for the determination of copper.

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
Chapter 1					
1	1-(2-Imidazolylazo)-2-naphthol-4-sulfonic acid	530 nm	3.0	1.94×10^4 L mol^{-1} cm^{-1} 0–0.8 µg Cu mL^{-1}	
2	1-(2-Pyridylazo)-2-naphthol	555 nm	6.5	5.21×10^4 L mol^{-1} cm^{-1} 0.08–4.00 µg mL^{-1}	1.22 ng cm^{-2} 4.0 ng mL^{-1}
3	1-(2-Pyridylazo)-2-naphthol (PAN)	556 nm	8.0		
4	1-[Pyridyl-(2)-azo]-naphthol-(2) (PAN)	520 nm	7.8–9.4	1.14×10^5 L mol^{-1} cm^{-1}	
5	1-(2-Pyridylazo)-2-naphthol (PAN)	565 nm	5.5	0.64–41.3 ng mL^{-1}	
6	1-(2-Pyridylazo)-2- naphthol (PAN)	558 nm		2.25×10^4 L mol^{-1} cm^{-1}	
7	1-(2-Pyridylazo)-2-naphthol	558 nm	2.5		0.031 µg mL^{-1}
8	1-(2-Pyridylazo)-2-naphthol (PAN)	558 nm for zero order and 580 for first-order derivative		1.82×10^4 L mol^{-1} cm^{-1}	0.038 g mL^{-1}
9	1-(2-Pyridylazo)-2-naphthol (PAN)	559 nm		2.45×10^4 L mol^{-1} cm^{-1}	2.6 ng cm^{-2}
10	Di-2-pyridylketone benzoylhydrazone (dPKBH)	483 nm	9	3.92×10^4 L mol^{-1} cm^{-1}	
11	1-Nitroso-2-naphthol	408 nm	4	2.04×10^4 L mol^{-1} cm^{-1}	
12	1-(2-Thiazolylazo)-2-naphtholin (TAN)	550–700 nm	5.9–7.1		0.003 ppm

13	1-(2-Thiazolylazo)-2-naphthol (TAN)	350–750 nm	10	1.0–300.0 ng mL^{-1}	
14	1-(2-Thiazolylazo)-2-naphthol (TAN)	580 nm	2.2	0.04–3.40 µg mL^{-1}	
15	2,7-Bi(5-carboxy-1,3,4-triazole)-1-amino-8-naphthol-3, 6-disulfonic acid, BCTZAHA)	540 nm	10.0	0.001–0.04 µg mL^{-1}	
16	4-(2-Thiazolylazo)resorcinol	520 nm		2.7×10^4 L mol^{-1} cm^{-1} 0–80 µg/50 mL	
17	4-(2-Pyridylazo)-resorcinol (PAR)	510 nm	6.5	1–12 ppm	0.6 ppm
18	4-(2-Pyridylazo)-resorcinol disodium salt dihydrate (PAR)	510 nm	10.0	7.12×10^4 L mol^{-1} cm^{-1}	
19	*o*-Nitrophenylfluorone	570 nm	5.6	5.61×10^4 L mol^{-1} cm^{-1}	
20	*o*-Bromophenylfluorone	570 nm		3.64×10^5 dm^3 mol^{-1} cm^{-1} 8–160 ng mL^{-1}	
21	*o*-Bromophenylfluorone (OBPF) in the presence of poly(*N*-vinylpyrrolidone)	570 nm		3.64×10^5 dm^3 mol^{-1} cm^{-1} 8–160 ng mL^{-1}	
22	2,4-Dichloro-phenylfluorone in the presence of cetylpyridinium bromide (CPB)	602 nm	5.82	8.98×10^4 L mol^{-1} cm^{-1}	
23	5′-Nitrosalicylfluorone	570 nm		1.4×10^5 L mol^{-1} cm^{-1}	
24	Phenylfluorone (PF)	595 nm	8.0	20–320 µg L^{-1}	3.4 µg L^{-1}
25	PM-picramazo	644 nm		2.65×10^4 L mol^{-1} cm^{-1}	
26	Picramazochromotropicacid[3-(2-hydroxy-3,5-dinitro phenyl) azo-4,5-dihydroxy-2,7-naphthyldisulfonic acid]	570 nm		1.36×10^4 L mol^{-1} cm^{-1}	

(continued)

Table 1 (continued)

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
27	Sulfochlorophenol S (SCPS)		4.5	0–0.80 mg L^{-1}	0.03 mg L^{-1}
28	Bromophenol blue (BPB)	590 nm		1.45×10^5 L mol^{-1} cm^{-1}	
29	4-(2,6-Diamino-4-pyrimidylazo)phenol (DAPP)	535 nm	6.0–7.3	5.8×10^4 L mol^{-1} cm^{-1} 0.0–1.27 ppm	1.1 ng cm^{-2}
30	Chlorosulfophenol S (CS)	650 nm	2.5–5.0	6.87×10^4 L mol^{-1} cm^{-1} , 0–20 g of Cu/10 mL	
31	2-(5-Nitro-2-pyridylazo)-5-[*N*-propyl-*N*-(3-sulfopropyl) amino] phenol (nitro-PAPS)	570 nm		7.95×10^4 L mol^{-1} cm^{-1}	
32	2,2′-{Ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol)	602 nm	6.0	0.12×10^2 L mol^{-1} cm^{-1}	2.438 g cm^{-2}
33	2-[{4-(1, 3-Benzoimidazole-2-yl) Ph}imino]–5-nitro phenols		5.6	0.1899×10 L $mol^{-\ 1}$ cm^{-1} 1–10 ppm	0.1315 µg cm^{-2}
34	2,6-Dithiol-4-ethylphenol (DTEP)	534–540 nm	6.2–7.7	0.05–4.0 µg mL^{-1}	8.5–8.7 ng mL^{-1}
35	Thenoyltrifluoroacetone (TTA)	535 nm	7.5	0–8 µg mL^{-1}	6 µg
36	*p*-Anisidine	533 nm		415 M^{-1} cm^{-1} 0.89408 g	
37	Ascorbic acid	340 nm	12	1–10 ppm	
38	L-Ascorbic acid	665 nm	2.2	0.2–1.0 µg mL^{-1}	

39	Hexadecyltrimethylammonium chloride (cetyltrimethyl-ammonium chloride) and sulfosalicylic acid		1.8	1.6×10^{-9}–8×10^{-8} mol/14 mL	
40	Naphthazarin(5,8-dihydroxy-1, 4-naphthoquinone; Naph)	330 nm	5.5–8.0	1.84×10^{4} L mol^{-1} cm^{-1} Up to 4.5 ppm	0.004 µg cm^{-2} 0.3 ppm
41	Dextran	680 nm	11.5	41 L mol^{-1} cm^{-1}	
42	Polysaccharides pullulan and dextran	640 nm		18–180 µg mL^{-1}	0.48 µg mL^{-1} (with pullulan) 0.53 µg mL^{-1} (with dextran)
43	Sodium pyrogallol-5-sulfonate (PS)	436.8 nm		10–300 ng cm^{-3}	
44	Arabinogalactan	238 nm	4.8–10.8	2,500 L mol^{-1} cm^{-1}	
45	Hydroquinone	500 nm		0–40 g L^{-1}	
46	*N*,*N*-Diethyl-*p*-phenylenediamine and thymoquinone	552 nm		$2.61\text{x}10^{6}$ L mol^{-1} cm^{-1}	
47	Bromocresol purple and neutral red	460 nm catalytic system 590 nm uncatalytic system	9.65	0.0060–0.072 g mL^{-1}	
48	6,7-Dihydroxy-4-methyl-2-phenylbenzopyrilium chloride		4.5		
49	6,7-Dihydroxy-4-methyl-2-phenylbenzopyrilium chloride (DHMPhB)	540 nm	4.5	8.5×10^{4} dm^{3} mol^{-1} cm^{-1} 0.02–0.95 µg L^{-1}	0.006 µg L^{-1}

(continued)

Table 1 (continued)

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
Chapter 2					
1	1-(4-Nitrophenyl)-3-(2-benzothiazol)triazene		8.37–9.38	1.17×10^5 L mol^{-1} cm^{-1}	
2	1-Azobenzene-3-(6-methoxy-2-benzothiazolyl) triazene (AMBT)	560 nm	10.0	5.36×10^4 L mol^{-1} cm^{-1}	
3	Biscyclohexanone oxalyldihydrazone.	595 nm			2.22×10^{-5} μg cm^{-2}
4	*N*,*N′*-Oxalylbis(salicylaldehyde hydrazone)	422 nm	2.0		0.4–1.8 μg mL^{-1}
5	*N*,*N′*-Oxalylbis(2-pyridyl-3′-sulfobenzoylhydrazone)	421 nm	1.89		
6	*p*-Dimethylaminobenzaldehyde benzothiazolylhydrazone (DBBH)	422 nm	4–8	7.6×10^4 L mol^{-1} cm^{-1} 0.5–5.0 μg/5 mL	0.84 ng cm^{-2}
7	Bis(cyclohexanone)oxalyldihydrazone	600 nm		20 μg mL^{-1}	0.13 μg mL^{-1}
8	2,4-Dihydroxybenzophenone benzoic hydrazone (DHBPBH)	380 nm	4	1.55×10^4 L mol^{-1} cm^{-1}	0.004 ng cm^{-2}
9	*p*-Methylisonitrosoacetophenone hydrazone	510 nm	7	6.28×10^3 L mol^{-1} cm^{-1}	
10	α-(2-Benzimidazolyl)- α′, α″-(*N*-5-nitro-2-pyridylhydrazone)toluene (BINPHT)	410 nm	6.0	3.8×10^4 L mol^{-1} cm^{-1} 0–2.5 μg mL^{-1}	0.06 μg mL^{-1}
11	2-Hydroxy-1-naphthaldehyde benzoylhydrazone (OHNABH)	443 nm	3–7	0.16–4.80 μg mL^{-1}	

12	Picolinaldehyde nicotinoylhydrazone (PANH)	380 nm	8.5–10.5	5.8×10^4 L mol^{-1} cm^{-1}	1.1 ng cm^{-2}
13	Di-2-pyridylketone benzoylhydrazone (dPKBH)	370 nm	8	3.92×10^4 L mol^{-1} cm^{-1} 3 mg L^{-1} of Cu	
14	2,5-Dihydroxyaceto phenonebenzoic hydrazone	400 nm		1.1×10^4 L mol^{-1} cm^{-1} 0.3–6.0 µg mL^{-1}	
15	Acetaldehyde-bis(cyclohexanone)oxaldihydrazone	540 nm		2–50 µg/100 mL	
16	3-Methoxy-4-hydroxybenzaldehyde-4-bromophenylhydrazone (3,4-MHBBPH)	462 nm	4.0	2.0520×10^4 L mol^{-1} cm^{-1}	0.2540 µg cm^{-2}
17	Diacetylmonoxime-4-hydroxybenzoylhydrazone (DM-4-HBH)	396 nm	10.5	1.8×10^4L mol^{-1} cm^{-1}	0.0035 mg cm^{-2}
18	2,4-Dimethoxy-4-hydroxylbenzaldehyde benzoyl hydrazone (DMBHBH)	384 nm	10.0	3.8×10^4 L mol^{-1} cm^{-1}	0.00585 mg cm^{-2}
19	3,5-Dimethoxy-4-hydroxybenzaldehydebenzoyl hydrazone (DMBBH)	435 nm		3.16×10^4 L mol^{-1} cm^{-1}	0.00633 mg cm^{-2}
20	2,3,4-Trihydroxyacetophenonephenyl hydrazone (THAPPH)	385 nm	2.5	1.0053×10^5 L mol^{-1} cm^{-1}	0.0006265 mg cm^{-2}
21	2-Hydroxynaphthaldehydebenzoyl hydrazone (HNABH)	427 nm		4.35×10^4 L mol^{-1} cm^{-1}	5.0 ng cm^{-2}
22	Bis(cyclohexanone)oxalyldihydrazone (BCO)	600 nm	8.6–10.0		0.02–4.00 mg L^{-1}
23	Salicyl salicylic acid hydrazone	420 nm		8.560×10^4 L mol^{-1} cm^{-1}	0.0007 µg cm^{-2}
24	Salicylaldehyde benzoylhydrazone (SAL-BH)	404 nm		1.4×10^5 L mol^{-1} cm^{-1} 0.01–18 mg L^{-1}	5.0 ng cm^{-2} ng mL^{-1}
25	Salicylaldehyde acetylhydrazone (SAAH)	372 nm		1.0×10^4 L mol^{-1} cm^{-1}	0.635 mg cm^{-2}

(continued)

Table 1 (continued)

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
26	Bis-cyclohexanone oxaldihydrazone	600 nm	8.5–10.0	1.6×10^4 L mol^{-1} cm^{-1}	
27	5-Bromo-2-hydroxy-3-methoxybenzaldehyde-*p*-hydroxybenzoichydrazone	405 nm	5.0	1.412×10^4 L mol^{-1} cm^{-1}	0.0045 µg cm^{-2}
28	Diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH)	412 nm	8–10.0	1.65×10^4 L mol^{-1} cm^{-1}	0.00606 µg cm^{-2}
29	*N″*,*N‴*-Bis[(*E*)-(4-fluorophenyl)methylidene] thiocarbonohydrazide [bis(4-fluoroPM)TCH]	375 nm		0.42545×10^5 L mol^{-1} cm^{-1}	0.0014 mg cm^{-2}
30	Pyridine-2-acetaldehyde benzoylhydrazone	380 nm	3.0	6.9–984.5 µg L^{-1}	1.8 µg L^{-1}
31	Furfuraldehyde fluorescein diacetate hydrazone (FFDH) and furfuraldehyde fluorescein hydrazone (FFH)	494 nm (FFDH) 498 (FFH)		7–33 µM	7×10^{-8} M (FFDH) 1.1×10^{-7} (FFH)
32	5-*p*-Methylphenylazo)-8-aminoquinoline (*p*-MPAQ)	117 nm	9.0–10.0	3.62×10^4 L mol^{-1} cm^{-1}	
33	5-(3-Carboxyphenylazo)-8-aminoquinoline (*m*-CPAQ)	554 nm		7.3×10^4 L mol^{-1} cm^{-1} 0–16 µg/25 mL	
34	5-(3-Carboxyphenylazo)-8-aminoquinoline	554 nm	6.6	7.3×10^4 L mol^{-1} cm^{-1} 0–16 µg/25 mL	
35	5-(4-Sulfophenylazo)-8-aminoquinoline [SPA]	550 nm	9	3.4×10^4 L mol^{-1} cm^{-1}	
36	*meso*-Tetrakis-(4-methoxyphenyl)-porphyrin (TMOPP)		7.05	9.14×10^6 L mol^{-1} cm^{-1}	

37	5-[4-*N*-(*p*-Chloro)-benzylammonium pyridyl] -10,15,20-tris (4-*N*-pyridyl) porphyrin chloride	428 nm	3.2	1.9×10^{5} L mol^{-1} cm^{-1}	
38	*meso*-Tetra-(4-methoxyphenyl-3-sulfo) porphine		4.4–5.9	0–1.4 μg/10 mL	
39	3,8,13,18-Tetramethyl-21H,23H-porphine-2,7,12,17-tetrapropionic acid or coproporphyrin-I (CPI)	380 nm	8		0.568 μg cm^{-2}
40	*meso*-Tetrakis(4-sulfonic acid phenyl) porphine (TPPS4)	489 nm	4–6	5.0×10^{5} L mol^{-1} cm^{-1} 0–0.2 μg mL^{-1}	
41	(5,10,20-Tetra-Ph-21 H,23 H-porphin tetrasulfonic acid)	413 nm	3–7		
42	*o*-Iodobenzenediazoaminobenzene-*p*-azobenzene (OIDAA)	500 nm	12	0–0.20 mg/L	0.008 mg L^{-1}
43	Dibromocarboxylbenzenediazoaminoazobenzene (DB-*O*-CDAA)	530 nm	10	1.08×10^{5} L mol^{-1} cm^{-1}	
44	4-(2,3-Dihydro-1,4-phthalazinedione-5-triazeno) azobenzene (PTAB)	520 nm	11.5	6.0×10^{4} L mol^{-1} cm^{-1} 0–6 mg L^{-1}	
45	Bis(acetylacetone)ethylenediiminate	370 nm	5.0	100 μg L^{-1}	
46	Bis(acetylacetone)ethylenediimine	545 nm		200 μm mL^{-1}	
47	*N*,*N*-Dimethyl-*N′*-(2-hydroxybenzyl)ethylenediamine	410 nm	8	890 L mol^{-1} cm^{-1}	
48	*N*,*N′*-Bis(salicylidene) ethylene-diamine (Salen)	550 nm	4–9	5.5×10^{3} and 1.3×10^{4} Lmol^{-1} cm^{-1}	0.005 mg L^{-1}
49	Cetyltrimethylammonium bromide	360 nm	0.5–3.5		
50	Hexadecyltrimethylammonium chloride (cetyl trimethylammonium chloride) and sulfosalicylic acid		1.8	1.6×10^{-9}–8×10^{-8} mol/14 mL	

(continued)

Table 1 (continued)

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
51	CAS and CTMAB		5.7	1.01×10^5 L mol^{-1} cm^{-1}	
52	Methyl thymol blue and cetyltrimethylammonium bromide	560–680 nm	6	0.10–3.00 g mL^{-1}	
53	Methylthymol blue (MTB) and cetyltrimethylammonium bromide (CTAB)	556 nm		6.1×10^4 L mol^{-1} cm^{-1}	6.7 ng mL^{-1}
54	BCO	610 nm	7–10	1.6×10^4 L mol^{-1} cm^{-1}	
55	Bis(cyclohexanone)oxalyldihydrazone (BCO)	600 nm	8.6–10.0		0.02–4.00 mg L^{-1}
56	Bisoxaldihydrazone (BCO)	600 nm	8.9–9.4		
57	Leucocrystal violet	590 nm		0.004–0.04 g mL^{-1}	
58	Leucocrystal violet	585 nm		1.9×10^5 L mol^{-1} cm^{-1}	0.001125 g cm^{-2}
59	DBC-arsenazo			0–0.8 µg Cu/25 mL	2.22×10^{-5} µg cm^{-2}
60	Eriochrome blue black R (EBBR)	550 nm	12	1.80×10^4 L mol^{-1} cm^{-1} 0–1.60 mg Cu L^{-1}	0.04 mg
61	Ethyl violet	612 nm	5	9.2×10^4 dm^3 mol^{-1} cm^{-1} (in freshwater) 8.1×10^4 dm^3 mol^{-1} cm^{-1} (In seawater) 0–5×10^{-7} mol dm^{-3} (31.8 ng cm^{-3})	

62	*N*-Ethyl-2-naphthylamine (NENA)	533 nm	5	1.72×10^5 M^{-1} cm^{-1}, 0–7.9 ng/5 mL	
63	Thiazolylazoacetylacetone (TAA)	445 nm	4.5–8.0		
64	VBB	570 nm		1.85×10^5 L mol^{-1} cm^{-1} 0–6 µg/25 mL	
65	3,3′,5,5′-Tetramethyl benzidine (TMB)	660 nm		2.54×10^5 L mol^{-1} cm^{-1}	
66	Azure B	647 nm	10	50–1,600 ng mL^{-1}	
67	Acridine yellow and fuchsin acid	450 nm uncatalytic 540 nm catalytic	5.5	0.60–32 µg L^{-1}	
68	Methyl violet	590 nm		0–32.0 g L^{-1}	
69	*N*-(Phenyl)-2-thioquinaldinamide (TQA)		1.5–3.8	8.1×10^3 L mol^{-1} cm^{-1}	7.7 ng cm^{-2}
70	2-(2-Quinolinylazo)-5-dimethylaminoaniline (QADMAA)	580 nm	4.0	1.14×10^5 L mol^{-1} cm^{-1}	
71	2-(5-Bromo-2-pyridylazo)-5-[*N*-*n*-propyl-*N*-(3-sulfopropyl) amino]aniline (5-Br-PSAA)	580 nm		0.1–2 mg L^{-1}	
72	2-(2′-Quinolylazo)-1,3-diaminobenzene (QADAB)	555 nm	4		
73	Thionine		9.76	0.004–0.480 g mL^{-1}	
74	Thionine	600 nm	10	1–160 ng mL^{-1}	0.7 ng mL^{-1}
75	Dimethylindodicarbocyanine polymethyne dye	(Cu I)	3–5	1.8×10^5 L mol^{-1} cm^{-1}	
76	Biquinoline	545 nm		0.2–20.0 mg L^{-1}	0.05 mg L^{-1}
77	2-Chloro-4-bromo-benzenediazoaminoazo benzene	520 nm	10.5	1.01×10^5 L mol^{-1} cm^{-1}	

(continued)

Table 1 (continued)

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
78	Rhodamine B and methylene blue	Catalytic system 540 nm and uncatalytic system 660 nm	4	0.00080–0.048 g mL^{-1}	
79	*N*,*N*-Diethyl-*p*-phenylenediamine and thymoquinone	552 nm		2.61×10^6 L mol^{-1} cm^{-1}	
80	Methyl orange		3.1	1.0×10^{-3} to 4.0×10^{-2} mg L^{-1}	4.6×10^{-4} mg L^{-1}
81	5-(4-Nitrophenylazo) salicylic acid (NPAS) and 2,2′-dipyridyl (Dp)	520 nm		2.60×10^4 L mol^{-1} cm^{-1}	
82	1-(2′,4′-Dinitroaminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol [2′,4′-dinitro APTPT]	645 nm	8.7–10.5	0.87×10^3 L mol^{-1} cm^{-1}	0.072 mg cm^{-2}
83	Neocuproin-hydroxylamine hydrochloride monohydrate	457 nm	4		0.75 μg L^{-1}
84	1-Amidino-*o*-methylurea (AMUH)	261 nm	4.6		
85	2-(5-Bromo-2-pyridylazo)-5-dimethylaminoaniline (5-Br-PADMA)	573 nm	3.75–5.75	5.89×10^4 L mol^{-1} cm^{-1} 0–18 μg/10 mL Cu	
86	Leucomalachite green	610 nm		3.8×10 L mol^{-1} cm^{-1} 0.016–0.176 μg mL^{-1}	0.00016 μg cm^{-2}
87	*O*-Methylphenyl thiourea (OMPT)	510 nm		1.0167×10^3 L mol^{-1} cm^{-1} 600 μg mL^{-1}	0.0625 μg cm^{-2}

1	4-Chloroisonitrosoacetophenonesemicarbazone	386 nm	7.2–8.0	1.79×10^5 L mol^{-1} cm^{-1}	
2	Phenanthrenequinone monosemicarbazone (PQSC)	480 nm	8	7.7×10^3 L mol^{-1} cm^{-1} Up to 8.9 ppm	
3	4-Chlorobenzaldehyde semicarbazone		7.2–8.0	2.3×10^4 L mol^{-1} cm^{-1}	
4	2-[2′-(6-Methyl-benzothiazolyl)azo]-5-dimethylamino benzoic acid (MBTAMB)	660 nm	2.0–5.0	7.0×10^4 L mol^{-1} cm^{-1} 0–0.72 μg mL^{-1}	
5	2-[2-(4-Methylbenzothiazolyl)azo]-5-dimethylamino benzoic acid (4-Me-BTAMB)	650 nm		3.1×10^4 L mol^{-1} cm^{-1} 0.04–2 mg L^{-1}	
6	2-(2-Benzothiazolylazo)-5-diethylaminobenzoic acid (BTAEB)	654 nm	3.8–5.5	5.7×10^4 L mol^{-1} cm^{-1} 0–20 μg Cu/25 mL	
7	2-Aminocyclopentene-1-dithiocarboxylic acid	462 nm	2.8–3.3	2.85×10^5 L mol^{-1} cm^{-1} 0.1–16.0 μg L^{-1}	
8	3-Hydroxy-3-phenyl-1-*p*-carboxyphenyltriazene			0.635–3.81 ppm	
9	3-Hydroxy-3-propyl-1-*p*-tolyltriazene	380 nm		1.27–7.62 ppm	
10	3-Hydroxy-3-methyl-1-*p*-methoxyphenyltriazene	430 nm	6–6.6	1,340 dm^3 mol^{-1} cm^{-1} 6.35–38.1 ppm	47.4 ng cm^{-2}
11	3-Hydroxy-3-m-tolyl-1-*o*-chlorophenyltriazene	390 nm	6.6–7.2	4,107 L mol^{-1} cm^{-1} 2.0×10^{-5} M 1.0×10^{-4} M	15.47 ng cm^{-2}
12	3-Hydroxy-3-m-tolyl-1-*p*-sulfonato (Na-salt) phenyltriazene	402 nm	6.4–6.9	037 L mol^{-1} cm^{-1}	9.02 ng cm^{-2}

(continued)

Table 1 (continued)

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
13	3-Hydroxy-3-methyl-1-(4-sulfonamidophenyl) triazene (HMST)	360 nm	6.7–7.3	6.158×10^3 L mol^{-1} cm^{-1}	10.31 ng cm^{-2}
14	3-Hydroxy-3-methyl-1-(4-sulfonamidophenyl) triazene (HMST)	360 nm	6.7–7.3	6.158×10^3 L mol^{-1} cm^{-1}	10.31 ng cm^{-2}
15	2-Pyridine carboxaldehyde isonicotinoyl hydrazone (2-PYAINH)	352 nm	9	5.2×10^4 L mol^{-1} cm^{-1}	0.0012 g cm^{-2}
16	2-Hydroxy-5-methylacetophenoneisonicotinoyl hydrazone (HMAINH)	440 nm	3.4	9.340×10^3 dm^3 mol^{-1} cm^{-1}	6.8 mg cm^{-2}
17	*N′*-(1-(Pyridin-2-yl)ethylidene)isonicotinohydrazide (ACPINH)	365 nm		10.52×10^4 L mol^{-1} cm^{-1}	0.01962 µg cm^{-2}
18	*o*-Hydroxyacetophenoneisonicotinoylhydrazone (OHAPINH)	420 nm	4	4.8×10^4 L mol^{-1} cm^{-1} 0.2–2.2 mg mL^{-1}	0.0006 mg mL^{-1}
19	2-Hydroxy-4-*n*-propoxybenzophenone oxime	390 nm		2.0×10^2 L mol^{-1} cm^{-1} 46.26 ppm	
20	2-Hydroxy- 4-*n*-butoxyacetophenone oxime ($C_{12}H_{17}NO_3$)	650 nm	3.5 & 6.0–10.0	108 L mol^{-1} cm^{-1}	0.58 µg cm^{-2}
21	Dehydroacetic acid oxime (DAO)	460 nm	5.8	2–100 ppm	
22	3-Isonitroso-5-methyl-2-hexanone (HIMH)	390 nm	6.5–8.5	1.001×10^4 L mol^{-1} cm^{-1}	6.1 ng cm^{-2}
23	4-Methylbenzaldehydeoxime	430 nm	10	0.5350×10^2 L mol^{-1} cm^{-1}	
24	Chloro-(phenyl) glyoxime	290.5 nm	4	0.8×10^4 L mol^{-1} cm^{-1}	

25	1,2-Propanedione-1-phenyl-1-(2-hydroxy-5-bromobenzilidineazine)-2-oxime	440 nm	9.6	5.9909×10^{3} L mol^{-1} cm^{-1}	10.6×10^{-3} mg cm^{-2}
26	Hydroxy oximes	540 nm		20–1,000 ppm	
27	Rhodamine B with tungstocuprate	570 nm		1.53×10^{6} L mol^{-1} cm^{-1} 0–0.5 g/25 mL	0.36 ng mL^{-1}
28	5-(4-Dimethylaminobenzylidene) rhodanine (DMABR)	480 nm	2 and 8	3.8×10^{3} L mol^{-1} cm^{-1} 7.6×103 L mol^{-1} cm^{-1}	
29	Rhodamine B and methylene blue	Catalytic system 540 nm and uncatalytic system 660 nm	4	0.00080–0.048 g mL^{-1}	
30	5-Br-PADAP	509 nm and 569 nm		0–12 μg/25 mL	
31	DDTC & 5-Br-PADAP	520 nm	9.2		
32	5-Br-PADAP	575 nm	9	1.04×10^{5} L mol^{-1} cm^{-1} 0–560 μg L^{-1}	
33	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol(5-Br-PADAP)	558 nm	0	0–2.0 μg mL^{-1}	
34	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol	568 nm	5		0.5 g L^{-1}
35	*o*-Aminophenol	424 nm	5.5	0.01–0.15 mg L^{-1}	
36	2-(5-Nitro-2-pyridylazo)-5-[*N*-propyl-*N*-(3-sulfopropyl) amino]phenol (nitro-PAPS)	565 nm	3.8	0.01–1 mg L^{-1}	
37	2-(5-Nitro-2-pyridylazo)-5-[*N*-propyl-*N*-(3-sulfopropyl) amino] phenol (nitro-PAPS)	570 nm		7.95×10^{4} L mol^{-1} cm^{-1}	

(continued)

Table 1 (continued)

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
38	Nitro-PAPS	580 nm		9.32×10^4 L mol^{-1} cm^{-1}	
39	2-(2-Thiazolylazo)-5-sulfopropylaminophenol (TASPAP)	552 nm	5.6	4.58×10^4 L mol^{-1} cm^{-1}	
40	*N*-(*o*-Methoxy benzaldehyde)-2-aminophenol (NOMBAP)	440 nm	5.7–6.8	25,739 L mol^{-1} cm^{-1}	0.00246 mg.cm^{-2}
41	DDTC (cuproine)	450 nm	3.6–9.0	9.05×10^3 L mol^{-1} cm^{-1} 0–30 µg L^{-1}	
42	Bathocuproine	477 nm	4.5	1.25×10^4 L mol^{-1} cm^{-1} 0–65 µg/25 mL	
43	Neocuproine (2, 9-dimethyl-1,10-phenanothroline)	460 nm		1.45×10^5 L mol^{-1} cm^{-1}	
44	Neocuproine	455 nm	5	2–500 µg L^{-1}	1.8 µg L^{-1}
45	Bathocuproine disulfonic acid	484 nm	4.5	Up to at least 40 µg L^{-1}	0.7 µg L^{-1}
46	*N*-*p*-Nitro-(2-mercapto) propionanilide	450 nm	3.0–6.5		

47	Primary ligand: cinnamoylhydroxamic acid (CHx) Secondary ligand: pyridine	390–399 nm (pyridine) 424–407 nm (piperidine) 364–393 nm (3-picoline) 359–340 nm (DMSO) 395–351.5 nm (EDA) 386–383 nm (DETA)	8.5	6112.6 L mol^{-1} cm^{-1} (for Cu–CHx–piperidine system)	0.01039 µg cm^{-2} (for Cu–CHx–piperidine system)
48	Dibromocarboxyarsenazo	585 nm		0–40 µg Cu/25 mL	
49	Cupron	445 nm	8	66,000 L mol^{-1} cm^{-1} Up to 7 ppm	
50	Ethyl *o*-carboxyphenyl hydrazonoacetoacetate (I)	415 nm	6.0–8.0	1.25×10^4 L mol^{-1} cm^{-1}	
51	1,5-Di(2-hydroxy-5-bromophenyl)-3-cyanoformazan (HBPCF)	640 nm	4.5	3.5×10^4 L mol^{-1} cm^{-1}	
52	Tetra-, penta-, hexaglycine	250 nm 365 nm		9.0×10^3 L mol^{-1} cm^{-1} 7.12×10^3 L mol^{-1} cm^{-1}	
53	1,5-Diazacycloctane-1,5-bis(*N*-methylacetohydroxamic acid) (DACOD-MAHA)	400 nm	5.52	960 L mol^{-1} cm^{-1}	
54	2-(2′-Quinolineazo)-4,5-dimethylhydroxybenzene (QADMP)	561 nm	4	4.56×10^4 L mol^{-1} cm^{-1}	
55	Xylenol orange		8	0–20 g/25 mL	
56	Cyclohexyldiamine tetraacetic acid (CyDTA)	700 nm	2 and 3	0–4 mg/50 mL	

(continued)

Table 1 (continued)

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
57	Sulfanilic acid	330 nm	6	0.05–6 mg mL^{-1}	0.028 mg mL^{-1}
58	SALAAP (condensation reaction between 2-hydroxybenzaldehyde and 4-aminoantipyrine)			0.20–2.5 g mL^{-1}	4.6×10^{-8} g mL^{-1}
59	Dibromocarboxyarsenazo (DBKKA)			0–0.032 mg L^{-1}	0.64 g L^{-1}
60	Isonitroso-*p*-methylacetophenone (HIMAP)	360 nm	5.8–7.5	1.016×10^{4} L mol^{-1} cm^{-1}	0.0062 mg cm^{-2}
61	Alanine		8	2.0–32.0 g L^{-1}	
62	8-Hydroxyquinoline (8-Ox)	395 nm	7	7.69×10^{5} L mol^{-1} $^{-1}cm^{-1}$	
63	*p*-Acetylchlorophosphonazo (CPApA)	554 nm		0.020–0.30 µg mL^{-1}	10.94 ng mL^{-1}
64	1-Nitroso-2-naphthol-3,6-disulfonic acid	636 nm			10 ng mL^{-1}
65	Amino acid (isoleucine)	230 nm	9	10–1000 mg L^{-1}	5 µg L^{-1}
66	8-Hydroxyquinoline	λ_{max} range 367–419 nm	4	2–12 µg mL^{-1}	
67	Light green SF	635 nm		0–20 ng mL^{-1}	
68	3,5-DiBr-DMPAP	580 nm	4	5.568×10^{4} L mol^{-1} cm^{-1}	
69	Ammonium purpurate (murexide)	457.5 nm	8	0.381–6.355 µg mL^{-1}	
70	[*N*-(*o*-Hydroxybenzylidene) pyridine-2-amine]	540 nm	6.8–7.5	3,494.84 L mol^{-1} cm^{-1}	0.0182 mg cm^{-2}
71	4-(2′-Benzothiazolylazo)-salicylic acid (BTAS)	485 nm	5	2.35×10^{4} L mol^{-1} cm^{-1}	

72	5-(4-Nitrophenylazo) salicylic acid (NPAS) and 2,2′-dipyridyl (Dp)	520 nm		2.60×10^4 L mol^{-1} cm^{-1}	
73	1-(2′,4′-Dinitroaminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol [2′,4′-dinitro APTPT]	645 nm	8.7–10.5	0.87×10^3 L mol^{-1} cm^{-1}	0.072 mg cm^{-2}
74	Fluoxetine hydrochloride (FX), fluvoxamine maleate (FV), sertraline hydrochloride (SE)	530 nm		1–18 µg mL^{-1} 1–16 µg mL^{-1} 0.25–10 µg mL^{-1}	
75	Indigo carmine		5	1–16 g/25 mL	3.4×10^{-9} g mL^{-1}
76	5-{α-Methyl-3-hydroxy benzylidene} rhodanine	430 nm	5.5	0.6027×10^4 L mol^{-1} cm^{-1} 0.05–13 µg mL^{-1}	0.01054 µg cm^{-2}
77	Schiff base	400 nm		7.68×10^4 L mol^{-1} cm^{-1}	
78	Dibromo-*p*-chloro-chlorophosphonazo (DBC-CPA)	550 nm		0.1–2.0 mg/10 mL	9.05 ng mL^{-1}
79	Nicotinohydroxamic acid	800 nm	9.2		
80	1-(2,4-Dimethylphenyl) azonaphthalen-2-ol (Sudan II)	537 nm	10	0.285–20 µg L^{-1}	0.085 µg L^{-1}
81	[*N*-(*o*-Hydroxybenzylidene)-4-Me aniline]	510 nm	5.8–6.8	890 L mol^{-1} cm^{-1}	0.07142 µg cm^{-2}
82	Esomeprazole	390 nm	3	0.5–10 ppm	0.022 µg cm^{-2}
83	3-((Benzothiazol-2-diazenylnaphthalene-2,7-diol]	588 nm	7	1.436×10^4 L mol^{-1} cm^{-1} 0.1–3.0 µg mL^{-1}	0.0044 µg cm^{-2}
84	*o*-Vanillidine-2-amino-4-ethylbenzothiazole (VEBT)	450 nm		0.41–3.78 µg mL^{-1}	
85	Hydroxy-3-[(2-hydroxyl phenyl) methylene amino] benzene sulfonic acid(II) (HVMAB)	430 nm	2	1.25×10^4 L mol^{-1} cm^{-1} (0.2–8) mg L^{-1}	0.006 mg L^{-1}

(continued)

Table 1 (continued)

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
86	2-[(4-Antipyrinyl)azo)]imidazole	578 nm	44,052	1×10^{-5}–1×10^{-4}mol L^{-1}	1×10^{-6} mol L^{-1}
87	2-[6-Nitro-2-benzothiazolylazo]-4-hydroxy benzoic acid (NO_2 BTAHB)	618 nm	6	$7.45 \times 10^{+3}$ L mol^{-1} cm^{-1} 0.1–6.0 µg mL^{-1}	0.0088 µg cm^{-2}
Chapter 4					
1	Thiophenealdehyde 4-phenyl-3-thiosemicarbazone (TPS)	360 nm	4–10	37×10^{3} L mol^{-1} cm^{-1} 2–20 µg/10 mL	
2	*N*-Salicylidenethiosemicarbazone (I)	630 nm	2.5		
3	2,4-Dihydroxy-5-bromoacetophenone thiosemicarbazone (DHBAT)	420 nm	6	0.145×10^{4} L mol^{-1} cm^{-1} 12.7 ppm	
4	Thiosemicarbazone of 2-carboxybenzaldehyde (2CBTSC)	346 nm		1.2×10^{4} L mol^{-1} cm^{-1}	
5	2H-Benzopyron-2-one-3-acetylthiosemicarbazone (BPAT)	410 nm	8.8–9.2	0.7×10^{3} L mol^{-1} cm^{-1} 2–25 mg mL^{-1}	0.086 µg cm^{-2}
6	Iso-nitrosopropiophenone thiosemicarbazone (HINPTC)	390 nm	10	5.826×10^{3} L mol^{-1} cm^{-1}	0.010 µg cm^{-2}
7	Diacetylmonoxime-4-phenyl-3-thiosemicarbazone		3.0–7.0	1.02×10^{4} L mol^{-1} cm^{-1}	0.0062 mg cm^{-2}
8	4-Chlorochalcone thiosemicarbazone	394 nm		3.76×10^{4} L mol^{-1} cm^{-1}	
9	2-Acetylthiophene-4-phenyl-3-thiosemicarbazone (ATPT)	420 nm	3.0–6.0		

10	9-Ethyl-3-carbazolecarboxaldehyde-thiosemicarbazone (ECCAT)	393 nm	4.75	0.2–1.9 mg mL^{-1}	
11	Thiosemicarbazone of citral	0	5.6	8.75×10^3 L mol^{-1} cm^{-1}	
12	2-Acetylthiophene thiosemicarbazone (ATT)	370 nm	43,958	1.83×10^4 L mol^{-1} cm^{-1}	0.0034 µg cm^{-2}
13	1-Phenyl-1,2-propanedione-2-oxime thiosemicarbazone (PPDOT)	500 nm	3.0–8.0	0.575×10^4 L mol^{-1} cm^{-1}	0.0118 µg cm^{-2}
14	Acetophenone-*p*-chlorophenylthiosemicarbazone (A-*p*-ClPT)	600 nm	43,930	5.5×10^3 L mol^{-1} cm^{-1}	0.244 µg cm^{-2}
15	3-Hydroxybenzaldehyde thiosemicarbazones (HBT)		5.5	8.75×10^3 L mol^{-1} cm^{-1}	
16	*N*-Ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone (ECCT)	380 nm	3	2.243×10^4 L mol^{-1} cm^{-1}	2.83×10^{-3} µg cm^{-2}
17	5-Bromo salicylaldehydethiosemicarbazone (5-BSAT)	390 nm		1.08×10^4 L mol^{-1} cm^{-1}	0.062 mg cm^{-2}
18	4-Hydroxy benzaldehyde thiosemicarbazone (4-HBTS)	370 nm		2.8×10^4 L mol^{-1} cm^{-1}	2.3×10^{-3} µg cm^{-2}
19	2-Acetylfuran thiosemicarbazone (AFT)	365 nm	6.0–8.0	3.33×10^4 L mol^{-1} cm^{-1}	2.0×10^{-3} mg cm^{-2}
20	2-Acetylpyridine-4-methyl-3-thiosemicarbazone (APMT)	380 nm	43,959	1.475×10^4 L mol^{-1} cm^{-1}	4×10^{-3} mg cm^{-2}
21	4-[*N*,*N*-(Dimethyl)amino]benzaldehyde thiosemicarbazone (DMABT)	420 nm	4.4–5.4	1.72×10^4 dm^3 mol^{-1} cm^{-1}	0.0036 mg cm^{-2}
22	2-Hydroxy-3-methoxy benzaldehyde thiosemicarbazone (2H3MB TS)	420 nm	6.2–7.6	1.0–10.0 mg mL^{-1}	0.327 mg mL^{-1}

(continued)

Table 1 (continued)

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
23	2-Acetylpyridine thiosemicarbazone (2-APT) and 3-acetylpyridine thiosemicarbazone (3-APT)	370 nm 350 nm	8.0–10.0	2.14×10^4 L mol^{-1} cm^{-1} 0.16–1.3 μg mL^{-1} 6.7×10^3 L mol^{-1} cm^{-1} 0.44–1.05 μg mL^{-1}	0.009 μg cm^{-2} 0.029 μg cm^{-2}
24	2-Hydroxy-3-Methoxy benzaldehyde thiosemicarbazone (HMBATSC)	395 nm	5	6.0×10^3 L mol^{-1} cm^{-1} 0.254–2.542 μg mL^{-1}	0.011 μg cm^{-2}
25	4-Hydroxybenzaldehydethiosemicarbazone	370 nm	6.5	16,347 L mol^{-1} cm^{-1} 0.06354–1.272 ppm	
26	5-Bromosalicylaldehyde thiosemicarbazone (5-BSAT)	378 nm	5	1.09×10^4 L mol^{-1} cm^{-1} 4.0×10^{-6}–9.6×10^{-6} M	
27	6-Phenyl-2,3-dihydro-asym-triazine-3-thione (PDTT)	540 nm		1.26×10^4 L mol^{-1} cm^{-1}	
28	3-Propyl-5-hydroxy-5-D-arabinotetrahydroxyl butyl-3-thiazolidine-2-thione (PHTTT)	480 nm	6.0–8.0	5.7×10^3 dm^3 mol^{-1} cm^{-1}	
29	6-(2-Naphthyl)-2,3-dihydro-1,2,4-triazine-3-thione (NDTT)	314 nm		0.5–6 μg mL^{-1}	0.106 μg mL^{-1}
30	6-(2-Naphthyl)-2,3-dihydro-1,2,4-triazine-3-thione (NDTT)	472 nm		1–30 g mL^{-1}	0.26 g mL^{-1}
31	6-(Anthracen-2-yl)-2,3-dihydro-1,2,4-triazine-3-thione (ADTT)	387 nm (second order)		5–35 μg mL^{-1}	1.40 μg mL^{-1}

32	6-(2-Methoxynaphthyl)-2, 3-dihydro-1,2,4-triazine-3-thione (MNDTT)	475 nm	12	4.4×10^3 L mol^{-1} cm^{-1} 2.5–20 mg mL^{-1}	0.33 mg mL^{-1}
33	6-(Phenanthrene-3-yl)-1,2,4,-triazine-3-thione (PhDTT)	460 nm	10	1.4–10 mg mL^{-1}	0.48 µg mL^{-1}
34	Dithizonate	550 nm		4.76×10^4 L mol^{-1} cm^{-1} 0.05–2.5 µg mL^{-1}	
35	Dithizonate	550 nm		0.05–2.5 µg mL^{-1}	
36	Dithizone	551 nm	3.8	6.8×10^4 L mol^{-1} cm^{-1}	
37	Dithizone	550 nm	3.4	10–250.0 ng mL^{-1}	2.6 ng mL^{-1}
38	Sodium diethylaminodithioformate	440 nm		1.3×10^4 L mol^{-1} cm^{-1} 0–3 µg mL^{-1}	
39	1,3,4-Thiadiazole-2,5-dithiol (DMTD)	350 nm		3×10^4 L mol^{-1} cm^{-1}	0.0056 µg cm^{-2}
40	2,5-Dimercapto-1,3,4-thiadiazole (DMTD)	390 nm		5.65×10^4 L mol^{-1} cm^{-1} 0.1–20 µg L^{-1}	10 ng cm^{-2}
41	Dithiocarbammonium hydroxide	452 nm	6.2		
42	Sodium pyrrolidine-1-carbodithioate	438 nm	7.0–10.0	1.33×10^4 L mol^{-1} cm^{-1}	
43	4,6-Dichloro-2-(imidazolidin-2-ylidenamino) pyrimidine (DTIAP)	383 nm		2.03×10^4 L mol^{-1} cm^{-1}	
44	4-Phenylpiperazinecarbodithioate (PPDTC)	305 and 450 nm	4	0.1–10 g mL^{-1}	0.12 µg mL^{-1}
45	Diethanoldithiocarbaminate potassium			1.24×10^4 L mol^{-1} cm^{-1}	

(continued)

Table 1 (continued)

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
46	4-(4′-Nitrobenzylidene imino)-3-methyl-5-mercapto -1,2,4-triazole (NBIMMT).	470 nm	6.2	2.825×10^3 L mol^{-1} cm^{-1} 4.75–16.13 ppm	0.0224 μg cm^{-2}
47	Schiff base 4-(4′-chlorobenzylideneimino)-3-methyl -5-mercapto-1,2,4-triazole [CBIMMT]	414 nm	4.2	0.33813×10^4 L mol^{-1} cm^{-1}, 17.5 μg mL^{-1}	0.01996 μg cm^{-2}
Chapter 5					
1	Piperidinedithiocarbamate	430–440 nm		7.0×10^4 L mol^{-1} cm^{-1} 0–0.72 μg mL^{-1}	0.0063 μg cm^{-2}
2	Diethanoldithiocarbamate	410 nm	10–11	0.04 and 2.00 μg mL^{-1}	
3	Diethyldithiocarbamate (DDTC)	436 nm	6.5–12.7		
4	Diethyldithiocarbamate (DDTC)	436 nm	7.6		
5	Diethyldithiocarbamate	400–500 nm	5–9		0.3 mg L^{-1}
6	Diethyldithiocarbamate	440 nm	8.5	1.5×10^5–7.0×10^5 mol dm^{-3}	
7	DDTC	460 nm	8.5	50–400 ng mL^{-1}	
8	Di-M dithiocarbamate (DDTC) Chlorosulfophenol S (CS)	436 nm 650 nm	4 2.5–5.0	1.16×10^4 L mol^{-1} cm^{-1} 6.87×10^4 L mol^{-1} cm^{-1}	
9	Sodium diethyldithiocarbamate trihydrate (DDTC)	450 nm	8.5–9.5	10–250 g mL^{-1}	
10	Sodium diethyldithiocarbamate	460 nm	9	1.34×10^4 L mol^{-1} cm^{-1}	
11	Sodium diethyldithiocarbamate(DDTC).	460 nm	4–5	1.0×10^4 L mol^{-1} cm^{-1}	

12	Sodium diethyldithiocarbamate	435 nm	9–10		
13	Diethyldithiocarbamate (DDTC)			0.002–0.08 g mL^{-1}	0.11 ng mL^{-1}
14	Diethyldithiocarbamate (DDTC)	440 nm	5	0.01–0.1 μg mL^{-1}	8.6×10^{-3} μg mL^{-1}
15	K 4-methylpiperidinedithiocarbamate (KMPDC)	435 nm		1.78×10^{4} L mol^{-1} cm^{-1} 0.0–20.0 μg Cu in 5 mL	
16	4-Methylpiperidinedithiocarbamate	435 nm	4.2	5–100 μg mL^{-1}	<0.5 μg mL^{-1}
17	4-Benzylpiperidinedithiocarbamate (4-BPDC)	437 nm	3.0–5.0	2.43×10^{4} L mol^{-1} cm^{-1} 2.5–100 mg L^{-1}	
18	Lead 4-benzyl piperidinedithiocarbamate (4-BPDC)	437 nm	43,926	8.197×10^{3} L mol^{-1} cm^{-1}	0.0013 μg cm^{-2}
19	4-Benzylpiperidine-dithiocarbamate (4-BPDC)	435 nm	6	2.75×10^{4} L mol^{-1} cm^{-1}	
20	MDTC (morpholinedithiocarbamte)			2.467×10^{4} L mol^{-1} cm^{-1}	
21	Ammonium pyrrolidine dithiocarbamate (APDC)	447.8 nm		1.08×10^{4} L mol^{-1} cm^{-1}	5.83 ng cm^{-2}
22	Chrome blue K, hydrogen peroxide			0.128–14.08 g/25 mL	0.016 g/25 mL
23	Chrome blue K (ACBK)	573 nm	12.7	4.56×10^{4} L mol^{-1} cm^{-1}	
24	Zincon	606 nm	5–9.5	0–5 μg mL^{-1}	
25	Zincon	610 nm	5.5–8.5	4.0×10^{4} L mol^{-1} cm^{-1} 0–1.5 mg L^{-1}	
26	Zincon	603 nm	5.3	Up to 5 mg L^{-1}	
27	Zincon		9.18	0.2–3.5 g mL^{-1}	

(continued)

Table 1 (continued)

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
28	Zincon (2-carboxy-2″-hydroxy-5″-sulfoformazylbenzene)	615 nm		5–500 ng mL^{-1}	3.4 ng mL^{-1}
29	Methylthymol blue (MTB)	631.9 nm	6	0.5–5.0 g mL^{-1}	
30	Methylthymol blue (MTB) and cetyltrimethylammonium bromide (CTAB)	556 nm		6.1×10^4 L mol^{-1} cm^{-1}	6.7 ng mL^{-1}
31	*N*-(2′-Thiazolyl)-2-Hydroxybenzamide (NTHB)			6.34×10^4 L mol^{-1} cm^{-1}	0.0010 µg cm^{-2}
32	*S*,*S*′-Bis(2-aminophenyl)oxalate	504 nm	3.0–8.0	5,365 M^{-1} cm^{-1} 0.4–150 µg mL^{-1}	11.5 µg mL^{-1}
33	4-Vanillindeneamino-3-methyl-5-mercapto-1,2,4-triazole (VAMMT)	430 nm	8.5	9.929×10 L mol^{-1} cm^{-1}	0.0646 g cm^{-2}
34	*N*-Benzoyl-*N*-methyl-*N*′-phenylthiourea	240–265 nm	5.9–7.3 and 9. 42–10.12		
35	*m*-Chloro-azo-antipyrine (MCAA)	624 nm	3.92	4.0×10^4 L mol^{-1} cm^{-1}	
36	5-Hydroxy-6-mercapto-benzo[a]phenazine (HMBP)	495 nm		7.39×10^3 dm^3 mol^{-1} cm^{-1}	0.012 mg cm^{-2}
37	Nitroso-R salt	450 nm		1.1×10^4 L mol^{-1} cm^{-1}	
38	6-Chloro-benzothiazolylazo benzoic acid (6-Cl-BTAEB)	650 nm	4	7.35×10^4 L mol^{-1} cm^{-1}	
39	1-(2-Hydroxyphenyl)thiourea (HPTU)	480 nm	7	0.003–0.9 ng mL^{-1}	0.003 ng mL^{-1}

40	2-(5-Bromo-2-oxoindolin-3-ylidene) hydrazine carbothioamide	510 nm	4.0–6.0	2538 L mol^{-1} cm^{-1} 1.0–8.0 μg cm^{-3}	25.0 ng cm^{-2}
41	2,6-Dithiol-4-methylphenol (DTMP)	629–635 nm	6.5–8.1	0.05–3.6 g mL^{-1}	8.6–8.8 ng mL^{-1}
Chapter 6					
1	CAS (chrome azurol S)	605 nm		5–40 and 40–200 g L^{-1}	
2	CAS and CTMAB		5.7	1.01 × 10^{5} L mol^{-1} cm^{-1}	
3	Chrome azurol S (CAS)	610 nm		7.93 × 10^{4} L mol^{-1} cm^{-1}	
4	Chrome azurol S	590 nm	5.0–8.0	5.16 × 10^{4} L mol^{-1} cm^{-1}	
5	CAS	618 nm		6.62 × 10^{5} L mol^{-1} cm^{-1}	
6	2-(4-Chloro-2-phosphonophenylazo)-7-(2,6-dibromo-4-chlorophenylazo)-1,8-dihydroxy – 3,6-naphthalene disulfonic acid (CPA-DBC)	606 nm	4.7	2.3 × 10^{4} L mol^{-1} cm^{-1}	
7	2,7-Bi(5-carboxy-1,3,4-triazole)-1-amino-8-naphthol -3,6-disulfonic acid, BCTZAHA)	540 nm	10	0.001–0.04 μg mL^{-1}	
8	2-Aminocyclopentene-1-dithiocarboxylic acid	462 nm	2.8–3.3	2.85 × 10^{5} L mol^{-1} cm^{-1} 0.1–16.0 μg L^{-1}	
9	2-Aminocyclopentene-1-dithiocarboxylic acid	462 nm	2.8–3.3	2.85 × 10^{5} L mol^{-1} cm^{-1}	
10	Calconcarboxylic acid	540 nm		0–3.0 g/25 mL	
11	BCA (2,2′-biquinoline-4,4′-dicarboxylic acid disodium salt)	562 nm	11	7.72 × 10^{3} L mol^{-1} cm^{-1}	
12	Alizarin red S	540 nm	9.2	2.00 × 10^{4} L mol^{-1} cm^{-1}	

(continued)

Table 1 (continued)

S.no./ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
13	Alizarin red S	578 nm	5	450–15,000 ng mL^{-1}	
14	Alizarin red S	Pair of absorbance is 546 and 484 nm	5.5	0.317–7.62 µg mL^{-1}	
15	Eriochrome cyanine R	590–595 nm		8.92×10^4 L mol^{-1} cm^{-1} and 9.70×10^4 L mol^{-1} cm^{-1}	
16	Tetramethylthiuram disulfide	430 nm	4.2–7.5	2.96×10^4 L mol^{-1} cm^{-1}	
17	2,7-Bi(5-carboxy-1,3,4-triazolylazo)-chromotropic acid (BCTZACA)	570 nm	5	4.58×10^4 L mol^{-1} cm^{-1}	
18	1-(2-Metoxiphenylamin)-3-metoksipropanthiol-2 (MPAMPT)	605 nm	5.4–6.8	4.32×10^4 dm^3 mol^{-1} cm^{-1} 16 µg mL^{-1}	1.48 ng cm^{-2}
Chapter 7					
1	5-Imiono-l-phenyl-3-ethyl-2-imidazolidinone			2.1×10^4 L mol^{-1} cm^{-1}	
2	Thiols such as cysteamine, L-cysteine, 2-mercaptoethanol and 2-mercaptopropionic acid		3–8	$0–1.1 \times 10^{-6}$ M	2.5 ng cm^{-3}
3	Cyanide ion	238 nm		0.55–5.8 µg mL^{-1}	
4	ARS-BOP3	526 nm	8.5	1.77×10^4 L mol^{-1} cm^{-1}	

5	Chlorophosphonazo-III (CPA-III)	610 nm	5	2.75×10^4 L mol^{-1} cm^{-1}	
6	Potassium Pr xanthate (KPX)	400 nm	6	1.0–16.0 μg mL^{-1}	12 mg mL^{-1}
7	Pyrophosphate	240 nm	9	2–50 ppm	
8	Cyanex 301 [bis(2,4,4-trimethylpentyl) dithiophosphinic acid]	440 nm		1.41×10^4 L mol^{-1} cm^{-1}	
9	4,4′-Tetraethyldiaminothiobenzophenone	500 nm	4.5	0–20 μg/25 mL	
10	4,5-Dimercapto-1,3-dithiol-2-thionate (DMIT)	430 nm	7.0	9.06×10^4 L mol^{-1} cm^{-1} 5.58×10^{-6}–1.67×10^{-5} mol L^{-1}	
11	Michler's thioketone (TMK)	500 nm	4.6	0–15 μg/25 mL	
12	Brilliant blue dye (RAWL)	626 nm	7.2		
13	2-(2-Imidazolylazo)-5-dimethylamino-HOBz(IZDBA)	600 nm	4	3.62×10^4 L mol^{-1} cm^{-1}	
14	Bromo-sulfonazo III (Br-SAZIII)	616.8 nm		3.3×10^5 L mol^{-1} cm^{-1}	
15	Potassium chlorate and hydrogen peroxide	624 nm	4.2	0.040–1.50 g/25 mL	
16	3,5-Bis(3-hydroxy-2-pyridylaminodiazo)-2,4,6-tribromobenzoic acid (BHPADTBBA)	570 nm	10	2.18×10^5 L mol^{-1} cm^{-1}	
17	7-Iodo-8-hydroxyquinoline-5-sulfonic acid	380 nm	5	7.35×10^3 L mol^{-1} cm^{-1}	
18	Losartan	530 nm		10–50 μg mL^{-1}	
19	Cefixime	450–510 nm	4.8	3.42×10^3 L mol^{-1} cm^{-1}	

Table 2: List of spectrophotometric reagents for the determination of iron.

S.no./ ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
Chapter 1					
1	2,6-Dithiol-4-methylphenol (DTMP)	550–556 nm	4.2–5.3	0.4–20 mg mL^{-1}	9.3–9.7 ng mL^{-1}
2	Polyphenol from green tea	570 nm	4.8	1.0×10^{-5} – 5.0×10^{-4} mol L^{-1}	
3	5-Bromosalicylidene-2-aminothiophenol (BSATP)		8.2	16,460 L mol^{-1} cm^{-1} , 1–10 ppm	0.01639 mg cm^{-2}
4	Green tea polyphenols	570 nm		4×10^{-5}–4×10^{-4} mol L^{-1}	
5	2,2^1-Ethylenebis(nitrilo-methylidene)diphenol (H_2EBNMDP)	383 nm	4	2.29×10^4 L mol^{-1} cm^{-1}	
6	5-[(Phenyliminoethyl)]-3-hydroxyphenol [PIEHP]	430 nm	3	0.726×10^4 L mol^{-1} cm^{-1}	0.07692 mg cm^{-2}
7	2,2′-Dipyridyl 1,10-Phenanthroline 1,10-Phenanthroline (phen)	520 nm 510 nm	4.5–5.5 4.5–5.5	$6.1 \pm 0.2 \times 10^3$ L mol^{-1} cm^{-1} $(6.9 \pm 0.3) \times 10^3$ L mol^{-1} cm^{-1}	~8 ppb
8	Tetrabromophenolphthalein Et ester (TBPE)	606 nm	6.5		
9	*p*-Aminophenylfluorone (APF)	620 nm		1–10 µg/10 mL	
10	9-(4-Carboxyphenyl)-2,3,7-trihydroxyl-6-fluorone	640 nm	6.5	1.06×10^5 L mol^{-1} cm^{-1}	3.9 ng cm^{-2}
11	Phenylfluorone	620 nm		9.355×10^4 L mol^{-1} cm^{-1} 0–16 µg/25 mL	

12	3,5,7,2′,4′-Pentahydroxyflavone (morin)	300–450 nm		0.83–27.00 mg L^{-1}	
13	Morin (3,5,7,2′,4′-pentahydroxy flavone)	424 nm	3.7	0.04–1.5 μg mL^{-1}	0.03 μg mL^{-1}
14	5-Sulfosalicylic acid Tiron	490 nm 670 nm		1.714×10^3dm^3 mol^{-1} cm^{-1} 1.870×10^3 dm^3 mol^{-1} cm^{-1}	32.5845 ng cm^{-2} 29.8553 ng cm^{-2}
15	Sulfosalicylic acid		1.8–3.0	1.70×10^3 L mol^{-1} cm^{-1} 4.00–28.00 mg L^{-1}	
16	Catechol and *p*-nitroaniline	540 nm		9.379×10^2 L mol^{-1} cm^{-1}	0.0595 mg cm^{-2}
17	Catechol and *m*-nitroaniline Catechol and *p*-anisidine Catechol and *p*-chloroaniline	540 nm 565 nm 545 nm		8.8032×10^2 L mol^{-1} cm^{-1} 1.7×10^3 L mol^{-1} cm^{-1} 1.6×10^3 L mol^{-1} cm^{-1}	0.0634 mg cm^{-2} 0.033 mg mL^{-1} 0.035 mg mL^{-1}
18	2-Thenoyltrifluoroacetone (TTA)	450–600 nm	4.8	95–1,070 mg L^{-1} (Fe II) and 31–350 mg L^{-1} (Fe III)	25 mg L^{-1} (Fe II), 8 mg L^{-1} (Fe III)
19	2,6-Dihydroxy benzoic acid (2,6-DHB)	560 nm	3	0.28–20 μg mL^{-1}	1.5×10^{-6} M
20	Chlortetracycline	435 nm	8	0.5–20.0 μg mL^{-1}	0.10 μg mL^{-1}
21	1,2-Dimethyl-3-hydroxypyrid-4-one (Hdmp)	450 nm	8.5	4.4 L mol^{-1} cm^{-1}	
22	Gallic acid (GA)	600 nm	5	0.2–15.0 μg mL^{-1}	0.07 μg mL^{-1}
23	Pyrogallol red	648 nm	5	3.24×10^4 L mol^{-1} cm^{-1} 0 ~ 25 mg/25 mL	
24	Rutin	620 nm		4.40×10^4 L mol^{-1} cm^{-1} 0–20 mg/25 mL	
25	Piperonal fluorine (PIF)	640 nm	9.6–10.3	0–25 ng mL^{-1}	

(continued)

Table 2 (continued)

S.no./ ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
26	Quercetin (Qu)	430 nm	4.05	2.0×10^{-5}–1.2×10^{-4} mol L^{-1}	2.0×10^{-5} mol L^{-1}
27	Resorcylic acid (2,4-dihydroxybenzoic acid, DHB)	520 nm		0.8×10^{4} L mol^{-1} cm^{-1}	
Chapter 2					
1	2,4,6-Tri(2′-pyridyl)-l,3,5-triazine (TPTZ)			5.0–100.0 mg L^{-1}	1.2 mg L^{-1}
2	1,10-Phenanthroline (1,10-phen) 1,10-Phenanthroline	508 nm 511 nm	3.0–10.0	1.11 × 104 M^{-1} cm^{-1} 1.21 × 104 L mol^{-1} cm^{-1}	
3	3-(2-Pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine (FST)	536.0 nm	4.75	21–200 mg L^{-1}	1.3 mg L^{-1}
4	3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT)			2.4×10^{4} L mol^{-1} cm^{-1} 0–0.3 mg L^{-1}	0.96 ng mL^{-1}
5	1,10-Phenanthroline		4.2	0.14–2.23 mg mL^{-1}	5.1 ng mL^{-1}
6	1,10-Phenanthroline (*o*-phen)	535 nm	5	0.1–2.0 mg mL^{-1}	
7	1,10-Phenanthroline (phen)	510 nm		0.07–1.43 mg L^{-1}	16 mg L^{-1}
8	4,7-Diphenyl-1,10-bathophenanthroline (DPBP)-eosin	542 nm	3.6–5.2	2.23 × 105 L mol^{-1} cm^{-1}	0.0025 ng cm^{-2} 0.076 and 0.045 mg mL^{-1}
9	Phenanthroline	515 nm		0.040–1.0 mg L^{-1}	3.09 and 1.55 mg L^{-1}

10	2,2′-Dipyridyl	520 nm	4.5–5.5	6.1 ± 0.2) × 10^3 L mol^{-1} cm^{-1}	
11	Phenanthrolinates	490 nm	5	0.2–5.6 mg L^{-1}	
12	1,10-Phenanthroline (phen)	606 nm	6.5		~8 ppb
13	1,10-Phenanthroline	511 nm	3.0–10.0	1.21 × 104 L mol^{-1} cm^{-1}	
14	1,10-Phenanthroline			0.10–8.00 mg mL^{-1}	
15	1,10-Phenanthroline	512 nm		0.25–5.0 mg L^{-1}	18 mg L^{-1}
16	4,7-Diphenyl-1,10-phenanthroline	534 nm	4	2 × 10^4 L mol^{-1} cm^{-1} 0–50 mg/25 mL	0.0025 mg cm^{-2}
17	5-Nitro-6-amino-1,10-phenanthroline (NAF)	520 nm	4	0.1–0.4 µg mL^{-1}	
18	Phenanthroline (phen)	515 nm		1.23 × 10^4 L mol^{-1} cm^{-1}	
19	Diphenylcarbazide and 1,10-phenanthroline		43,984	0.20–8.00	0.05 mg mL^{-1}
20	1,10-Phenanthroline	508 nm	5.8	1.1 × 104 L mol^{-1} cm^{-1}	
21	2,2′-Bipyridine	520 nm	3.5–6.0	5.0–500 mg L^{-1}	1.3 mg L^{-1}
22	2, 2′-Bipyridine	518 nm		1–60 ng mL^{-1}	
23	2,2′-Dipyridyl	520 nm	4.5–5.5	6.1 ± 0.2) × 10^3 L mol^{-1} cm^{-1}	
24	1,10-Phenanthroline	511 nm	3.0–10.0	1.21 × 10^4 L mol^{-1} cm^{-1}	
25	2,2′-Bipyridyl complex	534 nm		0.5–20 µg mL^{-1}	0.11 µg mL^{-1}
26	2,2′-Dipyridine	523 nm		8.7 × 10^3 M^{-1} cm^{-1}	

(continued)

Table 2 (continued)

S.no./ ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
27	Methyl green oxidized by potassium per-iodate	458 nm		20–120 mg L^{-1}	8.39 mg L^{-1}
28	Ferrozine				
29	*N*,*N*-Dimethyl-*p*-phenylenediaminedihydrochloride (DPD)	514 nm			0.40 nmol L^{-1}
30	Catechol and *p*-nitroaniline	540 nm		9.379×10^2 L mol^{-1} cm^{-1}	0.0595 mg cm^{-2}
31	Catechol and *p*-anisidine	565 nm		1.7×10^3 L mol^{-1} cm^{-1}	0.033 mg mL^{-1}
32	Diphenylamine-4-sulfonic acid sodium salt (DPA-4-SA)	410 nm	5.5	5 and 200 µg L^{-1}	1 µg L^{-1}
33	Variamine blue	560 nm	5	5.4–130 ng mL^{-1}	
34	Iminodibenzyl (IDB)	620 nm		0.2–4.8 mg mL^{-1}	
35	*N*,*N*-Dodecyltrimethylammoniumbromide (DTAB)		3.5	3.8×10^3 L mol^{-1} cm^{-1}	
36	Desipramine hydrochloride (DPH)	630 nm		3.288×10^3 L mol^{-1} cm^{-1}	0.0130 mg cm^{-2}
37	Cetylpyridinium chloride (CPC)	580 nm		1–100 ng mL^{-1}	0.52 ng mL^{-1}
38	8-Aminoquinaldine (AQ)	600 nm	5.5	1.157×10^4 L mol^{-1} cm^{-1}	
39	1,10-Phenanthroline			0.10–8.00 mg mL^{-1}	
40	*meso*-Tetra(4-methoxy-4-sulfonophenyl)porphyrin (*p*-OCH_3 $TPPS_4$)	446 nm	3.5–5.5	2.0×10^4 L mol^{-1} cm^{-1}	

1	[Methyl phenyl thiazolyl azo]-3-methyl-4-methoxy-2-naphthol (MPTAN)			0.05–10 ppm	0.016 ppm
2	3-5-(3-Methyl-1-phenylpyrazolazo)-1-nitroso-2-naphthol (MPANN)	454 nm	6	1.7982×10^4 L mol^{-1} cm^{-1}	0.01569 µg mL^{-1}
3	1-Nitroso-2-naphthol	443.6 nm		1.6×10^4 L mol^{-1} cm^{-1}	5.8 ng cm^{-2}
4	Disodium-1-nitroso-2-naphthol-3,6-disulfonate (nitroso-R salt)	720 nm	5	0.05–4.0 mg mL^{-1}	
5	1-(2-Pyridyl-azo)-2-naphthol (PAN)	768 nm		8.936×10^4 L mol^{-1} cm^{-1}	
6	1-(2-Pyridylazo)-2-naphthol (PAN)	600–850 nm	5		0.07 ng mL^{-1}
7	1-(2-Pyridylazo)-2-naphthol (PAN)			1.51×10^4 L mol^{-1} cm^{-1}	
8	1-(2-Pyridylazo)-2-naphthol (PAN)		4	0.30–5.00 mg mL^{-1}	
9	1-Nitroso-2-naphthol	420 nm	4	2.57×104 L mol^{-1} cm^{-1}	0.06 µg mL^{-1}
10	2,2′-Ethylenebis(nitrilomethylidene)diphenol (Salen)	366 nm Fe(II), 383 nm Fe(III)	8 Fe(II) 4 Fe(III)	1.84×10^4 Fe(II), 2.29×10^4 Fe(III) L mol^{-1} cm^{-1}	
11	2-Aminophenol (OAP)	402 nm	Acidic	6.65×10^5 L mol^{-1} cm^{-1}	5 ng cm^{-2}
12	*N*-(*o*-Methoxybenzaldehyde)-2-aminophenol (NOMBAP)	470 nm	5.6–6.8	3166 L mol^{-1} cm^{-1}	0.0176 mg cm^{-2}
13	2-(5-Bromo-pyridylazo)-5-diethylaminophenol (5-Br-PADAP)	744 nm		3.09×10^5 L mol^{-1} cm^{-1}	
14	5-Br-PADAP			4.48×10^4 L mol^{-1} cm^{-1}	
15	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP)	749 nm	3.6–6.4	3.1×10^4 L mol^{-1} cm^{-1}	
16	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol	560 nm	9.5	7.32×10^4 L mol^{-1} cm^{-1}	

(continued)

Table 2 (continued)

S.no./ ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
17	2-Hydroxy-3-methoxybenzaldehydeisonicotinoyl hydrazone (HMBAINH)	442 nm	5	0.14–1.396 mg mL^{-1}	0.013 mg mL^{-1}
18	2,2′-Dipyridylketone picolinoylhydrazone (DPKPH)	700 nm	4.9		0.005 mg L^{-1}
19	2-Hydroxy-3-methoxy benzaldehyde-*p*-hydroxy benzoic hydrazone (HMBAHBH)	390 nm	3	1.87 × 10^{4} L mol^{-1} cm^{-1}	2.9 × 10^{-3} mg cm^{-2}
20	2-Hydroxy-1-naphthaldehyde-*p*-hydroxybenzoic hydrazone (HNAHBH)	405 nm		5.6 × 10^{4} L mol^{-1} cm^{-1}	
21	Diacetylmonoximebenzoyl hydrazone	360 nm	6.25	1.25 × 10^{4} L mol^{-1} cm^{-1}	0.0045 mg cm^{-2}
22	2,4-Dihydroxybenzaldehydeiso nicotinoylhydrazone (2,4-DHBINH)	400 nm	3	1.75 ± 0.025 × 10^{4} L mol^{-1} cm^{-1}	0.0034 mg cm^{-2}
23	Di-2-pyridyl ketone salicyloylhydrazone (DPKSH)	375 nm		4.21 × 10^{4} L mol^{-1} cm^{-1} [Fe (II)]	0.09 μM [Fe(II)]
24	2-Hydroxy-1-naphthaldehyde benzoylhydrazone (OHNABH)	540 nm	44,015	0.14–4.20 mg mL^{-1}	
25	Pyridine-2-amidoxime	360–700 nm		2.0–100 mg mL^{-1} [Fe(II)], 3.0–200 mg mL^{-1} [Fe(III)]	0.4 mg L^{-1} [Fe(II)], 0.8 mg L^{-1} [Fe(III)]
26	*p*-Bromophenylazo-bis-acetoxime	370 nm	3.5–4.5	1030 dm^{3} mol^{-1} cm^{-1}	54.22 ng cm^{-2}
27	*o*-Carboxy phenylazo-bis-acetoxime	376 nm	2.8–4.0	2.446 dm^{3} mol^{-1} cm^{-1}	22.83 ng cm^{-2}

28	Phenylazo-bis-acetoxime	362 nm		1.852×10^{3} dm^{3} mol^{-1} cm^{-1}	30.15 ng cm^{-2}
29	5-Bromosalicylaldoxime (5-BSO)	460 nm	7.2	0.018×10^{4} L mol^{-1} cm^{-1}	3.2×10^{-6} mg cm^{-2}
30	*p*-Sulfonamidophenylazobis acetoxime	405 nm	2.5–3.0	1.853×10^{3} dm^{3} mol^{-1} cm^{-1}	30.14 ng cm^{-2}
31	8-Hydroxyquinoline	359 nm	43,862	1–14 mg mL^{-1}	
32	5-(4-Carboxy-phenylazo)-8-hydroxyquinoline (5-CPAHQ)	448 nm	4.2–5.6	4.14×10^{4} L mol^{-1} cm^{-1}	
33	Pyridine 2,5-dicarboxylic acid	492 nm	4.0–7.0	1.55×10^{2} L mol^{-1} cm^{-1}	
34	PAR, i.e., 4-(2-pyridylazo) resorcinol		8.1	0.3–1.1 ppm	
35	Acetophenone 2′,4′-dihydroxy semicarbazone [A24DHS]	350 nm	3.4	3,899.2 L mol^{-1} cm^{-1}	0.0288 mg cm^{-2}
36	*N*-Benzoyl-*N*-phenylhydroxylamine (BPHA)		4.5		2.5 mg L^{-1}
37	KSCN solution and Et rhodamine B	620 nm		1.08×10^{5} L mol^{-1} cm^{-1}	
38	3-Hydroxy benzyl aminobenzoic acid	480 nm	5		
39	3-Hydroxy3-*m*-tolyl-1-*p*-chlorophenyltriazene	397 nm	3.0–4.0	$1.0\text{–}5.0 \times 10^{5}$ L mol^{-1} cm^{-1}	9.466 ng cm^{-2}
40	*N*-(*o*-Hydroxybenzylidene)pyridine-2-amine (NOHBPA)	530 nm		4469.27 L mol^{-1} cm^{-1}	0.0125 mg cm^{-2}
41	5-(4-Nitrophenyl azo) salicylic acid (NPAS)	545 nm		2.81×10^{4} L mol^{-1} cm^{-1}	
42	Dibromo-*p*-nitro-chlorophosphonazo	610 nm		1.63×10^{4} L mol^{-1} cm^{-1}	
43	Catechol and *p*-anisidine	565 nm		1.7×10^{3} L mol^{-1} cm^{-1}	0.033 mg mL^{-1}
44	Methyl red	522 nm		0.4–2.0 mg mL^{-1}	0.07 mg mL^{-1}
45	Desipramine hydrochloride (DPH)	630 nm		3.288×10^{3} L mol^{-1} cm^{-1}	0.0130 mg cm^{-2}
46	1-Phenyl-3-methyl-4-stearoyl-5-pyrazolone			0.5–10 mg	0.1 mg

(continued)

Table 2 (continued)

S.no./ ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
47	Diphenylcarbazone (HDcO)	500 nm	6	0.4×10^4 L mol^{-1} cm^{-1}	
48	Piroxicam (PR)	510 nm	5	1.82×10^4 L mol^{-1} cm^{-1}	17.32 ng cm^{-2}
49	*p*-Methylisonitrosoacetophenone (MINAP)	650 nm	7.5–8.5	6.515×10^3 L mol^{-1} cm^{-1}	
59	Diformylhydrazine (DFH)	470 nm	7.3–9.3	0.3258×10^4–0.3351×10^4 L mol^{-1} cm^{-1}	0.0168 mg cm^{-2}
51	Diphenylcarbazide and 1,10-phenanthroline		43,984	0.20–8.00	0.05 mg mL^{-1}
52	*N*,*N′*-Bis(2-hydroxy-5-bromo-benzyl)1,2 diaminopropane (HBDAP)	500 nm	3.75	9×10^3 L mol^{-1} cm^{-1} 0.056–1.68 mg L^{-1}	1.23×10^{-7} M
53	EDTA	420 nm		87.4 L mol^{-1} cm^{-1}	
54	Diantipyrylphenylethylenemethane	540 nm		1.44×10^6 L mol^{-1} cm^{-1}	
55	Chrome azurol S and 8-quinolinol	520 nm		2.777×10^5 L mol^{-1} cm^{-1}	
56	*N*-2-Hydroxyphenylamino-*N*-2-hydroxy-1-cyclobutene-3,4-dione	455 nm		1.7×10^3 L mol^{-1} cm^{-1}	
57	4-(2-Pyridylazo)pyrocatechol (PAPC)	494 nm	6.0–7.5	4.96×10^4 L mol^{-1} cm^{-1}	

Chapter 4

1	2,2′-Azinobis(3-ethylbenzothiazoline-6-sulfonate) (ABTS)	415 nm			25.5 mg L
2	4,7-Diphenyl-1,10-bathophenanthroline (DPBP)-eosin	542 nm		2.23 × 10 L mol cm	0.0025 ng cm
3	Solid-phase extraction	644 nm		1.09 × 10 L mol cm	0.51 ng cm
4	2-Amino-2′,5-dichlorobenzophenone (MCB) or 2-Amino-5-chloro-2′-fluorobenzophenone (MFB)	520 nm		0.31–1.2121 mg mL^{-1} or 0.42–1.41 mg mL^{-1}	
5	SCN(I) and rhodamine B	620 nm		3.38 × 10 L mol cm	
6	Acetophenone 2′,5′-dihydroxy thiosemicarbazone (ADHTS)	430 nm	3.6	646.06 L mol cm	0.0869 mg cm^{-2}
7	Chromazurol S (CAS) in the presence of tetradecyltrimethylammonium bromide (TTA) and Triton X-100 (TX100)	650 nm		1.12 × 10^{5} L mol^{-1} cm^{-1}	
8	Phenanthroline	510 nm		2.10 × 10^{4} L mol^{-1} cm^{-1}	
9	Dibromo-*p*-sulfonic acid-arsenazo (DBS-arsenazo, DBS-ASA)	520 nm		0.20–6.0 ng mL^{-1}	0.17 ng mL^{-1}
10	*p*-Acetylarsenazo (ASApA)	540 nm		0.10–4.0 ng mL^{-1}	0.031 ng mL^{-1}
11	Dibromo-*p*-chloroarsenazo	518 nm		0.2–6.0 ng mL^{-1}	0.025 ng mL^{-1}
12	Picolinaldehyde-4-phenyl-3-thiosemicarbazone (PAPT)	406 nm	3	4.6 × 10^{4} L mol^{-1} cm^{-1}	0.013 μg mL^{-1}
13	Methylthymol blue	440 nm			0.6 ng mL^{-1}
14	4-(2-Thiazolylazo) resorcinol	733 nm		6.98 × 10^{4} L mol^{-1} cm^{-1}	
15	1,2-Dihydroxybenzene-3,5-disulfonic acid (Tiron)	667 nm	1.7		
16	Thiocyanate (SCN^{-})	480 nm		2.9565 × 10^{4} L mol^{-1} cm^{-1}	0.002 mg cm^{-2}
17	SCN	480 nm		2.60 × 10^{5} L mol^{-1} cm^{-1}	

(continued)

Table 2 (continued)

S.no./ ref. no.	Name of analytical reagent	Absorption maximum (λ_{max})	pH	Molar absorptivity	Sandell's sensitivity
18	8-Hydroxyquinadine	595 nm		7.82×10^3 L mol^{-1} cm^{-1}	
19	Potassium isobutylxanthate (KIBX)	378 nm	5	2.58×10^3 dm^3 mol^{-1} cm^{-1}	
20	Thiocyanate with cetyltrimethylammonium (CTMA)	473 nm		3.55×10^4 L mol^{-1} cm^{-1}	
21	PPT (pyridoxal-4-phenyl-3-thiosemicarbazone)	440 nm	2.5–6.5	0.5–8.0 mg mL^{-1}	
22	8-Hydroxyquinaldine	600 nm	8	7.17×10^3 L mol^{-1} cm^{-1}	
23	5,5-Dimethylcyclohexane-1,2,3-trione 1,2-dioxime 3-thiosemicarbazone (DCDT)	550 nm			115 ng mL^{-1}
24	Norfloxacin (NRF)	435 nm		0.2–1.4 mg mL^{-1}	0.01 mg mL^{-1}
25	Tiron	635 nm		0.002–0.026 M	
26	5-Bromosalicylaldehyde thiosemicarbazone (5-BSAT)	385 nm	5.0–6.0	1.72×10^4 L mol^{-1} cm^{-1}	0.032 mg cm^{-2}
27	*N*-(*o*-Methyl)phenyl-*N*-hydroxy-*N′*-(*o*-methyl) phenylbenzamidine hydrochloride	470 nm		1.1480×10^4 L mol $^{-1}$ cm^{-1}	0.0047 cm^{-2}
28	PAN-S	756 nm	4.5	1.72×10^4 L mol^{-1} cm^{-1}	
29	2-Aminocyclo-1-pentenedithiocarboxylic acid (ACDA)	650 nm		8.46×10^3 L mol^{-1} cm^{-1}	0.11 µg mL^{-1}
30	Zincon		4.74	0.0–2.0 ng mL^{-1}	2.2×10^{-11} g mL^{-1}
31	*N*,*N′*-Bis(2-hydroxy-5-bromo-benzyl)-1,2-diamino-propane (HBDAP)		43,985	0.056–1.68 mg L^{-1}	~1.23×10^{-7} M
32	Sulfosalicylic acid		1.8–3.0	1.70×10^3 L mol^{-1} cm^{-1}	

Section A

Chapter 1
Analytical reagents having oxygen (O) as donor atom

1.1 Naphthols

1.1.1 1-(2-Imidazolylazo)-2-naphthol-4-sulfonic acid

Pan Fuyou et al. [1] have described spectrophotometric method for the detection of trace Cu in Mg alloys and Fe ores. For this 1-(2-imidazolylazo)-2-naphthol-4-sulfonic acid as a color reagent is used for the detection of Cu(II) in pH 3.0 solutions. The apparent molar absorptivity of the complex is 1.94×10^4 L mol^{-1} cm^{-1} at 530 nm. The 1:1 complex has an apparent stability constant of 6.96×10^6 and Beer's law is obeyed in the range of 0–0.8 μg Cu mL^{-1}.

1.1.2 1-(2-Pyridylazo)-2-naphthol

Agnihotri Narinder Kumar et al. [2] have reported a photometric method for trace analysis of Cu(II) with 1-(2-pyridylazo)-2-naphthol (PAN) in the presence of a neutral surfactant, Triton X-100 in normal and derivative modes. At 555 nm the molar absorptivity ($\mathcal{E}$) and Sandell's sensitivity (S) of PAN–Cu(II) complex is 5.21×10^4 L mol^{-1} cm^{-1} and 1.22 ng cm^{-2}, respectively. The detection limit of Cu(II) is 4.0 ng mL^{-1} and Beer's law is obeyed in the range 0.08–4.00 μg mL^{-1} of the analyte. Cu content of a number of alcoholic beverages, biological and standard alloy samples is reported using this method.

Li Rong et al. [3] have developed β-cyclodextrin polymer adsorbed resin phase spectrophotometry with PAN for determination of copper at the μg level in soybean and human hair. Cobalt, nickel, zinc and manganese, which form colored species with PAN in the resin phase, can be completely masked using a solution composed of phenanthroline (2.78×10^{-5} mol L^{-1}) and sodium hexametaphosphate (3.27×10^{-3} mol L^{-1}). The method can be used to determine copper in the presence of cobalt, nickel, zinc and magnesium.

Thakur Manisha et al. [4] have described a simple and sensitive field detection and spectrophotometric method for determination of Cu that is based on the formation of a red-colored species of Cu(II) with 1-[pyridyl-(2)-azo]-naphthol-(2) (PAN), TX-100 and *N*,*N*′-diphenylbenzamidine (DPBA) at pH range 7.8–9.4. The red-colored Cu(II)–PAN–(TX-100)–DPBA complex in $CHCl_3$ shows maximum absorbance at 520 nm with molar absorptivity value of 1.14×10^5 L mol^{-1} cm^{-1}. The detection limit of the method

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is 2 ng mL^{-1} organic phase. The system obeys Beer's law up to 0.6 μg Cu(II) mL^{-1} in organic solution. Most of the common metal ions generally found associated with Cu do not interfere. As reported by authors the repeatability of the method is checked by finding relative standard deviation (RSD, $n = 10$) value for solutions each containing 0.2 μg mL^{-1} of Cu(II), and the RSD value of the method is 1.5%. The validity of the method is found satisfactory for the determination of Cu in soil and airborne dust particulate samples.

Hejazi Leila et al. [5] have presented a novel, sensitive and simple spectrophotometric method for rapid extraction, pre-concentration and simultaneous determination of trace amounts of Co, Ni and Cu as their PAN complexes using polytetrafluoro ethylene filter as solid phase. The proposed method has been successfully applied by authors to the simultaneous determination of Co, Ni and Cu in tap and pit water samples.

Wang Airong et al. [6] have presented a spectrophotometric method for the determination of Cu^{+2} in H_2SO_4 medium anodizing liquor and PAN. Cu forms a stable complex with PAN in acid solution with a solubilizing and sensitizing agent Triton X-100 and gelatine as a protecting agent. The maximum absorption of the complex is 558 nm with apparent molar absorptivity of 2.25×10^4 L mol^{-1} cm^{-1}. The linear range of the method was 0–3.2 mg mL^{-1}, and the detection limit is 0.028 mg mL^{-1}. In this study, no interference was found in the presence of other coexisting ions as reported.

Karim-Nezhad Ghasem et al. [7] have developed multivariate calibration models (principal component regression (PCR) and partial least square (PLS)) for simultaneous determination of Fe(III) and Cu(II) with PAN. In this method AOT has been used as a micellizing agent, due to which spectrum of Fe(III)–PAN complex has been shifted to higher wavelength and the overlapping with Cu–PAN spectrum is decreased. It seems that this anionic surfactant enters the structure of the Fe–PAN complex to cause a shift in the absorption spectrum of it. The method has also been successfully applied to simultaneous determination of Cu and Fe in biological samples.

Karim-Nezhad Ghasem et al. [8] have developed a simple and selective derivative spectrophotometric for detection of copper and iron in human hair and serum samples. For this PAN in bis-2-Et hexyl sulfosuccinate (AOT) micellar solution has been used. In the presence of AOT, the absorption spectrum of Fe(III)–PAN complex shifts to higher wavelengths and the overlapping with Cu–PAN spectrum has been decreased under these conditions. In this condition, in ordinary spectrophotometry, Cu(II) has no interference in the detection of iron, but Fe(III) interfered in the detection of copper. In the first-order derivative mode the spectra of Cu(II)–PAN and Fe(III)–PAN complexes completely resolved together and can selectively detect them, as mentioned. The zero- and first-order derivative spectrophotometric calibration curves were drawn at working wavelengths of 558 and 580 nm for copper and 600 and 630 nm for iron. Molar absorptivity is found 1.82×10^4 and 2.75×10^4 L mol^{-1} cm^{-1}, respectively, for

Cu(II)–PAN and Fe(III)–PAN complexes. In derivative mode, the limits of detection (LOD) for Cu(II) and Fe(III) were 0.038 and 0.025 g mL^{-1}, respectively, as reported.

Afshan Soomro et al. [9] have reported a simple rapid new spectrophotometric method for the determination of copper at trace level using PAN in cationic micellar solution of cetyltrimethyl ammonium bromide (CTAB). By using this micellar system previous solvent extraction method can replaced, which reduces the cost and toxicity, while enhancing the sensitivity, selectivity and the molar absorptivity. At λ_{max} 559 nm the average molar absorption coefficient and Sandell's sensitivity is found to be 2.45×10^4 L mol^{-1} cm^{-1} and 2.6 ng cm^{-2}. Beer's law linear calibration graph is obtained over the concentration range from 0.12 to 5.0 µg mL^{-1} and the stoichiometric composition of the chelate is 1:2 (Cu:PAN). The developed method is successfully applied for the determination of copper from alloys and real samples as described by authors.

1.1.3 1-Nitroso-2-naphthol

Shar G. A. and Bhanger M. I [10] have reported a method for the spectrophotometric determination of Cu(II)-1-nitroso-2-naphthol complex in aqueous phase in the presence of Tween-40, non-ionic surfactant. The method obeys Beer's law in the concentration range of 0.25–2.0 mg mL^{-1}. The detection limit of Cu(II) is 0.25 mg mL^{-1}. The method has been used for the determination of copper in industrial waste samples, and the results are comparable with those by flame atomic absorption spectroscopy.

Abdollahi H. et al. [11] have presented a spectrophotometric method for the simultaneous determination of Fe, Co and Cu together in many natural samples by using the reagent 1-nitroso-2-naphthol that forms complexes with these metals in the presence of aqueous solution of non-ionic surfactant, Triton-X 100. For individual determinations, molar absorptivity and the limit of detection have been obtained. The total relative standard error for applying the method on synthetic samples is 2.02%. The proposed method has been successfully applied to the determinations of Fe, Co and Cu in several synthetic alloy solutions.

1.1.4 1-(2-Thiazolylazo)-2-naphtholin

Low Kah Hin et al. [12] have developed multivariate models for the simultaneous spectrophotometric determination of copper(II), nickel(II) and zinc(II) in water with chromogenic reagent 1-(2-thiazolylazo)-2-naphtholin in the presence of Triton X-100. PCR and PLS multivariate calibration approaches have been applied to overcome the drawback of spectral interferences. In this method there is no significant difference in analytical performance between PLS and PCR models. The root mean square error of prediction (RMSEP) using three components for Cu^{2+}, Ni^{2+} and Zn^{2+} was 0.018, 0.010, 0.011 ppm, respectively. High reliability is achieved when the proposed procedure is applied to simultaneous determination of Cu^{2+}, Ni^{2+} and Zn^{2+} in synthetic mixture and tap water.

Moradi R. et al. [13] have reported simultaneous spectrophotometric detection of mixtures using PLS modeling that is a powerful multivariate statistical tool. 1-(2-Thiazolylazo)-2-naphthol (TAN) has been used for simultaneous detection of copper and cobalt. The TAN complexes are quantitatively extended into dichloromethane and the resolution of the mixtures is accomplished by PLS. Orthogonal signal correction (OSC) is a suitable preprocessing method (based on constrained principal component analysis) for PLS calibration of mixtures without loss of prediction capacity using spectrophotometric method. In this study calibration model is based on absorption spectra in the 350–750 nm range for 25 different mixtures of copper and cobalt. For copper and cobalt calibration matrixes ranges are 1.0–300.0 and 1.0 –200 ng mL^{-1}, respectively. To check the prediction ability of the PLS and OSC-PLS models a series of synthetic solution containing different concentrations of copper and cobalt are used. The RMSEP for copper and cobalt with OSC and without OSC was 0.266 and 0.378, 0.513 and 0.643, respectively. The method can be successfully applied to the analysis of spiked water (river, tap and well) samples.

Bagherian, Ghadamalie et al. [14] have developed the H-point standard addition method (HPSAM) for the simultaneous determination of Cu(II) and Pd(II). In this technique, the complex is formed of Cu(II) and Pd(II) with 1-(2-thiazolylazo)-2-naphthol (TAN) at pH 2.2. As a micellizing agent sodium dodecyl sulfate (SDS) has been used that improves the sensitivity and selectivity of the method. In an acidic medium Cu(II) and Pd(II) can be determined in the concentration ranges of 0.04–3.40 and 0.12–6.0 µg mL^{-1}, respectively, with satisfactory accuracy and precision. The proposed method has been used for the simultaneous determination of Cu(II) and Pd(II) in water and various synthetic alloy samples with different concentration ratios of Cu(II) and Pd(II) with good accuracy and precision, as reported by authors.

1.1.5 2,7-Bi(5-carboxy-1,3,4-triazole)-1-amino-8-naphthol-3,6-disulfonic acid (BCTZAHA)

Ge Changhua et al. [15] have reported a catalytic kinetic spectrophotometric determination of trace copper that is based on the linear relationship between fading reaction extent and the content of copper(II) in certain range. The fading reaction and kinetic condition between copper(II) and 2,7-bi (5-carboxy-1,3,4-triazolylazo) – H-acid (i.e., 2,7-bi(5-carboxy-1,3,4-triazole)-1-amino-8-naphthol-3,6-disulfonic acid, BCTZAHA) in the medium of $NH_3{\cdot}H_2O\text{-}NH_4Cl$ buffer solution at pH 10.0 are studied. The maximum absorption wavelength of fading system is at 540 nm. The calibration curve was linear for copper(II) in the range of 0.001–0.04 µg mL^{-1}. The detection limit has been found to be 1.32×10^{-11} g mL^{-1}. The method has been applied to the direct determination of trace copper in river water, tap water and well water samples without separation, as described.

1.2 Resorcinol

1.2.1 4-(2-Thiazolylazo)resorcinol

Zheng Lisheng et al. [16] have used 4-(2-thiazolylazo) resorcinol for spectrophotometric detection of Cu in Al alloy. The apparent molar absorptivity is 2.7×10^4 L mol^{-1} cm^{-1} at 520 nm. Beer's law is obeyed in the range of 0–80 μg/50 mL. The interferences of Al, Cr and Zn were eliminated by precipitation with NaOH. The interferences of iron and nickel were eliminated by using citric acid as masking agent.

1.2.2 4-(2-Pyridylazo)-resorcinol disodium salt dihydrate (PAR)

Zenki Michio et al. [17] have determined copper spectrophotometrically with 4-(2-pyridylazo)-resorcinol (PAR) in the presence of EDTA. The main reagent, PAR is successfully regenerated by the ligand-exchange reaction with EDTA, allowing the adoption of circulatory FIA and the repetitive determination of Cu(II). The proposed method has been applied for 100 repetitive determination of 2.5 ppm Cu(II) with only a 100 mL reservoir solution, as reported by authors.

Ramadan Abdul Aziz et al. [18] have developed method for spectrophotometric determination of Cu(II) with 4-(2-pyridylazo)-resorcinol disodium salt dihydrate (PAR) in aqueous phosphate buffer at pH = 10. In this method the authors suggest that two types of complexes are formed. The first is Cu(PAR) with absorption maxima at 510 nm, $\varepsilon = 4.0 \times 10^4$ L mol^{-1} cm^{-1}, and the second is $Cu(PAR)_2$ with absorption maxima in the range 495–500 nm, $\varepsilon = 7.62 \times 10^4$ and 7.12×10^4 L mol^{-1} cm^{-1} in the absence and presence of EDTA, respectively. The formation constant p*K* for the Cu $(PAR)_2$ complex is in the order of 1012. Beer's law is obeyed for Cu–PAR complex, ratio of 1:2, on the range of 1×10^{-6}–2.5×10^{-5} M and 0.1×10^{-6}–2.5×10^{-5} M with RSD 1.7 and 2.2% in the absence and presence of EDTA, respectively. Cr^{3+}, As^{3+}, Ni^{2+}, Co^{2+}, Fe^{3+} and Pb^{2+} do not cause any considerable interference, whereas, Hg^{2+}, Zn^{2+} and Cd^{2+} do not interfere in the presence of EDTA. As reported by the authors, this method can also applied for determination of Cu(II) in some pharmaceuticals in the presence of EDTA. The RSD did not exceed ±1.5%.

1.3 Phenylfluorones

1.3.1 *o*-Nitrophenylfluorone

Wang Hongmei et al. [19] have reported a method for the spectrophotometric determination of Cu with *o*-nitrophenylfluorone in the presence of cetylpyridinium bromide (CPB). Cu(II) and the reagent form a complex within the ratio of 1:1 in pH 5.6 HOAc–NaOAc buffer solution. The observed absorption maximum of the complex is at 570 nm having the apparent molar absorptivity 5.61×10^4 L mol^{-1} cm^{-1}, and Beer's law is obeyed at 0–7 µg/25 mL. As described by authors the method has been used in the determination of Cu in Al alloy with the RSD 0.007–0.014% and the recovery 96.0–97.7%.

1.3.2 *o*-Bromophenylfluorone

Yamaguchi Takako et al. [20] have used a novel chemical probe *o*-bromophenylfluorone (OBPF) for a simple, reliable and sensitive spectrophotometric determination of copper(II). OBPF, in the presence of poly(*N*-vinylpyrrolidone), forms a complex with copper(II). Beer's law is obeyed in the range of 8–160 ng mL^{-1}, at 570 nm with an apparent molar absorptivity 3.64×10^5 dm^3 mol^{-1} cm^{-1}. This method has also been applied to the recovery tests of copper(II) in human urine, bovine serum and tap water, with satisfactory results.

1.3.3 2,4-Dichloro-phenylfluorone

Huang Zhen-zhenet al. [21] have studied a color reaction of copper with 2,4-dichloro -phenylfluorone in the presence of CPB. Complex of copper with 2,4-dichloro-phenylfluorone was formed in the buffer solution of pH 5.82, showed the maximum absorption wavelength 602 nm. The apparent molar absorption coefficient has been found as 8.98×10^4 L mol^{-1} cm^{-1} which obeyed Beer's law in the range of 0–0.8 mg L^{-1}. This method can be successfully applied to the determination of copper in environmental water samples as mentioned.

1.3.4 5′-Nitrosalicylfluorone

Wu Lixiang et al. [22] have used 5′-nitrosalicylfluorone as chromogenic agent for spectrophotometric determination of trace copper(II) in oil sample. In this study buffer system KH_2PO_4–Na_2HPO_4 and micro-emulsion (cetyl tri-methyl ammonium bromide (CTMAB) + Bu alcohol + heptane + water) as medium is used. The maximum absorbance of the complex of copper with chromogenic agent is obtained at 570 nm. Beer's law is obeyed for copper(II) content in the range of 0–9 mg mL^{-1} with the apparent molar absorptivity of 1.4×10^5 L mol^{-1} cm^{-1}. The ascorbic acid is used by authors to mask Ni^{2+}, Fe^{3+}, Al^{3+} and so on in the determination. The method has been used successfully to the determination of copper(II) in Daqing crude oil and oil sand with the average recoveries of 99.6% and 97.8%, and the RSD of 0.74% and 0.84%, respectively.

1.3.5 Phenylfluorone (PF)

Caldas Luiz Fernando S. et al. [23] have reported a multivariate optimization of a spectrophotometric method for copper detection in sugarcane spirits, exploring the reaction of Cu(II) with phenylfluorone (PF) in the presence of cetylpyridinium chloride (CPC) and Triton X-100. The highest sensitivity is achieved when the pH is 8.0 and the PF and TX-100 concentration are 6.2×10^{-5} and 1.0×10^{-2} mol L^{-1}, respectively. The optimized method presented a limit of detection of 3.4 μg L^{-1} and a limit of quantification of 11 μg L^{-1} and was applied in the determination of Cu in 17 samples, as reported.

1.4 Picramazo

1.4.1 Picramazo[3-(2-hydroxy-3,5-dinitrophenyl)azo-4,5-dihydroxy-2,7-Naphthyldisulfonic acid]

Tan Xiufang et al. [24] have reported the synthesis of PM-picramazo and the conditions for spectrophotometric determination of copper. The results show that copper forms a blue-colored complex (1:1) in H_3PO_4 solution. The complex has a maximum absorption at 644 nm with a molar absorptivity of 2.65×10^4 L mol^{-1} cm^{-1}. Beer's law is obeyed for 0–16 μg of Cu in 25 mL solution. As described by authors the method is simple and selective and has been used for the determination of Cu in aluminum alloys with satisfactory results.

Zhong Guoxiu et al. [25] have developed a new spectrophotometric method for the determination of Cu which is based on the color reaction of Cu with picramazo chromotropic acid [3-(2-hydroxy-3,5-dinitrophenyl)azo-4,5-dihydroxy-2,7-naphthyldisulfonic acid] in 0.1 mol L^{-1} HCl medium. The observed maximum absorbance of the complex formed by Cu with picramazo-chromotropic acid is at 570 nm. Beer's law is obeyed at 2–70 mg/25 mL for Cu with apparent molar absorptivity of 1.36×10^4 L mol^{-1} cm^{-1}. The proposed method has also been applied by authors to the determination of Cu in Al alloy standard samples.

1.5 Phenol and bromo phenols

1.5.1 Sulfochlorophenol S (SCPS)

Xu Wenqing et al. [26] have reported that Cu^{2+} can react with sulfochlorophenol S (SCPS) at pH 4.5 to change the colored solution from red to blue. In this ß-correction spectrophotometric principle has been applied for the detection of trace Cu in wastewater. The sensitivity and accuracy were both higher than that by the ordinary spectrophotometry. In additional the complex's characteristic parameters can be detected accurately and easily. Results show that Beer's law is obeyed over the concentration range 0–0.80 mg L^{-1} copper with the detection limit to be equal to 0.03 mg L^{-1}. The analysis of samples resulted that recovery of copper is between 93.5% and 109% and the RSD less than 3.7%, as reported.

1.5.2 Bromophenol blue (BPB)

Liu Baosheng et al. [27] have used and reported that bromophenol blue (BPB) into the aqueous phase (pH = 10 having NaOH solution) added to Cu(biq)2BPB by trichloromethane and isoamyl alcohol (20:1) are extracted and then crystal violet (CV) with benzene solution BPB is floated by CV. The flotation is dissolved in ethanol and the absorbance of the solution measured at 590 nm. Because of the two dyes assistant effect the sensitivity is raised. The observed molar absorptivity is 1.45×10^5 L mol^{-1} cm^{-1}. Copper in the sample is separated first with trichloromethane and isoamyl alcohol by extracting the $Cu(biq)_2BPB$ complex, thus achieving a high selectivity. Beer's law is obeyed in the range of 0–0.4 mg L^{-1} with a RSD of 3.6%. The recoveries are 97.8–101.7% for 4.8×10^{-8} g mL^{-1} copper solution as reported by authors.

1.5.3 4-(2,6-Diamino-4-pyrimidylazo)phenol (DAPP)

Singh Ishwar et al. [28] have used, 4-(2,6-diamino-4-pyrimidylazo)phenol (DAPP) reagent for the spectrophotometric determination of copper(II). As authors reported, DAPP interacts with Cu(II) to give 1:2 violet complex. The Sandell's sensitivity of the color reaction is 1.1 ng cm^{-2} at 535 nm. Optical constants for the metal complex have been evaluated. Effect of foreign ions in the determination of Cu(II) ions has also been studied.

1.5.4 Chlorosulfophenol S (CS)

Hu Qiu-luan et al. [29] have reported a spectrophotometric method to detect micro-copper content in fruits and vegetables by means of its color reaction in the presence of chlorosulfophenol S (CS). The results showed that Cu(II) could react with CS to generate the blue complex in the Britton–Robinson buffer medium at a pH range of 2.5–5.0, which displayed a maximum absorption at 650 nm with 86 nm of bathochromic shift compared to CS itself. Beer's law is followed within the range of 0–20 g of Cu/10 mL, and the apparent mole absorptivity is 6.87×10^4 L mol^{-1} cm^{-1} (0.1% DBS), as reported.

1.5.5 2-(5-Nitro-2-pyridylazo)-5-[*N*-propyl-*N*-(3-sulfopropyl)amino]phenol (nitro-PAPS)

Zhou Tieli et al. [30] have established a simple and sensitive method for detection of serum copper by spectrophotometry. 2-(5-Nitro-2-pyridylazo)-5-[*N*-propyl-*N*-(3-sulfopropyl) amino] phenol (nitro-PAPS) is used as a coloring agent for serum copper in the presence of surfactants Tween–80 and Triton X–100, and the formed complex is measured by spectrophotometry. The maximum absorption wavelength of the complex is 570 nm, and the molar absorption coefficient was 7.95×10^4 L mol^{-1} cm^{-1}. The linearity of the method was up to 63.0 mol L^{-1}, and the recoveries ranged from 98.6% to 103.1%, as reported.

1.5.6 2,2′-{Ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol)

Kumar R. Kishore et al. [31] have developed a simple, sensitive and selective extractive spectrophotometric method for the detection of Cu(II) in various water and alloy samples using newly synthesized reagent 2,2′-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis (4-bromophenol). Cu(II) forms a green-colored complex with 2,2′-{ethane-1,2-diylbis [nitrilo-methylylidene]}bis(4-bromophenol) in acetate buffer medium (pH 6), which increases the sensitivity and complex is extracted into chloroform. Under optimum conditions the maximum absorption of the complex is measured at 602 nm. Beer's law is obeyed in the range of 0.4 to 5.0 g mL^{-1} of copper. The molar absorptivity and Sandell's sensitivity of the complex have been found to be 0.12×10^2 L mol^{-1} cm^{-1} and 2.438 g cm^{-2}, respectively. The detection limit is 0.044 g mL^{-1}, as reported.

1.5.7 2-[{4-(1,3-Benzoimidazole-2-yl)Ph}imino]-5-nitrophenols

Sonawane, Ratnamala P. et al. [32] have developed a spectrophotometric method for the determination of Cu(II). As extractive reagent 2-[{4-(1,3-benzoimidazole-2-yl) Ph}imino]-5-nitrophenols are used. The reagent forms a colored complex (pH-5.6) which can be quantitatively extracted into *n*-butanol. In the reported method Beer's law is obeyed over a range from 1 to 10 ppm. The molar absorptivity and Sandell's sensitivity calculated was 0.1899×10 L mol^{-1} cm^{-1} and 0.1315 μg cm^{-2}, respectively. The proposed method has been successfully applied to synthetic and commercial samples, as reported.

1.5.8 2,6-Dithiol-4-ethylphenol (DTEP)

Kuliev, Kerim A. et al. [33] have used 2,6-dithiol-4-ethylphenol (DTEP) as a photometric reagent for the extractive spectrophotometric determination of copper(II). The reagent DTEP forms complex with copper(II) in the presence hydrophobic amines that give instantaneous and stable blue color in the pH range 6.2–7.7. Beer's law is obeyed in the range of 0.05–4.0 μg mL^{-1} at 534–540 nm. The LOD is found to be 8.5–8.7 ng mL^{-1}. By equilibrium shift method, the stoichiometry of the complex is established as 1:1:1 (M:L:Am). The standard deviation and the coefficient of variance have also been presented. The results of the prescribed procedure applied for the determination of the micro amounts of Cu(II) in pharmaceutical, food and in plant samples have been presented by authors.

1.6 Miscellaneous reagents

1.6.1 Thenoyltrifluoroacetone (TTA)

Maheswari V. et al. [34] have described a sensitive spectrophotometric method for the detection of trace amount of Cu in alloys and pharmaceutical samples. The method is based on the detection of the ligand thenoyltrifluoroacetone (TTA) associated with Cu(II)–TTA complex, which is formed at pH of 7.50. The insoluble complex is collected over lead sulfate. The complex along with lead sulfate is solubilized using NaOAc at a pH of 5.50. The released TTA is coupled with diazonium chloride generated by the reaction of para-nitroaniline with Na nitrite to form an azo dye with an absorption maximum at 535 nm in aqueous medium. The color system obeys Beer's law over the 0–8 μg range of Cu. The coefficient of variation is 2.1% for 10 detections at the 6 μg level, as reported.

1.6.2 *p*-Anisidine

Murthy N. Krishna et al. [35] have described a spectrophotometric method for the determination of copper(II). Copper(II) solution gives an instantaneous stable pink-colored product with 0.2% aqueous *p*-anisidine in the presence of 0.03 N acetic acid. The wavelength of maximum absorption is 533 nm and obeys Beer's law up to 0.89408 g copper(II). It is also recommended as a spot test for copper(II).

1.6.3 Ascorbic acid

Majeed Abdul et al. [36] have detected Cu spectrophotometrically by using ascorbic acid as a chromogenic reagent. The complex formed in basic medium is measured for its absorbance at 340 nm. Interference for 23 cations and 9 anions was checked. Effect of pH, time, temperature, NH_3, reagent concentration and interference is reported in the method.

Khan M. Nasiruddin et al. [37] have developed a sensitive and selective kinetic-spectrophotometric method for the determination of trace amounts of Cu(II). It is based on the catalytic effect of Cu(II) ions on the oxidation of L-ascorbic acid by methylene blue in a strongly acidic medium. The working wavelength is 665 nm at $pH = 2.20$. The RSD for 0.4 mg mL^{-1} Cu(II) is 3.60% (6 determinations). The method has been satisfactorily applied to the determination of Cu(II) in electric copper wire samples and pharmaceutical products.

1.6.4 Sulfosalicylic acid

Endo Masatoshi et al. [38] have described a highly sensitive method for the determination of copper(II) based on preconcentration of copper(II)-*N*,*N*-diethyldithiocarbamate as a aggregate film. Traces of copper(II) have quantitatively collected into a thin film consisting of hexadecyltri-methylammonium chloride (cetyltrimethylammonium chloride) and sulfosalicylic acid. The film is easily detached from a membrane filter support and the copper(II) complex is determined spectrophotometrically by dissolving in DMF. The calibration graph is linear from 1.6×10^{-9} to 8×10^{-8} mol copper(II) in 14 mL of test solution. The RSD observed is 3.1% ($n = 5$) at 3×10^{-6} M copper(II). The membrane filter can be used repeatedly. The method has been applied to the determination of trace copper(II) added to river water.

1.6.5 Naphthazarin (5,8-dihydroxy-1,4-naphthoquinone; Naph)

Chaisuksant R et al. [39] have reported spectrophotometric determination of Cu using naphthazarin (5,8-dihydroxy-1,4-naphthoquinone; naph) as a chromogenic reagent. The Cu(II)–naphthazarin complex shows an absorption maximum at 330 nm with a molar absorptivity of 1.84×10^4 L mol^{-1} cm^{-1}. Beer's law is obeyed up to 4.5 ppm of Cu(II). The polynuclear complex has a mole ratio of Cu:Naph = 4:6 in a 50% (vol./vol.) ethanol/water medium containing 0.1 M ammonium acetate and 1.5% (wt./vol.) SDS. The method has been applied by authors for the determination of Cu(II) in alloy samples with satisfactory results.

1.6.6 Dextran

Norkus E. et al. [40] have proposed spectroscopic method of Cu(II) complex formation with dextran at 20 °C and showed that complexation of Cu(II) ions begins at pH over 7. The formation of Cu(II) hydroxyl complexes with deprotonated dextran monomer units has been observed at pH 8–12. The concentration of uncomplexed Cu(II) ions is determined in the solutions containing 5 mmol L^{-1} Cu(II) and 10–30 g L^{-1} dextran. Concentration of free Cu(II) ions diminishes by 14 orders of magnitude at pH 12.75 comparing with pH 7.

Savic I. et al. [41] have developed gel-permeation chromatography (GPC) and visible spectrophotometric methods and validated for quantitative analysis of complexes of copper(II) with the polysaccharides pullulan and dextran (active pharmaceutical compound in new anti-hypocupremical formulations). Linearity, precision, accuracy, specificity, and LOD and quantification (LOQ) have been detected in accordance with ICH Q2(R1) guidelines. GPC is performed isocratically with redistilled water as mobile phase at a flow rate of 1 mL min^{-1}. Visible spectrophotometry has been performed in water, using 640 nm for direct assay of the copper(II) complex with pullulan and dextran. The calculated F and t values at the 95% confidence level were less than the theoretical values, as reported.

1.6.7 Sodium pyrogallol-5-sulfonate (PS)

Mitic Snezana S. et al. [42] have developed a catalytic kinetic spectrophotometric method for the determination of trace amounts of Cu(II). The method is based on the oxidation of sodium pyrogallol-5-sulfonate (PS) by H_2O_2 in acidic medium. The reaction is monitored spectrophotometrically at 436.8 nm. The optimum operating conditions regarding concentration of reagents, pH and temperature have been established. The working curve is linear in the concentration range from 10 to 300 ng cm^{-3}. The interference of diverse ions has been studied. The proposed method has been successfully applied to the spectrophotometric determination of trace copper in water and milk.

1.6.8 Arabinogalactan

Grishchenko L. A. et al. [43] have developed a spectrophotometric method for the determination of copper(II) that was based on its complexation reaction with arabinogalactan. Copper ions form complexes with arabinogalactan in a wide pH range from 5.0 to 12.5. Arabinogalactan forms two complex species with copper metal. The composition and formation constant of the complex formed at pH lower than 10.8 have been determined.

1.6.9 Hydroquinone

Jian Tie-zhu et al. [44] have described a spectrophotometric method with reverse FIA catalytic kinetics which has been developed for the detection of trace copper in sea water. This method is based on the obvious catalytic effect of copper on the oxidation of hydroquinone by hydrogen peroxide in the slightly alkaline solution. The quinone produced is detected by spectrophotometry at 500 nm by authors. Under the optimum condition, the good linearity of a standard calibration was obtained over the ranges of 0–40 g L^{-1} of copper, and the relative coefficient was 0.9993, as reported.

1.6.10 *N*,*N*-Diethyl-*p*-phenylenediamine and thymoquinone

Suizu Tomoki et al. [45] have described a spectrophotometric method for the determination of copper(II) with *N*,*N*-diethyl-*p*-phenylenediamine and thymoquinone. In this determination Beer's law is obeyed in a concentration range of 1.0–10 ng mL^{-1} of copper(II). The apparent molar absorptivity is 2.61×10^6 L mol^{-1} cm^{-1} at 552 nm. The RSD for five replicate determinations for 6.3 ng mL^{-1} was 1.81%. As authors mention, the proposed method is superior to the other catalytic methods of determination for copper(II) with regard to the liner range and the RSD. The recovery of copper(II) from real samples (tap water and supplement tablet) were within 96–103%.

1.6.11 Bromocresol purple and neutral red

Zhu Qing-ren et al. [46] have developed a dual-wavelength dual-indicator catalytic kinetic spectrophotometric method for the detection of trace copper in flour and rice. This method is based on the catalytic effect of copper on the oxidation of bromocresol purple and neutral red by hydrogen peroxide in NH_3-NH_4Cl medium at $pH = 9.65$. The absorbance of catalytic system and uncatalytic system is measured at 460 nm and 590 nm, respectively. Under the optimum conditions, the linear range of the detection of trace copper was 0.0060–0.072 g mL^{-1}. The detection limit is 8.0×10^{-12} g mL^{-1}, and the RSD was 2.9% ($n = 11$), as reported.

1.6.12 6,7-Dihydroxy-4-methyl-2-phenylbenzopyrilium chloride

Chebotarev, A. N. et al. [47] optimized the conditions for extraction n of the Cu(II) complex with 6,7-dihydroxy-4-methyl-2-phenylbenzopyrilium chloride of composition 1:2. The complex is formed at pH 4,5 in the solution. Isoamyl alcohol is the best extractant as reported. The extraction equilibrium is reached within 1 min, and the optimum ratio of organic and aqueous phases is 1:5. A high-sensitivity (LOD = 0.007 g cm^{-3}) extraction-spectrophotometric procedure for the determination of Cu(II) using 6,7-dihydroxy-4-methyl-2-phenylbenzopyrilium chloride is developed by authors. The calibration graph is linear in the range of 0.02–0.96 pg cm^{-3}. The reported method has been successfully applied to analysis of various categories of waters.

Snigur, Denys et al. [48] have discovered the novel cloud point extraction procedure for pre-concentration of copper(II), which is a simple chemical method for initiating the cloud point extraction (CPE). The formation of surfactant-rich phase in a system containing a non-ionic surfactant Triton X-100, copper(II), 6,7-dihydroxy-4-methyl-2-phenylbenzopyrilium chloride (DHMPhB) and ammonium benzoate has been observed immediately upon addition of the sulfuric acid into solution. Under the optimal conditions (absorption maximum has been 540 nm, concentration 1.5×10^{-4} mol dm^{-3} of DHMPhB, 1.0 vol.% of Triton X-100, 2.0 cm^3 of 0.75 mol dm^{-3} ammonium benzoate, and 1.0 cm^3 of 0.5 mol dm^{-3} sulfuric acid solution for obtaining benzoic-benzoate buffer solution with pH 4.5 and initiation immediate surfactant rich phase formation) the calibration plot for spectrophotometrie determination of copper(II) obeys a linearity in the range of copper(II) concentration 0.02–0.95 μg cm^{-3}. The limit of detection has been calculated to be 0.006 μg cm^{-3}. The water samples have also been analyzed according to a suggested procedure with satisfactory results.

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Chapter 2
Analytical reagents having nitrogen (N) as donor atom

2.1 Triazenes

2.1.1 1-(4-Nitrophenyl)-3-(2-benzothiazol)triazene

Long Yue et al. [1] have synthesized a new reagent 1-(4-nitrophenyl)-3-(2-benzothiazol) triazene and applied to the spectrophotometric detection of Cu(II). At pH 8.37–9.38 in the presence of CTMA (cetyltrimethyl ammonium bromide) it forms complex with copper and the molar absorptivity of this complex is found to be 1.17×10^5 L mol^{-1} cm^{-1} and without CTMAB and the molar absorptivity is 9.20×10^4 L mol^{-1} cm^{-1}.

2.1.2 1-Azobenzene-3-(6-methoxy-2-benzothiazolyl)triazene

Luo Dao-cheng et al. [2] have proposed a new method for the detection of trace copper using the coloration reaction between 1-azobenzene-3-(6-methoxy-2-benzothiazolyl)triazene (AMBT) and Cu^{2+}, which gives 2:1 complex compound in the presence of Triton-X100 in Na_2CO_3-$NaHCO_3$ buffer at pH of 10. The generated species exhibits a maximum absorption at 560 nm with an apparent molar absorptivity of 5.36×10^4 L mol^{-1} cm^{-1}. The system obeys Beer's law in the copper concentration range from 0 to 12 g/25 mL, as reported.

2.2 Hydrazones

2.2.1 Bis(cyclohexanone)oxalyldihydrazone

Chen Jun et al. [3] have described that Cu can be detected in supernatant fluids in wet Zn metallurgical process spectrophotometrically by measuring the absorbance at 595 nm after introducing ammonium citrate solution NH_4OH–NH_4Cl (1.0:2.1 M) buffer solution and biscyclohexanoneo-xalyldihydrazone.

Chimpalee N. et al. [4] have found that copper can be detected spectrophotometrically at 600 nm based on the reaction of copper(II) and bis(cyclohexanone)oxalyldihydrazone using flow-injection analysis. The carrier stream are distilled water and the reagent streams are 27% (wt./vol.), citric acid solution, 37% (vol./vol.) ammonia solution and 0.18% (wt./vol.) bis(cyclohexanone) oxalyldihydrazone solution. The calibration graph is linear up to 20 µg mL^{-1} copper and the relative standard

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deviation for the detection of 5 µg mL^{-1} of copper was 0.92% ($n = 10$); the detection limit is 0.13 µg mL^{-1} copper, both based on injection volume of 250 µL. The system can be applied to the detection of copper in steels, copper-based alloys and pig feeds and to monitor copper in an alkaline scale removal process, as reported.

Liu Tingrong et al. [5] have described a method for determination of Cu in pure Al by spectrophotometry with acetaldehyde-bis(cyclohexanone)oxaldihydrazone. The suitable conditions are as follows: acetaldehyde amount 5 mL, temp. 20–30 °C, pH 8–10 and absorption maxima is 540 nm. Beer's law is obeyed in a range of 2–50 µg/ 100 mL solution. The detection limit is 0.02 µg mL^{-1}. The method has been used for standard samples, showing satisfactory results.

Qi Yanshan et al. [6] have developed a spectrophotometric method based on the color reaction of copper with bis(cyclohexanone)oxalyldihydrazone (BCO) to detection of copper in zincate solution. By using ammonium citrate as the masking agent, ammonium chloride-ammonia solution as the buffer solution to adjust the pH value of the solution within 8.6–10.0, copper and BCO react to form a blue product stably existing in the aqueous phase. It has been found that the color solution shows a maximum absorption peak at 600 nm, and Cu^{2+} in the zincate solution can be detected in a concentration range of 0.02–4.00 mg L^{-1}, as reported.

An Shen-jing et al. [7] have discussed optimum chromogenic conditions for high copper content in alloy. As a chromogenic reagent bis-cyclohexanone oxalydihydrazone has been used. Cu(II) and used chromogenic reagent show blue complex in pH 8.5–10.0 having maximum absorbance at 600 nm. The coloration temperature and concentration of bis-cyclohexanone oxaldihydrazone are 20 °C and 0.1 g L^{-1}, respectively. The coloration time of complex is 10 min. For copper Beer's law is obeyed in the range of 0.4–4.0 µg mL^{-1} and molar absorptivity (ε) found is 1.6×10^4 L mol^{-1} cm^{-1}. This method could be applicable for detection of high content copper in high-temperature alloy and copper alloy CRMs. In this method relative error was less than 1% and RSD was less than 6.5%, as described.

2.2.2 *N*,*N′*-Oxalylbis(salicylaldehydehydrazone)

Kim Yongnam et al. [8] have developed a spectrophotometric method for the detection of copper using *N*,*N′*-oxalylbis(salicylaldehydehydrazone) as a chromogenic reagent. Detection has been performed by measuring the absorbances of the copper complex in solution containing 60% DMF (pH 2) at 422 nm. The method allows the detection of 0.4–1.8 µg mL^{-1} of copper and has been applied to its detection in synthetic mixtures and alloy samples, as reported.

2.2.3 *N*,*N′*-Oxalylbis(2-pyridyl-3′-sulfobenzoylhydrazone)

Kim Yong Nam et al. [9] have synthesized a water-soluble chromogenic reagent *N*, *N′*-oxalylbis(2-pyridyl-3′-sulfobenzoylhydrazone). Spectrophotometric and first- and second-derivative spectrophotometric methods for the detection of copper with the reagent have been developed. Values of the copper complexes in aqueous solution at pH 1.89 are 379, 395, 363 and 421 nm, respectively. The method allows the detection of 0.12–1.20 μg mL^{-1} of copper and has been applied to the analysis of aluminum alloy samples. The best results have been obtained from the measurements of the second-derivative values at 421 nm, as reported.

2.2.4 *p*-Dimethylaminobenzaldehydebenzothiazolylhydrazone (DBBH)

Yamamoto Motonari et al. [10] have studied an extraction-spectrophotometric method for the detection of Cu(II) using *p*-dimethylaminobenzaldehydebenzothiazolylhydrazone (DBBH). The method is based on the formation of the Cu(II)–DBBH complex, which is extractable into toluene from aqueous solution in the pH range from 4.0 to 8.0 by shaking for 5 min. The absorbance is measured at 442 nm. The apparent molar absorptivity is 7.6×10^4 L mol^{-1} cm^{-1} at 442 nm and the spectrophotometric sensitivity is 0.84 ng cm^{-2} according to Sandell's expression. Beer's law is obeyed over the range 0.5–5.0 μg of Cu(II) in 5 mL toluene. The stoichiometric ratio of the Cu(II)–DBBH complex into toluene phase was examined by Job's continuous variation method that gave ratio 1:2, Cu(II)-to-DBBH. This method is satisfactorily applied to the detection to Cu in Mg alloys, as reported.

2.2.5 2,4-Dihydroxybenzophenone benzoic hydrazone (DHBPBH)

Reddy V. Krishna et al. [11] have employed 2,4-dihydroxybenzophenone benzoic hydrazone (DHBPBH) as an analytical reagent for the spectrophotometric determination of Cu and Fe. The reagent forms 1:1 greenish yellow-colored complex with Cu(II) at pH 4.0 and λ_{max} 380 nm ($\mathcal{E} = 1.55 \times 10^4$ dm^3 mol^{-1} cm^{-1}); Sandell's sensitivity 0.004 μg cm^{-2}, and Beer's law range 0.31–2.2 μg mL^{-1}. The same analytical reagent forms a brown-colored complex with Fe(III) in 2:3 at pH 5.0 and λ_{max} 380 nm ($\mathcal{E} = 2.8 \times 10^4$ dm^3 mol^{-1} cm^{-1}); Sandell's sensitivity 0.002 μg cm^{-2} and Beer's law range 0.14–1.0 μg mL^{-1}. The method could also be applied for the determination of Cu in soil and alloy samples and Fe(III) in cement sample.

2.2.6 *p*-Methylisonitrosoacetophenonehydrazone

Lokhande R. S. et al. [12] have studied a simple and rapid extractive spectrophotometric method for the determination of Cu(II). The complex formed between Cu(II) and *p*-methylisonitroso-acetophenonehydrazone is extracted into $CHCl_3$ from aqueous solution of pH 7.0. The extracted species has an absorption maximum at 510 nm and obeys Beer's law at 0.1–1.0 μg mL^{-1} of Cu(II), the molar absorptivity being 6.28×10^3 L $mole^{-1}$ cm^{-1}. Interference from foreign ions also has been studied.

2.2.7 α-(2-Benzimidazolyl)-α′, α″-(*N*-5-nitro-2-pyridylhydrazone)toluene

Park Chan-Il et al. [13] have studied the spectrophotometric determination of Cu(II) with α-(2-benzimidazolyl)-α′, α″-(*N*-5-nitro-2-pyridylhydrazone)toluene. The optimum conditions of pH, stability, concentration of ligand and surfactant have been evaluated by the authors. This method is a simple and sensitive for determination of Cu(II) and offers a selective separation of Cu(II) from sample solution containing 1 ppm below amount of Ni(II), Co(II), Zn(II) and Sn(II). Cu has been determined by measuring the absorbance at 410 nm of Cu(II)–BINPHT complex extracted with benzene in Brij 58 surfactant. Beer's law is obeyed over the concentration range 0–2.5 μg mL^{-1} and the detection limit ($S/N = 2$) is 0.06 μg mL^{-1}. The relative standard deviation at the 0.3 μg mL^{-1} is 2.4% ($N = 7$). The method has also been applied for the determination of Cu(II) in various milks.

2.2.8 2-Hydroxy-1-naphthaldehyde benzoylhydrazone (OHNABH)

Reddy V. Krishna et al. [14] have proposed a simple, highly sensitive and selective spectrophotometric method for the determination of Cu(II) in trace (microgram) quantities. Cu(II) reacts with 2-hydroxy-1-naphthaldehyde benzoylhydrazone (OHNABH) in the pH range 3–7 forming greenish-yellow-colored solution. The maximum absorbance of the solution is at 443 nm. Beer's law is obeyed in the range of 0.16–4.80 mg mL^{-1} of Cu(II) at 443 nm. This method has been applied by the authors for the determination of copper in some copper-based alloys and some plant samples.

2.2.9 Picolinaldehydenicotinoylhydrazone (PANH)

Pawar R. B. et al. [15] have mentioned a sensitive method for the extraction and spectrophotometric determination of Cu(II) at trace levels using picolinaldehydenicotinoylhydrazone (PANH) as an analytical reagent. The yellow-colored PANH–Cu(II) complex, extracted into $CHCl_3$ in the pH range 8.5–10.5, shows maximum absorbance at 380 nm. Beer's law is obeyed over the range of 10–300 ng mL^{-1} of Cu(II). The molar absorptivity and Sandell's sensitivity for PANH–Cu(II) system is 5.8×10^4 L mol^{-1} cm^{-1} and 1.1 ng cm^{-2}, respectively. The ratio of Cu to the reagent in the complex is 1:2. As the authors reported, the proposed method has been applied for the accurate determination of copper in alloys and pharmaceutical samples.

2.2.10 Di-2-pyridylketone benzoylhydrazone (dPKBH)

Pinto Juan J. et al. [16] have developed a sensitive spectrophotometric method for the direct determination of Cu in aqueous samples without a preconcentration step. The method is based on the formation of yellow complex with the chromogenic reagent di-2-pyridylketone benzoylhydrazone (dPKBH) in an alkaline medium. The complex stoichiometry is 1:2 (Cu:dPKBH) and presents maximum absorbance at 370 nm. The influence of variables affecting the behavior of the system such as pH, concentration of dPKBH, buffer solution and ethanol, order of addition of reagents and stability of complex are evaluated. The molar absorptivity is 3.92×10^4 L mol^{-1} cm^{-1} and Beer's law is obeyed up to 3 mg L^{-1} of Cu. The limit of detection is 2.5 mg L^{-1} and hence the method is more sensitive than the direct methods reported previously.

2.2.11 2,5-Dihydroxyaceto phenonebenzoichydrazone

Kudapali Y. S. et al. [17] have developed a new reagent 2,5-dihydroxyaceto phenonebenzoichydrazone for the detection and spectrophotometric determination of Cu(II) in acidic medium. The yellow-colored complex containing Cu and the ligand in 1:1 molar ratio shows maximum absorption at 400 nm, and the molar absorptivity is 1.1×10^4 L mol^{-1} cm^{-1}. Beer's law is obeyed for 0.3–6.0 mg mL^{-1} of Cu(II). The method is applied to the determination of Cu in alloy steels and plant leaves with good precision and accuracy.

2.2.12 3-Methoxy-4-hydroxybenzaldehyde-4-bromophenylhydrazone (3,4-MHBBPH)

Rekha D. et al. [18] have described a facile, sensitive and selective extractive spectrophotometric method for the determination of Cu(II) in various H_2O and alloy samples using 3-methoxy-4-hydroxybenzaldehyde-4-bromophenylhydrazone (3,4-MHBBPH). Cu(II) forms an orange-colored complex with (3,4-MHBBPH) in acetate buffer medium (pH 4) that increases the sensitivity. The complex was extracted into $CHCl_3$. Under optimum conditions, the maximum absorption of the extracted complex is measured at 462 nm. Beer's law is obeyed at 0.20–4.0 μg mL^{-1} of Cu. The molar absorptivity and the Sandell's sensitivity of the complex were 2.0520×10^4 L mol^{-1} $cm^{-1}$and 0.2540 μg cm^{-2}, respectively. The detection limit is 0.0270 μg mL^{-1}. The method has been successfully applied for the determination of Cu(II) in H_2O and alloy samples, as mentioned by the authors.

2.2.13 Diacetylmonoxime-4-hydroxybenzoylhydrazone (DM-4-HBH)

Kiran Kumar V. et al. [19] have reported derivative spectrophotometric determination of Cu(II) and Ni(II) based on the formation of their complexes with diacetylmonoxime-4-hydroxy-benzoylhydrazone (DM-4-HBH) reagent in basic medium. The reagent gives yellowish-green and light green–colored complex at pH 10.5 and 9.0, respectively. The maximum absorbance measured at λ_{max} is reported at 396 nm and 380 nm for Cu(II) and Ni(II) complexes. The molar absorptivity and Sandell's sensitivity are 1.8×10^4, 2×10^4 L mol^{-1} cm^{-1} and 0.0035, 0.0029 mg cm^{-2}, respectively. Cu(II) and Ni(II) form (M:L) 1:1 complex and stability constant of the complexes are 4.2×10^6 and 7.5×10^5, respectively. The derivative amplitude is measured at λ_{max} 433 nm and 404 nm, respectively.

2.2.14 2,4-dimethoxy-4-hydroxylbenzaldehydebenzoylhydrazone (DMBHBH)

Ramakrishna Reddy K. et al. [20] have developed a rapid, simple, sensitive and selective spectrophotometric method for the determination of Cu(II) using newly synthesized chromogenic reagent 2,4-dimethoxy-4-hydroxylbenzaldehydebenzoylhydrazone (DMBHBH). In the presence of cationic surfactant, CTAB (5%) (micellar medium) it forms an orange-colored Cu(II) water-soluble complex in the pH range 8.0–12.0. This complex shows maximum absorbance at λ_{max} 384 nm and in the pH range 9.0–10.0. At this λ_{max} of complex the reagent blank shows negligible absorbance. The studies are carried out at pH 10.0 (phosphate buffer) against reagent blank. Beer's law is obeyed in the range 0.1588–1.9063 mg mL^{-1}, and the optimum concentration range obtained from Ringbom plot is 0.3177–1.5886 mg mL^{-1} of Cu(II) as mentioned by the authors. The molar absorptivity and Sandell's sensitivity for the colored solution are found to be 3.8×10^4 L mol^{-1} cm^{-1} and 0.00585 mg cm^{-2}, respectively. The interference effect of various diverse ions has also been studied. The stoichiometry of the complex, 1:1 [Cu(II): DMBHBH] with stability constant 1.150260×10^5 obtained from Job's method has been reported. The standard deviation of the method in the determination of 0.3177 mg mL^{-1} of Cu(II) is 0.003 and the RSD is 3.50%. First- and second-order derivative spectroscopic method has also been developed at λ_{max} 440 nm and 455 nm, respectively, for determination of Cu(II), which is more sensitive than the zero-order method, as reported. The developed method has been used for the determination of Cu(II) in grape leaves, in biological materials and in alloy samples.

2.2.15 3,5-Dimethoxy-4-hydroxy benzaldehydebenzoylhydrazone (DMBBH)

Aruna Bai K. et al. [21] have developed a simple and sensitive spectrophotometric method for the determination of copper(II) in beer, wine and biological samples using 3,5-dimethoxy-4-hydroxy benzaldehydebenzoylhydrazone (DMBBH) as analytical reagent. Copper(II) forms an orange-colored water-soluble complex in basic medium in the presence of surfactant CTAB (5%). The molar absorptivity and Sandell's sensitivity of colored species are 3.16×10^4 L mol^{-1} cm^{-1} and 0.00633 mg cm^{-2}, respectively, as reported by the authors. Beer's law is obeyed in the range 0.1588–1.907 mg mL^{-1} of copper(II) at 435 nm (λ_{max}). Copper(II) forms a 1:1 complex and stability constant of the complex is 8.58×10^5 and interference ions also studied systematically.

2.2.16 2,3,4-Trihydroxy acetophenonephenylhydrazone (THAPPH)

Chalapathi P. V. et al. [22] have developed a simple, sensitive and selective kinetic spectrophotometric method for the determination of Cu(II) using 2,3,4-trihydroxy acetophenonephenylhydrazone (THAPPH) as analytical reagent. The metal ion forms 1:2 (M:L) bluish green–colored complex with THAPPH in HCl-KCl buffer of pH 2.5. Beer's law is obeyed in the range 0.04–0.64 mg mL^{-1} of Cu(II) at λ_{max} of 385 nm. The sensitivity of the method has been calculated in terms of molar absorptivity (1.0053×10^5 L mol^{-1} cm^{-1}) and Sandell's sensitivity is 0.0006265 mg cm^{-2} which explain the sensitivity of the method. The standard deviation (0.0024), RSD (0.47%), confidence limit (±0.0017) and standard error (0.0008) found precision and accuracy of the developed method. The stability constant has been calculated by Ausmu's (2.35×10^{-11}) and Edmonds and Birnbaum's (2.44×10^{-11}) methods at room temperature. The interfering effect of various cations and anions has also been studied. The reliability of the method has been assured by analyzing the standard alloys, Brass (BCS 5 g) H.T. Bronze (BCS 10 g) and Phosphor-Bronze (BCS 7a). The proposed method is successfully employed by the authors for the determination of Cu(II) in food and medicinal leafy samples, as described.

2.2.17 2-Hydroxynaphthaldehydebenzoyl hydrazone (HNABH)

Jamaluddin Ahmed M. et al. [23] have reported a very simple, ultra-sensitive and highly selective spectrophotometric method for the rapid determination of Cu at a trace level. As analytical reagent 2-hydroxynaphthaldehydebenzoyl hydrazone (HNABH) is proposed for the direct non-extractive spectrophotometric determination of Cu(II). HNABH reacts with Cu in a slightly acidic medium in 50% DMF media. This analytical reagent produces a highly absorbent green chelate with a molar ratio 1:1 with λ_{max} at 427 nm which remain stable for 24 h. The average molar absorptivity and Sandell's sensitivity are found to be 4.35×10^4 L $\mathrm{mol^{-1}\,cm^{-1}}$ and 5.0 ng $\mathrm{cm^{-2}}$ of Cu(II), respectively. The detection limit and quantification limit of the reaction system have been found to be 1 and 10 μg $\mathrm{L^{-1}}$, respectively. The method could be successfully used for the determination of Cu in several standard reference materials (steels and alloys) as well as in some environmental waters (potable and polluted), biological (human blood and urine) and soil samples and solutions containing both Cu(I) and Cu(II) as well as some complex synthetic mixtures.

2.2.18 Salicylsalicylicacidhydrazone (SSAH)

Aluru Raghavendra et al. [24] have developed a spectrophotometry method for the determination of trace amounts of copper in spiked water and alloy samples without any prior separation or extraction. In this study salicylsalicylicacidhydrazone (SSAH) is used as spectrophotometric reagent. Cu(II) and SSAH produce greenish-yellow color in acidic medium and show absorption maximum at 420 nm. Beer's law is obeyed in the concentration range 0.2497 to 2.2471 μg $\mathrm{mL^{-1}}$. Several parameters like stability constant (1.13×10^7), molar absorption coefficient (8.560×10^4 L $\mathrm{mol^{-1}\,cm^{-1}}$), Sandell's sensitivity (0.0007 μg $\mathrm{cm^{-2}}$), linear calibration range, stoichiometry of the complex (1:1), method detection limit (0.0299 μg $\mathrm{mL^{-1}}$), limit of quantification (0.0598 μg $\mathrm{mL^{-1}}$) and standard deviation (2.624–3.567%) have been calculated. The effect of foreign ions on determination is presented by the authors.

2.2.19 Salicylaldehydebenzoylhydrazone (SAL-BH)

Ahmed M. Jamaluddin et al. [25] have mentioned that spectrophotometry is ultrasensitive, selective and non-extractive method for the detection of trace amounts of Cu(II). For this study an analytical reagent salicylaldehydebenzoylhydrazone (SAL-BH) is used. SAL-BH reacts with Cu(II) in slight acidic media and gives greenish-yellow chelate having 1:1 (Cu:SALBH). This complex shows maximum absorption at 404 nm and is stable for 72 h. The average molar absorptivity and Sandell's sensitivity are found to be 1.4×10^5 L $\mathrm{mol^{-1}\,cm^{-1}}$ and 5.0 ng $\mathrm{cm^{-2}}$ for Cu(II), respectively. Linear calibration graphs were obtained for 0.01–18 mg $\mathrm{L^{-1}}$ of Cu(II). As the authors reported the detection limit and quantification limit of the reaction system are found to be 1 ng $\mathrm{mL^{-1}}$ and 10 μg $\mathrm{L^{-1}}$, respectively. A large excess of over 50 cations, anions and complexing agents do not interfere in the determination. The method is highly selective for Cu and was successfully used for the determination of Cu in several standard reference materials as well as in some environmental samples, waters, biological, food and soil samples and solution containing both Cu(I) and Cu(II) as well as some complex synthetic mixtures, as mentioned.

2.2.20 Salicylaldehyde acetylhydrazone (SAAH)

Renuka M. et al. [26] have reported spectrophotometric method for the determination of trace amounts of copper(II). As analytical reagent, salicylaldehyde acetylhydrazone (SAAH) is proposed for the direct non-extractive spectrophotometric determination of copper(II). The reagent reacts with copper(II) in a slightly acidic medium in the presence of sodium acetate and acetic acid buffer to form instantaneous, pale yellow–colored 1:1(M:L) complex. The complex shows absorption maximum (λ_{max}) at 372 nm that has stability for 3 h. As the authors described molar absorptivity and Sandell's sensitivity are found to be 1.0×10^4 L mol^{-1} cm^{-1} and 0.635 mg cm^{-2}, respectively. The system obeys Beer's law in the range for 1.0–9.0 mg mL^{-1} of copper(II). The method has been successfully used for the determination of copper in several standard reference materials such as copper alloys.

2.2.21 5-Bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydroxybenzoichydrazone

Devireddy Madhavi et al. [27] have reported a direct visible spectrophotometric method for determination of copper(II) in alloy, fruit, leaf and biological samples. It is a rapid, simple, sensitive and selective method for determination of Cu(II). 5-Bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydroxybenzoichydrazone reacts with Cu(II) forming brown-colored soluble complex in aqueous DMF in the pH range 3.0–8.0. It has λ_{max} at 405 nm, at pH-5.0. The method obeys Beer's law in the range 0.317 to 3.81 μg mL^{-1}. The molar absorptivity is 1.412×10^4 L mol^{-1} cm^{-1} and Sandell's sensitivity is 0.0045 μg cm^{-2} as reported by the authors. The standard deviation of the method for ten determinations of 1.59 μg mL^{-1} of Cu(II) is 1.22×10^{-3}. The correlation coefficient (γ) of the calibration equation of the experimental data is 0.9999. The effect of various diverse ions is also studied. The formula of the complex has been found to be 1:1 by reported results and its stability constant was 3.13×10^5.

2.2.22 Diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH)

Nagalakshmi B. N. et al. [28] have used a novel chromogenic organic reagent diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) for the determination of copper(II) by spectrophotometry. In basic buffer (pH 8.0–10.0) medium this reagent forms bright yellow-colored water-soluble complex with Cu(II), which shows maximum absorbance at 412 nm. This system obeys Beer's law in the concentration range of 0.3178–3.813 μg mL^{-1}. For accurate determination from Ringbom's plot the optimum copper(II) concentration range is evaluated as 0.6355–3.4953 μg mL^{-1}. The observed molar absorptivity and Sandell's sensitivity are 1.65×10^4 L mol^{-1} cm^{-1} and 0.00606 μg cm^{-2}, respectively. Copper(II) forms M:L (I:I) color complex with DMAHBH and stability constant of the complex has been found to be. 7.15×10^5. As mentioned by the authors this developed method can applied for the determination of copper(II) in food samples like vegetables and milk samples.

2.2.23 *N″*,*N‴*-Bis[(E)-(4-fluorophenyl)methylidene]thiocarbonohydrazide [bis(4-fluoroPM)TCH]

Nalawade Rekha A. et al. [29] have developed a rapid and simple spectrophotometric method for the determination of copper(II) by using newly synthesized chromogenic reagent, *N*'',*N*'''-bis[(E)-(4-fluorophenyl)methylidene]thiocarbonohydrazide [bis (4-fluoroPM)TCH]. The reagent is highly sensitive and forms yellow-colored ternary complex in the acidic pH range with copper(II) in the presence of pyridine having composition 1:1:2 (M:L:Py). Absorption of colored complex is observed in amyl acetate with reagent as a blank at $\lambda_{\max}$ 375 nm. In the organic phase pyridine is forming adduct with reagent due to which the synergistic effect is observed. The complex solution obeys Beer's law in the concentration range from 2.0 to 14 mg mL^{-1}. Molar absorptivity and Sandell's sensitivity values for Cu(II)-bis(4-fluoroPM)TCH]-Py complex are 0.42545×10^5 and 0.0014 mg cm^{-2}, respectively. The selectivity of the developed method has also been checked in the presence of various foreign ions. The developed method showed relative standard deviation (R.S.D.) of 0.13% for $n = 10$. The composition of Cu(II)-[bis(4-fluoroPM)TCH]-Py complex is determined by using Job's method of continuous variation, mole ratio method and slope ratio method. The ternary complex is stable for more than 24 h. Various factors influencing the degree of complexation such as the effect of pH, reagent concentration, synergent concentration and solvent have been studied. As mentioned by the authors this method is found to be simple, rapid and reproducible.

2.2.24 Pyridine-2-acetaldehyde benzoylhydrazone

Granado-Castro M. D. et al. [30] have presented a tandem system based on the coupling of a bulk liquid membrane and a flow injection analysis for the separation, preconcentration and spectrophotometric determination of copper in saline water. As a carrier in the liquid membrane as well as a spectrophotometric reagent for UV-VIS detection as a ligand pyridine-2-acetaldehyde benzoyl-hydrazone has been used. Simultaneous and sequential experimental designs have been used to optimize the chosen variables of each technique. The metal has been separated and preconcentrated from the sample with an efficiency of 100.5 ± 0.9% and a metal preconcentration factor of 16.1. The online FIA determination has been accomplished after metal complexation by the reagent at pH 3. A linear response has been obtained in a range from 6.9 to 984.5 µg L^{-1} Cu(II), provides a detection limit of 1.8 µg L^{-1}. The proposed tandem system has been successfully tested using a TMDA-62-certified reference material providing a relative error of +1.9%. It has also been applied to the Cu(II) determination in coastal seawater samples with low relative errors ranging from −3.8% to 0.0% (using DPASV as reference method).

2.2.25 Furfuraldehyde fluorescein diacetate hydrazone (FFDH) and furfuraldehyde fluorescein hydrazone (FFH)

Haishuang Jia et al. [31] have proposed two novel methods for spectrophotometric determination of Cu^{2+} ion using furfuraldehyde fluoresceindiacetatehydrazone (FFDH) and furfuraldehyde fluorescein hydrazone (FFH). The solutions of FFDH and FFH result in a rapid color change from colorless to dark yellow on addition of Cu^{2+}. As reported by the authors, these solutions can provide a rapid, selective and sensitive response to Cu^{2+} within a linear dynamic range of 7–33 μM and the detection limits of 1.1×10^{-7} and 7×10^{-8} M, respectively. Apparently, the detection limit of FFDH is lower than that of FFH, which indicates that FFDH forms a more stable complex with Cu^{2+}. In addition, the detection of Cu^{2+} in water samples was also studied; as a result, the developed FFDH is more applicable than FFH for spectrophotometric determination of Cu^{2+} in environmental water samples. Particularly, as a lipid chemical compound, FFDH may be transported across the cell membrane to detect Cu^{2+} in vivo. It has a great significance in many fields, such as biology, biochemistry, medicine and environment.

2.3 Aminoquinolines

2.3.1 5-*p*-(Methylphenylazo)-8-aminoquinoline (*p*-MPAQ)

Wang Yuzhi et al. [32] have found that copper reacts with 5-*p*-(methylphenylazo)-8-aminoquinoline (*p*-MPAQ) in the presence of cationic surfactant cetyltrimethylammonium bromide in Na_2CO_3 buffer solution of pH 9.0–10.0 to form 1:1 Cu:p-MPAQ red-brown complex. The molar absorptivity and wavelength are 3.62×10^4 L mol^{-1} cm^{-1} and 117 nm, respectively. Beer's law is obeyed in the range of 0–13 μg Cu/10 mL. The stability constant of the complex is 1.50×10^8. This method has been applied to the direct detection of micro amount of copper in aluminum alloys with sodium fluoride as a masking agent.

2.3.2 5-(3-Carboxyphenylazo)-8-aminoquinoline (*m*-CPAQ)

Xu Qiheng et al. [33] have synthesized 5-(3-carboxyphenylazo)-8-aminoquinoline (*m*-CPAQ). Cu(II) reacts with *m*-CPAQ to form a stable red violet complex with the composition of 1:3. The absorption maximum of the chelate is observed at 554 nm with an apparent molar absorptivity of 7.3×10^4 L mol^{-1} cm^{-1}. Beer's law is obeyed in the 0–16 µg/25 mL range for Cu(II). This method could be applied to the analysis of iron ores and cast iron with satisfactory results.

Wang Yufei et al. [34] have reported a method for the spectrophotometric determination of Cu(II) with 5-(3-carboxyphenylazo)-8-aminoquinoline (*m*-CPAQ). *m*-CPAQ forms a purple-red complex with the ratio of 1:3 with Cu(II) in pH 6.6 KH_2PO_4-$Na_2B_4O_7$ buffer solution. The absorption maximum of the complex is observed at 554 nm. The molar absorptivity is 7.3×10^4, and Beer's law is obeyed at 0–16 µg/25 mL. Pd^{+2} had positive interference on the determination. The method has also been used for the determination of Cu in Fe ore and cast Fe samples with the relative standard deviation 2.8–4.5% as described by the authors.

2.3.3 5-(4-Sulfophenylazo)-8-aminoquinoline [SPA]

Morales Libby et al. [35] have described a derivative spectrophotometric method that can be applied successfully for the detection of copper in mineral residuals and natural water samples. For this, chromophore 5-(4-sulfophenylazo)-8-aminoquinoline [SPA] is used as a reagent. The Cu(II) reacts with the reagent chromophore SPA that is previously retained in the anionic exchange DEAE Sephadex A25. The 1:2 stoichiometry of the Cu(II)-SPA complex has been detected at pH 9 by Job and molar ratio methods. The analysis measures have been executed directly in the solid phase containing the complex of Cu(II) and reagent chromophore SPA at 605 nm. The quantification range is in between $(3.2 \pm 0.3 \times 10^{-1}) \times 10^{-8}$ and $(94.4 \pm 0.9) \times 10^{-8}$ mol L^{-1} $(3.2 \pm 0.3 \times 10^{-1}) \times 10^{-8}$, and $(94.4 \pm 0.9) \times 10^{-8}$ mol L^{-1}, as reported.

2.4 Porphyrins

2.4.1 meso-Tetrakis-(4-methoxyphenyl)-porphyrin (TMOPP)

Wu Qingsheng et al. [36] have investigated the common color reaction conditions and the derivative spectral conditions for meso-tetrakis-(4-methoxyphenyl)-porphyrin (TMOPP) with Cu(II) and Zn(II). A derivative spectrophotometric partial least squares (PLS) method for the simultaneous detection of copper, zinc and their ratio has been developed. Heating for 16 min in a boiling water bath in a neutral medium of pH 7.05 in the presence of Tween-80 allows the color reaction of TMOPP-Cu and -Zn to proceed. Their 4th-derivative molar responsive coefficients (peak-to-peak) are 9.14×10^6 and 1.53×10^7, respectively. The proposed method is applied to the detection of Cu, Zn and Cu/Zn in artificial samples (Cu:Zn = 0.03:0.5–0.40:0.02 µg/25 mL).

2.4.2 5-[4-*N*-(*p*-chloro)-benzylammonium pyridyl]-10,15,20-tris(4-*N*-pyridyl) porphyrin chloride

Zhang Zhi-hua et al. [37] have proposed a method to detect trace amounts of copper in environmental water. For this a new chromogenic reagent 5-[4-*N*-(*p*-chloro)-benzylammonium pyridyl]-10,15,20-tris(4-*N*-pyridyl) porphyrin chloride is used. In a phthalate buffer medium of pH 3.2, a coordination complex is formed between the new porphyrin reagent and Cu^{2+} ion with its absorption maximum at the wavelength of 428 nm. Apparent molar absorptivity is found to be 1.9×10^5 L mol^{-1} cm^{-1}. Beer's law is obeyed within 0.1 mg of Cu^{2+} in 1 L of solution in respect to its linear regression equation of $A = 0.0152 + 0.31\,C$ ($r = 0.9991$), as reported.

2.5 Porphines

2.5.1 meso-Tetra-(4-methoxyphenyl-3-sulfo) porphine

Huang Zexing et al. [38] have prepared meso-Tetra-(4-methoxyphenyl-3-sulfo) porphine as a reagent for copper by spectrophotometry. The reagent forms a 1:1 complex with Cu in solution of pH 4.4–5.9. The absorption of the complex is linear with Cu concentration of 0–1.4 µg/10 mL. The method is applied to Cu detection in Al alloy, rice and wheat powder, wastewater and human hair.

2.5.2 3,8,13,18-Tetramethyl-21H,23H-porphine-2,7,12,17-tetrapropionic acid

Giovannetti R. et al. [39] have used the reagent 3,8,13,18-tetramethyl-21H,23H-porphine-2,7,12,17-tetrapropionic acid or coproporphyrin-I (CPI) for the spectrophotometric determination of copper(II) and cobalt(II) in the presence of pyridine and imidazole catalysts. Optimum conditions were investigated and the methods are applied to the determination of parts per billion levels of copper(II) and cobalt(II). The Sandell sensitivities of the recommended procedures are 0.568 µm $cm^{(-2)}$ and 0.464 µg $cm^{(-2)}$ (for $A = 0.001$) for copper and cobalt, respectively. The relative standard deviations are 2.0% for copper and 1.0% for cobalt. The kinetics of the reaction of CPI with copper(II) and cobalt(II) in the presence of the catalysts and the influence of the temperature were studied, and their kinetic constants determined. The influence of light on the photodecomposition of CPI was also studied, as reported.

2.5.3 meso-Tetrakis(4-sulfonic acid phenyl)porphine (TPPS4)

Zhang Yinhan et al. [40] have developed a spectrophotometric method for detection of Cu^{2+} and lead in tap water using meso-tetrakis (4-sulfonic acid phenyl)porphine (TPPS4). The method is based on the Cu^{2+}-TPPS4 complex formation to cause the decrease of TPPS4 dimer. The characteristic absorption peak of the TPPS4 dimer is at 489 nm in sodium acetate solution at pH 4–6. Hydroxylamine hydrochloride accelerated the complex formation and NaF was used as a masking agent. Beer's law is obeyed at 0–0.2 μg mL^{-1} Cu^{2+} and the apparent molar absorptivity is 5.0×10^5 L mol^{-1} cm^{-1}.

2.5.4 (5,10,20-Tetra-Ph-21H,23H-porphin tetrasulfonic acid)

Watanabe Shugo et al. [41] have developed a spectrophotometric method to determine concentration of copper in a solder alloy sample. For this, solder alloy sample is dissolved and diluted by adding a color reagent to form a Cu complex that is then measured by spectrophotometry. The complex is formed by Cu and color reagent (5,10,20-tetra-Ph-21H,23H-porphin tetrasulfonic acid) in a solution of pH 3–7. Ascorbic acid is used as a reaction accelerator. The complex has a maximum optical absorption at 413 nm, as mentioned.

2.6 Azobenzenes

2.6.1 *O*-Iodobenzenediazoaminobenzene-p-azobenzene (OIDAA)

Zhang Peng Fei et al. [42] have synthesized a ligand *o*-iodobenzenediazoaminobenzene-p-azobenzene (OIDAA) for detection of trace amounts of Cu in metals at pH 12. The extraction with $CHCl_3$ in the presence of 2,9-dimethyl-1,10-phenanthroline can remove other metal ions. By the beta-correction principle, the complex ratio of Cu to OIDAA can be detected easily as 1:2 and the chelate's practical molar absorptivity at 500 nm and its instability constant at pH 12 were worked out. Beer's law is obeyed over the concentration range of 0–0.20 mg L Cu with the detection limit of 0.008 mg L^{-1}.

2.6.2 Dibromocarboxylbenzenediazoaminoazobenzene (DB-*O*-CDAA)

Wang Guangjian et al. [43] have studied the highly sensitive, selective color reaction of dibromocarboxylbenzenediazoaminoazobenzene (DB-*O*-CDAA) with Cu^{2+}. Results show that in the presence of Triton X-100 in a pH 10.0 borax buffer solution the reagent reacts with Cu to form a red complex with a molar ratio of 1:2, which has a maximum absorption at 530 nm and molar absorptivity is 1.08×10^5 L mol^{-1} cm^{-1}. Cu obeyed Beer's law in the range of 0–0.32 µg Cu mL^{-1}. The method was used to detect trace Cu in alloy and synthetic water samples with satisfactory results.

2.6.3 4-(2,3-Dihydro-1,4-phthalazinedione-5-triazeno)azobenzene (PTAB)

Ma Huimin et al. [44] have synthesized, purified and identified 4-(2,3-dihydro-1,4-phthalazinedione-5-triazeno)azobenzene (PTAB) and used as color developing agent with Cu(II). PTAB reacts with Cu^{2+} in a $Na_2B_4O_7$-NaOH buffer solution (pH 11.5) in the presence of Tween-80 to from a stable red complex having an absorption maximum at 520 nm with a molar absorptivity 6.0×10^4 L mol^{-1} cm^{-1}. The linear range for determination of Cu is 0–6 mg L. A simple method for determination of Cu has been developed and can be used to determine Cu in Al alloys.

2.7 Ethylenediamine salt (en)class

2.7.1 Bis(acetylacetone)ethylenediiminate

Chimpalee N. et al. [45] have detected copper by flow injection spectrophotometry at 370 nm after extraction of copper(II) bis(acetylacetone)ethylenediiminate chelate into chloroform. The carrier stream was deionized water and the reagent streams were acetate buffer (pH 5.0) and 0.2% (w/v) bis (acetylacetone) ethylenediimine solutions. The sampling rate was 20 h^{-1}. The calibration graph was linear up to 100 µg L^{-1} copper, based on injection volumes of 250 µL. The relative standard deviation was 1.95% for 20 µg mL^{-1} copper. The system has been applied to the detection of copper in copper-based alloys and pig feeds, as reported.

Chimpalee N. et al. [46] have detected Cu by spectrophotometrically at 343, 370 and 545 nm, based on the reaction of Cu(II) and bis (acetylacetone) ethylenediimine after extraction of the chelate into $CHCl_3$. The calibration graphs were linear up to 20 µg mL^{-1} Cu at 343 nm, 80 µm mL^{-1} Cu at 370 nm and 200 µm mL^{-1} Cu at 545 nm. The relative standard deviation for the detection of 50 µm mL^{-1} of Cu (at 545 nm) was 1.4% ($n = 10$). The system was applied to the detection of Cu in Cu-based alloys and pig feeds, as reported.

2.7.2 *N*,*N*-Dimethyl-*N′*-(2-hydroxybenzyl)ethylenediamine (HL)

Sal'nikov Yu et al. [47] have studied the acidic-basic and complexing properties of *N*,*N*-dimethyl-*N*'-(2-hydroxybenzyl)ethylenediamine (HL) in aqueous 2-proponal and characterized using spectrophotometric techniques. Dimer H_2L_2 has been found to predominate in solution at $c_{HL} = 0.01$ mol L^{-1}. Three protonated dimeric (H_3L^{2+}, $H_4L_2{}^{2+}$ and $H_5L_3{}^{2+}$), diprotonated monomeric (H_3L^{2+}) and triprotonated tetrameric forms ($H_7L_4{}^{3+}$) have been detected in the system, depending on pH. At lower ligand concentrations ($c_{HL} = 0.0015$ mol L^{-1}), the solution contains both dimmers and monomers of the compound. The higher dentate number of HL compared to 2-alkylaminomethylphenols allows it to form more number of both mono-and binuclear complexes with copper(II), ($[Cu(HL)]^{2+}$, $[Cu(HL)_2]^{2+}$, $[CuL_2]$, $[CuL_2OH]^{-}$, $[Cu_2(HL)_2]^{4+}$, and $[Cu_2(HL)_2\ L_2]^{2+}$), making them more stable.

2.7.3 *N,N′*-bis (salicylidene)ethylenediamine (Salen)

Rajavel R. et al. [48] have developed a facile, highly sensitive and selective spectrophotometric procedure for the determination of Cu(II) in thermal boiler water using a newly synthesized reagent, *N,N′*-bis (salicylidene)ethylenediamine (Salen). As the authors described this method is based on the reaction at pH 4–9 between the Salen and Cu(II), forming a deep green complex. Cu(II) Salen (1:1) complex floats quantitatively with oleic acid surfactant. It exhibits a constant and maximum absorbance at 550 nm in both aqueous and surfactant layers. Beer’s law is obeyed over the concentration range 0.25–6.35 mg L^{-1} with a detection limit of 0.005 mg L^{-1} for a standard aqueous solution of Cu(II) with a concentration of 3.82 mg L^{-1}, molar absorptivity is 5.5×10^3 and 1.3×10^4 L mol^{-1} cm^{-1} in aqueous and surfactant layers, respectively. Sandell’s sensitivity has been calculated to be 0.244 mg cm^{-2} and the relative standard deviation ($n = 9$) has been found to be 0.19%. The proposed procedure has been successfully applied to the analysis of Cu(II) in natural waters and high-purity thermal water samples.

2.8 Cetyltrimethylammonium bromides (CTMAB)

Paria P. K. et al. [49] have detected copper(II) by extraction of its yellow complex with cetyltrimethylammonium bromide from acidic solution (pH 0.5–3.5) into $CHCl_3$ and measured the absorbance at 360 nm.

Endo Masatoshi et al. [50] have described a highly sensitive method for the determination of copper(II), which is based on preconcentration of copper(II)-N,N-diethyldithiocarbamate as an aggregate film. Traces of copper(II) have quantitatively collected into a thin film consisting of hexadecyltrimethylammonium chloride (cetyltrimethylammonium chloride) and sulfosalicylic acid. The film is easily detached from a membrane filter support and the copper(II) complex has been determined spectrophotometrically by dissolving in DMF. The calibration graph is linear from

1.6×10^{-9} to 8×10^{-8} mol copper(II) in 14 mL of test solution. The relative standard deviation observed is 3.1% ($n = 5$) at 3×10^{-6} M copper(II). The membrane filter can be used repeatedly. The method has been applied to the determination of trace copper(II) added to river water.

Zhang Shu-fang et al. [51] have developed an absorbance ratio-derivative method for the simultaneous detection of Cu(II) and Cr(III) in surrounding H_2O. In the HOAc-NaOAc buffer solution at pH 5.7 with heating, Cr^{3+} or Cu^{2+} with CAS and CTMAB formed a blue ternary complex. The molar absorptivities of Cr(III)-CAS-CTMAB and Cu(II)-CAS-CTMAB are 2.52×10^5 L mol^{-1} cm^{-1} and 1.01×10^5 L mol^{-1} cm^{-1}, respectively, as reported. Beer's law is obeyed at 0.08–1.2 g mL^{-1} for Cu(II) and 0.05–0.52 g mL^{-1} for Cr(III), as reported.

Pouretedal H. R. et al. [52] have proposed a spectrophotometric partial least-square method for simultaneously detection of cobalt, nickel, copper and zinc in micellar media. Methyl thymol blue and cetyltrimethylammonium bromide are used as a color reagent and a surfactant, respectively. Absorbance measurements are made in the amplitude of 560–680 nm with 1.5 nm steps in buffered solution at pH 6. The linear ranges have been obtained in the intervals of 0.05–3.00, 0.10–4.00, 0.10–3.00 and 0.05–3.50 g mL^{-1} for Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions, respectively, as reported.

Pourreza Nahid et al. [53] have used a flotation spectrophotometric methods for the detection of copper(II) by formation of a ternary ion-associated complex from Cu(II), methylthymol blue (MTB) and cetyltrimethylammonium bromide (CTAB). These are floated at the interface of aqueous phase and n-hexane by shaking in a separating funnel. The adsorbed ion associated are separated in funnel and dissolved in small volume of methanol. This adsorbed ion associated mixture shows absorption maximum at 556 nm. The apparent molar absorptivity (ε) of the ion associated is found to be 6.1×10^4 L mol^{-1} cm^{-1}. The calibration curve is linear in the concentration range of 10–400 ng mL^{-1} of Cu^{2+} with a correlation coefficient of 0.9994. The limit of detection (LOD) was 6.7 ng mL^{-1}.The relative standard deviation (RSD) for 50 and 300 ng mL of Cu^{2+} was 3.9% and 1.3% ($n = 7$), respectively, as described.

2.9 Bis(cyclohexanone)oxalyldihydrazones (BCO)

Li Li [54] has reported the spectrophotometric method which is convenient and fast with high sensitivity for determination of Cu(II). BCO form blue-colored complex with Cu^{2+} and under the condition of pH value is 7–10 which is adjusted by NH_3/H_2O solution showing absorption maximum at 610 nm. The concentration of copper is 0.2–4 mg mL^{-1} that followed Beer's law and the molar absorptivity is 1.6×10^4 L mol^{-1} cm^{-1} as reported. The best conditions, acidity and effect of BCO content to determination of copper are studied, as reported.

Qi Yanshan et al. [22] have developed a spectrophotometric method based on the color reaction of copper with bis(cyclohexanone)oxalyldihydrazone (BCO) to detection of copper in zincate solution. By using ammonium citrate as the masking agent, ammonium chloride-ammonia solution as the buffer solution to adjust the pH value of the solution within 8.6–10.0, copper and BCO react to form a blue product stably existing in the aqueous phase. It is found that the color solution shows a maximum absorption peak at 600 nm, and Cu^{2+} in the zincate solution that can be detected in a concentration range of 0.02–4.00 mg L^{-1}, as reported.

Liu Xian-bin et al. [55] have proposed spectrophotometric method for determination of copper in a novel material (fire smelting nickel substrate material). In ammonium chloride-ammonium hydroxide buffer solution at pH 8.9–9.4, the stable chelate formed by Cu^{+2} with bisoxaldihydrazone (BCO) shows maximum absorption wavelength at 600 nm. The determination of copper is interfered by matrix iron, nickel, chromium and cobalt. Chromium volatilized with hydrochloric acid and the interference can be eliminated by matrix matching and citric acid masking method. The copper content in four actual samples has been determined by this method with relative standard deviation in the range of 1.4%–4.0%, as described.

2.10 Leucocrystal violet reagents

Mathew Sunitha B. et al. [56] have developed a sensitive spectrophotometric method for detection of trace Cu using leucocrystal violet as chromogenic reagent. The proposed method is based on the reaction of Cu(II) with KI in acid medium to liberate I, which oxidizes leucocrystal violet to crystal violet dye having absorption maximum at 590 nm. The reaction between Cu and KI is accelerated by irradiating the mixture with microwave energy for 15 s at 480 W. Beer's law is obeyed in the concentration range 0.004–0.04 g mL^{-1}, as mentioned.

Pataila Girija et al. [57] have developed a sensitive spectrophotometric method for the trace detection of copper oxychloride (protective fungicide) using leucocrystal violet as chromogenic reagent in soil, agricultural runoff water, fruits and plant material samples. The proposed method is based on the reaction of Cu(II) with KI in acid medium to liberate I_2, which oxidizes leucocrystal violet to crystal violet dye having absorption maximum at 585 nm. The reaction between copper oxychlori de and KI is accelerated by irradiating the mixture with microwave energy for 40 s at 970 W. Beer's law is obeyed in the concentration range 0.1–0.8 g mL^{-1}. The molar absorptivity and Sandell's sensitivity are found to be 1.9×10^5 L mol^{-1} cm^{-1} and 0.001125 g cm^{-2}, respectively, as reported.

2.11 Miscellaneous reagents

2.11.1 DBC-arsenazo

Chen Xiantong et al. [58] have developed a method for detection of trace copper based on the catalytic effect of copper on the reduction of DBC-arsenazo by ascorbic acid in HOAc-NaOAc medium. Sandell sensitivity is 2.22×10^{-5} µg cm^{-2}, and Beer's law is obeyed in the range of 0–0.8 µg Cu/25 mL. The method was used to detect copper in iron ores with satisfactory results, as reported.

2.11.2 Eriochrome blue black R (EBBR)

Gao Hongwen et al. [59] have developed a modified dual-wavelength spectrophotometric (DWS) method, using the reaction of Cu" with eriochrome blue black R (EBBR) at pH 12. It is sensitive and selective in the presence of both pentadecyltrimethylammonium bromide (PTMAB) and ascorbic acid. As described by the authors the modified DWS can completely eliminate the effect of excess EBBR in its Cu" solution and give the real absorbance of the produced chelate of Cu" with EBBR, with increased analytical sensitivity and decreased error. The complex obeyed Beer's law over the concentration range of 0–1.60 mg Cu per liter and the true molar absorbance of chelate Cu(EBBR), at 550 nm has been computed as $1.80.\ 10^4$ mol^{-1} cm^{-1}. The detection limit of Cu is 0.04 mg. This method has been applied for the determination of trace amounts of copper in waste water with satisfactory results, as reported.

2.11.3 Ethylviolet

Yamamoto Koichi et al. [60] have presented a spectrophotometric method for the detection of Cu in water by solvent extraction of an ion-association complex of the dichlorocuprate(I) ion with ethyl violet. Cu at 1 ppb concentration in water and seawater corresponds to 0.029 and 0.026 absorbance, respectively.

2.11.4 *N*-Ethyl-2-naphthylamine (NENA)

Mori Itsuo et al. [61] have studied spectrophotometric detection of benzoylperoxide (BPO) and copper(II) by using the color reaction for *N*-ethyl-2-naphthylamine (NENA), BPO and copper(II) as metal ion at various concentrations of acetonitrile-water mixed solution as acidic media. The calibration graphs are linear at 0–200 µg BPO with apparent molar coefficient ($\mathcal{E}$) of 8.5×10^3 M^{-1} cm^{-1} at 530 nm, and 0–2.4 µg per 10 mL copper(II) with $\mathcal{E} = 1.72 \times 10^5$ M^{-1} cm^{-1} at 533 nm, respectively. In addition, the FIA method for copper(II) is proposed with NENA-BPO. The calibration graph for FIA is linear at 0–7.9 ng copper(II) per 5 µL at 533 nm. These proposed methods are selective and simple in comparison to previous methods such as cuproin kinetic reactions. The spectrophotometry for copper(II) with NENA-BPO is very specific, and the effect of foreign ions is negligible, as reported.

2.11.5 Thiazolylazoacetylacetone(TAA)

Awadallah R. M. et al. [62] have studied solvent extraction and spectrophotometric determination of trace amounts of Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+}. As complexing agent thiazolylazoacetylacetone (TAA) is used in various organic solvents. As revealed Cu^{2+}, Zn^{2+} or Ni^{2+} forms complexes with $\lambda_{max} = 445$, 450, 450 and 460 nm, at pH values 4.5–8.0, 6.0–9.0, 5.0–9.0 and 6.5–8.5 and after 10, 10, 10 and 5 min shaking time in the case of Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} thiazolylazoacetylacetonate complexes, respectively. The stoichiometric ratios of the formed chelates determined by molar ratio and continuous variation methods equal 2.0 and 0.35, respectively, indicating the formation of 1:2 (M^{2+}: L) complexes. The stability of the complexes is in the order: $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$ TAA complexes. Determination of Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} in admixtures and in the presence of other ingredients [cations (Ca^{2+}, Cd^{2+}, Mg^{2+}, Sr^{2+}, Fe^{2+}, $Fe^{3+}Mn^{2+}$) and (F^-, $NO3^-$, $SO_4{}^{2-}$, $S_2O_3{}^{2-}$, $PO_4{}^{3-}$, AcO^-, tartrate, citrate)] has also been carried out.

2.11.6 VBB

Liang Guozhu et al. [63] have presented a method for the spectrophotometric determination of Cu(I) in Al alloy with Cu(I)-I–VBB. A ternary ionic complex having ratio of 1:2:1 is formed by Cu(I), KI and VBB in 4 mL 0.05M H_2SO_4 solution, which shows absorption maximum at 570 nm. The molar absorptivity 1.85×10^5, and Beer's law is obeyed at 0–6 µg/25 mL. On the determination Cd^{+2} and Hg^{+2} had great interference. As mentioned by the authors the presented method could be used for the determination of Cu in Al alloy with the relative standard deviation 0.51–0.71% having recovery 95–97%.

2.11.7 3,3′,5,5′-Tetramethyl benzidine (TMB)

Di Junwei et al. [64] have proposed a new type of colored complex, the charge transfer complex for the spectrophotometric determination of copper. The method is based on the formation of a colored product, the charge transfer colored complex of Cu substituted tungstophosphate with 3,3′,5,5′-Tetramethyl benzidine (TMB), which is stabilized and sensitized by the addition of polyvinyl alcohol (PVA) in aqueous solution. The optimum reaction conditions and other analytical parameters are studied. Beer's law is obeyed in the Cu(II) concentration range of 0.003–0.1 mg mL^{-1}. The molar absorptivity at 660 nm is 2.54×10^5 L mol^{-1} cm^{-1}. The proposed method is simple, selective and sensitive; it has been applied to the analytical samples with satisfactory results.

2.11.8 Azure B

Safavi A. et al. [65] have presented a flow injection analysis (FIA) method as a sensitive catalytic kinetic method for the determination of nanogram amounts of Cu. This method is based on the catalytic effect of Cu(II) on the reduction of azure B by sulfide in the presence of cetyltrimethyl-ammonium bromide (CTAB). Spectrophotometrically, the reaction is monitored at 647 nm. The linearity range of the calibration graph is dependent on the concentration of sulfide. The method is simple, rapid, precise, sensitive, and widely applicable. The limit of detection is 9.2 ng mL^{-1}, the calibration range is 50–1,600 ng mL^{-1} of Cu(II), sampling rate is >60 detns./h, and the relative std. deviation of seven determinations of 400 ng mL^{-1} Cu(II) was 0.9%. The method has been applied by the authors to the determination of Cu in H_2O samples.

2.11.9 Acridine yellow and fuchsin acid

Sun Dengming et al. [66] have used a simple new dual-wavelength dual-indicator catalytic kinetic spectrophotometric method to detect trace copper(II) in water with satisfactory results. The method is based on the copper(II) catalyzing oxidation of acridine yellow and fuchsin acid by hydrogen peroxide in the Na_2HPO_4-NaH_2PO_4 at pH 5.5. The absorbances of the catalytic and un-catalytic systems are measured at 450 nm and 540 nm, respectively. Under the optimum conditions, the linear range of detection is 0.60–32 µg L^{-1}, as described.

2.11.10 Methyl violet

Yan Xiaoping et al. [67] have applied spectrophotometric method to the detection of trace copper(II) in food with satisfactory results. This method is based on its catalytic effect on the oxidative discoloration of hydrogen peroxide with methyl violet in hydrochloric acid medium. The maximum wavelength of absorbance is located at 590 nm when HCl concentration is 0.10 mol L^{-1}, H_2O_2 concentration is 1% and methyl violet concentration is 2×10^{-4} mol L^{-1}, reacting at 70 °C for 15 min. The liner range of the detection is found to be 0–32.0 g L^{-1} and the detection limit was 1.98×10^{-9} g mL^{-1}, as reported.

2.11.11 *N*-(Phenyl)-2-thioquinaldinamide (TQA)

Chakrabarti A. K. et al. [68] have presented a method for determination of Cu(II) in typical synthetic mixtures, environmental H_2O samples, alloy and steels in ultra trace level. Presented method is sensitive, selective and almost specific for determination of Cu. With *N*-(phenyl)-2-thioquinaldinamide (TQA), Cu(II) formed a 1:3 blue-violet anionic chelate in 1:1 water-EtOH (vol./vol.) and over the pH ranges of 1.5–3.8. The system obeyed Beer's law at 0.25–12 μg mL^{-1} at pH = 2.7 with the optimum range of determination of 0.5–8 μg mL of Cu(II). The molar absorptivity and Sandell's sensitivity are 8.1×10^3 and 1.05×10^4 (TMA) L mol^{-1} cm^{-1} of Cu(II) and 7.7 ng cm^{-2}. The log Kσ value obtained is 12.81 at 25 ± 1°.

2.11.12 2-(2-Quinolinylazo)-5-dimethylaminoaniline (QADMAA)

Liu Fei et al. [69] have studied a reagent 2-(2-quinolinylazo)-5-dimethylaminoaniline (QADMAA) that reacts with copper(II) to form a stable 2:1 complex in pH = 4.0, phosphatic salt buffer solution and in the presence of CTMAB. The molar absorptivity is 1.14×10^5 L mol^{-1} cm^{-1} at 580 nm. Beer's law is obeyed at 0.01–0.6 μg mL^{-1} of copper. This method has been applied by the authors to the determination of copper in environmental samples with good results.

2-(5-Bromo-2-pyridylazo)-5-[*N*-n-propyl-*N*-(3-sulfopropyl) amino]aniline (5-Br-PSAA)

Ohno Shinsuke et al. [70] have studied complex formation of 2-(5-bromo-2-pyridylazo)-5-[*N*-n-propyl-*N*-(3-sulfopropyl) amino]aniline (5-Br-PSAA) with copper(II) and iron(II) at pH 4.6. Copper(II) reacts with 5-Br-PSAA to form a complex showing an absorption maximum at 580 nm but iron(III) does not react. In the presence of a reducing agent only iron(II)-5-Br-PSAA complex is formed and detected at 558 nm. Under the optimum experimental conditions, the determinable ranges are 0.1–2 mg L^{-1} for copper and 0.1–5 mg L^{-1} for iron, respectively, with a sampling rate of 18 h^{-1}. The limits of detection are 50 microg L^{-1} for copper and 25 μg L^{-1} for iron. The relative standard deviations ($n = 15$) are 2% for 0.5 mg L^{-1} copper and 1.8% for 0.5 mg L^{-1} iron when determined in standard solutions. The proposed method can be successfully applied to the simultaneous determination of copper and iron in multi-element standard solution and in industrial waste water samples, as reported.

2-(2′-Quinolylazo)-1,3-diaminobenzene (QADAB)

Wu Fangping et al. [71] have described a method for detection of Cu contents in more than ten kinds of Chinese herbal medicines by microwave digestion-solid phase extraction spectrophotometry. The method comprises allowing Cu to react in the Chinese herbal medicines with 2-(2′-quinolylazo)-1,3-diaminobenzene (QADAB) in the presence of phosphate buffer solution (pH 4.0) and cetyltrimethylammonium bromide to obtain complex. This complex showed maximum absorbance at 555 nm. The range of Cu content was 0–1.0 μg mL^{-1} as reported.

Thionine

Chai Hong-mei et al. [72] have proposed a new catalytic kinetic spectrophotometric method for the determination of trace copper ion. It is based on the catalysis effect of copper on the oxidation of thionine by H_2O_2 in a buffer solution of NH_3-NH_4Cl at pH value of 9.76, and under conditions of the anionic surfactants of SDS and SDBS. The linear range of this method is 0.004–0.480 g mL^{-1}, the detection limit is 2.50×10^{-3} g mL^{-1} and apparent activation energy is 32.05 kJ mol^{-1}, as reported.

Bagheri H. et al. [73] have developed a simple, rapid and sensitive method for determination of trace amount of Cu(II) in real samples. This method is based on catalytic effect of Cu(II) on the oxidation of thionine by hydrogen peroxide in an alkaline media and in the presence of o-phenanthroline as an activator. The reaction is monitored spectrophotometrically by measuring the decrease in absorbance of thionine at 600 nm by the fixed time method. The detection limit is 0.7 ng mL^{-1}.

Dimethylindodicarbocyanine polymethyne dye (DIDC)

Balogh Ioseph S. et al. [74] have used 1,3,3-trimethyl-2-[5-(1,3,3-trimethyl-1,3-dihydro-indol-2-ylidene)-penta-1,3-dienyl]-3H-indolium – more commonly known as dimethylindodicarbo-cyaninepolymethyne dye (DIDC) as reagent for the detection of Cu(I), Cu(II) ion. Cu(I) and Cu(II) in the presence of chloride ions and DIDC reagent are extractable by a variety of organic solvents. The extraction of the Cu ion associates with DIDC by amyl acetate and the detection of Cu(I) and Cu(II) are at pH 3–5 and pH 3–6 and chloride concentration of 0.5–0.8 mol L^{-1} and 3–6 mol L^{-1} for Cu(I) and Cu(II), respectively. The molar absorptivities for Cu(I) and Cu(II) are 1.8×10^5 L mol^{-1} cm^{-1} and 1.2×10^5 L mol^{-1} cm^{-1}, respectively, as reported.

Biquinoline

Do Nascimento Rocha Sarah Adriana et al. [75] have proposed a method for molecular spectrophotometric determination of copper in sugarcane spirits. The copper(I) reacts with biquinoline forming a pink complex with maximum absorption at 545 nm. The reaction occurs in the presence of hydroxylamine, ethanol and Triton X-100. Determination of copper is possible in a linear range 0.2–20.0 mg L^{-1} with a detection limit 0.05 mg L^{-1}, as reported.

2-Chloro-4-bromo-benzenediazoaminoazo benzene

Li Yanhui et al. [76] have reported the color reaction of the new reagent 2-chloro-4-bromo-benzenediazoaminoazo benzene with Cu(II) in the presence of Triton X-100. This reagent forms a stable red complex (1:2) with Cu(II) in the presence of $Na_2B_4O_7$-NaOH buffer medium at pH 10.5. The λ_{max} of the complex is 520 nm, and the apparent molar absorptivity is found to be 1.01×10^5 L mol^{-1} cm^{-1}. Beer's law is obeyed in the range of 0–400 mg L^{-1} Cu(II). The coexisting ions could be separated from Cu (II) in sample by mercapto-containing dextran gel. The method has been applied by the authors to the determination of water samples, with the recovery of 100–102% and the RSD of 2.0–2.4%.

Methylene blue

Zhao Li et al. [77] have proposed a new dual-wavelength and dual-indicator catalytic kinetic spectrophotometric method for the detection of trace amount of copper in water. This method is based on copper(II) catalyzing oxidation of rhodamine B and methylene blue by hydrogen peroxide in a buffer medium of HAc-NaAc (pH 4.0). The absorbances of the catalytic and uncatalytic systems have been measured at 540 nm and 660 nm. The linear range of detection is 0.00080–0.048 g mL^{-1}, as reported.

N,*N*-Diethyl-*p*-phenylenediamine

Suizu Tomoki et al. [78] have described a spectrophotometric method for the determination of copper(II) with *N*,*N*-diethyl-*p*-phenylenediamine and thymoquinone. In this determination Beer's law is obeyed in a concentration range of 1.0–10 ng mL^{-1} of copper(II). The apparent molar absorptivity has been 2.61×10^6 L mol^{-1} cm^{-1} at 552 nm. The relative standard deviation for five replicate determinations for 6.3 ng mL^{-1} was 1.81%. As the authors mentioned, the proposed method is superior to the other catalytic methods of determination for copper(II) with regard to the liner range and the relative standard deviation. The recovery of copper(II) from real samples (tap water and supplement tablet) were within 96–103%.

Methyl orange

Liu Yong-he et al. [79] have proposed a micelle-sensitized catalytic spectrophotometric method for detection of trace amount of copper(II). In a hydrochloric acid solution of pH 3.1 and in the presence of CTMAB, the color-fading of methyl orange by oxidation with hydrogen peroxide is catalyzed by cupric ion, and the sensitivity of the color-fading reaction is found to be 2–3 times higher than that of the reaction in the absence of CTMAB. Based on these facts, linear relationship between the magnitude of decrease in absorbance $A(A_0\text{-}A)$ and mass concentration of copper(II) is obtained in the range of 1.0×10^{-3} to 4.0×10^{-2} mg L^{-1}. Detection limit (3S/N) found was 4.6×10^{-4} mg L^{-1}. By the proposed method authors detected copper(II) in river water samples and values of recovery found by standard addition method were in the range from 98.4% to 103.0%, as reported.

2,2′-Dipyridyl (Dp)

Hashem E. Y. et al. [80] have developed a spectrophotometric method that is easy to perform for the determination of copper in pharmaceutical, biological and water samples having safety to the environment too as there are no uses of hazardous solvents, which may harm our environment. Copper(II) forms a stable ternary complex with 5-(4-nitrophenylazo) salicylic acid (NPAS) and 2,2′-dipyridyl (Dp) in ethanol at room temperature showing maximum absorption at 520 nm with a molar absorptivity 2.60×10^4 L mol^{-1} cm^{-1}.The linear range for copper determination is 2.2–6.3 mg L^{-1} as reported by the authors. This method is sensitive, accurate and tolerant to many foreign ions.

1-(2′,4′-Dinitroaminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol [2′,4′-dinitro APTPT]

Kamble Ganesh S. et al. [81] have proposed that this spectrophotometric method is rapid, reproducible and successfully applied to the determination of copper(II) in binary and synthetic mixtures, alloys, pharmaceutical formulations, environmental and fertilizer samples. In the determination of copper(II) a chromogenic reagent, 1-(2′,4′-dinitroaminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol [2′,4′-dinitro APTPT] has been chosen. In this procedure copper(II) with 2′,4′-dinitro APTPT in the presence of pyridine gives green-colored ternary complex of a molar ratio 1:2:2 (M:L:Py) in the pH range 8.7–10.5 which is based on the synergistic extraction of complex formed. It exhibits a maximum absorption of colored complex at 445 nm and 645 nm in chloroform against the reagent blank. Beer's law is followed in the concentration range 10–80 mg mL^{-1} of copper(II) and optimum range of 20–70 mg mL^{-1} of the metal as evaluated from Ringbom's plot. The molar absorptivity and Sandell's sensitivity of copper(II)-2′,4′-dinitro APTPT-pyridine complex in chloroform is 0.87×10^3 L mol^{-1} cm^{-1} and 0.072 mg cm^{-2}, respectively. As reported by the authors the use of suitable masking agents enhances the selectivity of the method.

Neocuproin-hydroxylamine hydrochloride monohydrate

Jiang Yu-chun and Fu Bing [82] have presented a study that is based on the yellow complex formed by copper and neocuproin-hydroxylamine hydrochloride monohydrate. This yellow complex shows maximum absorption at 457 nm, and 732 type ion exchange resin as sorbent, a method of spectrophotometric determination of copper in molybdenum concentrations is proposed by the authors after separation and enrichment by ion exchange resin. Copper(II) is separated and enriched by the ion exchange resin at a flow rate of 1.4 mL min^{-1} in the pH range 3 to 4, then eluted by

HCl, which eliminated most of the interference from coexisting ions. As reported by the authors, the detection limit and precision of the method have been obtained to be 0.75 μg L^{-1} and 4.5%, respectively. The method could be successfully used to determination trace amounts of copper in real samples.

1-Amidino-*o*-methylurea

Singh L. Jadumani et al. [83] have determined the stoichiometry's and stability constants of copper(II) ions with 1-amidino-*o*-methylurea in aqueous solution at different temperatures with constant ionic strength of 0.5 M KNO_3 by using Job's continuous variation method spectrophotometrically. In all cases, the Job's curves display a maximum at a mole fraction $X_{\mathrm{metal}} = 0.5$ indicating the formation of complex with 1:1 metal to ligand ratio. It has been observed that metal–ligand stability constant decreases with increasing temperature indicating exothermic nature of the reaction. Plots of thermodynamic stability constants vs. $1/T$ give linear curves indicating high temperature sensitivity for the -NH group of the ligand.

Liu, Weihao and Liu, Genqi [84] have studied the color reaction of 2-(5-bromo-2-pyridylazo)-5-dimethylaminoaniline (5-Br-PADMA) with copper. The experimental results show that copper reacts with 5-Br-PADMA at room temperature to form a stable purplish red complex in pH = 3.75–5.75 HAc-NaAc buffer solution. The apparent molar absorptivity of the complex is 5.89×10^4 L mol^{-1} cm^{-1} at 573 nm. As described by the authors, the molar ratio of copper to 5-Br-PADMA in the complex is 1:2 that obeyed Beer's law in the range of 0–18 μg/10 mL for copper. The proposed method has been applied to spectrophotometric determination of copper in mine samples with satisfactory results.

Tiwari, Kishore K. et al. [85] have developed a simple and sensitive microwave supported spectrophotometric method for the determination of copper using new reagent leucomalachite green. In this method, the reaction of copper(II) with potassium iodide in the presence of hydrochloric acid to liberate iodine and the liberated iodine selectively oxidizes LMG to MG dye, which shows absorption maximum at 610 nm. As the authors report the complex obeyed Beer's law over the concentration range of 0.016–0.176 μg mL^{-1}. The molar absorptivity, Sandell's sensitivity and detection limit of method are found to be 3.8×10 L mol^{-1} cm^{-1}, 0.00016 μg cm^{-2} and 0.002 μg mL^{-1}, respectively. The method described has been satisfactorily applied for the determination of copper in environmental, biological and pharmaceutical samples.

Kuchekar, Shashikant R et al. [86] have developed a simple and rapid method for solvent extraction and spectrophotometric determination of copper(II) using *o*-methylphenyl thiourea (OMPT) as a sensitive reagent. The basis of proposed method is formation of copper(II)-OMPT complex which show maximum absorbance at 510 nm. Copper(II) was extracted with 0.020 mol L^{-1} OMPT in chloroform from aqueous solution in 0.075 mol L^{-1} potassium iodate. The formed complex obeyed Beer's law up to 600 μg mL^{-1} for copper(II). As reported by the authors, the molar absorptivity and Sandell's sensitivity of the complex are found to be 1.0167×10^3 L mol^{-1} cm^{-1} and 0.0625 μg cm^{-2}, respectively.

Correlation coefficient of the method is found to be 0.93. From slope ratio, mole ratio and Job's continuous variation methods the stoichiometry of copper(II)-OMPT complex has been established as 1:1 having stability >24 h. The proposed method is free from interferences from large number of foreign ions, as described. The proposed method can be successfully applied for separation and determination of copper(II) from real samples (vegetable and environmental samples), binary and ternary synthetic mixtures.

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Chapter 3

Analytical reagents having nitrogen (N) and oxygen (O) as donor atoms

3.1 Semicarbazones

3.1.1 4-Chloroisonitrosoacetophenonesemicarbazone

Lokhande R. S. et al. [1] have developed a spectrophotometric method for the determination of Cu(II) and reagent 4-chloroisonitrosoacetophenonesemicarbazone has been used. Upon reaction with Cu(II) the reagent gives a slight blue-colored complex at pH 7.2–8.0. This complex could be quantitatively extracted into $CHCl_3$ having molar absorptivity 1.79517×10^5 L mol^{-1} cm^{-1} at 386 nm. Beer's law is obeyed in the range 0.1 µg to 10 µg. As reported by the authors the present method can be used for analysis of Cu(II) in real samples as well as in binary mixtures.

3.1.2 Monosemicarbazone

Rai H. C. et al. [2] have proposed a spectrophotometric method for the determination of copper(II) by using phenanthrenequinone monosemicarbazone as a colorimetric reagent. The optimum conditions for the determination and the selectivity of the method have also been studied.

3.1.3 4-Chlorobenzaldehyde semicarbazone

Khiwani N. et al. [3] have presented a spectrophotometric method for analysis of Cu(II) in the samples of milk using 4-chlorobenzaldehyde semicarbazone as a reagent. The reagent reacts with Cu(II) giving a brown-colored complex that can be quantitatively extracted into chloroform at pH 7.2–8.0. Observed molar absorptivity at 388 nm is 2.3×10^4 L mol^{-1} cm^{-1} that obeyed Beer's law in the range 0.1 ppm to 10 ppm.

3.2 Alkylaminobenzoic acids

3.2.1 2-[2′-(6-Methyl-benzothiazolyl)azo]-5-dimethylaminobenzoic acid (MBTAMB)

Zhu Youyu et al. [4] have synthesized 2-[2′-(6-methyl-benzothiazolyl)azo]-5-dimethylaminobenzoic acid (MBTAMB) and employed as a new reagent for the spectrophotometric

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detection of copper(II). A blue complex is formed from MBTAMB and Cu(II) in the range of pH 2.0–5.0 in aqueous ethanol. The maximum absorption of the complex is at 660 nm; its apparent molar absorptivity is 7.0×10^4 L mol^{-1} cm^{-1}. Beer's law is obeyed for copper in the range of 0–0.72 µg mL^{-1}. The method has been used for the detection of micro amount of copper in aluminum alloy. The proposed method is simple, rapid and accurate, as reported.

3.2.2 2-[2-(4-Methylbenzothiazolyl)azo]-5-dimethylaminobenzoic acid (4-Me-BTAMB)

Furukawa Masamichi et al. [5] have synthesized chromogenic reagent 2-[2-(4-methylbenzothiazolyl)azo]-5-dimethylaminobenzoic acid (4-Me-BTAMB), which reacts with Cu(II) to form a 1:1 complex. In aqueous 1,4-dioxane solution a blue color is obtained with an absorbance peak at 650 nm. The apparent molar absorptivity of the 4-Me-BTAMB Cu(II) complex is 3.1×10^4 L mol^{-1} cm^{-1}. The optimum range for measurement in 1.0-cm cells is 0.04–2 mg Cu(II) L^{-1}. The proposed method is simple and very selective, and was applied to the detection of Cu in Al alloys, as reported.

3.2.3 2-(2-Benzothiazolylazo)-5-diethylaminobenzoic acid (BTAEB)

Chen Tongsen et al. [6] have developed a new dual-wavelength spectrophotometric method for the detection of Cu(II) with 2-(2-benzothiazolylazo)-5-diethylaminobenzoic acid (BTAEB)-Triton X-100. In the HAc-NaAc buffer medium at pH 3.8–5.5 and in the presence of Triton X-100, Cu(II) reacts with BTAEB to form a 1:2 blue violet complex. The maximum wavelength and apparent molar absorptivity of the complex are 654 nm and 5.7×10^4 L mol^{-1} cm^{-1}, respectively. Beer's law is obeyed at 0–20 µg Cu/25 mL. The molar absorptivity is 9.02×10^4 L mol^{-1} cm^{-1} of dual-wavelength spectrophotometry. The method is highly sensitive and selective. It was applied to the direct detection of Cu in Al alloy with satisfactory results, as reported.

3.2.4 2-Aminocyclopentene-1-dithiocarboxylic acid

Gholivand Mohammad B. et al. [7] have proposed a very sensitive, selective and economical method for preconcentration and determination of trace amounts of Cu in drugs and alloy samples. In this method, a solid uncharged complex is produced from 2-aminocyclopentene-1-dithiocarboxylic acid (synthetic reagent) on naphthalene. The 2-aminocyclopentene-1-dithiocarboxylate of copper is retained quantitatively on microcrystalline naphthalene in the pH range 2.8–3.3. After filtration the solid mass consisting of Cu complex-naphthalene is dissolved in DMF. The absorbance is measured at 462 nm against the reagent blank and molar absorptivity is 2.85×10^5 L mol^{-1} cm^{-1}. Beer's law is obeyed over the concentration of 0.1–16.0 mg of Cu in 4 mL of the DMF solution. Detection limit is 3 ng mL^{-1} of Cu(II). The interference of a large number of anions and cations has also been studied by the authors.

3.3 Hydroxytriazenes

3.3.1 3-Hydroxy-3-phenyl-1-*p*-carboxyphenyltriazene

Mehta Chayan et al. [8] have prepared 3-hydroxy-3-phenyl-1-*p*-carboxyphenyltriazene, and used this as a metallo-chromic indicator for complexometric detection of lanthanides, Cd and Zn. The present communication deal with spectrophotometric detection of Cu. Beer's law was obeyed for 0.635–3.81 ppm. The standard deviation was ± 0.01 ppm for 3.17 ppm Cu.

3.3.2 3-Hydroxy-3-propyl-1-*p*-tolyltriazene

Mehta Chayan et al. [9] have used 3-hydroxy-3-propyl-1-*p*-tolyltriazene for the spectrophotometric detection of Cu(II) at 380 nm. Beer's law is obeyed for 1.27–7.62 ppm. The conditional stability constant of the 1:3 Cu-reagent complex are 16.64 and 16.59. The interference of diverse ions has also been studied.

3.3.3 3-Hydroxy-3-methyl-1-*p*-methoxyphenyltriazene

Mehta Chayan et al. [10] have synthesized a reagent 3-hydroxy-3-methyl-1-p-methoxyphenyltriazene that forms in EtOH-solution a brown complex with Cu in the pH range 6–6.6. The max wavelength for this complex is at 380 nm and the working wavelength is 430 nm. Color development is instantaneous and all the solutions are made up to desired volume with EtOH. Maximum color development takes place when the reagent is in eightfold excess. Validity of Beer's law is observed in the range 6.35–38.1 ppm of Cu. Molar absorptivity, and Sandell's sensitivity is 1,340 dm^3 mol^{-1} cm^{-1} and 47.4 ng cm^{-2} respectively. Standard deviation is ± 0.14 for 15.88 ppm of Cu(II). Composition of the complex is found as 1:2 (Cu:R) by Job's method, slope-ratio method and mole-ratio methods.

3.3.4 3-Hydroxy-3-*m*-tolyl-1-*o*-chlorophenyltriazene

Sharma Kavita et al. [11] have used the reagent 3-hydroxy-3-*m*-tolyl-1-*o*-chlorophenyltriazene for spectrophotometric determination of Cu(II). The composition of yellow-colored complex is 1:2 (Cu:reagent) with absorption maximum at 390 nm in the pH range 6.6–7.2. Absorbance measurements are made at 400 nm. Beer's law is followed in the concentration range 2.0×10^{-5} M to 1.0×10^{-4} M. The value of molar absorptivity, Sandell's sensitivity, stability constant and free energy of formation are 4,107 L mol^{-1} cm^{-1}, 15.47 ng cm^{-2}, 10.10 and −13.77 kcal mol^{-1} respectively. Interference of 25 diverse ions is also examined by the authors.

3.3.5 3-Hydroxy-3-*m*-tolyl-1-*p*-sulfonato (Na-Salt) phenyltriazene

Sharma Kavita et al. [12] have used 3-hydroxy-3-*m*-tolyl-1-*p*-sulfonato (Na-Salt) phenyltriazene for the spectrophotometric determination of Cu(II). The reagent forms 1:2 yellow complexes with copper at pH 6.4 to 6.9 with λ_{max} at 402 nm. At absorption maximum 418 nm, values of molar absorptivity, Sandell's sensitivity, stability constant and free energy of formation are 7,037 L mol^{-1} cm^{-1}, 9.02 ng cm^{-2}, 9.02 (from Harvey and Manning's method) and −12.30 K Cal mol^{-1} respectively. Beer's law is obeyed in the entire concentration range studied, i.e. 2.0×10^{-5} M to 1.2×10^{-4} M. As described by the authors it is possible to determine copper (6.35 mg) in the presence of equimolar amount of eighteen cations and anions.

3.3.6 3-Hydroxy-3-methyl-1-(4-sulfonamidophenyl) triazene

Naulakha Neelam et al. [13] have used the reagent 3-hydroxy-3-methyl-1-(4-sulfonamidophenyl) triazene (HMST) for the spectrophotometric determination of copper(II). The light brown–colored complex absorbs at 360 nm at pH 6.7–7.3 (Cu:R = 1:2). The molar absorptivity and Sandell's sensitivity are 6.158×10^{3} L mol^{-1} cm^{-1} and 10.31 ng cm^{-2}, respectively.

3.4 Isonicotinoyl hydrazones and isonicotinoyl hydrazides

3.4.1 2-Pyridine carboxaldehyde isonicotinoyl hydrazones (2-PYAINH)

Guzar Sajid H. and Jin Qin-han [14] have reported spectrophotometric method for the detection of Ni, Cu, Co and Fe. A selective and sensitive reagent 2-pyridine carboxaldehyde isonicotinoyl hydrazone (2-PYAINH) has been chosen for Ni, Cu, Co and Fe at pH value of 7.0, 9.0, 9.0 and 8.0 respectively, which greatly increased the selectivity. As the authors describe Ni, Cu, Co and Fe reacted with 2-PYAINH to form 1:2 yellow-orange, 1:2 yellow-green, 1:2 yellow and 1:1 yellow complexes, with absorption peaks at 363, 352, 346, and 359 nm respectively. Under the optimal conditions, Beer's law is obeyed at 0.01–1.4, 0.01–1.5, 0.01–2.7 and 0.01–5.4 mg L^{-1} respectively. The apparent molar absorptivity and Sandell's sensitivities have been found 8.4×10^4, 5.2×10^4, 7.1×10^4, and 3.9×10^4 L mol^{-1} cm^{-1} and 0.00069, 0.0012, 0.00078, and 0.0014 g cm^{-2} respectively. The detection limits are 0.001, 0.002, 0.003 and 0.01 mg L^{-1} respectively, as reported.

3.4.2 2-Hydroxy-5-methylacetophenoneisonicotinoyl hydrazone (HMAINH)

Aswar A. S. and Joshi M. D [15] have reported spectrophotometry as new, simple and sensitive extractive method for the determination of Cu(II) with reagent 2-hydroxy-5-methylacetophenoneisonicotinoyl hydrazone (HMAINH). The reagent HMAINH reacts with Cu(II) to give a yellow-colored complex, which can be extracted quantitatively in chloroform at 3.4 pH. The complex shows absorption maximum at 440 nm. Beer's law is obeyed in the concentration range of 0.5–4.0 ppm of Cu(II). The molar absorptivity and Sandell's sensitivity of extracted species are 9.340×10^3 dm^3 mol^{-1} cm^{-1} and 6.8 ng cm^{-2}, respectively. The stoichiometry of the complex is found to be 1:1. The effect of various diverse ions on the estimation of Cu(II) is studied.

3.4.3 *N′*-(1-(pyridin-2-yl)ethylidene)isonicotinohydrazide (ACPINH)

Reddy P. Nityananda Kumar et al. [16] have developed a simple spectrophotometric method for the determination of copper(II) by using *N′*-(1-(pyridin-2-yl)ethylidene)isonicotinohydrazide (ACPINH) as a sensitive and selective analytical reagent. At pH 6.0 this reagent forms a greenish yellow–colored metal-ligand (M-L) complex (1:2), which shows maximum absorbance (λ_{max}) at 365 nm, while the ligand shows maximum absorbance at 284 nm. The method obeys Beer's law in the concentration range of 0.0636–0.636 µg L^{-1} with linear regression 0.99867. The molar absorptivity coefficient and Sandell's sensitivity of the complex are found to be 10.52×10^4 L mol^{-1} cm^{-1} and 0.01962 µg cm^{-2}, respectively. The proposed method is successfully applied for the determination of Cu(II) in water and food samples collected in and around the city of Kadapa city in Andhra Pradesh as reported by the authors.

3.4.4 *o*-Hydroxyacetophenoneisonicotinoylhydrazone (OHAPINH)

Reddy, G. Trivikram et al. [17] have developed a rapid extractive spectrophotometric method for the determination of copper(II) using *o*-hydroxyacetophenoneisonicotinoylhydrazone (OHAPINH) as an analytical reagent. OHAPINH reacts with Cu(II) to form an yellowish brown–colored complex at pH 4.0, which can be extracted with dichloromethane (DCM). It is observed that the color development is instantaneous and stable for more than 96 h. Cu(II) obeyed Beer's law in the range of 0.2 = 2.2 μg mL^{-1}, with a correlation coefficient 0.9998. The molar absorptivity and Sandell's sensitivity of the complex are 4.8×10^4 L mol^{-1} cm^{-1} and 0.0006 μg mL^{-1}, respectively. The metal to reagent ratio has been determined by Job's continuous variation, mole ratio, Asmus and slope ratio methods and is found to be 1:2. The optimized method can be successfully applied for the determination of copper(II) in the presence of diverse ions and also in biological, geological and pharmaceutical samples. The proposed method is selective, sensitive and reproducible, and the obtained results are in agreement with ICP-MS and AAS methods as reported.

3.5 Oximes

3.5.1 2-Hydroxy-4-*n*-propoxybenzophenone oxime (I)

Desai Anila et al. [18] have used 2-hydroxy-4-*n*-propoxybenzophenone oxime (I) for both gravimetric and spectrophotometric detection of copper(II). The buff-colored precipitate formed by Cu(II) and I was quantitatively detected and weighed as $Cu(C_{16}H_{16}O_8N)_2$. The precipitate is extracted into benzene for spectrophotometric detection at 390 nm. Beer's law is obeyed up to 46.26 ppm Cu(II). The molar absorptivity was 2.0×10^2 L mol^{-1} cm^{-1}. The mole ratio method and slope ratio method gave a Cu:I ratio of 1:2. The stability constant was 9.4×10^6.

3.5.2 2-Hydroxy-4-*n*-butoxyacetophenone oxime

Talati J. D. et al. [19] have used 2-hydroxy-4-*n*-butoxyacetophenone oxime ($C_{12}H_{17}NO_3$) for gravimetric estimation of Pd(II), Cu(II) and Ni(II) from their mixture at pH values of 1.5, 3.5 and 5.5, respectively. The reagent can also be used for extraction spectrophotometric detection of Cu(II) in the pH range 6.0–10.0. The mole ratio, slope ratio and Job's method show the metal-ligand ratio in the complex to be 1:2 with a stability constant of 2.4×10^9. The yellowish-green complex formed and extracted in benzene layer obeys Beer's law up to 326.7 ppm. The optimum concentration range, the photometric sensitivity and molar absorptivity are 197.2–326.7 ppm, 0.58 μg cm^{-2} and 108 L $mole^{-1}$ cm^{-1} at 650 nm respectively. The complex is fairly stable for 24 h and 50° ($\Delta G = -12.96$ Kcal mol^{-1}).

3.5.3 Dehydroacetic acid oxime (DAO)

Aminuddin M. et al. [20] have used dehydroacetic acid oxime (DAO) as a ligand for spectrophotometric determination of copper. The reaction takes place in slightly acidic medium and the Cu-DAO complex absorbs radiation in the visible region at 460 nm. As mentioned by the authors the absorption is free from any spectral interference as far as the reagent itself is concerned.

3.5.4 3-Isonitroso-5-methyl-2-hexanone (HIMH) and 5-methyl-2,3-hexanedione dioxime (H_2MHDDO)

Tandel S. P. et al. [21] have proposed a simple and selective method for the extraction of Cu(II) and its spectrophotometric determination using 3-isonitroso-5-methyl-2-hexanone (HIMH) and 5-methyl-2,3-hexanedione dioxime (H_2MHDDO). Cu(II) forms a greenish-yellow-colored complex with HIMH that can be extracted into isoamyl alcohol at pH 6.5–8.5. It shows absorption maximum at 390 nm and calibration curves are linear in the concentration ranges of 0.1–7.0 mg mL^{-1} of Cu(II). The molar absorptivity of the complex is 1.001×10^4 L mol^{-1} cm^{-1} and Sandell's sensitivity is 6.1 ng cm^{-2}. With H_2MHDDO, Cu(II) forms a greenish-yellow-colored complex that can be extracted into $CHCl_3$ at pH 7.0–8.5. The absorption maximum is observed at 370 nm and calibration curves are linear in the concentration ranges of 0.1–10 mg mL^{-1} of Cu(II). The molar absorptivity of the complex is 6.61×10^3 L mol^{-1} cm^{-1} and Sandell's sensitivity is 9.2 ng cm^{-2}. As the authors describe, both the reagents have been used for the determination of Cu in synthetic mixtures, pharmaceuticals, dyes and alloy samples.

3.5.5 4-Methylbenzaldehydeoxime

Lokhande R. S. et al. [22] have developed spectrophotometric method for the determination of copper(II) using 4-methylbenzaldehydeoxime as an analytical reagent that reacts with Cu(II) giving a green-colored complex. This complex can be quantitatively extracted in butan-1-ol at pH 10.0. Molar absorptivity of the complex at 430 nm is 0.5350×10^2 L mol^{-1} cm^{-1} and it obeyed Beer's law in the range 5 to 50 μg mL^{-1}. By using the present method Cu(II) was analyzed in synthetic mixtures, alloys as well as pharmaceutical samples, as reported by the authors.

3.5.6 Chloro-(phenyl)glyoxime

Turkoglu Orhan et al. [23] have developed a simple method for the determination of trace amounts of copper by spectrophotometry. This is based on the formation of the copper-chloro-(phenyl) glyoxime complex at pH 4.0 at 290.5 nm. The molar absorptivities of the complex is 0.8×10^4 L mol^{-1} cm^{-1}. The effects of the foreign ions were also studied. The method has been successfully applied by the authors for determinations of copper in some natural waters and pharmaceutical samples.

3.5.7 1,2-Propanedione-1-phenyl-1-(2-hydroxy-5-bromobenzilidineazine)-2-oxime (PDPHBBAO)

Lokhande Rama S. et al. [24] have used 1, 2-propanedione-1-phenyl-1-(2-hydroxy-5-bromobenzilidineazine)-2-oxime (PDPHBBAO) for extractive spectrophotometric determination of Cu(II). Copper forms a dark yellow-colored complex, which can be extracted in chloroform at pH 9.6, showing absorption maxima at 440 nm. Beer's law is obeyed in the concentration range 1–10.00 mg. As reported by the authors the molar absorptivity and Sandell's sensitivity are calculated on the basis of total Cu(II) taken and found to be 5.9909×10^3 L mol^{-1} cm^{-1} and 10.6×10^{-3} mg cm^{-2}, respective. This method can be applied satisfactorily for the determination of copper in the synthetic mixtures, alloys, beverages, milk samples which is highly sensitive, selective, simple, rapid and accurate.

3.5.8 Hydroxy oximes

Pathan A. Z. et al. [25] have developed a simple and selective method for spectrophotometric determination of Cu(II) using hydroxy oximes as the reagent. Copper (II) reacts with hydroxy oximes in aqueous solution to form the blue-colored complex. When 1 cm cells are used, the aqueous solutions of the chelates obeyed Beer's Law in the concentration range of 20 to 1,000 ppm. As reported by the authors, this method is mainly useful for the analysis of ores and alloys that contain different percentages of copper.

3.6 Rhodamines

Li Zubi et al. [26] have developed a spectrophotometric method for determination of Cu that is based on the reaction of rhodamine B with tungstocuprate in the presence of poly(vinyl alcohol). The absorption maximum of the ion-association complex has been observed at 570 nm in 0.96 M H_2SO_4. The apparent molar absorptivity of the complexes is 1.53×10^6 L mol^{-1} cm^{-1} and Beer's law is obeyed at 0–0.5 g/25 mL of Cu. The detection limit is 0.36 ng mL^{-1} ($n = 12$). A 0.018 µg mL^{-1} Cu solution is analyzed with relative standard deviation of 0.83% ($n = 11$). The ion-association complex is stable for at least 240 h. The molar composition of ion-associated complex is Cu:W:rhodamine

B = 1:12:5. Most common ions showed no interference. The method has also been used for the determination of Cu in natural water, running water, human hair, carrots and vegetables with satisfactory results as reported.

Ojeka E. O. et al. [27] have synthesized a new analytical reagent 5-(4-dimethylaminobenzylidene) rhodamine (DMABR) and its spectral characteristics have been studied. The extraction-spectrophotometric method using the reagent has been developed for the determination of copper and manganese. The method is based on the extraction of metal ions into ethanol with DMABR from a weakly acidic medium. Cu and Mn compounds react with the reagent DMABR in the molar ratio 1:1, 1:2 and 1:3 (metal:ligand) at pH 1.09 to 11.0 in a solution containing 20% (vol./vol.) of ethanol. For complete complexation a concentration of DMABR three times greater than the metal concentration is essential. The Cu and Mn complexes have an absorption maximum at 480 nm. For Cu-DMABR the molar absorptivity is 3.8×10^3 L mol^{-1} cm^{-1} at pH 2 and 7.6×10^3 L mol^{-1} cm^{-1} at pH 8. The interferences of some metal ions are also studied by the authors.

Zhao Li et al. [28] have proposed a new dual-wavelength and dual-indicator catalytic kinetic spectrophotometric method for the detection of trace amounts of copper in water. This method is based on copper(II) catalyzing oxidation of rhodamine B and methylene blue by hydrogen peroxide in a buffer medium of HAc-NaAc (pH 4.0). The absorbances of the catalytic and uncatalytic systems are measured at 540 nm and 660 nm. The linear range of detection is 0.00080–0.048 g mL^{-1}, as reported.

3.7 Aminophenols

3.7.1 5-Br-PADAP

Zhang Mingying et al. [29] have proposed micelle solubilization and dual-wavelength spectrophotometric determination of copper and zinc. Cu and Zn were detected by using 5-Br-PADAP in the presence of OP. The measuring wavelengths were 509 and 569 nm for Cu, and 530 and 573 nm for Zn. The calibration curves were linear in the range of 0–12 and 0–10 µg/25 mL for Cu and Zn respectively, with satisfactory sensitivity and accuracy.

Ge Xuanning et al. [30] have reported extraction of trace copper with chloroform as Cu-DDTC complex. In Tris buffer solution at pH 9.2, Cu-DDTC and 5-Br-PADAP were under ligand exchange to form Cu-5-Br-PADAP complex. Cu is detected by measuring the absorbances of Cu-5-Br-PADAP complex at 520 nm. Copper can be detected in food, wastewater and urine samples with satisfactory results, as reported.

Sa Mu-Ga et al. [31] have developed a spectrophotometric method for determination of copper and nickel in presence of Triton X-100. In borax buffer medium at pH 9.0, copper and nickel react with 5-Br-PADAP and form a purplish-red complex with

$X = 575$ nm, $c = 1.04 \times 10^5$ L mol^{-1} cm^{-1} and $A = 575$ nm, Ni = 1. 14×10^5 L mol^{-1} cm^{-1} that obeyed Beer's law in the concentration ranges of 0–560 μg L^{-1} for copper and 0–440 μg L^{-1} for nickel. The method is also applied by the authors to the determination of Cu and Ni in standard steel sample. As reported by the authors the precision of <5% relative standard deviation (n = 5) shows that results agree with recommended values.

Yu Ping et al. [32] have reported a rapid method for the detection of copper in diesel oil with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol(5-Br-PADAP) as a chromogenic reagent by flow injection spectrophotometry. It was studied in the medium of non-ionic microemulsion, which was composed of OP/*n*-butanol/*n*-heptane/water. In the optimum condition, Beer's law is obeyed in the range of 0–2.0 μg mL^{-1} for copper at 558 nm.

Xie Xiafeng [33] has described a method for detection of trace amount of cobalt and copper in water samples. After cloud point extraction with Triton X-114, an RH-HPLC method with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) chelates on a ODS column by using methanol-acetonitrile-water (volume ratio is 67 + 8 + 25) containing 2.0 mmol L^{-1} CTMAB and acetate buffer solution (pH 5.0) as mobile phase. This spectrophotometric detection is performed at 568 nm. The detection limit is 0.5 g L^{-1} for copper(II), and 0.8 g L^{-1} for cobalt(II), as reported.

3.7.2 *o*-Aminophenol

Sun Dengming et al. [34] have proposed a method for determination of Cu(II) by extraction-catalytic spectrophotometry. The method is based on Cu(II) catalyzed oxidation of o-aminophenol by H_2O_2 in weak acidic medium at pH 5.5. The reaction time, concentration of *o*-aminophenol in aqueous phase and degree of reaction are controlled by extraction equilibrium. The absorbance of organic phase is measured at 424 nm. The linear range of the method for Cu(II) is 0.01–0.15 m L^{-1}. The method has been applied by the authors to the determination of Cu in water, soybean and human hair with satisfactory results.

3.7.3 2-(5-Nitro-2-pyridylazo)-5-[*N*-propyl-*N*-(3-sulfopropyl)amino]phenol (nitro-PAPS)

Teshima Norio et al. [35] have proposed an affordable flow injection method for simultaneous spectrophotometric detection of copper, iron and zinc in patients' sera. The use of a newly designed multi-compartment flow cell allowed the simultaneous detection of the three metals with a single injection (one-shot') and a double beam spectrophotometer. The chemistry relied on the reactions of these metals with 2-(5-nitro-2-pyridylazo)-5-[*N*-propyl-*N*-(3-sulfopropyl)amino]phenol (nitro-PAPS) to form corresponding colored complexes. At pH 3.8, only copper-nitro-PAPS complex is formed in the presence of pyrophosphate as a masking agent for iron, and then the copper and iron(II) complexes are formed in the presence of reductant (ascorbic acid) at the same pH, and finally all three metals react with nitro-PAPS at pH 8.6. The characteristics are introduced into the flow system to detect each metal selectively and sensitively. Under the optimum conditions, linear calibration curves for the three metals are obtained in the range of 0.01^{-1} mg L^{-1}. The limits of detection are found 3.9 g L^{-1} for copper, 4.1 g L^{-1} for iron and 4.0 g L^{-1} for zinc as reported.

Zhou Tieli et al. [36] have established a simple and sensitive method for detection of serum copper by spectrophotometry. 2-(5-Nitro-2-pyridylazo)-5-[*N*-propyl-*N*-(3-sulfopropyl) amino] phenol (nitro-PAPS) has been used as a coloring agent for serum copper in the presence of surfactants Tween-80 and Triton X-100, and the formed complex has been measured by spectrophotometry. The maximum absorption wavelength of the complex was 570 nm, and the molar absorption coefficient was 7.95×10^4 L mol^{-1} cm^{-1}. The linearity of the method was up to 63.0 mol L^{-1}, and the recoveries range from 98.6% to 103.1%, as reported.

Wang Yi et al. [37] have developed a simple sensitive and stable method of detection of copper in human hair by UV-spectrophotometry. Nitro-PAPS is used as a coloring reagent in the presence of surfactants Brij-35 and Triton X-100. The results show that the maximum absorption of the complex compound is at 580 nm. The linearity of test is up to 0.5 g mL^{-1}. The molar absorption coefficient is 9.32×10^4 L mol^{-1} cm^{-1}. The recoveries range from 99.2% to 102.5%, as reported.

3.7.4 2-(2-Thiazolylazo)-5-sulfopropylaminophenol (TASPAP)

Ma Weixing et al. [38] have developed a chromogenic reaction of 2-(2-thiazolylazo)-5-sulfopropylaminophenol (TASPAP) with copper(II) in aqueous solution. The proposed method is applied to the direct detection of copper in aluminum alloy, for this pure aluminum or aluminum alloy samples which is dissolved in HCl when H_2O_2 and NH_3/H_2O and added to the sample solution. Cu^{2+} reacts with TASPAP to forming a stable purple complex at pH 5.6. The maximum absorption peak of this complex lies at 552 nm and its $A = 4.58 \times 10^4$ L mol^{-1} cm^{-1}. Beer's law is obeyed in the range of 0–2.0 mg L^{-1} for Cu^{2+}, as reported.

3.7.5 *N*-(*o*-Methoxybenzaldehyde)-2-aminophenol (NOMBAP)

Makhijani Ritika M et al. [39] have described spectrophotometry as simple, rapid, and sensitive method for the determination of Cu(II) by *N*-(*o*-methoxybenzaldehyde)-2-aminophenol (NOMBAP) as an analytical reagent. NOMBAP extracts Cu

(II) quantitatively into chloroform from an aqueous solution in pH range 5.7–6.8. The chloroform extract shows an intense peak at 440 nm (λ_{max}). Beer's law is obeyed over the Cu(II) concentration range of 0.1–4.0 mg mL^{-1}. The Sandell's sensitivity and molar absorptivity for Cu-NOMBAP system are 0.00246 mg cm^{-2} and 25,739 L $mole^{-1}$ cm^{-1}, respectively. The composition of extracted species is found to be 1:2 (Cu: NOMBAP) by Job's continuous variation and mole ratio method. The standard deviation is ±0.079. Interference by various ions has been studied by the authors and it is suggested that this method can be successfully applied for determination of Cu(II) in alloy and pharmaceutical samples.

3.8 Cuproines

3.8.1 Diethyldithiocarbonate (cuproine)

Zhang Zhenxin et al. [40] have studied the spectrophotometric determination of Cu by using DDTC (cuproine) as extractant and color developing agent with nonorganic solvents in poly ethylene glycol (PEG-DDTC) $(NH_4)_2SO_4$ system. The complex has been extracted by PEG phase from the water solutions of pH 3.6–9.0 (NaOAc-HOAc, NH_4Cl-$NH_3{\cdot}H_2O$). The maximum absorption of the complex is at 450 nm and the molar absorptivity is 9.05×10^3 L mol^{-1} cm^{-1}. Beer's law is obeyed at 0–30 μg L^{-1} Cu. Cu and DDTC form a stable complex with a molar ratio of 1:2; the proposed method could be applied to the determination of Cu in Al alloys with satisfactory results as reported by the authors.

3.8.2 Bathocuproine

Li Xiuling et al. [41] have described a method for the spectrophotometric determination of Cu(I) in alloys with bathocuproine in microemulsion medium. A complex with the ratio of 1:2 is formed by bathocuproine and Cu(I) in the presence of microemulsion in pH 4.5 HOAc-NH_4OAc buffer solution having absorption maximum at 477 nm. The apparent molar absorptivity is 1.25×10^4 L mol^{-1} cm^{-1}, and Beer's law is obeyed at 0–65 μg/25 mL. Ascorbic acid eliminates the interference of Fe^{+3}. The method is applied to determination of Cu in Al alloy, iron and steel, Pb-based alloy, and Sn-based alloy with the RSD 0.14–0.67%.

3.8.3 Neocuproine (2,9-dimethyl-1,10-phenanothroline)

Shrivas Kamlesh [42] has proposed a simple, sensitive and selective spectrophotometric method for the detection of copper in water and soil samples. The method is based on the reaction of Cu(I) with neocuproine (2,9-dimethyl-1,10-phenanothroline) and extracted with *N*-Phbenzimidoyl-thiourea in chloroform. The value of molar absorptivity of the complex in the term of Cu(I) is 1.45×10^5 L mol^{-1} cm^{-1} at maximum 460 nm in chloroform. The detection limit of copper in water and soil is 2 ng mL^{-1} and 4 ng g^{-1}, as reported. The method is free from the interference of the ions commonly found to be associated with the Cu detection in water and soil samples, as demonstrated by the authors.

Shariati Shahab et al. [43] have used UV-visible spectrophotometry for determination of trace amounts of copper. In aqueous solution copper ions form complexes with neocuproine; then Triton X-114 (0.15%, w/v) is added and phase separation occurs upon heating to 60°. These copper complexes are preconcentrated into the small volume of the surfactant-rich phase; after centrifugation, the surfactant-rich phase is diluted with methanol and absorbance is measured at 455 nm. By using UV-Visible spectrophotometry the applicability of Taguchi method to optimize cloud point extraction for preconcentration has also been confirmed.

3.8.4 Bathocuproine disulfonic acid

Peixoto Patricia S. et al. [44] have developed a reverse configured flow injection system for the determination of copper in water samples. Bathocuproine disulfonic acid has been used as a complexing agent. This complexing agent forms a complex in the presence of a reducing agent (hydroxylamine). The λ_{max} of the complex is monitored at 484 nm. The determination range is extended from 1 to 40 µg L^{-1}, with an applicable determination rate. As reported by the authors this method could be applied to the determination of copper in water samples (estuarine, river and drinking water) and showed good accuracy. The detection limit of 0.7 µg L^{-1} copper is consistent with the requirement of the target water samples.

3.9 Miscellaneous

3.9.1 *N-p*-Nitro-(2-mercapto)propionanilide

Kalani Rekha et al. [45] have synthesized a water-insoluble complex using Cu and the reagent *N-p*-nitro-(2-mercapto)propionanilide over the pH range of 3.0–6.5 that is easily adsorbed on microcryst naphthalene. The adsorbed mixture can be separated through filtration from the aqueous solution and then be dried and the complex is dissolved in DMF. Trace amount of Cu is detected by spectrophotometry at the wavelength of 450 nm.

3.9.2 Cinnamoylhydroxamic acid (CHx)

Hassiruzzaman M. et al. [46] have developed a simple and selective method for the spectrophotometric detection of trace amount of divalent copper with cinnamoylhydroxamic acid (CHx) in the presence of pyridine, piperidine, 3-picoline, DMSO, ethylenediamine (EDA) and diethylenetriamine (DETA). Both direct and extracting spectrophotometries show that colored hydroxamates are stable only in basic medium. The intense greenish yellow–colored products are formed above pH 8.5 with an absorption maximum at 390 and 399 nm (pyridine), 424 and 407 nm (piperidine), 364 and 393 nm (3-picoline), 359 and 340 nm (DMSO), 392 and 351.5 nm (EDA) and 386 and 383 nm (DETA) both in direct and Me iso-Bu ketone (MIBK) or isoamyl alcoholic (IAA) extracted system, respectively. Results indicate that the highest sensitivity and molar absorptivity were 0.01039 µg Cu(II) cm^{-2} and 6112.6 L mol^{-1} cm^{-1}, respectively, for Cu-CHx-piperidine system in direct spectrophotometry, while MIBK extracted Cu- CHx-pyridine system is found to give a sensitivity of 0.00832 µg Cu(II) cm^{-2} and molar absorptivity of 7,637.6 L mol^{-1} cm^{-1} being the highest of all the systems. The effects due to variation of pH, reagent concentration order of addition of reagents, time, temperature and solvent media on the absorption spectra have been investigated and the optimum conditions are detected.

3.9.3 Dibromocarboxyarsenazo

Xie Zhimin et al. [47] have found that in Na_2HPO_4-citrate buffer solution at pH 8 Cu(II) reacts with dibromocarboxyarsenazo to form a 1:1 complex. Cu was detected by measuring the absorbance at 585 nm. Beer's law is obeyed for 0–40 µg Cu/25 mL. The method can be applied to detecting Cu in aluminum alloys with satisfactory results, as reported.

3.9.4 Cupron

Rajput Nisha et al. [48] have developed an aqueous spectrophotometric method for the estimating of nanogram quantities of Cu(II) using cupron in the presence of Brij 35. The molar absorptivity of the complex is 66,000 L mol^{-1} cm^{-1} at pH 8 and wavelength 445 nm, and Beer's law is obeyed up to 7 ppm. The method is free from the interferences and was successfully employed in the analysis of alloys and H_2O, as reported.

Sirry S. M. et al. [49] have proposed extraction-spectrophotometric method for the determination of trace amounts of Cu and Co based on their extraction into *n*-pentanol with ethyl *o*-carboxyphenylhydrazonoacetoacetate (I). Copper has been extracted from pH 6.0–8.0 and ionic strength 0.5 M KCl. The maximum absorption of the extracted Cu(II)-(I) complex (1:1 and 1:2 species) occurs at 415 nm. As the authors describe, the proposed method has been successful in assaying the Cu concentration of 3–63 mg/10 mL of *n*-pentanol (e = 1.25×10^4 L mol^{-1} cm^{-1}).

3.9.5 1,5-Di(2-hydroxy-5-bromophenyl)-3-cyano formazan (HBPCF)

JinWen-Bin et al. [50] have reported the conditions for the color reaction of (HBPCF) with copper. In acetic acid-sodium acetate medium of pH 4.5 in the presence of CTMAB, 1,5-di(2-hydroxy-5-bromophenyl)-3-cyanoformazan (HBPCF) reacts with copper and forms a stable blue complex (mole ratio 1:3) with maximum absorption wavelength of 640 nm and molar absorptivity of 3.5×10^4 L mol^{-1} cm^{-1}. Beer's Law is obeyed in the concentration range of 0–28 mg/25 mL for copper. The method has also been applied by the authors to the determination of copper in tea and hair with satisfactory results.

3.9.6 Tetra, penta and hexaglycine

Alipazaga Maria V. et al. [51] have proposed a spectrophotometric studies on Cu(II) complexes with tetra, penta and hexaglycine. The oxidation of Cu(II) with tetra, penta and hexaglycine in borate buffer aqueous solution by dissolved oxygen is strongly accelerated by sulfite. The formation of Cu(II) complexes with maximum absorbance at 250 nm (e = 9.0×10^3 L mol^{-1} cm^{-1}) and 365 nm (e = 7.12×10^3 L mol^{-1} cm^{-1}) is observed. The concentration of Cu(II) complexes is proportional to the amount of added sulfite.

3.9.7 1,5-Diazacycloctane-1,5-bis(*N*-methylacetohydroxamicacid) (DACOD-MAHA)

Gaspar Margarida et al. [52] have studied the complexation behavior of the ligand 1,5-diazacycloctane-1,5-bis(*N*-methylacetohydroxamicacid) toward Cu(II) in aqueous solution by UV-visible spectroscopy. The copper(II) complexation involves the formation of a mononuclear species with a tetradentate mixed amine/hydroxamate coordination mode.

3.9.8 2-(2′-Quinolineazo)-4,5-dimethylhydroxybenzene (QADMP)

Han Yong et al. [53] have studied the color reaction of Cu(II) with 2-(2′-quinolineazo)-4,5-dimethylhydroxybenzene (QADMP). QADMP reacts with Cu(II) to form a stable 2:1 complex in the presence of pH = 4.0 HOAc-NaOAc buffer solution and CTMAB medium. The molar absorption is 4.56×10^4 L mol^{-1} cm^{-1} at 561 nm. Beer's law is obeyed with satisfactory results.

3.9.9 Xylenol orange (XO)

Song Yue-yuan et al. [54] have established a simultaneous detection method for copper and cobalt in cobalt ore by K-coefficient spectrophotometry. Beer's law is obeyed when the contents of copper and cobalt are in the range of 0–20 g/25 mL and 0–40 g/25 mL respectively. Color reaction takes place between copper(II) and cobalt(II) and xylenol orange (XO) in the presence of cetyl trimethyl ammonium bromide (CTMAB) under pH = 8.00. The relative standard deviation of this method is 3.5% for copper and 4.9% for cobalt, and the recovery percentage is 103.3% for copper and 92.6% for cobalt, as reported.

3.9.10 Cyclohexyldiamine tetra acetic acid (CyDTA)

Jia Hong-wu et al. [55] have applied spectrophotometric detection of high Cu concentration in copper electrolyte directly. This method uses cyclohexyldiamine tetra acetic acid (CyDTA) as developer in the test, which combined with Cu(II) in the liquid of acid whose pH is between 2 and 3 to form a kind of blue-green complex. This complex shows maximum absorption at 700 nm and follows Beer's law in the concentration range of 0–4 mg/50 mL for Cu. The interference of nickel and ferrite is subtracted with subtraction method, as reported.

3.9.11 Sulfanilic acid

Ghasemi Jahan et al. [56] have developed a very sensitive and selective kinetic catalytic spectrophotometric method for the detection of Cu(II). The method is based on the catalytic effect of Cu(II) on the reaction of sulfanilic acid with hydrogen peroxide at pH 6 and 25 °C in aqueous solution. As mentioned by the authors, the increase in the absorbance of the reaction mixture at 330 nm at a fixed time is proportional to the concentration of Cu(II) over the range of 0.05–6 g mL^{-1}. Partial least squares modeling as a powerful multivariate statistical tool is also applied and compared for detection of Cu(II) in aqueous solution. The root mean squares error prediction (RMSEP) and the relative error prediction REP(%) are 0.11% and 3.78%, as reported.

3.9.12 SALAAP

Wang Qing-Hua et al. [57] have established a new spectrophotometric method for the detection of trace copper(II) in river water that is based on SALAAP (a Schiff-base, synthesized by the condensation reaction between 2-hydroxybenzaldehyde and 4-aminoantipyrine). The linear range is 0.20–2.5 g mL^{-1} and regression equation is

$A = 0.0462 + 0.1885\,[Cu^{2+}]$ (g mL^{-1}), $r = 0.9990$, and the detection limit is 4.6×10^{-8} g mL^{-1}, as reported.

3.9.13 Dibromocarboxyarsenazo (DBKKA)

Li Bei-gang and Qi Jiao [58] have developed a new catalytic kinetic spectrophotometric method (in the medium of sulfuric acid) for the detection of trace copper in the foodstuffs. This method is based on the catalytic effect of trace Cu(II) on discoloring reaction of dibromocarboxyarsenazo (DBKKA) with hydrogen peroxide. The result shows that the catalytic reaction is a quasi-zero-order reaction. The apparent rate constant and the activation energy of the reaction are 1.38×10^{-4} s^{-1} and 53.97 kJ mol^{-1}, respectively. The linear range of the detection is 0–0.032 mg L^{-1}, and the detection limit is 0.64 g L^{-1} for Cu(II), as reported.

3.9.14 Isonitroso-*p*-methoxyacetophenone (HIMAP)

Barhate V. D. and Patil M. R. [59] have reported that isonitroso-*p*-methoxyacetophenone (HIMAP) extracts copper(II) quantitatively (99.00%) into chloroform from an aqueous solution of pH 5.8–7.5. The chloroform extract shows an intense peak at λ_{max} 360 nm. Beer's law is obeyed over the Cu(II) concentration range 0.1–10 mg mL^{-1}. The molar absorptivity and Sandell's sensitivity of colored species are 10,165 L $mole^{-1}$ cm^{-1} and 0.0062 mg cm^{-2}, respectively. The composition of extracted species is found to be 1:2 (Cu:HIMAP) by Job's continuous variation and mole ratio method. The method can be successfully applied for determination of Cu(II) in aluminum alloy and also for the sequential separation of Cu(II) and Co(II).

3.9.15 Alanine

Wei Liang et al. [60] have reported that the copper can catalyze the fading reaction of neutral red reduced by hydrogen peroxide using the alanine as a sensitizer in NH_4C1-$NH_3 \cdot H_2O$ medium (pH 8.0). On the basis of this, a new flow injection, catalytic spectrophotometric method is proposed for online detection of trace copper in sea water. Beer's law is obeyed in the concentration range of 2.0–32.0 g L^{-1} for copper, as reported.

3.9.16 8-Hydroxyquinoline (8-Ox)

Li Ying-jie et al. [61] have described a new spectrophotometric method with cloud point extraction for the detection of trace copper in water sample. The method is based on the complexation of Cu(II) with 8-hydroxyquinoline (8-Ox), which forms a hydrophobic complex and subsequently enters surfactant-rich phase at pH 7.0. At NH_3-NH_4Cl buffer solution, the maximum wavelength of absorption of Cu(II)-8-Ox complex is 395 nm, $A = 7.69 \times 10^5$ L mol^{-1} cm^{-1}, as reported.

3.9.17 *p*-Acetylchlorophosphonazo(CPApA)

Zhai Qing-Zhou [62] has proposed a novel catalytic kinetic-spectrophotometric method for the detection of copper in tomato and cucumber samples. The method is based on copper(II) catalyzes the oxidation of p-acetylchlorophosphonazo(CPApA) by hydrogen peroxide in 0.10 M phosphoric acid. Copper(II) could be detected spectrophotometrically by measuring the decrease in the absorbance of CPApA at the wavelength of 554 nm using the fixed-time method. The optimum reaction conditions are as follows: H_3PO_4 (1.00 M) 1.0 mL, CPApA (2.19×10^{-4} M) 1.5 mL, H_2O_2 (4.30×10^{-2} M) 1.2 mL, reaction temperature 100° and reaction time 13 min. The linear range for the detection of copper(II) is 0.020–0.30 g mL^{-1}, as reported.

3.9.18 1-Nitroso-2-naphthol-3,6-disulfonic acid

Makipour Paymaneh and Moghimi Ali [63] have introduced a simple and fast method for extraction and determination of trace amounts of Cu(II) ions using octadecyl-bonded silica membrane disks modified with 1-nitroso-2-naphthol-3,6-disulfonic acid and visible spectrophotometry at a wavelength maximum of 636 nm. Maximum capacity of the membrane disks modified with 2 mg of the anthraquinone derivative used has been found to be 489 mg Cu^{2+}. The limit of detection of the proposed method is 10 ng mL^{-1}. The method could be applied to the recovery of Cu^{2+} from different synthetic samples and water samples, as reported by the authors.

3.9.19 Amino acid (isoleucine)

Liang Pei and Yang Juan [64] have proposed cloud point extraction preconcentration and spectrophotometry that is a new method for the determination of trace copper. In the proposed approach, amino acid (isoleucine) has been used as the chelating agent, and Triton X-100 has been selected as the surfactant. Some factors including pH of sample solution, concentration of the chelating agent and surfactant, and equilibration temperature and time, which affected the extraction efficiency of Cu and its subsequent determination are studied and optimized. Under the optimum conditions, the calibration graph is linear in the range of 10–1,000 mg L^{-1} preconcentration of 25 mL sample give an enhancement factor of 22 and a detection limit of 5 mg L^{-1}. The method could be successfully applied to the determination of Cu in food and water samples, as reported.

3.9.20 8-Hydroxyquinoline

Alula Melisew Tadele et al. [65] have proposed a spectrophotometric method for simultaneous determination of copper(II) and iron(II) in synthetic mixtures and pharmaceutical mixtures. For this 8-hydroxyquinoline is used as a chromogenic reagent. The absorption spectra are recorded in the wavelength range of 350–600 nm. Four chemometrics methods such as first derivative spectrophotometry (1D zero crossing), first derivative ratio (1D ratio), classical least squares (CLS) and principal component regression (PCR) are used to predict the concentration of the metal ions. The calibration curves are found linear in the range of 2–12 g mL^{-1} for both ions, as reported.

3.9.21 Light green SF

Chen Zongbao et al. [66] have proposed a novel method for the catalytic kinetic spectrophotometric detection of copper(II), which is based on the catalytic effects of trace copper(II) on the fading reaction of light green SF oxidized by H_2O_2 in the presence of dilute nitric acid with CTMAB as sensitizer. The experimental method is optimized, and the detection wavelength is selected as 635 nm. The results showed that this reaction has zero-order reaction for light green SF and first-order reaction for trace copper. Under the optimal conditions, the detection limit of this method is 0.23×10^{-9} g mL^{-1}. The change of absorbance (A) has good linearity with the mass concentration of Cu^{2+} in the range of 0–20 ng mL^{-1}. The interference of other coexisting ions can be effectively eliminated by adding proper masking reagents. The relative standard deviations (RSD) are 3.8% and 2.4%, as reported.

3.9.22 3,5-DiBr-DMPAP

Ma Meiping et al. [67] have developed a new spectrophotometric method for highly selective detection of water samples of pools with 3, 5-diBr-DMPAP in the presence of OP at pH 4.0 buffer solution. The maximum absorption of the complex compound is 580 nm, the linearity of test is up to 0.6 g mL^{-1} and the molar absorption coefficient is 5.568×10^4 L mol^{-1} cm^{-1}, as reported. It has been used for the detection of Cu(II) in every kind of water samples of pools.

3.9.23 Ammonium purpurate (murexide)

Kachbi A. et al. [68] have applied partial least squares (PLS) modeling based on SIMPLS algorithm for the simultaneous spectrophotometric detection of Co(II), Ni(II) and Cu(II) with ammonium purpurate (murexide) as the complexing agent. An analytical wavelengths of (400 to 490) nm have chosen and an experimental calibration matrix for PLS has been designed with 21 samples of (0.354 to 5.893) g mL^{-1}, (0.352 to 5.869) g mL^{-1} and (0.381 to 6.355) g mL^{-1} for cobalt, nickel and copper, respectively. A leave one out cross-validation procedure has been used for selecting the number of components using Rybicki Press. The method has been successfully applied by the authors to the simultaneous detection of these metals in industrial alloys.

3.9.24 *N*-(*o*-hydroxybenzylidene)pyridine-2-amine (NOHBPA)

Gupta Anand Kumar S. and Barhate V. D. [69] have presented a simple and sensitive extractive spectrophotometric method for the determination of copper(II) using [*N*-(*o*-hydroxybenzylidene)pyridine-2-amine] (NOHBPA) as an analytical reagent. NOHBPA forms a reddish-brown color complex of copper(II) showing an intense peak at 540 nm (λmax) and extracts quantitatively (99.40%) into benzene from an aqueous solution of pH range 6.8–7.5. The system obeys Beer's law over the Cu(II) concentration range of 0.1–14 mg mL^{-1}. The Sandell's sensitivity and molar absorptivity for Cu-NOHBPA system are 0.0182 mg cm^{-2} and 3494.84 L $mole^{-1}$ cm^{-1} respectively, as described. The composition of extracted species is found to be 1:2 (Cu:NOHBPA) by Job's continuous variation and mole ratio method. Interference by various ions has also been studied. This method can be successfully employed for the determination of Cu(II) in pharmaceutical samples.

3.9.25 4-(2′-Benzothiazolylazo)-salicylic acid (BTAS)

Hashem E. Y. et al. [70] have reported that spectrophotometry is a highly sensitive method for determination of copper(II) in different biological specimens like some drugs and water samples. For this purpose analytical reagent 4-(2′-benzothiazolylazo)-salicylic acid (BTAS) is taken by the authors. Cu(II) forms a stable complex with 4-(2′-benzothiazolylazo)-salicylic acid (BTAS) at room temperature and pH of 5.0. The complex gives a maximum absorption at $\lambda = 485$ nm with a molar absorptivity coefficient of 2.35×10^4 L mol^{-1} cm^{-1}. The linear range for the copper determination is 0.63–5.04 mg L^{-1}.

3.9.26 5-(4-Nitrophenylazo) salicylic acid (NPAS)

Hashem E. Y. et al. [71] have reported that the spectrophotometric method is easy to perform for the determination of copper in pharmaceutical, biological and water samples having safety to the environment as there are no uses of hazardous solvents, which may harm our environment. Copper(II) forms a stable ternary complex with 5-(4-nitrophenylazo) salicylic acid (NPAS) and 2,2′-dipyridyl (Dp) in ethanol at room temperature showing maximum absorption at 520 nm with a molar absorptivity 2.60×10^4 L mol^{-1} cm^{-1}. The linear range for copper determination is 2.2–6.3 mg L^{-1} as reported by the authors. This method is sensitive, accurate and tolerant to many foreign ions.

3.9.27 1-(2′,4′-Dinitroaminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol [2′,4′-dinitro APTPT]

Kamble Ganesh S. et al. [72] have proposed that spectrophotometric method is rapid, reproducible and can be successfully applied to the determination of copper(II) in binary and synthetic mixtures, alloys, pharmaceutical formulations, environmental and fertilizer samples. For the determination of copper(II) a chromogenic reagent, 1-(2′, 4′-dinitroaminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol [2′,4′-dinitro APTPT] is chosen. In this procedure copper(II) with 2′,4′-dinitro APTPT in the presence of pyridine gives a green-colored ternary complex of a molar ratio 1:2:2 (M:L:Py) in the pH range 8.7–10.5 that is based on the synergistic extraction of complex formed. It exhibits a maximum absorption of colored complex at 445 nm and 645 nm in chloroform against the reagent blank. Beer's law is followed in the concentration range 10–80 mg mL^{-1} of copper(II) and optimum range of 20–70 mg mL^{-1} the metal as evaluated from Ringbom's plot. The molar absorptivity and Sandell's sensitivity of copper(II)-2′,4′-dinitro APTPT-pyridine complex in chloroform are 0.87×10^3 L mol^{-1} cm^{-1} and 0.072 mg cm^{-2}, respectively. Use of suitable masking agents enhances the selectivity of the method.

3.9.28 Fluoxetine hydrochloride (FX), fluvoxamine maleate (FV)

Soliman Suzan M. et al. [73] have developed two simple and sensitive spectrophotometric and spectro-fluorimetric procedures and validated for analysis of selective serotonin reuptake inhibitors (SSRIs) namely, fluoxetine hydrochloride (FX), fluvoxamine maleate (FV) and sertraline hydrochloride (SE). Both methods are based on the formation of ternary complex between the cited drugs, eosin and copper sulfate, spectrophotometrically. For determination of complex two procedures are used; the first procedure depends on the extraction of the ternary complex with chloroform. The second spectrophotometric method depends on the direct measurement of the complex after addition of sodium lauryl sulfate. The ternary complexes show an absorption maximum at 530 nm for the 3 cited drugs. The formed complexes obey Beer's law in concentration ranges 1–18, 1–16 and 0.25–10 μg mL^{-1} using the extractive method and 0.4–12, 0.5–14 and 0.1–8 μg mL^{-1} using surfactant with good correlation coefficients. A fluorescence quenching method for the determination of the (SSRIs) through the formed ternary complexes is also investigated to enhance the sensitivity of the analysis. The formed fluorophores are measured at λ_{max} 310 nm and λ_{max} 510 nm for the three drugs. The proposed methods are validated and successfully applied by the authors to the analysis of the three drugs in drug substances and drug products with good accuracy. No interference is observed from common pharmaceutical excipients.

3.9.29 Indigo carmine

A novel method for the detection of copper(II) by catalytic spectrophotometry based on the catalytic effect of copper on the oxidation fading reaction of indigo carmine with potassium bromate in phosphate buffer solution at pH = 5 is reported by **Shen Li** [74]. Under the optimized conditions, the absorbance shows good linearity with the concentration of copper(II) in the range of 1–16 g/25 mL, and the detection limitation is 3.4×10^{-9} g mL^{-1}, as reported. The method is applied to detection of copper (II) in water sample with satisfactory results.

3.9.30 5-{α-Methyl-3-hydroxy benzylidene} rhodanine

Ashok Rao K. et al. [75] have reported a simple and sensitive spectrophotometric method for the quantification of copper in water, vegetables, foodstuffs, human hair and pharmaceutical samples. Cu(II) forms an orange-red-colored complex with 5-{a-methyl-3-hydroxy benzylidene} rhodamine [5 M, 3 H-BR], sodium acetate and acetic acid buffer. The maximum absorbance is measured at 430 nm. Beer's law is obeyed in the range of (0.05 μg–13 μg mL^{-1}). The molar absorptivity (ε) and the Sandell's sensitivity of the complex is 0.6027×10^{40} L mol^{-1} cm^{-1} and 0.01054 μg cm^{-2}, respectively. First, second and third derivative spectrophotometry is proposed and employed successfully for the determination of copper in the supra, as reported.

3.9.31 Schiff base (salicylaldehyde-adenine)

Hong Tao et al. [76] have established a spectrophotometric method for the determination of trace Cu(II) by using Schiff base as color reagents. The conditions of the reaction between SASB and Cu(II) are optimized. The linear range and apparent molar absorptivity at 400 nm is 0.05–0.60 mg mL^{-1} and 7.68×10^4 L mol^{-1} cm^{-1}, respectively. The method, which is free from the interference of much common ions, can used for the determination of copper in the presence of 75 times of Al^{3+} and 25 times of Fe^{3+} after 2 mL of 10.0 g L^{-1} NH_4F is added as a screening agent. The results for the determination of trace copper in aluminum alloys obtained by this method with the standard deviation of less than 2.5% are in agreement with that obtained by AAS.

3.9.32 Dibromo-*p*-chloro-chlorophosphonazo (DBC-CPA)

Hu Wei-Hua et al. [77] have proposed kinetic-spectrophotometric method for the determination of copper. The method is based on the catalytic effect of copper(II) on the oxidation of dibromo-p-chloro-chlorophosphonazo (DBC-CPA) by hydrogen peroxide in 1 mol L^{-1} phosphoric acid medium. Copper can be spectrophotometrically determined by measuring the decrease in the absorbance of dibromo-p-chloro-chlorophosphonazo at the wavelength of 550 nm using the fixed-time method. The linear range of the present method is 0.1–2.0 mg in 10 mL of solution and the limit of detection is 9.05 ng mL^{-1}. The method can be successfully applied to the determination of copper in apple and banana. The relative standard deviations of 13 determinations of the method are 0.82–1.03% and the recoveries of the present method are 101.3–103.6%.

3.9.33 Nicotinohydroxamic acid

Muthuselvi R. et al. [78] have developed a simple, direct, highly sensitive and selective spectrophotometric method for the determination of Cu(II). The proposed procedure is successfully applied to the analysis of Cu(II) in natural samples, industrial effluents and alloy. This method is based on the reaction between nicotinohydroxamic acid and Cu(II) at pH 9.2, forming a stable green-colored complex. It exhibits a constant and maximum absorption at 800 nm. The system obeys Beer's law over a wide range of concentration. The proposed method can be applied for the determination of Cu(II) without interference from a variety of ions, as described.

3.9.34 1-(2,4-Dimethylphenyl) azonaphthalen-2-ol (Sudan II)

Gurkan Ramazan et al. [79] have developed spectrophotometry for the separation and preconcentration of copper(II) in different beverage samples. Prior to spectrophotometric analysis cloud point extraction (CPE) method is used. Here as chelating agent 1-(2,4-dimethylphenyl) azonaphthalen-2-ol (Sudan II) is used. For pH adjustment borate buffer is taken. Polyethylene glycol tert-octylphenyl ether (Triton X-114) is used as an extracting agent in the presence of sodium dodecylsulfate (SDS). The surfactant-rich phase is diluted with acetone after phase separation, based on the cloud point of the mixture. The enriched analyte is determined spectrophotometrically and shows absorption maximum at 537 nm. The calibration curve is linear within the range 0.285–20 µg L^{-1} with a detection limit of 0.085 µg L^{-1}, as mentioned.

3.9.35 [*N*-(*o*-Hydroxybenzylidene)-4-Me aniline] (NOHBMA)

Hankare Asmita S. et al. [80] have developed a spectrophotometric method for the determination of Cu(II) using [*N*-(*o*-hydroxybenzylidene)-4-Me aniline] (NOHBMA) as an analytical reagent. As reported by the authors it is a simple, rapid and sensitive method for determination of Cu(II). NOHBMA extracts Cu(II) quantitatively (99.64%) into n-amyl alcohol from an aqueous solution of pH range 5.8–6.8. The n-amyl alcohol extraction shows an intense peak at 510 nm (λ_{max}). Beer's law is obeyed over the Cu(II) concentration range of 1.0–20.0 µg mL^{-1}. The Sandell's sensitivity and molar absorptivity for Cu-NOHBMA system are 0.07142 µg cm^{-2} and 890 L $mole^{-1}$ cm^{-1} respectively. The composition of extracted species is found to be 1:2 (Cu:NOHBMA) by Job's continuous variation and mole ratio method. The average of ten determinations of 100 µg of Cu(II) in 10 cm^3 of solution is 100.2 µg that is varied between 100.05 µg and 100.36 µg at 95% confidence limit and standard deviation is ±0.155. The authors have also studied interference by various ions. The proposed method is successfully applied for determination of Cu(II) in alloy sample.

3.9.36 Esomeprazole

Ranganath, B. et al. [81] have used esomeprazole as a new chromogenic reagent for the determination of copper(II) by direct and derivative spectrophotometric method. Esomeprazole forms a yellow-colored complex with copper(II) at pH 3. The method obeys Beer's law over 0.5 to 10 ppm and Sandell's sensitivity is 0.022 µg cm^{-2}. The method can also be useful for determination of copper in biological, alloys, synthetic mixture and water samples.

3.9.37 3-Benzothiazol-2-diazenylnaphthalene-2,7-diol

Khazaal, Fatma A. et al. [82] have synthesized the azo reagent 3-benzothiazol-2-diazenylnaphthalene-2,7-diol and characterized by various characterization techniques. At glassy carbon disk GCE electrode in different supporting electrolyte at concentration 1 M and scan rate 100 mv s^{-1}, the electrochemical behavior of the azo reagent and its complex with Cu(II) has been studied. Spectrophotometric determination of copper(II) is based on the formation of a 2:1 complex with above reported reagent showing λ_{max} at 588 nm. The molar absorptivity (e_{max}) of 1.436 × 10 L mol^{-1} cm^{-1}. A linear correlation 0.1–3.0 mg mL^{-1} is found between absorbance at λ_{max} and concentration. The effect of diverse ions on the determination of copper(II) to investigate the selectivity of the method are studied. The stability constant of the product has value 1.1 × 10. As described by the authors, the proposed method can be successfully applied to the analysis of honey sample.

3.9.38 *o*-Vanillidine-2-amino-4-ethylbenzothiazole (VEBT)

Shanthalakshmi, K. et al. [83] have proposed a simple spectrophotometric method for the determination of copper using *o*-vanillidine-2-amino-4-ethylbenzothiazole (VEBT). The copper ions react with the given Schiff's base at room temperature to a form 1:2 [Metal:Ligand] brownish yellow-colored complex that follows Beer's law over the range 0.41 m g mL^{-1} to 3.78 m g mL^{-1} of copper. The complex formed is measured at lmax 450 nm in aqueous methanol solution. The proposed method offers the sensitivity, rapidity, selectivity without any prior separation and extraction. The method is free from the interference of metal ions like zinc, cadmium, cobalt, iron, lead and mercury, as reported by the authors. The method can be successfully applied for the determination of trace amount of copper in industrial effluents.

3.9.39 Hydroxy-3-[(2-hydroxyl phenyl) methylene amino] benzene sulfonic acid(II)(HVMAB)

Maarouf, Mohammad et al. [84] have proposed the potential formation of a colored complex in aqueous solution between Cu^{+2} and hydroxy-3-[(2-hydroxyl phenyl) methylene amino] benzene sulfonic acid(II)(HVMAB) in the spectrophotometric determination of copper. It is found that a greenish yellow–colored complex of Cu^{+2} and HVMAB is formed in aqueous medium at pH = 2. Experimetally, λ_{max} of complex solution with Cu^{+2} is found to be 430 nm by the spectral survey. Other spectral parameters for the same complex are determined on this absorption maximum .The stoichiometric composition of complex is Cu:HVMAB = (1:2), molar absorbance coefficient e = 1.25×10^4 L mol^{-1} cm^{-1} and complex formation constant $K_b = 1.67 \times 10^4$, as reported by the authors. Moreover, all factors effecting the complex formation are investigated from which it is found that the complex obeyed Beer Lambert Law in the range (0.2–8.0) mg L^{-1} and the detection limit is 0.006 mg L^{-1}. Further, it is reported that this method can be successfully applied to standard copper solutions, the relative standard deviation didn't exceed 3.89% at low concentration of copper, as determined by the authors, the higher copper concentration the lowest RSD and the highest recovery occurred, namely, at 5 mg L^{-1} of copper the RSD and the recovery are 0.2% and 100.2% respectively. The minimum recovery is 96.3%.

3.9.40 2-[(4-Antipyrinyl)azo)]imidazole

Ali, Khdeeja Jabbar et al. [85] have prepared a ligand 2-[(4-antipyrinyl) azo)] imidazole that reacts with metal salt in ethanol:water as a solvent in 1:1 ratio (metal:ligand). The characterization of metal complex having general formula $[CuLCI_2H_2O]$ indicates that the ligand coordinates with the metal(II) ion in neutral tridentate manner. All the studies reveal coordination six for the metal in the complex that has a octahedral structure. The absorption maximum of complex observed is 578 nm, which is directly proportional to copper(II) concentration. At pH 8–9, with reagent concentration of 1×10^5 mol L^{-1} the complex is observed to be stable at various at temperatures (5–60) °C for a longer period of time 1,440 min. The calibration graph observed is linear in the range of 1×10^{-5}–1×10^{-4} mol L^{-1} and detection limit has been 1×10^{-6} mol L^{-1}.

3.9.41 2-[6-Nitro-2-benzothiazolylazo]-4-hydroxy benzoic acid ((NO2 BTAHB)

Jreo, Aqeel Mahdi [86] is synthesized a new 2-[6-nitro-2-benzothiazolylazo]-4-hydroxy benzoic acid (NO_2BTAHB) organic reagent and proposed a sensitive and selective spectrophotometric method for the rapid determination of Cu(II) using (NO_2BTAHB) reagent. This reaction is instantaneous at pH = 6.0 and the absorbance remains stable for over 24 h. The method allows for the determination of Cu(II) over the range (0.1–6.0) mg mL^{-1}, with molar absorptivity of $(7.45 \times 10^{+3})$ L mol^{-1} cm^{-1} and a detection limit of 0.0245 mg mL^{-1}. Recovery and relative error values of precision and accuracy of method are found to be R.S.D = 1.7%, Re = 98.6% and $E_{rel} = -1.4\%$. The properties of complex has been studied and show (M:R) ratio was 1:2 at pH = 6.0, and the stability constant of $7.796 \times 10^{+9}$ L^2 mol^{-2}. The interference of ions (Ni^{2+}, CrO_2^-, Ca^{2+}, Pb^{2+}, Cu^{+2}, WO_4^{-2}, MO_4^{-2}, Co^{2+}, Mg^{2+}, Cd^{2+}, Ba^{2+}, Bi^{3+}) and masking agents effect on absorbance.

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Chapter 4
Analytical reagents having nitrogen (N) and sulfur (S) as donor atoms

4.1 Thiosemicarbazones

4.1.1 Thiophenealdehyde 4-phenyl-3-thiosemicarbazone (TPS)

Nishioka H. et al. [1] have developed a simple method for the extraction spectrophotometric detection of copper(II) using thiophenealdehyde 4-phenyl-3-thiosemicarbazone (TPS). The method is based on the formation of the copper(II)–TPS complex, which is extractable into chloroform from aqueous solution in the pH range 4–10 by shaking 15 min. The extracted species shows maximum absorption at 380 nm with the molar absorptivity of 37×10^3 L mol^{-1} cm^{-1}at 360 nm. Beer's law is obeyed over the range 2–20 µg of copper(II) in 10 mL of chloroform at 360 nm. The proposed method is relatively selective for copper(II) and has been satisfactorily applied to the detection of copper(II) in some alloys, as reported.

4.1.2 *N*-Salicylidenethiosemicarbazone

Gao Chengxiang et al. [2] have found that Cu can be detected in $CuSO_4.5H_2O$, $CuCl_2.2H_2O$, $Cu(NO_3)_2.3H_2O$, and CuO (powder) spectrophotometrically by measuring the absorbance at 630 nm of the green complex of Cu and *N*-salicylidenethiosemicarbazone in pH 2.5 HCl-NaOAc buffer solution containing ascorbic acid as a masking agent.

4.1.3 2,4-Dihydroxy-5-bromoacetophenone thiosemicarbazone (DHBAT)

Desai M. J. et al. [3] have synthesized 2,4-dihydroxy-5-bromoacetophenone thiosemicarbazone (DHBAT) and used as a spectrophotometric reagent for Cu and Fe. Both the metal ions form yellow-colored complex at pH 6.0 and 4.0 and show maximum absorption at 420 nm and 380 nm, respectively. Molar absorptivity for Cu(II)-DHBAT and Fe(III)-DHBAT is 0.145×10^4 lit mol^{-1} cm^{-1} and 0.6×10^4 lit mol^{-1} cm^{-1} respectively. Cu(II) complexes with DHBAT in 1:1 (M:L) stoichiometry while Fe(III) complexes DHBAT in 1:2 (M:L) stoichiometry. Solution of Cu(II) ion obeys Beer's law up to 12.7 ppm whereas Fe(III) ion solution at 9.41 ppm. As mentioned by the authors the reagent shows satisfactory results for the analysis of Cu in brass and Fe in pharmaceutical preparations.

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4.1.4 Thiosemicarbazone of 2-carboxybenzaldehyde (2CBTSC)

Lopez-de-Alba et al. [4] have studied the formation of yellow complex between Cu(II) and thiosemicarbazone of 2-carboxybenzaldehyde (2CBTSC), spectrophotometrically. The use of 2CBTSC as an analytical reagent in photometric estimation of Cu(II) is described. The method is suitable at 0.5–5.0 ppm of Cu(II) ($\lambda_{max} = 346$ nm, $\varepsilon = 1.2 \times 10^4$ L mol^{-1} cm^{-1}) with a relative error of 1.12%. The interferences caused by numerous ions have been studied. The stoichiometry of the complex originated by the 2CBTSC with Cu(II) is determined by spectrophotometric methods and it is 1:1 (reagent: cation). The method could be applied by the authors for the determination of Cu in medical formulations, drinking H_2O and wheat bran with satisfactory results.

4.1.5 2-H-Benzopyron-2-one-3-acetylthiosemicarbazone (BPAT)

Lokhande R. S. et al. [5] have reported synthesis of 2*H*-benzopyron-2-one-3-acetylthiosemicarbazone (BPAT) which can be used for the extraction and spectrophotometric determination of Cu(II) at microgram level. The Cu(II)-BPAT complex is yellow in color and can be extracted in methylisobutylketone (MIBK) in the pH range 8.8 to 9.2 under optimum condition at 410 nm. Beer's law is obeyed at 2–25 mg mL^{-1} of Cu(II). The molar absorptivity is 0.7×10^3 L mol^{-1} cm^{-1} and Sandell's sensitivity is 0.086 mg cm^{-2}. The stoichiometric ratio of the complex is 1:2. The interference of diverse cations and anions has been studied. The method has been applied to commercial samples, as described.

4.1.6 Iso-nitrosopropiophenone thiosemicarbazone (HINPTC)

Kocharekar Archana R. et al. [6] have proposed a reagent iso-nitrosopropiophenone thiosemicarbazone (HINPTC) for extraction and spectrophotometric determination of copper. The reagent HINPTC reacts with Cu to give a yellow-colored complex that can be quantitatively extracted into isoamyl alcohol at pH 10. The organic extract shows maximum absorption at 390 nm. Beer's law is followed in the concentration range of 0.5–6.0 mg mL^{-1} of Cu. The molar absorptivity of the complex is 5.826×10^3 L mol^{-1} cm^{-1} and Sandell's sensitivity is 0.010 mg cm^{-2}. The stoichiometry of the complex is 1:2 (M: L). The proposed method is rapid, sensitive and reproducible and has been applied for the determination of copper in synthetic mixtures and real samples like pharmaceuticals, Al alloys and brass ash.

4.1.7 Diacetylmonoxime-4-phenyl-3-thiosemicarbazone

Prasad N. B. L. et al. [7] have described analytical properties of diacetylmonoxime-4-phenyl-3-thiosemicarbazone. The reagent gives intense yellowish-green and reddish-yellow–colored complexes with copper(II) and nickel(II) in sodium acetate acetic acid buffer(pH 3.0–7.0) medium respectively. The molar absorptivity and Sandell's sensitivity of the Cu(II) and Ni(II) complexes of DAMOPT are 1.02×10^4, 1.75×10^4 L mol^{-1} cm^{-1} and 0.0062, 0.0035 mg cm^{-2}, respectively. DAMOPT has also been used for the spectrophotometric determination of nickel(II) in hydrogenated vegetable oil and chocolate.

4.1.8 4-Chlorochalcone thiosemicarbazone

Zhang Xia et al. [8] have presented a new method for analysis of trace copper. In the presence of emulsifier OP and HAc-NaAc buffer solution, the 4-chlorochalcone thiosemicarbazone and copper(II) could form a stable yellow complex, which shows maximum absorbance at 394 nm, and a molar absorptivity 3.76×10^4 L mol^{-1} cm^{-1}, as reported.

4.1.9 2-Acetylthiophene-4-phenyl-3-thiosemicarbazone (ATPT)

Reddy K. Hussain et al. [9] have used, 2-acetylthiophene-4-phenyl-3-thiosemicarbazone (ATPT) for the spectrophotometric determination of Cu(II) in aqueous medium. In NaOAc-HOAc buffer medium, this reagent gives intense color reaction with Cu(II) in the pH range 3.0–6.0. First and second derivative methods have been developed for the determination of Cu(II) in aqueous medium. First derivative spectrum of Cu-ATPT complex has maximum amplitude at 420 nm that is selected in analytical studies. However, the second derivative spectrum of Cu-ATPT complex exhibits maximum amplitude at 410 nm (peak) and 455 nm (valley) and the zero cross at 485 nm. The amplitude at 410 nm is proportional to the amount of Cu(II).

4.1.10 9-Ethyl-3-carbazolecarboxaldehyde-thiosemicarbazone (ECCAT)

Bingoel H. et al. [10] have described kinetics of complexation reaction of Cu(II) with 9-ethyl-3-carbazolecarboxaldehyde-thiosemicarbazone (ECCAT) spectrophotometrically. In a DMF-H_2O medium at 35° the complex shows maximum absorbance at 393 nm. By the Arrhenius and Eyring equations, kinetic and activation parameters of the complexation reaction can be calculated using the data obtained from studying the effect of temperature on reaction rates under the specified conditions. Based on the studied complexation reaction, a simple kinetic method for the spectrophotometric determination of Cu(II) has been developed by the authors. The calibration graphs are linear in the concentration range 0.2–1.9 μg mL^{-1}. The species that cause interference have also been studied.

4.1.11 Thiosemicarbazone of citral

Bansal Anil Kr et al. [11] have studied on thiosemicarbazone of citral that is a condensation product of industrially and eco-friendly terpenoid serves as very good analytical reagent for biologically important metal Cu and Ni. In NaOAc buffer medium of 5.6 and 2.6, the reagent gives a brown-colored complex with Cu and gray color complex with Ni, respectively. The molar absorptivities of Cu and Ni complexes are 8.75×10^3 and 1.25×10^4 L mol^{-1} cm^{-1}, respectively. These color reactions are studied for the spectrophotometric determination of Cu(II) and Ni(II) in aqueous medium as reported.

4.1.12 2-Acetylthiophene thiosemicarbazone (ATT)

Rao M. Sayaji et al. [12] have proposed a new analytical reagent 2-acetylthiophene thiosemicarbazone (ATT), which gives an intense yellowish green–colored complex ($\lambda_{max} = 370$ nm) with copper(II) in sodium acetate–acetic acid buffer (pH 5–7) medium. The molar absorptivity and Sandell's sensitivity of the copper(II) complex of ATT are 1.83×10^4 L mol^{-1} cm^{-1} and 0.0034 μg of Cu(II) cm^{-2}, respectively. The method is used for the determination of copper(II) in alloys, edible oils and seeds, as described.

4.1.13 1-Phenyl-1,2-propanedione-2-oxime thiosemicarbazone (PPDOT)

Prasad N. B. L. et al. [13] have proposed a spectrophotometric method for the determination of Cu(II) and Ni(II) by using, 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone (PPDOT) as chromogenic reagent. The reagent gives intense color reactions with Cu(II) and Ni(II) in NaOAc-HOAc buffer medium in the pH range 3.0–8.0. The molar absorptivity and Sandell's sensitivity of the methods for the determination of Cu(II) and Ni(II) are 0.575×10^4, 1.20×10^4 L mol^{-1} cm^{-1} and 0.0118 and 0.00503 μg cm^{-2}, respectively. Job's and molar ratio methods are used for determining the compositions of Cu and Ni complexes of PPDOT that is obtained in the ratio 1:2 (M:L). First derivative methods are developed for the determination of Cu(II) and Ni(II). Simultaneous spectrophotometric determination of Cu(II) and Ni(II) is carried out by measuring the peak-base line technique at 500 and 467.5 nm respectively. The method can be applied also in the determination of Cu(II) and Ni(II) in synthetic mixtures and in edible oils and seeds without the need for employing simultaneous equations.

4.1.14 Acetophenone-*p*-chlorophenylthiosemicarbazone (A-*p*-ClPT)

Ghazy S. E. et al. [14] have developed a spectrophotometric procedure for the determination of copper(II). This method is based on the reaction at pH 4–9 between the synthesized acetophenone-p-chlorophenylthiosemicarbazone (A-*p*-ClPT) and Cu(II) forming a green-colored complex. Cu(II): A-*p*-ClPT (1:2), that floats quantitatively with oleic acid (HOL) surfactant and exhibits a constant and maximum absorbance at 600 nm in both aqueous and surfactant layers. Beer's law is obeyed by this standard aqueous solution of Cu(II) with a concentration of 3.82 mg L^{-1} over the concentration range 0.25–6.35 mg L^{-1} with a detection limit of 0.021 mg L^{-1} for a and molar absorptivities of 5.5×10^3 and 1.3×10^4 mol L^{-1} cm^{-1} in aqueous and surfactant layers, respectively. Sandell's sensitivity is 0.244 μg cm^{-2} and the relative standard deviation ($n = 9$) is 0.19%. The proposed procedure can be successfully applied to the analysis of Cu(II) in natural waters, certified scrap steel samples and vitamin samples as described. Also, the flotation mechanism is suggested based on some physical and chemical studies on the solid complexes isolated from aqueous and surfactant layers.

4.1.15 3-Hydroxybenzaldehyde thiosemicarbazones (HBT)

Babu S. et al. [15] have proposed a reagent 3-hydroxybenzaldehyde thiosemicarbazones (HBT) as analytical reagent for spectrophotometric determination of Cu(II) and Pd(II) in aqueous medium. The reagent gives yellowish green–colored complexes with Cu(II), Pd(II) in NaOAc-HOAc buffer medium of pH 5.5 and 2.5 respectively. The molar absorptivities of Cu and Pd complexes are 8.75×10^3, and 1.25×10^4 L mol^{-1} cm^{-1}, respectively.

4.1.16 *N*-Ethyl-3-carbazolecarboxaldehyde-3-thio-semicarbazone (ECCT)

Reddy K. Janardhan et al. [16] have used *N*-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone (ECCT) as new analytical reagent for the development of a highly sensitive extractive spectrophotometric method for the determination of copper(II). The ECCT forms a greenish-yellow-colored 1:1 (M:L) complex with copper(II) at pH 3.0, which is well extracted into n-butanol and shows maximum absorbance at 380 nm. The system obeys Beer's law in the range 0.4–3.6 with 2.243×10^4 L mol^{-1} cm^{-1}, 2.83×10^{-3} μg cm^{-2} molar absorptivity and Sandell's sensitivity respectively. The regression coefficient is 0.412 with 0.99 correlation coefficient. This developed method has been successfully employed by the authors for the determination of copper(II) in environmental and pharmaceutical samples.

4.1.17 5-Bromo salicylaldehydethiosemicarbazone (5-BSAT)

Ramanjaneyulu G. et al. [17] have used 5-bromo salicylaldehydethiosemicarbazone (5-BSAT) in acidic medium for a rapid and sensitive spectrophotometric determination of Cu(II) in aqueous DMF medium. The metal ion forms a light greenish yellow–colored complex with the above chromogenic reagent, which shows absorption maximum at 390 nm. Beer's law is obeyed in the range 0.31–6.35 mg mL^{-1} of Cu (II). The molar absorptivity (ε) and Sandell's sensitivity are 1.08×10^4 L $mole^{-1}$ cm^{-1} and 0.062 mg cm^{-2}, respectively. The methods have been employed successfully for the determination of Cu in grape leaves and Al-based alloy samples, as described.

4.1.18 4-Hydroxy benzaldehyde thiosemicarbazone (4-HBTS)

Padmanabha Satheesh and Rao V. Suryanarayana [18] have reported that spectrophotometry is a sensitive, selective and simple method for detection of trace amount of copper. As chromogenic reagent 4-hydroxy benzaldehyde thiosemicarbazone (4-HBTS) is used. In the presence of the neutral surfactant triton X-100 (micellar medium), it forms a green-colored water-soluble complex showing absorption maximum at 370 nm. The molar absorptivity and Sandell's sensitivity of the colored solution are found to be 2.8×10^4 L mol^{-1} cm^{-1} and 2.3×10^{-3} μg cm^{-2} respectively. The complex has 1:2 [M: L2] stoichiometry with stability constant 5.94×10^{10}. This method could be applied for the detection of trace copper in industrial waste water, as recommended.

4.1.19 2-Acetylfuran thiosemicarbazone (AFT)

Reddy K. Vasudeva et al. [19] have applied the spectrophotometric method for the determination of copper in alloys and in biological samples by using 2-acetylfuran thiosemicarbazone (AFT) as a selective reagent for determination of copper. It reacts with Cu(II) in the pH range 6.0–8.0 to form a yellow-colored complex showing absorption maximum at 365 nm. The system obeys Beer's law up to 0.915 mg mL^{-1} of copper(II). The molar absorptivity and Sandell's sensitivity of Cu(II)-2-acetylfuran-thiosemicarbazone are 3.33×10^4 L mol^{-1} cm^{-1} and 2.0×10^{-3} mg cm^{-2} at 365 nm.

4.1.20 2-Acetylpyridine-4-methyl-3-thiosemicarbazone (APMT)

Reddy K. Vasudeva et al. [20] have proposed a new sensitive reagent 2-acetylpyridine-4-methyl-3-thiosemicarbazone (APMT) for spectrophotometric determination of Cu(II). It reacts with Cu(II) in the pH range 5–8 to form a yellow-colored complex. To ascertain the stability of the complex the absorbance value of Cu(II)–APMT complex is measured at different intervals of time at 380 nm. It is observed that the color development is instantaneous and stable for >48 h. The system obeys Beer's law 2.54 mg $mL^{-1}$of Cu(II). At 380 nm the molar absorptivity and Sandell's sensitivity of the species are 1.475×10^4 L mol^{-1} cm^{-1} and 4×10^{-3} mg cm^{-2}, respectively. To determine the composition of the Cu(II) complex with APMT Job's continuous variation and molar ratio methods are used and for evaluating the accuracy of the developed method, various biological samples and certified reference materials have been tested.

4.1.21 4-[*N*,*N*-(Dimethyl)amino]benzaldehyde thiosemicarbazone (DMABT)

Karthikeyan J. et al. [21] have selected 4-[*N*,*N*-(dimethyl)amino]benzaldehyde thiosemicarbazone (DMABT) as an analytical reagent, for the extractive spectrophotometric determination of copper(II). DMABT forms a yellow-colored complex with copper(II) in the pH range 4.4–5.4 with absorption maximum at 420 nm. Beer's law is obeyed in the concentration range ≤4.7 mg mL^{-1}. The optimum concentration range for min. photometric error as detected by Ringbom plot method is 1.2–3.8 mg mL^{-1}. The molar absorptivity of complex formed is 1.72×10^4 dm^3 mol^{-1} cm^{-1} and Sandell's sensitivity of the complex obtained from Beer's data is 0.0036 mg cm^{-2}. The composition of the Cu(II)-DMABT complex is found to be 1:2 (M:L). The interference of various cations and anions in the method has been studied. Thus the method can be employed for the determination of trace amount of copper(II) in water, alloys and other natural samples of significant importance, as claimed by the authors.

4.1.22 2-Hydroxy-3-methoxy benzaldehyde thiosemicarbazone (2H3MB TS)

Patil, Y. K. et al. [22] have presented 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (2H3MB TS) as a photometric reagent for the extractive spectrophotometric determination of copper(II). The reagent forms an instantaneous and stable blue-colored complex with copper(II) in the pH range 6.2 to 7.6. The concentration range in which the complex followed Beer's law is found to be 1.0 µg mL^{-1} to 10.0 µg mL^{-1} at 420 nm. The limit of detection (LOD) is calculated by using standard deviation of blank solution at confidence limit 98.3%, which is found to be 0.327 µg mL^{-1} The stoichiometry of the complex is 1:2 (M:L) by Job's method of continuous variation and confirmed by mole ratio method. The standard deviation and the coefficient of variance have also been presented. The results of the prescribed procedure can be applied for the determination of the micro amounts of Cu(II) in standard steel samples, alloys, pharmaceutical and synthetic samples.

4.1.23 2-Acetylpyridine thiosemicarbazone (2-APT) and 3-acetylpyridine thiosemicarbazone (3-APT)

Admasu, Daniel et al. [23] have used two selective and sensitive reagents, 2-acetylpyridine thiosemicarbazone (2-APT) and 3-acetylpyridine thiosemicarbazone (3-APT) for the spectrophotometric determination of Cu(II). Both reagents forms yellowish Cu(II) complex at a pH range of 8.0–10.0 that obeys Beer's law for Cu(II)-2-APT and Cu(II)-3-APT in the concentration range of 0.16–1.3 and 0.44–1.05 µg mL^{-1}, respectively. The molar absorptivity and of Cu(II)-2-APT and Cu(II)-3-APT are found to be 2.14×10^4 at 370 nm, and 6.7×10^3 L $mol^{-}1$ cm^{-1} at 350 nm, respectively. The values of Sandell's sensitivity obtained are 0.009 and 0.029 µg cm^{-2}, respectively. The correlation coefficient of the standard curves of Cu(II)-2-APT and Cu(II)-3-APT are 0.999 and 0.998, and the detection limit of the Cu(II)-2-APT and Cu(II)-3-APT are 0.053 and 0.147 µg mL^{-1}, respectively. The results demonstrate that the procedure is precise (relative std. deviation <2%, n = 10). The method has also been tested for Cu(II) determination in soil and vegetable samples and comparisons of the results is made with those obtained using a flame atomic absorption spectrophotometer for Cu(II) determination. The validity of the methods also tested using paired sample t-test at the 0.05 level showing a good agreement between them.

4.1.24 2-Hydroxy-3-methoxy benzaldehyde thiosemicarbazone

Sreevani, I. and Swetha, M. [24] have developed a highly sensitive and selective spectrophotometric method for the determination of trace amount of copper(II) in aqueous DMF medium. A light green–colored complex is formed between 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) and copper ion in an acidic buffer of pH 5.0. The complex shows absorbance maximum at 395 nm, which is stable for more than 48 h. Beer's law is obeyed in the range 0.254–2.542 µg mL^{-1} and the molar absorptivity and Sandell's sensitivity have been found as 6.0×10^3 L mol^{-1} cm^{-1} and 0.011 µg cm^{-2}, respectively. The complex has 1:1 (Cu(II)–HMBATSC) stoichiometry with light green color. The stability constant of the complex is determined by Job's continuous variation method as 12.306×10^5. A sensitive and selective second order derivative spectrophotometry for the determination of Cu(II). The interference of various cations and anions is also studied by the authors. The reported methods are successfully used in the determination of Cu(II) in water and real samples.

4.1.25 4-Hydroxybenzaldehyde thiosemicarbazone

Satheesh, K. P. et al. [25] have developed an organic reagent "4-hydroxybenzaldehyde thiosemicarbazone" for determination of Cu(II) spectrophotometrically. The results reveal that Cu(II) shows favorable conditions for complex formation under weak acidic condition (pH 5–6). By using standard procedures the metal ions can be determined quantitatively in µg quantities, as results show. The suitability of this method for the determination of copper lies in the range 0.127–1.27 µg mL^{-1}. The above-mentioned method has been extended by the authors, for the determination of Cu(II) present in wastewater sample and the obtained results have been compared with other previously reported methods.

4.1.26 5-Bromosalicylaldehyde thiosemicarbazone (5-BSAT)

Tu, Le Ngoc et al. [26] have described the simultaneous spectrophotometric method for the determination of Cu(II) and Co(II) by using partial least squares regression method. For this purpose as a ligand, 5-bromosalicylaldehyde thiosemicarbazone (5-BSAT) has been selected. The ligand reacts to form greenish yellow– and brown-colored [Cu(II)-5-BSAT] and [Co(II)-(5-BSAT)2] complexes, respectively. The absorption peaks (λmax) of these complexes have been found at 378 nm and 381 nm, respectively. At pH 5.0, the formation of both these complexes is complete within 20 min. The linear ranges are 4.0×10^{-6} M–9.6×10^{-6} M for Cu(II) and 8.0×10^{-6} M–8.0×10^{-5} M for Co(II). The molar absorptivity (ε) was 1.09×10^{4} L mol^{-1} cm^{-1} and 1.42×10^{4} L mol^{-1} cm^{-1}, respectively. In the reported method, partial least squares (PLS) regression method is proposed for the simultaneous determination of these ions between wavelengths 370 and 446 nm at an interval of 4 nm. As reported by the authors the test set garnered a root mean square error (RMSE) of 0.192 for copper and 0.489 for cobalt. The relatively small RMSE suggests only a small difference between predicted vs. measured concentrations that shows the accuracy of the method. The developed method is successfully employed in the analysis of water sample for determining concentrations of copper and cobalt.

4.2 Thione class

4.2.1 6-Phenyl-2,3-dihydro-asym-triazine-3-thione (PDTT)

Edrissi M. et al. [27] have described a sensitive and highly selective spectrophotometric method by the detection of 12–120 µg of copper using 6-phenyl-2,3-dihydro-asym-triazine-3-thione (PDTT) as a complexing agent. Complex has been measured at 540 nm and molar absorptivity is 1.26×10^{4} L mol^{-1} cm^{-1}. The method is applied for the detection of copper in standard steels, as reported.

4.2.2 3-Propyl-5-hydroxy-5-*D*-arabinotetrahydroxylbutyl-3-thiazolidine-2-thione (PHTTT)

Ojeka E. O. and Iyun J. F [28] have used 3-Pr homolog of 3-propyl-5-hydroxy-5-D-arabinotetrahydroxyl butyl-3-thiazolidine-2-thione (PHTTT) as a reagent in the colorimetric determination of copper and chromium in effluent samples. The complex formed at pH 6.0–8.0 shows absorption maximum at 480 nm. The molar absorptivity of Cu $(PHTTT)_3$ is $5.7 \times 10^3\ dm^3\ mol^{-1}\ cm^{-1}$ and $Cr(PHTTT)_3$ is $6.7 \times 10^3\ dm^3\ mol^{-1}\ cm^{-1}$ respectively. The stoichiometry of PHTTT reagent with the metal ion studied using the methods of continuous variation and titration respectively gave the ratio of copper to PHTTT as 1:3 and chromium to PHTTT as 1:3. Simple and direct spectrophotometric methods developed have been described for the estimation of Cu and Cr metal ions with the reagent with practical applicability to effluent water sample.

4.2.3 6-(2-Naphthyl)-2,3-dihydro-1, 2, 4-triazine-3-thione (NDTT)

Tehrani Maliheh Barazandeh et al. [29] have described a simple and accurate spectrophotometric method for determination of copper in serum using 6-(2-naphthyl)-2, 3-dihydro-1,2,4-triazine-3-thione (NDTT). Copper forms a red-colored complex with a reagent,6-(2-naphthyl)-2,3-dihydro-1,2,4-triazine-3-thione. The Cu-NDTT complex is soluble in chloroform and shows maximum absorbance at 314 nm. In this study, derivative spectrophotometric method has been proposed for determination of Cu(II) in serum based on the reaction between copper and new chromogenic compound NDTT. Serum is first treated with trichloroacetic acid for de-proteination and ascorbic acid to release Cu from protein. After addition of tartaric acid and NDTT, complex is extracted by chloroform. Beer's law is obeyed in the copper concentrated range of 0.5–6 mg mL^{-1} of serum and the detection limit is 0.106 mg. The linear regression equation was $A = 0.04507\ C–0.0001$. The within-day and between-day variations in four selected concentration (0.5, 1, 4, 6 mg mL^{-1}) are less than 2.68 and 3.07%, respectively. The proposed method is simple, selective and sensitive for determination of copper in serum, as reported by the authors.

Tehrani Maliheh Barazandeh et al. [30] have developed a simple and sensitive derivative spectrophotometric method for simultaneous detection of Ni and Cu using 6-(2-naphthyl)-2,3-dihydro-1,2,4-triazine-3-thione (NDTT) as a selective analytical reagent. The complexes of metal ions with NDTT are formed immediately in basic media and extracted with chloroform. The zero-crossing measurement technique has been found suitable for the direct measurement of the third-derivative value of Ni-NDTT and Cu-NDTT at 501 and 472 nm respectively. Beer's law is obeyed in the concentration range 1–30 g mL^{-1} for both cations with different ratios. The limit of detection is 0.26 g mL^{-1} and 0.13 g mL^{-1} for Cu and Ni, respectively, as reported.

4.2.4 6-(Anthracen-2-yl)-2,3-dihydro-1,2,4-triazine-3-thione (ADTT)

Tehrani M. Barazandeh et al. [31] have described derivative spectrophotometric simultaneous determination of Cu and Ni using 6-(anthracen-2-yl)-2,3-dihydro-1,2,4-triazine-3-thione (ADTT) as analytical reagent. After derivatization in basic medium Cu and Ni are detected by zero-crossing method in the second-, third- and fourth-order derivative spectra. Beer's law is obeyed in the range of 5–35 μg mL^{-1} for Cu at 387 nm (second order) and 554 nm (third order) and 5–35 μg mL^{-1} Ni at 447 nm (first order), 400 nm (third order) and 385 nm (fourth order). For both cations the limit of quantification is 5 μg mL^{-1}. The within-day and between-day variations in three concentrations are less than 3.36 and 4.73% in all measurements respectively, as described.

4.2.5 6-(2-Methoxynaphthyl)-2,3-dihydro-1,2,4-triazine-3-thione (MNDTT)

Tehrani Maliheh Barazandeh et al. [32] have mentioned that spectrophotometric method is accurate, and green method for the determination of Cu(II) using 6-(2-methoxynaphthyl)-2,3-dihydro-1,2,4-triazine-3-thione (MNDTT) as analytical reagent. MNDTT produces a dark red complex with copper in methanol in 1:2 stoichiometries. Beer's law is obeyed over the concentration range of 2.5–20 μg mL^{-1} with $r^2 = 0.992$. The limit of detection and limit of quantification were 0.33 and 1.10 μg mL^{-1}, respectively, within-day and between-day precision values were <3.68%. Finally, the method was applied to a dental alloy (110-plus) successfully.

4.2.6 6-(Phenanthrene-3-yl)-1,2,4,-triazine-3-thione(PhDTT)

Maskoot, Marzieh et al. [33] have developed a simple, sensitive and non-extractive spectrophotometric method for the determination of copper(II) using 6-(phenanthrene-3-yl)-1,2,4,-triazine-3-thione(PhDTT), in Tween 80 neutral surfactant. Copper(II) forms a red-colored complex with the above reagent. This complex shows maximum absorbance at 460 nm in the pH range 9.0–11.0. Beer's law is obeyed over the concentration range of 1.4–10 μg mL^{-1} Cu^{2+} with $r^2 = 0.999$. The limit of detection is 0.48 μg mL^{-1} of copper(II). The reported method was also tested by analyzing the amalgam samples, and the results were in good agreement as given by the authors.

4.3 Dithizone class

Kundu Dipali et al. [34] have described a spectrophotometric method for the detection of trace amount of copper and silver when present together in special glasses. The method involves selective extraction of copper dithizonate on polyurethane foam after masking of silver with chloride. Silver is extracted in ammoniacal medium after masking of copper with EDTA. Both the complexes, i.e., copper and silver dithizonates are eluted from foam with acetone. Detection is carried out spectrophotometrically. Beer's law is obeyed for the concentration range of 0.05–2.5 μg Cu mL^{-1} at 550 nm and 0.10–6.0 μg Ag mL^{-1} at 500 nm. The method yields agreeable results.

Kundu D. et al. [35] have proposed an analytical method that involves the decomposition of the glass matrix with hydrofluoric and nitric acids, formation of secondary copper(II) in 0.30 M hydrochloric acid and 3×10^{-5} M dithizone, extraction of copper dithizonate over 1 h at 50°–60 °C on polyether-based polyurethane foam, elution of copper dithizonate in acetone and finally measurement of absorbance at 550 nm. The method obeys Beer's law for copper contents at 0.05–2.5 μg mL^{-1}. Satisfactory results are obtained when the method is applied to different glasses, as reported.

Li Xing-yang et al. [36] have reported a dithizone extraction spectrophotometry that could be applied to the successive detection of Cu(II) and Pb(II) in water samples. Carbon tetrachloride (CCl_4) is used as extraction solvent in both cases. The extraction of Cu(II) dithizonate is carried out in an acetate buffer medium of pH 3.8, and the absorbance of the complex in CCl_4 is measured at the wavelength 551 nm. An ammonical buffer solution of pH 10 is added to the aqueous phase, which remains after extraction of Cu(II), and appropriate amount of 1 mol L^{-1} NaOH solution is added to adjust the pH of the solution to pH 9.2. Lead(II) has been then extracted as its dithizonate by CCl_4 from the solution and its absorbance measured at the wavelength of 525 nm. Value of molar absorptivity of Cu-dithizonate and Pb-dithizonate in CCl_4 are found to be (Cu) 6.8×10^4 L mol^{-1} cm^{-1} and (Pb) 1.3×10^5 L mol^{-1} cm^{-1}, as reported.

Niazi A. et al. [37] have used a new dispersive liquid-liquid micro extraction (DLLME) preconcentration and orthogonal signal correction-partial least square (OSC-PLS) for simultaneous spectrophotometric determination of copper and mercury. For the study dithizone has been used as chelating agent and as extraction and dispersive solvents carbon tetrachloride and acetonitrile have been selected. All factors affecting the sensitivity are optimized by the Box-Behnken design and the linear dynamic range for detection of copper and mercury is found. Under the optimum conditions, the calibration graphs are linear in the range of 10.0–250.0 and 10–300 ng mL^{-1} with detection limit of 2.6 and 2.8 ng mL^{-1} (3δB m^{-1}) and the enrichment factor of this method for copper and mercury, reaches 180 and 175, respectively. Simultaneous detection of copper and mercury by using spectrophotometry is not easy so PLS modeling is used for the multivariate calibration of the spectrophotometric data. The OSC is used for preprocessing of data matrixes and the prediction results of model, with and without using OSC, are statistically compared. For 25 samples, calibration matrix is designed by keeping absorbance over the range of 400–700 nm. The root mean squares error of prediction for copper and mercury with and without OSC varies as

0.010, 0.026 and 0.055, 0.086, respectively. This method can be applied for detection of copper and mercury in spiked water and synthesis samples, as described.

4.4 Miscellaneous

4.4.1 Sodium diethylaminodithioformate

Du Bin et al. [38] have proposed a spectrophotometric method for the detection of copper naphthenate in gasoline that is based on the reaction between copper and sodium diethylaminodithioformate. The maximum absorbance occurs at 440 nm, and its apparent molar absorptivity is 1.3×10^4 L mol^{-1} cm^{-1}. Beer's law is obeyed for the concentration range of 0–3 μg mL^{-1} for copper.

4.4.2 2,5-Dimercapto-1,3,4-thiadiazole (DMTD)

Khader A. M. A. et al. [39] have used 1,3,4-thiadiazole-2,5-dithiol (DMTD) as a new chromogenic reagent for the spectrophotometric detection of Cu(II) in K dihydrogen phosphate-NaOH buffer medium. Beer's law is obeyed up to concentration limit of 4.5 ppm. The Cu(II)–DMTD complex has the highest absorption at 350 nm. The molar absorptivity and Sandell's sensitivity of the complex are 7.3×10^4 L mol^{-1} $cm^{-1}$and 0.0056 μg cm^{-2} respectively. The effects of diverse ions are also studied and conditions are established for the detection of Cu in synthetic samples and alloys.

Ahmed M. Jamaluddin et al. [40] have reported a simple spectrophotometric method for the rapid determination of copper at a trace level using 2,5-dimercapto-1,3,4-thiadiazole (DMTD) as a new spectrophotometric reagent. The method is based on the reaction of nonabsorbent DMTD in a slightly acidic (0.002–0.014 mol dm^{-3}sulfuric acid) aqueous solution with Cu(II) to produce a highly absorbent greenish-yellow chelate that has an absorption maximum at 390 nm. The reaction is instantaneous and the absorbance remains stable for 24 h. The average molar absorptivity of Cu(II) is 5.65×10^4 L mol^{-1} cm^{-1} and Sandell's sensitivity is 10 ng cm^{-2}. The stoichiometric composition of the chelate is 1:2 (Cu:DMTD). Linear calibration graphs are obtained for 0.1–20 mg cm^{-3} of Cu(II). The method is successfully used for the determination of copper in several standard reference material and in some environmental water samples, biological samples, soil samples, and solutions containing both Cu(I) and Cu(II) and complex synthetic mixtures.

4.4.3 Dithiocarbammonium hydroxide

Yang Run-ping et al. [41] have established a spectrophotometric method for the detection of copper in polluted water. In the ammonium hydroxide solution with pH value 6.2, copper ions react with dithiocarbammonium hydroxide and produce yellow-amber colloidal compound. This compound gives maximum absorbance at 452 nm. The concentration of copper ions is between 0.10 and 2.5 g mL^{-1}, as reported.

4.4.4 Sodium pyrrolidine-1 carbodithioate

Ma Weixing et al. [42] have developed a new spectrophotometric method for the detection of copper in pure aluminum and alloy samples that is based on the chromogenic reaction of copper(II) with the sodium pyrrolidine-1 carbodithioate to form a stable yellow complex (1:2) in the presence of emulsifier OP and in the medium of $NH_4Cl\text{-}NH_3{\cdot}H_2O$ buffer at pH 7.0–10. The maximum absorption wavelength of the complex is 438 nm at room temperature. Beer's law is obeyed in the range of 0–70 g in 25 mL solution with the apparent molar absorptivity of 1.33×10^4 L mol^{-1} cm^{-1}, as reported.

4.4.5 4,6-Dichloro-2-(imidazolidin-2-ylidenamino)pyrimidine (DTIAP)

Ding Runmei et al. [43] have developed a new simple spectrophotometric method for detection of trace copper in rice and tea samples. A yellow-colored solution is produced by reagent 4,6-dichloro-2-(imidazolidin-2-ylidenamino)pyrimidine (DTIAP) with copper(II) in $Na_2HPO_4\text{-}KH_2PO_4$ buffer medium. The Cu(II)–DTIAP complex shows an absorbance maximum at 383 nm. A calibration graph is obtained from 0 to 0.9 mg L^{-1}. The observed molar absorptivity is 2.03×10^4 L mol^{-1} cm^{-1}, as reported. Most of the common coexisting metal ions show no interference with the color reaction.

4.4.6 Diethanoldithiocarbaminate potassium salt (HHDDTC)

Zhang Qian and Zhang et al. [44] have used spectrophotometry as a method for determination of trace copper(II) in tea samples after disabling the common ions by masking agent. For this purpose diethanoldithiocarbaminate potassium salt (HHDDTC) is adopted. The linear regression equation that obeys Beer's law in the range of 0–3.40 μg mL^{-1} is $A = 0.1915\,C + 0.0039$ (C: μg mL^{-1}, $R = 0.9998$, $n = 18$) with the molar absorption coefficient = 1.24×10^4 L mol^{-1} cm^{-1}, as reported.

4.4.7 4-Phenylpiperazinecarbodithioate (PPDTC)

Kaur Varinder et al. [45] have described a new, simple, inexpensive and sensitive method for the simultaneous spectrophotometric detection of Cu(II) and Pd(II) by H-point standard addition method and derivative spectrophotometry. 4-Phenylpiperazinecarbodithioate (PPDTC) in an anionic micellar solution of SLS is used as a reagent at pH 4. The linear ranges of the method are 0.1–10 and 0.1–11 g mL^{-1} for Cu(II) and Pd(II), respectively. The results of applying H-point standard addition and fourth derivative spectrophotometry showed that Cu(II) and Pd(II) can be detected simultaneously with detection limits of 0.12 and 0.11 g mL^{-1}, respectively. Therefore, the method of H-point standard addition and fourth derivative spectrophotometry are used for resolving overlapped spectra for the detection of Cu(II) and Pd(II). This method can be successfully applied to the detection of these metals in synthetic and real samples, as reported.

4.4.8 4-(4′-Nitrobenzylidene imino)-3-methyl-5-mercapto-1, 2, 4-triazole (NBIMMT)

Shaikh, Abdul B. et al. [46] have developed a simple, selective and rapid extractive spectrophotometric method for the extraction and determination of Cu(II) with 4-(4′-nitrobenzylidene imino)-3-methyl-5-mercapto-1,2,4-triazole, (NBIMMT). The reagent (NBIMMT) instantly forms stable orange-red-colored complex with Cu(II) at room temperature. This complex can be quantitatively extracted in chloroform at pH 6.2. Against reagent blank, the extracted species shows absorption maximum at 470 nm and follow Beer's law in concentration range 4.75 to 16.13 ppm of Cu(II) and optimum concentration range obtained from Ringbom's plot is found to be 5 to 17.5 ppm. The molar absorptivity and Sandell's sensitivity of Cu(II)-NBIMMT in chloroform are found to be 2.825×10^3 L mol^{-1} cm^{-1} and 0.0224 µg cm^{-2}, respectively. The optimum extraction conditions are evaluated by studying various parameters. As described by the authors, the use of masking agents enhances the selectivity of method. The composition of the extracted species is determined by using Job's method, mole ratio method and verified by log-log plot. The ratio of Cu(II):NBIMMT is found to be 1:2. The proposed method can be successfully applied for the determination of Cu(II) in synthetic mixtures, pharmaceutical samples and alloys.

4.4.9 Schiff base 4-(4′-chlorobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole [CBIMMT]

Barache, Umesh B. et al. [47] have been developed efficient, simple and selective cost-effective method for the extractive spectrophotometric determination of copper(II) by using the Schiff base 4-(4′-chlorobenzylideneimino)-3-methyl-5-mercapto-1,2,4-triazole [CBIMMT]. The reported chromogenic reagent forms a yellow-colored complex with copper(II) in acetate buffer at pH 4.2 at maximum absorbance 414 nm. The copper(II) complex with ligand is instantly extracted into chloroform and remains stable for >48 h. The composition of extracted complex is ascertained by using Job's method of continuous variation, mole ratio method and slope ratio method that is obtained as 1:2 [copper(II): reagent] . Under optimal conditions, the copper(II) complex in chloroform adheres to Beer's law up to 17.5 μg mL^{-1} of copper(II). The optimum concentration range obtained from Ringbom's plot is from 5 μg mL^{-1} to 17.5 μg mL^{-1}. The molar absorptivity, Sandell's sensitivity and enrichment factor of the extracted copper(II) chelate are 0.33813×10^4 L mol^{-1} cm^{-1}, 0.01996 μg cm^{-2} and 2.49, respectively. In the extraction of copper(II), several affecting factors including the solution pH, ligand concentration, equilibrium time, effect of foreign ions are optimized. The interfering effects of various cations and anions can be studied and use of masking agents enhances the selectivity of the method. As reported by the authors, the method can be successfully applied for the determination of copper(II) in various synthetic mixtures, complexes, fertilizers, and environmental samples such as food samples, leafy vegetables and water samples. By comparison with reference procedure the result obtained indicates that the reported method is a convenient, fast method for the extraction and quantification of micro levels of copper(II) from various environmental matrixes without use of sophisticated instrumentation and procedure.

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Chapter 5
Analytical reagents having nitrogen (N), oxygen (O) and sulfur (S) as donor atoms

5.1 Thiocarbamate class

5.1.1 Piperidinedithiocarbamate

Kumar Ashok Jain et al. [1] mention that copper reacts with piperidinedithiocarbamate to form a water-insoluble thermally stable 1:2 complex. This complex is easily adsorbed onto microcrystalline naphthalene from an acetone solution and absorbs in the range 430–440 nm. Beer's law is obeyed over the concentration range 4.0–72.0 μg of copper in 10 mL of DMF solution. The molar absorptivity and Sandell's sensitivity are 1.00012×10^4 L mol^{-1} cm^{-1} and 0.0063 μg cm^{-2} respectively. Replicate analyses of a sample solution containing 40.0 μg of copper gave a mean absorbance of 0.630 with a relative standard deviation of 0.43%. The interference of various ions was studied and conditions were developed for the detection of copper in some alloy samples, as reported.

5.1.2 Diethanoldithiocarbamate

Pedrazzi Eluzir Moraes et al. [2] have proposed a flow injection system for the spectrophotometric determination of copper in rocks. Samples are mineralized by treatment with hydrofluoric and perchloric acids and the solution is analyzed after iron(III) precipitation. Copper is preconcentrated in a small CHELEX-100 resin column placed in the flow system, eluted with 2.5 M nitric acid and further mixed with diethanoldithiocarbamate in basic medium. The colored complex is monitored at 410 nm. With the proposed system, about 2–30 samples are run per h with low reagent consumption. Beer's law is followed within 0.04 and 2.00 μg mL^{-1}. Precision and accuracy were assessed by using reference rock standard from USGS and GSJ with copper content as low as 0.4 μg g^{-1} with good precision and accuracy, as reported.

San Andres et al. [3] have detected Cu(II), Ni(II) and Co(II) as diethyldithiocarbamate (DDTC) complexes in the presence of aqueous solution of cationic surfactants of hexadecyltrimethyl-ammonium bromide, chloride and hydroxide (CTAB, CTAC, CTAOH). The presence of micellar systems avoids the previous step of solvent extracting necessary to the formation of the DDTC complexes in the absence of micelles. The influence of the different micellar counter ions on the analysis characteristics (sensitivity and detection limits) of the proposed method for spectrophotometric detecting of Cu(II), Ni(II) and Co(II) is studied.

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San Andres et al. [4] have presented a spectrophotometric method for the detection of copper(II), Ni(II) and Co(II) as their complexes with diethyldithiocarbamate (DDTC) in the presence of aqueous anionic micellar media of sodium and ammonium dodecylsulfate. The presence of micellar systems allows one to eliminate the previous solvent extraction step that is necessary for the detection of metal-DDTC complexes in the absence of micelles. This reduces the cost and toxicity of the method. The influence of anionic micelles on the analytical characteristics (sensitivity and detection limits) was studied. The proposed method is applied to the detection of Cu(II) in industrial waste water and in nickel covered metallic samples, and the results are compared with those obtained by flame atomic absorption spectrometry, as reported.

Pereira Edenir R. et al. [5] have reported spectrophotometric procedure for copper determination in fungicides and fertilizers, based on the reaction of Cu^{2+} with diethyldithiocarbamate, which has been improved by combining suitable micellar medium. Effects of different micellar media are studied after addition of the surfactants SDS, CTAB, Triton X-100, Brij-35 and Tween-80. With Triton X-100, a remarkable improvement in the determination is observed.

Shar G. A. et al. [6] have reported a method for the spectrophotometric determination of Cu(II)- Diethyldithiocarbamate (DDTC) complex in aqueous phase in the presence of polyoxyethylene-dodecylether (Brij-35), non-ionic surfactant. The method obeys Beer’s law in the concentration range of 1.5×10^{-5} to 7.0×10^{-5} mol dm^{-3}. The detection limit of Cu(II) is 3.0×10^{-6} mol dm^{-3}. As described by the authors, the method has been used for the determination of Cu in goat liver and fly ash samples and the results are comparable with those by flame atomic absorption spectroscopy (FAAS).

de Moraes Sandra et al. [7] have proposed 1,3-diaminepropane-3-propyl-anchored silica gel (DAPPS) as a sorbent in a spectrophotometric flow system for the preconcentration of Cu^{2+} in digests of biological materials (maize powder, soybean, citrus leaves, corn stalks) as well as H_2O samples (river, stream, streamlet, spring H_2O and well). The system presents a minicolumn packed with DAPPS, where the sample solution is passed through it for a period of time, and, subsequently, an eluent solution, stripped-out the retained analyte that is further determined with DDTC at 460 nm. The better preconcentration conditions used are: 120 s loading, 60 s elution, 30 s regeneration of the column, loading flow rate 6.5 mL min^{-1}, buffer solution for the preconcentration and regeneration of the column-borate buffer pH 8.5, elution flow rate 2.3 mL min^{-1}, time of elution 60 s, eluent composition, 0.4 mol L^{-1} HNO_3. Under these conditions, the preconcentration factor obtained was 36, and the detection limit achieved was 8.4 ng mL^{-1} in H_2O samples and 0.84 µg g^{-1} in biological material. The maximum adsorption capacity of DAPPS to Cu^{2+} was 0.49 mmol g^{-1} (31.1 mg. g^{-1}) obtained in a batch system. The recovery of Cu in the H_2O samples ranges from 96.9 to 102.4% and in the biological materials ranges from 97.0 to 102.6%.

Yang Feng-xia et al. [8] have applied a method for detection of copper in the sample of nickel plating solution. For this chloroformic solution of lead di-M dithiocarbamate [Pb(DDTC)$_2$] as the extracting agent has been used to exchange trace Cu^{2+} in the nickel plating solution by primary extraction method. The extracted Cu (DDTC)$_2$ to the organic phase and detected content of copper is at the wave length of 436 nm by spectrophotometry at pH 4. The result shows that the molar absorption coefficient of Cu (DDTC)$_2$ is 1.16×10^4 L mol^{-1} cm^{-1} within the range of 0–3.2 g mL^{-1}. The existence of a lot of nickel ion has no interference on the detection of copper. The method has much higher sensitivity, accuracy and precision, suitable to the on-site analysis of trace copper in nickel plating solution, as reported.

Dai Yong-sheng et al. [9] have presented a method for detection of Cu and Mo in rifle color coating by spectrophotometry. In ammoniacal or slightly alkaline solution (pH = 8.5–9.5), sodium diethyldithiocarbamate trihydrate (DDTC) reacts with Cu(II) to form yellow brown coordination compound and its maximum absorbance is observed at 450 nm. In 50 mL coloration system, Beer's law is obeyed at 10–250 g mL^{-1} Cu(II). Thiocyanate salts can react with Mo^{5+} to form orange-red coordination compound and its maximum absorbance is observed at 460 nm. Thiourea is added as reductant, ferrous sulfate is added to stabilize the coloration solution and copper sulfate is added as catalyst to accelerate the coloration rate, as mentioned.

Ding Zongqing [10] has presented a new spectrophotometric method for the detection of copper with sodium diethyldithiocarbamate in water solution. Ammoniacal buffer medium at pH 9.0 and the presence of Triton X-100 have been used by the author. The complex shows maximum absorbance of at 460 nm and apparent molar absorption coefficient has been found 1.34×10^4 Lmol^{-1}cm^{-1}. Beer's law is obeyed in range of 0–5.0 mg L^{-1}, as reported.

Bai Litao et al. [11] have established a method to detect the content of copper in a sample of silver-coated copper powder by spectrophotometry with sodium diethyldithiocarbamate (DDTC). The results indicated that under the medium of pH 4–5, the maximum absorption wavelength of the Cu(II) and DDTC micellar complex is at 460 nm, the apparent molar absorptivity coefficient is 1.0×10^4 L mol^{-1} cm^{-1}. Beer's law is obeyed in the range of 0–2.4 g mL^{-1}. The recovery is 94.9–104.1%, with relative standard deviation, is 3.1–5.7%, as reported. It is an excellent method to detect constant copper at acidic conditions as well as exclude the interference of a large number of ions by choosing the appropriate conditions.

Li Liqing et al. [12] have presented a method for detection of copper ions with spectrophotometry by using sodium diethyldithiocarbamate as copper reagent. The maximal absorption peak of the copper complex is 435 nm, and the pH should be controlled at 9–10. Masking agent (EDTA and ammonium citrate) is adopted to eliminate the ion interference. The method has the advantages of simple operation, wide applicability, low cost and good application value, as reported by the authors.

Liao Xiaoxiang et al. [13] have developed a new Na_2SO_4 salting-out extraction method for preconcentration of trace amounts of copper as a prior step to its detection by UV-visible spectrophotometry. In this diethyldithiocarbamate (DDTC) is used as a complexing agent, with chloroform as extraction solvent. Under the optimal conditions, the calibration curve is linear in the range of 0.002–0.08 g mL^{-1} of copper, detection limit is 0.11 ng mL^{-1} in original solution (3Sbc m^{-1}) and the relative standard deviation for seven replicate detection of 0.002 g mL^{-1} copper is ±1.9%. The proposed method has been applied by the authors for detection of copper in Honeysuckle, Radix Glycyrrhiza, Lycium samples with satisfactory results.

Sabzi, Reza Emamali et al. [14] have investigated a dispersive liquid-liquid microextraction (DLLME) process based on the complexation reaction of Cu(II) with diethyldithiocarbamate (DDTC) from aqueous solutions. Using one variable at a time method, the effect of various experimental parameters in the extraction such as, dispersive solvent, extracting solvent, the volume of extraction and disperser solvent, pH of the aqueous solution, ionic strength and extraction time are optimized, and the analytical characteristics of the method have been obtained. Under the optimum conditions the calibration graph obeys linearity over the range 0.01 to 0.1 mg mL^{-1} of Cu(II) ion with a correlation coefficient of 0.994. The value of limit of detection ($S/N = 3$) obtained in this method is 8.6×10^{-3} mg mL^{-1}. Relative standard deviation (RSD) for 7 replicate determinations of 0.08 mg mL^{-1} Cu(II) has been found to be 3.3%. The interference effect of some anions and cations has also been tested. The reported extraction method has been successfully applied to the determination of copper in human blood serum sample.

5.1.3 K 4-Methylpiperidinedithiocarbamate (KMPDC)

Bati Bekir et al. [15] have developed a spectrophotometric method for detection of Cu(II) by using K 4-methylpiperidinedithiocarbamate (KMPDC) as a new analytical reagent. This method is based on the separation of Cu complex $Cu(MPDC)_2$ from some other metal complexes by thin-layer chromatography and the absorption measurement at 435 nm after the extracting of the complex with $CHCl_3$. Beer's law is obeyed for a concentration range of 0.0–20.0 μg Cu in 5 mL of the final $CHCl_3$ solution and the calculated average molar absorptivity of the complex is 1.78×10^4 L mol^{-1} cm^{-1}. The thin-layer chromatography studies show that Cu complex can be separated effectively using pure *o*-xylene, benzene-toluene (1 + 1, V/V) and benzene-toluene (1 + 2, V/V) from Fe(III), Co(II), Ni(II), manganese(II), Sn(II), Se(IV) and Te(IV). The method was also used for the detection of Cu in certain alloys.

5.1.4 4-Methylpiperidinedithiocarbamate

Isildak Ibrahim et al. [16] have reported a simple, highly sensitive and fast spectrophotometric flow-injection method for the determination of Cu(II). When the Cu solution is introduced into a tertiary reagent stream containing 4-methylpiperidinedithiocarbamate colored Cu(II)-(4-methylpiperidinedithio carbamate)$_2$ complex is formed that is selectively monitored at 435 nm. A micro-column containing strong cation exchange resins has been placed by the authors between injection manifold and spectrophotometer to increase interactions between Cu(II) and analytical reagent and preconcentration of Cu(II). The calibration graph is linear in the range 5–100 μg L^{-1}. The detection limit is <0.5 μg L^{-1} for 20 μL injection volume of Cu(II) ion solution. As described by the authors the developed method could be applied to environmental, Cu processing H_2O, and ore samples.

5.1.5 4-Benzylpiperidinedithiocarbamate (4-BPDC)

Asan Adem et al. [17] have synthesized and used a new type of dithiocarbamate derivative, 4-benzylpiperidinedithiocarbamate (4-BPDC) for spectrophotometric determination of Cu(II) ions in the low mg L^{-1} ranges. As the authors reported, this method is based on the reaction of Cu(II) ions with 4-BPDC in the carrier solution to develop a colored complex. The accuracy of the method has been demonstrated by the analysis of certified reference materials.

Cesur Hasan and Bati Bekir [18] have reported a method for solid-phase extraction of copper with lead 4-benzyl piperidinedithiocarbamate [Pb(4-BPDC)$_2$] and its spectrophotometric determination. In this method, Cu in large volumes liquid phase quantitatively replaces lead on colorless [Pb(4-BPDC)$_2$] complex and naphthalene solid phase mixture forming colored Cu-4-benzyl piperidinedithiocarbamate complex [Cu(4-BPDC)$_2$]. The solid phase containing colored [Cu(4-BPDC)$_2$] is dissolved in $CHCl_3$ and its absorbance is measured at 437 nm against the reagent blank. The range of linearity is 0.4–10 mg mL^{-1} of Cu(II) in $CHCl_3$, the molar absorptivity of the complex determined from the linear portion of Beer's law plot is 8.197×10^3 L mol^{-1} cm^{-1} and Sandell's sensitivity is 0.0013 mg cm^{-2}.

Shemirani Farzaneh et al. [19] have studied that copper(II) is determined spectrophotometrically as a complex with 4-benzylpiperidine-dithiocarbamate (4-BPDC). The analyte is preconcentrated applying cloud point extraction with Triton X-114 as a surfactant. Molar absorptivity of Cu-(4-BPDC)$_2$ complex has been determined as 2.75×10^4 L mol^{-1} cm^{-1} at $\lambda_{max} = 435$ nm. Under optimum conditions (pH = 6.0, 3.0×10^{-5} mol L^{-1} 4-BPDC, 0.2% (m/v) Triton X-114, 50° equilibrium temperature) calibration plot is constructed and found linear in the analyte concentration range 5–200 ng mL^{-1}; the corresponding detection limit was 1.6 ng mL^{-1}. Precision (% RSD) of 10 replicate determinations of 50.0 ng mL^{-1}. The proposed procedure has been successfully applied by the authors to the determination of Cu(II) in natural water samples.

5.1.6 MDTC (morpholinedithiocarbamte)

Kaur Varinder et al. [20] have proposed a spectrophotometric method for the determination of trace amount of Cu(II) and Pd(II) with MDTC (morpholinedithiocarbamte) as a reagent in the presence of CTAB (a solubilising agent). Molar absorptivity and analytical sensitivities of the 1:2 $Cu(MDTC)_2$ and $Pd(MDTC)_2$ complexes are 2.467×10^4 and 2.989×10^4> L mol^{-1} cm^{-1}, respectively. The developed derivative procedure has been applied for the rapid and selective simultaneous determination of Cu(II) and Pd(II) at 0.2–15 and 0.1–10 mg mL^{-1}, respectively as reported. Complex matrices including alloys, biological samples, pharmaceutical samples and synthetic mixtures have been successfully analyzed for trace amounts of two metal ions.

5.1.7 Ammonium pyrollidinedithiocarbamate

Soomro Gul Afshan et al. [21] have developed a simple rapid new spectrophotometric method for the determination of copper using ammonium pyrollidinedithiocarbamate in the presence of anionic aqueous micellar solution 1.0% sodium dodecyl sulfate. This reagent reacts with copper(II) to form bis(ammonium pyrollidinedithiocarbamato) copper complex. The use of micellar system in this system replaces the previous solvent extraction steps and enhancing the sensitivity, selectivity and the molar absorptivity and reduces cost. The average molar absorption coefficient and Sandell's sensitivity is found to be 1.08×10^4> L mol^{-1} cm^{-1} and 5.83 ng cm^{-2} at l_{max} 447.8 nm, respectively. Linear calibration graph is obtained over the concentration range 0.12–4.0 mg>mL^{-1}; the stoichiometric composition of the complex is found to be 1:2 (Cu:$[APDC]_2$). The developed method could be successfully applied for the determination of copper from alloy and brass samples as reported.

5.2 Chrome blue K class

Sun Xue-hua et al. [22] have reported a new catalytic-spectrophotometric method, for the detection of trace copper in agricultural products. The method is based on the oxidation of acid chrome blue K by hydrogen peroxide in H_2SO_4 medium using copper as the catalyst. The sample is dissolved with HNO_3 and H_2O_2 in a tightly closed PTFE vessel and heated in a microwave oven under prescribed program. Working conditions of the instrument and conditions of chemical reaction are optimized. A linear range of detection is 0.128–14.08 g/25 mL, the detection limit is 0.016 g/25 mL and recoveries are in the range of 98.1% to 101.6%, as reported.

Huang Ze-nan et al. [23] have proposed an AN = 0 dual-wavelength compensation coefficient spectrophotometric method for detection of copper(II) in water samples. The method is based on the red dark chelate formation between copper(II) and acid chrome blue K (ACBK) in NaOH medium (pH = 12.7). This method could detect the real absorbance of the chromogenic Cu (ACBK) through eliminating the destructive interference of discolored ACBK on Cu (ACBK) and could also detect the similar real absorbance of the ACBK through eliminating the destructive interference of Cu (ACBK) on the discoloration of ACBK. The compensation coefficient of absorbance signal is 4.135 at wavelength of AN 573 nm and AN 533 nm and the signal molar absorptivity is 4.56×10^4 L mol^{-1} cm^{-1}, as reported.

5.3 Zincon(2-carboxy-2″-hydroxy-5″-sulfoformazylbenzene) class

Liu R. M. et al. [24] have described a flow injection system for the simultaneous determination of copper and zinc with a single detector. Two sample plugs are injected into the same carrier stream sequentially. One is for zinc determination and the other is for the sum of copper and zinc. For zinc determination, copper masking reagent is simultaneously injected into a parallel carrier stream and merged with the sample plug by using the merging zone technique. Zincon is used as the color reagent for the spectrophotometric determination of copper and zinc.

Deng Fanzheng et al. [25] have developed a new spectrophotometric method with phase-separation for the detection of Cu in Al alloys using Zincon as color reagent. The method is based on the reaction of Cu(II) with zincon to form a stable blue complex and the extraction of the complex with PEG phase in the presence of $(NH_4)_2SO_4$ at pH 5.5–8.5 (KH_2PO_4-K_2HPO_4). The extracted complex exhibits a maximum absorption at 610 nm with an apparent molar absorptivity of 4.0×10^4 L mol^{-1} cm^{-1}. Beer’s law was obeyed at 0–1.5 mg L^{-1} for Cu.

Morais Ines et al. [26] have developed a double-line sequential injection system for the spectrophotometric determination of several metal ions in waters. The proposed double-line configuration is used to enable adding sample and chromogenic reagents as merging zones. The methodology is applied to the spectrophotometric determination of copper, iron, manganese and zinc in samples of diverse origins at the range of 0.15–5.00, 0.10–10.0, 0.48–4.00 and 0.11–5.00 mg L^{-1}, respectively. Different chromogenic reagents and detection wavelengths are used. The chromogenic reagents for iron and manganese are 1,10-phenanthroline and formaldoxime, respectively. Copper and zinc both are determined using the analytical reagent zincon. Analytical characteristics of the methodology, such as manifold parameters, buffer pH, and reagent concentrations, are optimized, and interference of some of the metal ions commonly present in water sample is assessed.

Shpigun L. K. et al. [27] have developed a flow injection spectrophotometric method for the simultaneous detection of copper(II) and zinc(II) in mixtures utilizing metal-Zincon complex formation and kinetic differences in the ligand substitution reaction of amino-polycarboxylic acid at pH 9.18. The linear range for the detection of zinc is 0.2–9.7 g mL^{-1} and for copper is 0.2–3.5 g mL^{-1}, as mentioned.

Bahram, Morteza et al. [28] have developed a new coacervative extraction using pH-sensitive hydrogel for pre-concentration and spectrophotometric determination of Cu(II) based on the complex formation with Zincon (2-carboxy-2″-hydroxy-5″-sulfoformazylbenzene) in water samples. In the extraction step, appropriate amounts of poly (styrene-alt-maleic anhydride), as a pH-sensitive hydrogel, has been added by the authors into the aqueous solution, so a rather cloudy solution is formed. Organic and inorganic compounds having the potential to interact with polymer particles could be extracted into the organic phase. The equilibrium state is achieved quickly because of the surface area between the polymer particles and the aqueous sample becomes very large. After centrifuging, hydrogel-rich phase is sedimented in the bottom of sample tube. The sedimented phase is diluted with methanol and the absorbance of the solution is measured at 615 nm (λ_{max} of the complex in hydrogel media). To optimize the main experimental parameters including concentration of hydrogel, HCl, Zincon and salting-out effect, central composite design (CCD) is performed at five levels. Under the optimum conditions the linear analytical range obtained is 5–500 ng mL^{-1} with a correlation coefficient of 0.991 and the limit of detection is found to be 3.4 ng mL^{-1}. The proposed method can be successfully applied for the determination of copper in various water samples and is an efficient, rapid, simple and inexpensive micro-extraction technique, as reported.

5.4 Methylthymol blue class

Pouretedal Hamid Reza et al. [29] have applied a second-derivative spectrophotometric method successfully for the simultaneous detection of Cu and Ni in synthetic binary mixtures and real samples. This method is based on zero-crossing-over technique. In this procedure methylthymol blue (MTB) acts as a chromogenic reagent and cetyltrimethylammonium bromide acts as a surfactant. All measurements are carried out in buffered solution at pH 6 and at a temperature of 25 °C. The amplitude of derivative spectra is measured at wavelengths of 631.9 and 587.7 nm for the simultaneous detection of Ni^{2+} and Cu^{2+}. Respective linearity is obtained at 0.5–5.0 g mL^{-1} for both ions in the presence of 0.0–5.0 g mL^{-1} of the other ion as an interfering ion, as described.

Pourreza Nahid et al. [30] have used a flotation spectrophotometric methods for the detection of copper(II) by formation of a ternary ion-associated complex from Cu(II), methylthymol blue (MTB) and cetyltrimethylammonium bromide (CTAB). These are floated at the interface of aqueous phase and *n*-Hexane by shaking in a separating funnel. These are separated in funnel and dissolved in small volume of methanol. This adsorbed ion associated mixture shows absorption maximum at 556 nm. The apparent molar absorptivity (ε) of the ion associated is found to be 6.1×10^4 L mol^{-1} cm^{-1}. The calibration curve is linear in the concentration range of 10–400 ng mL^{-1} of Cu^{2+} with a correlation coefficient of 0.9994. The limit of detection (LOD) was 6.7 ng mL^{-1} The relative standard deviation (RSD) for 50 and 300 ng mL^{-1} of Cu^{2+} was 3.9% and 1.3% (n = 7), respectively, as described.

5.5 Miscellaneous

5.5.1 *N*-(2′-Thiazolyl)-2-hydroxybenzamide (NTHB)

Garg B. S. et al. [31] have developed a new method for the spectrophotometric detection of copper with *N*-(2′-thiazolyl)-2-hydroxybenzamide (NTHB) in a Triton X-100 micellar medium. The proposed method is simple, convenient, faster and provides sensitive detection of copper with very less interference. The molar absorptivity and Sandell's sensitivity calculated are found as 6.34×10^4 L mol^{-1} cm^{-1} and 0.0010 µg cm^{-2}, respectively.

5.5.2 *S*,*S*′-bis(2-aminophenyl)oxalate

Nohut Sinan et al. [32] have described a new selective reagent, *S*,*S*'-bis(2-aminophenyl) oxalate (H_2L), for the extractive spectrophotometric determination of copper. In methanol the ligand, H_2L, forms a 1:1 complex with copper(II). The molar absorptivity of Cu(II)-*S*,*S*'-bis(2-aminophenyl)oxalate complex in methanol is 5,365 M^{-1} cm^{-1} at 504 nm. The method has been applied for the determination of copper in pharmaceutical formulations, environmental and foodstuff samples as reported by the authors.

5.5.3 4-Vanillindeneamino-3-methyl-5-mercapto-1,2,4-triazole (VAMMT)

Nazareth Ronald Aquin et al. [33] have reported a rapid and sensitive spectrophotometric method for the determination of Cu(II) with 4-vanillindeneamino-3-methyl-5-mercapto-1,2,4-triazole (VAMMT). VAMMT reacts with Cu(II) at pH 8.5 to give a green-colored complex that shows an absorption maximum at 430 nm. Sandell's sensitivity and the molar absorptivity of the complex are 0.0646 mg cm^{-2} and 9.929 × 10 L mol^{-1} cm^{-1}. The effect of foreign ions and other experimental variables is also studied by the authors. Cu(II) is successfully determined in various alloy samples.

5.5.4 *N*-Benzoyl-*N*-methyl-*N′*-phenylthiourea

Khorrami Saeid A. et al. [34] have performed spectrophotometric determination of Cu(II) using *N*-benzoyl-*N*-methyl-*N*'-phenylthiourea. The ligand forms mononuclear 1:1 and 1:2 complexes with the Cu(II) ion. The stability constants for complexation of the Cu(II) ion with *N*-benzoyl-*N*-methyl-*N*'-phenylthiourea are determined at different wavelengths in the range 240–265 nm in 0.02 mol dm^{-3} of sodium chloride as a background salt in the mixed solvent system of 75% THF in water (vol./vol.) in the pH ranges 5.90–7.30 and 9.42–10.12 with high ligand to metal ratios at 23.5 ± 0.5 °C.

5.5.5 *M*-Chloro-azo-antipyrine (MCAA)

Ma Xiaobei et al. [35] have proposed a spectrophotometric method for detection of copper in tea. In NaAc-HAc buffer solution of pH = 3.92, copper reacts with *M*-chloro-azo-antipyrine (MCAA) to form a blue substance and can be detected by spectrophotometry at 624 nm with apparent molar absorptivity 4.0×10^4 L mol^{-1} cm^{-1}. Beer's law is obeyed for the mass concentration of copper in the range of 0–1.6 g mL^{-1}. The correlation coefficient is 0.9980, the relative standard deviation (RSD) is 4.2%, the detection limit is 0.047 g mL^{-1} and the recovery of standard addition varies from 93% to 103% as reported.

5.5.6 5-Hydroxy-6-mercapto-benzo[a]phenazine (HMBP)

Reiss Aurora et al. [36] have proposed a extractive spectrophotometric method for determination of Cu(II) ion by using 5-hydroxy-6-mercapto-benzo[a]phenazine (HMBP) as a sensitive and selective analytical reagent. Cu reacts with HMBP to gives a dark red complex which shows a maximum absorbance at 495 nm which is solute in $CHCl_3$, with molar absorptivity and Sandell's sensitivity values of 7.39×10^3 dm^3 mol^{-1} cm^{-1} and 0.012 mg cm^{-2}, respectively. Beer's law is obeyed in the concentration range 0.67–26.90 mg mL^{-1}. The composition of the Cu(II)-HMBP complex has been established by the authors as 1:2 by Job's continuous variation method and molar ratio method. The instability constant of the complex calculated by Job's relation for non-isomolar series is 4.65×10^{-9}, at room temperature. The detection limit is 0.59 mg mL^{-1}. The method is successfully employed for the determination of Cu(II) in environmental samples.

5.5.7 Nitroso-*R*-salt

Qiu Huidong et al. [37] have described a spectrophotometric method for the determination of Cu and Fe in Mg alloy. In acid system, Cu and Fe react with nitroso-*R*-salt to form a yellow green complex with λ_{max} (Cu) = 450 nm and λ_{max}720 nm for Fe. The apparent molar absorptivity of Cu and Fe complexes is found to be 1.1×10^4 L mol^{-1} cm^{-1} and 0.7×10^4 L mol^{-1} cm^{-1}, respectively. The calibration curves obtained are linear at 0.2–12 mg mL^{-1} and 0.1–16 mg mL^{-1} for Cu and Fe, respectively. The method could also be applied to the determination of Cu and Fe in Mg alloy with the relative standard deviation of 2.06–3.25%, as described.

5.5.8 6-Chloro-benzothiazolylazo benzoic acid (6-Cl-BTAEB)

Luo Daocheng et al. [38] have established a new spectrophotometric method for the detection of trace copper(II) in fine coal ash, on the basis of the color reaction of copper(II) with 6-chloro-benzothiazolylazo benzoic acid (6-Cl-BTAEB). Copper(II) reacts with 6-Cl-BTAEB in HAc-NaAc buffer solution at pH 4.0. In the presence of emulsifier OP, they form a stable 2:1 complex showing absorption maximum at 650 nm. Beer's law is obeyed in range of 0–400 g L^{-1} for copper and the apparent molar absorptivity is 7.35×104 L mol^{-1} cm^{-1}, as reported.

5.5.9 1-(2-Hydroxyphenyl)thiourea (HPTU)

Sunil A. and Rao S. Jagadeeswara [39] have reported a sensitive simultaneous determination of copper(II) and nickel(II) using first derivative spectrophotometry based on zero-crossing-over technique. In this method, 1-(2-hydroxyphenyl)thiourea (HPTU) is used as a chromogenic reagent. As activator pyridine is used and cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) are used as surfactants to enhance the sensitivity in the method. Analytical parameters such as pH, reagent concentration and reaction time are also studied. The ranges of determination for copper(II) and nickel(II) are 0.003–0.9 ng mL^{-1} and 0.5–100 ng mL^{-1}, respectively. The proposed method is applied by the authors to plant samples for the determination of copper(II) and nickel(II), simultaneously.

5.5.10 2-(5-Bromo-2-oxoindolin-3-ylidene)hydrazine carbothioamide

Madan, Parinita Umesh et al. [40] have developed a simple, rapid and sensitive spectrophotometric method for the determination of Cu(II) by using 2-(5-bromo-2-oxoindolin -3-ylidene)hydrazine carbothioamide as an analytical reagent. 2-(5-Bromo-2-oxoindolin

-3-ylidene)hydrazine carbothioamide extracts Cu(II) quantitatively (99.92%) into *n*-amyl alcohol from an aqueous solution of pH range 4.0–6.0 and in the presence of 3 cm^3 of phosphate buffer (pH 5.0). The *n*-amyl alcohol extract shows an intense peak at 510 nm (λ_{max}). Beer's law is obeyed over the Cu(II) concentration range of 1.0–8.0 μg cm^{-3}. The Sandell's sensitivity and molar absorptivity for complex are 25.0 ng cm^{-2} and 2,538 L $mole^{-1}$ cm^{-1}, respectively. By using Job's continuous variation and mole ratio method, the composition of extracted species is found to be 1:2. Interference by various ions is also studied by the authors. As described, the proposed method is rapid, sensitive, reproducible and has been successfully applied for determination of Cu(II) in alloy and pharmaceutical samples.

5.5.11 2,6-Dithiol-4-methylphenol (DTMP)

Kuliev, Kerim A [41] proposed 2,6-dithiol-4-methylphenol (DTMP) as a photometric reagent for the extractive spectrophotometric determination of copper(II). The reagent gives instantaneous and stable blue color with copper(II) in the presence hydrophobic amines, in the pH range 6.5 to 8.1. Beer's law shows linearity in the range of 0.05–3.6 μg mL^{-1} at 629–635 nm. The limit of detection (LOD) is found to be 8.6–8.8 ng mL^{-1}. By equilibrium shift method, the stoichiometry of the complex is established as 1:1:1 (M:L:Am). The results of the prescribed procedure are applied for the determination of the micro amounts of Cu(II) in pharmaceutical, food and plant samples.

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Chapter 6
Analytical reagents having oxygen (O) and sulfur (S) as donor atoms

6.1 Chrome azurol S class

Zhang Wangxia et al. [1] have developed a flow injection analytical micelle-solubilized spectrophotometry for detection of copper in environmental water. This method can detect copper quickly and conveniently. In the buffering solution of $Na_2B_4O_7$-HCl, copper reacts with CAS (chrome azurol S) in the presence of CTMAB (hexadecyltrimethylammonium bromide), and a Kelly substance is made and then detected at 605 nm. Under the optimum condition, standard curve with good linearity and broad linear range can be obtained among the ranges of 5–40 g L^{-1} and 40–200 g L^{-1}. The detection limit was 0.76 g L^{-1}, the relative standard deviation (slope) was 1.59% (n = 11), and the range of recovery was 90.2–104%, as reported.

Zhang Shu-fang et al. [2] have developed an absorbance ratio-derivative method for the simultaneous detection of Cu(II) and Cr(III) in surrounding H_2O. In the HOAc-NaOAc buffer solution at pH 5.7 heating, Cr^{3+} or Cu^{2+} with CAS and CTMAB forms a blue ternary complex. The molar absorptivities of Cr(III)-CAS-CTMAB and Cu(II)-CAS-CTMAB are 2.52×10^5 L mol^{-1} cm^{-1} and 1.01×10^5 L mol^{-1} cm^{-1} respectively, as reported. Beer's law is obeyed at 0.08–1.2 g mL^{-1} for Cu(II) and 0.05–0.52 g mL^{-1} for Cr(III), as reported.

Liu Fang and Shen Chunjiang [3] have used naphthalene phase spectrophotometric method to detect copper in crude oil samples with chrome azure S (CAS) as chromogenic agent. The apparent molar absorptivity at 610 nm is 7.93×10^4 L mol^{-1} cm^{-1}. The linear range is 0–8 g, as reported.

Deng Fanzheng et al. [4] have developed a novel method of extractive spectrophotometric determination of Cu in ionic liquid aqueous 2-phase system (ATPS) formed by a hydrophilic ionic liquid 1-butyl-3-Me imidazoliumtetrafluoroborate and NaH_2PO_4. In the ionic liquid aqueous 2-phase system of pH 5.0–8.0, the complex formed by chrome azurol S and Cu^{2+} shows high absorbance with the maximum absorption of 590 nm. Beer's law is obeyed at 0–4.0 mg mL^{-1} for Cu^{2+} with the apparent molar absorptivity of 5.16×10^4 L mol^{-1} cm^{-1}. The complex ratio of chrome azurol S and Cu^{2+} is 3:1. The method is applied to the determination of Cu in standard Al alloy. As reported by the authors, the ionic liquid could be repeatedly used after simple treatment.

Cui Xinyu et al. [5] have developed determination of trace copper by spectrophotometry that is based on the color reaction of Cu^{2+} and CAS in the presence of Triton X-100 and OP. Cu^{2+} and CAS-TritonX-100-OP form polybasic complexes with higher sensitivity

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to measure the concentration of copper. The maximal absorption wavelength of the complex is at 618 nm with apparent molar absorptivity of 6.62×10^5 L mol^{-1} cm^{-1}. The content of Cu^{2+} obeys Beer law in the range of 0–20 μg/25 mL. The method has been applied by the authors to the determination of trace copper in mung with satisfactory results.

6.2 Disulfonic acid class

6.2.1 2-(4-Chloro-2-phosphonophenylazo)-7-(2,6-dibromo-4-chlorophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid (CPA-DBC)

Zhai Qing-zhou et al. [6] have reported the color reaction of copper(II) with 2-(4-chloro-2-phosphonophenylazo)-7-(2,6-dibromo-4-chlorophenylazo)-1,8-dihydroxy -3,6-naphthalene disulfonic acid (CPA-DBC). In a buffer medium of HOAc-NaOAc (pH 4.7), copper(II) reacts with CPA-DBC to form a blue-violet complex with a molar ratio (M:R) of 1:2. The molar absorptivity is 2.3×10^4 L mol^{-1} cm^{-1} and maximum absorption wavelength is 606 nm. Beer's law is obeyed in the range of 0–25 μg/25 mL of Cu(II) solution. The method can be applied to the determination of copper in rice, as described.

6.2.2 2,7-Bi(5-carboxy-1,3,4-triazolylazo)-H acid (i.e., 2,7-bi(5-carboxy-1,3,4-triazole)-1-amino-8-naphthol-3,6-disulfonic acid, BCTZAHA)

Ge Changhua et al. [7] have reported a catalytic kinetic spectrophotometric determination of trace copper that is based on the linear relationship between fading reaction extent and the content of copper(II) in certain range. The fading reaction and kinetic condition between copper(II) and 2,7-bi(5-carboxy-1,3,4-triazolylazo)-H acid (i.e., 2,7-bi(5-carboxy-1,3,4-triazole)-1-amino-8-naphthol-3,6-disulfonic acid, BCTZAHA) occur in the medium of $NH_3 \cdot H_2O$-NH_4Cl buffer solution at pH 10.0. The maximum absorption wavelength of fading system is at 540 nm. The calibration curve is linear for copper(II) in the range of 0.001–0.04 μg mL^{-1}. The detection limit is found to be 1.32×10^{-11} g mL^{-1}. The method has been applied to the direct determination of trace copper in river water, tap water and well water samples without separation, as described.

6.3 Carboxylic acid and thiocarboxylic acid class

6.3.1 2-Aminocyclopentene-1-dithiocarboxylic acid

Gholivand Mohammad B. et al. [8] have proposed a very sensitive, selective and economical method for preconcentration and determination of trace amounts of Cu in drugs and alloy samples. In this method, a solid uncharged complex produced from 2-aminocyclopentene-1-dithiocarboxylic acid (synthetic reagent) on naphthalene. The 2-aminocyclopentene-1-dithiocarboxylate of copper is retained quantitatively on microcrystalline naphthalene in the pH range 2.8–3.3. After filtration the solid mass consisting of Cu complex-naphthalene is dissolved in DMF. The absorbance is measured at 462 nm against the reagent blank and molar absorptivity is 2.85×10^5 L mol^{-1} cm^{-1}. Beer's law is obeyed over the concentration of 0.1–16.0 mg of Cu in 4 mL of the DMF solution. Detection limit is 3 ng mL^{-1} of Cu(II). The interference of a large number of anions and cations has also been studied by the authors.

6.3.2 Chlorophosphonazo-mA

Garidi Zhaorigetu B. et al. [9] have reported a new catalytic kinetic spectrophotometric method for the determination of trace Cu(II) that is based on the fact that Cu(II) could catalyze the indicating oxidation reaction of Chlorophosphonazo-mA by H_2O_2 in the medium of H_3PO_4. The method has been used for determination of Cu(II) in Mongolian medicine and human hair with the relative standard deviation of 1.8–4.0% and recovery of 96–105% as described by the authors.

6.3.3 Calconcarboxylic acid

Li Yanhui et al. [10] have developed a new inhibitory kinetic spectrophotometric method for the detection of trace copper in water. It is found that the discoloring reaction of calconcarboxylic acid with hydrogen peroxide is inhibited by trace amount of copper(II) in the medium of 0.1 mol L^{-1} HCl. Based on this, the maximum absorption wavelength of inhibitory system is located at 540 nm. The linear range of the detection is 0–3.0 g/25 mL, as reported.

6.3.4 BCA (2,2′-Biquinoline-4,4′-dicarboxylic acid disodium salt)

Liu Xuan and Feng Zhiming [11] have developed the color reaction between BCA (2,2′-biquinoline-4,4′-dicarboxylic acid disodium salt) and copper for determining trace copper in foods. In the presence of pH 11.0 buffer solution and hydroxylamine hydrochloride, BCA could react with copper(II) to form a purple complex with a ratio of 2:1. The molar absorbance constant is found to be 7.72×10^3 L mol^{-1} cm^{-1} at 562 nm. The absorbance obeys Beer's law in the range of 0–4.8 μg mL^{-1} Cu(II). The established method has been used by the authors for the determination of trace copper in tea and kelp.

6.4 Alizarin red S class

Wu Xiao-hua et al. [12] have proposed a method that is applied to the determination of Cu(II) in alloy. The color reaction of Cu(II) with alizarin red S is studied in borax buffer solution. Alizarin red S reacts with borax form a stable 1:4 chelate complex having yellow color in pH 9.20 borax buffer solution. Purple shift occurs in ARS's absorption spectra. The apparent molar absorptivity of this chelate is 2.00×10^4 L mol^{-1} cm^{-1} at 540 nm. Beer's law is obeyed at 0–0.96 μg mL^{-1} for Cu(II), as reported.

Safavi A. et al. [13] have presented a spectrophotometric method for simultaneous detection of Fe(III), Al(III) and Cu(II) in several synthetic alloy solutions using Alizarin Red S as a chelating agent. A partial least squares multivariate calibration method is used for the analysis of ternary mixtures of Fe(III), Al(III) and Cu(II) at 450–6,000, 140–4,000 and 450–15,000 ng mL^{-1} respectively as reported. Absorbance data are taken between 400 and 800 nm.

Rohilla Rajni et al. [14] have used H-point standard addition method (HPSAM) for simultaneously determination of Cu^{2+} and Pb^{2+} in micellar media. As chromogenic reagent alizarin red S is used by the authors to form Cu^{2+} and Pb^{2+} complexes. For measurements Tween-80 is used as a micelle agent in buffered solution at pH 5.5 and linearity is 0.317–7.62 mg mL^{-1} Cu^{2+} and 0.345–6.14 mg mL^{-1} Pb^{2+}, respectively. Cu^{2+} and Pb^{2+} can be determined simultaneously at 11:1 and 1:20 Cu:Pb concentration ratios by using H-point standard additional method as shown by results. The proposed procedures successfully determine Cu^{2+} and Pb^{2+} simultaneous in synthetic binary mixtures, some natural waters and industrial wastewater.

6.5 Miscellaneous class

6.5.1 Eriochrome cyanine R

Evtimova Bisera et al. [15] have applied simplex optimization and factorial design for four spectrophotometric systems, with each system consisting of copper(II), eriochrome cyanine R and cationic surfactant. It is shown that the addition of surfactants results in substantial changes in the spectral characteristics of the metal-metallochromic dye complex. The optimization makes it possible to find optimal conditions to reach increased sensitivity of the system and the development of a reliable and sensitive method for detecting low concentration of copper. The molar absorptivities at 590–595 nm are 8.92×10^4 L mol^{-1} $cm^{-1}$and 9.70×10^4 L mol^{-1} cm^{-1}.

6.5.2 Tetramethylthiuram disulfide

Malik Ashok Kumar et al. [16] have defined a rapid and economical method that provides preconcentration of Cu from various samples. Cu forms a complex with tetramethylthiuramdisulfide supported on naphthalene in the column at pH 4.2–7.5. The method is applied for the detection of Cu in various alloys, synthetic samples and environmental samples, as reported.

6.5.3 2,7-Bi(5-carboxy-1,3,4-triazolylazo)-chromotropic acid (BCTZACA)

Chen Hong et al. [17] have proposed the conditions of color reaction of a novel reagent 2,7-bi(5-carboxy-1,3,4-triazolylazo)-chromotropic acid (BCTZACA) with Cu^{2+}. The reagent reacts with Cu^{2+} to form a stable 1:1 purple complex in HAc-NaAc buffer (pH 5.0). The complex formed shows an absorption maximum at 570 nm and apparent molar absorptivity 4.58×10^4 L mol^{-1} cm^{-1} that obeys Beer's law in the range of 0–0.8 mg L^{-1} for Cu^{2+}. As masking agent NH_4F and Na bi-tartrate are used. The method has been used for the direct determination of Cu in Al alloy and Mg alloy, and the results are satisfactory, as reported.

6.5.4 1-(2-Metoxiphenylamin)-3-metoksipropanthiol-2 (MPAMPT)

Maharramov, Abel M. et al. [18] have proposed an analytical reagent 1-(2-metoxiphenylamin)-3-metoksipropanthiol-2 (MPAMPT) for the extractive spectrophotometric determination of copper(II). This reagent forms blue colored complex with copper(II) in the pH range 5.4–6.8 that follows Beer's law in the concentration range up to 16 μg mL^{-1}. The complex of Cu(II)-MPAMPT shows a maximum absorbance at 605 nm, with molar absorptivity of 4.32×10^4 dm^3 mol^{-1} cm^{-1} and Sandell's sensitivity of the complex obtained is 1.48 ng cm^{-2}, as reported by the authors. The composition of the complex has been found to be 1:2 (M/L). The interference of various cations and anions in the method has also been studied. The method can be used for the determination of trace amount of copper(II) in pharmaceutical, food and plant sample, as reported.

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Chapter 7
Analytical reagents having other combination of donor atoms

7.1 5-Imiono-l-phenyl-3-ethyl-2-imidazolidinone

Abd El-Mottaleb et al. [1] have described spectrophotometric detection of Cu(II) and Ni(II) ions. For this 5-Imiono-l-phenyl-3-ethyl-2-imidazolidinone is used as color reagent that which reacts in aqueous ethanolic solution with Cu(II) and Ni(II) ions to produce violet and red complexes, respectively. These two complexes have 1:2 (M:L) molar ratio and also the complexes obey Beer's law over the useful range of Cu(II) and Ni(II) ions concentration. The molar absorptivities are 2.1×10^4 L mol^{-1} cm^{-1} and 1.5×10^4 L mol^{-1} cm^{-1} for Cu(II) and Ni(II) complexes respectively.

7.2 Thiols-catalyzed cysteamine, *L*-cysteine, 2-mercaptoethanol and 2-mercaptopropionic acid

Katayama Atsushi et al. [2] have developed a new kinetic method for the detection of trace amounts of copper(II). For this the Cu(II)-catalyzed oxidation of water-soluble thiols such as cysteamine, *L*-cysteine, 2-mercaptoethanol and 2-mercaptopropionic acid is examined in water or in a mixture of water and aprotic solvents like *N*,*N*-dimethylformamide (DMF), DMSO and acetonitrile. In this method the decrease in the concentration of thiols is measured spectrophotometrically for the detection of Cu(II). The best sensitivity is achieved using 60% DMF solution as the reaction media and *L*-cysteine as water-soluble thiols. The calibration curve of Cu(II) is linear over the range $0–1.1 \times 10^{-6}$ M. The detection limit is 3.9×10^{-8} M (2.5 ppb) for Cu (II). The selectivity achieved by the proposed method is excellent, since most of diverse ions tested are tolerated in high ratios. The proposed method has been applied successfully to the detection of Cu(II) in waste waters, as reported.

7.3 Cyanide ion

Wang Naixing et al. [3] have proposed method for the simultaneous detection of copper and nickel by third-derivative spectrophotometry based on the absorption spectra of their complexes with cyanide ion in the UV range. The method allows the detection of 0.55–5.8 μg mL^{-1} of copper and 0.55–6.8 μg mL^{-1} of nickel. The relative standard deviation for 11 detection of 1.5 μL mL of copper and nickel are 0.78 and 0.72%, respectively. The detection limits are 0.10 μg mL^{-1} for nickel and 0.13 μg mL

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for copper. The method has been applied to direct detection of copper and nickel in iron alloys and an aluminum alloy without any separation, as reported.

7.4 ARS-BOP3

Khalifa M. E. et al. [4] have applied simple matching standard procedure for the detection of Cu(II) in standard alloys and in simulated references multielement standard. The ARS reacts with Cu(II) in the presence of borate at pH 8.5 to form a stable ternary complex with Cu:ARS-BOP$_3$ = 1:3–3. At 526 nm the molar absorptivity of the complex is 1.77 × 104 L mol^{-1} cm^{-1}. The interfering effect of various ions is detected.

7.5 Chlorophosphonazo-III (CPA-III)

Gao Hong-Wen et al. [5] have developed a dual wavelength spectrophotometric method for the detection of Cu in waste water with chlorophosphonazo-III (CPA-III) at pH 5. The Cu(II)-CPA-III reaction is sensitive and selective if DDTC is used to preconcentration trace amounts of Cu and separating other metal ions. The ß-correction method can eliminate the effect of excess CPA-III from its Cu(II) colored solution to give the real absorbance of the Cu-CPA-III chelate. Beer's law is obeyed over at 0–1.20 mg L^{-1} Cu concentration, and the molar absorptivity of Cu(CPA-III) at 610 nm is 2.75×10^4 L mol^{-1} cm^{-1}. The detection limit of Cu is 0.005 mg L^{-1}.

7.6 Potassium Pr xanthate (KPX)

Balaji T. et al. [6] have described a simple, rapid and sensitive procedure for the detection of copper in waste water and food samples. Copper forms a bright yellow-colored complex with potassium Pr xanthate (KPX) at pH 6.0. The complex is extracted into Me isoBu ketone and measured at 400 nm spectrophotometrically. Beer's low is obeyed over a concentration range of 1.0 to 16.0 μg mL^{-1}. Sandell's sensitivity deviation and coefficient of variation for 10 detection of 12 mg mL^{-1} of copper are 0.0385 and 0.032%, respectively.

7.7 Pyrophosphate

Haj-Hussein et al. [7] have described a flow-injection analytical (FIA) method for the UV spectrophotometric detection of copper in copper ores. The ore samples are dissolved in concentration perchloric acid, the excess acid is neutralized with ammonia solution and the resulting solution is used for the detection of copper. The

UV-FIA system is based on the reaction of copper(II) ions with pyrophosphate and subsequent measurement of the absorbance of the dipyrophosphatocuprate(II) complex at 240 nm. The main factors that control the formation of this complex and the FIA variables influencing the system are described. The calibration graph is linear from 2–50 ppm copper. At a sampling rate of about 70 samples h^{-1} with 50 µL sample injections, precision is about 1% relative standard deviation.

7.8 Cyanex 301 [bis(2,4,4-trimethylpentyl)dithiophosphinic acid]

Argekar Anant P. et al. [8] have proposed cyanex 301 [bis(2,4,4-trimethylpentyl) dithiophosphinic acid] as a selective reagent for the extractive spectrophotometric detection of copper. The molar absorptivity of Cu(II)–cyanex 301 complex in toluene is 1.41 × L mol^{-1} cm^{-1} at 440 nm. The method was applied for the detection of copper in pharmaceutical formulations, human hair and foodstuffs as described.

7.9 4,4′-Tetraethyldiaminothiobenzophenone

Yang Jun et al. [9]**.** have reported a method for the FIA photometric determination of micro Cu based on the color reaction of Cu with 4,4′-tetraethyldiaminothiobenzophenone. An orange-red complex is formed by Cu(I) and the reagent in pH 4.5 HOAc-NaOAc buffer medium in the presence of emulsifying agent OP-10 and reducing agent ascorbic acid. The observed detecting wavelength is at 500 nm and Beer's law is obeyed at 0–20 µg/25 mL. The interferences of Fe^{3+} and Al^{3+} could be eliminated by NaF. The method has been used in the determination of Cu in ore samples with the relative standard deviation 2.1–2.8%, the recovery 92–102% as authors mentioned.

7.10 4,5-Dimercapto-1,3-dithiol-2-thionate

Barreto Sonia R. G. et al. [10] have studied a novel and sensitive spectrophotometric method for the determination of Cu in the presence of high concentrations of interfering ions. The new method, based on the complex formed between Cu and 4,5-dimercapto -1,3-dithiol-2-thionate, can be applied to the determination of Cu in metallic alloys used in dental amalgams with high amounts of Sn and Ag. The lowest detectable Cu concentration is 64 µg L^{-1} and the range of concentrations that follow Beer's law is 0.350 to 1.06 µg mL^{-1}. The average Cu concentration found in metallic amalgams is 10.54% with a standard deviation of ± 0.76% and recovery of 97.5%.

7.11 Michler's thioketone (TMK)

Fu Dayou et al. [11] have applied a simple spectrophotometric method for determination of trace copper in water samples. Copper reacts with Michler's thioketone (TMK) to form a stable 1:4 complex in the presence of surfactant poly(ethylene glycol)octylphenyl ether (OP) medium at pH 4.6. The complex Cu(II)-TMK-OP shows maximum absorbance at 500 nm. Beer's law is obeyed by the copper complex solution in the concentration range of 0–15 µg/25 mL with satisfactory results, as reported.

7.12 Brilliant blue dye (RAWL)

Qi Yanxia et al. [12] have applied a new kinetic-spectrophotometric method to the detection of copper(II) in freshwater samples and seawater samples. The method is based on the catalytic effect of copper(II) on the oxidation of weak acid brilliant blue dye (RAWL) by hydrogen peroxide. The copper(II) can be detected spectrophotometrically by measuring the decrease of absorbance of RAWL at 626 nm. The optimum reaction conditions are as follows: pH 7.20, buffer solution $NaOH\text{-}KH_2PO_4$, RAWL (200 mg L^{-1}) 5.00 mL, H_2O_2(30%) 0.50 mL, reaction temperature 80 °C and reaction time 20 min, as stated.

7.13 2-(2-Imidazolylazo)-5-dimethylamino-HOBz(IZDBA)

Ge Changhua et al. [13] have reported a spectrophotometric method using a new reagent 2-(2-imidazolylazo)-5-dimethylamino-HOBz(IZDBA) that shows color reaction with Cu(II). The IZDBA reacts with Cu(II) to form a 2:1 stable purple complex that shows absorption maximum at 600 nm in the buffer solution of HAc-NaAc at pH 4.0. The apparent molar absorptivity is 3.62×10^4 L mol^{-1} cm^{-1}. Beer's law is obeyed at 0.08–0.8 mg L^{-1} for Cu(II). The method has also been used by authors for the direct determination of Cu in Al alloy and Mg alloy samples.

7.14 Bromo-sulfonazo III (Br-SAZIII)

Jiang Zhang et al. [14] have investigated a novel chromogenic reaction between copper(II) and bromo-sulfonazo III (Br-SAZIII) in hexamethyleneamine-hydrochloric buffer solution. The results show that a blue complex of copper(II) and bromosulfonazo III is formed with a molar ratio of 1:1. The molar absorptivity is 3.3×10^5 L $mol^{-1}cm^{-1}$, and the maximum absorption peak was at 616.8 nm. The proposed procedure is used by authors for quantitative estimation of Cu(II) in the concentration range of 0–1.024 mg mL^{-1} with the detection limit (3s) of 7.03×10^{-4} mg mL^{-1} (n = 20).

Under the optimized conditions, total copper contents in vegetables and tea have been successfully determined by authors.

7.15 Brilliant green

Ying Zhen-Xing [15] has established a new catalytic kinetic spectrophotometric method for the detection of trace copper that is based on the copper catalyzing oxidation of brilliant green by potassium chlorate and hydrogen peroxide in potassium hydrogen phthalate-sodium hydrate buffer solution at pH = 4.20. The absorbance is measured at 624 nm. The linear range of the detection of copper is 0.040–1.50 g/25 mL. The observed detection limit is 8.6×10^{-11} g mL^{-1}, as reported.

7.16 3,5-Bis(3-hydroxy-2-pyridylaminodiazo)-2,4,6-tribromobenzoic acid (BHPADTBBA)

Fan Yueqin et al. [16] have proposed a new spectrophotometric method for the detection of micro copper(II) in aluminum alloys. For this a new chromogenic reagent, 3,5-bis(3-hydroxy-2-pyridylaminodiazo)-2,4,6-tribromobenzoic acid (BHPADTBBA) has been synthesized by authors, and the color reaction of BHPADTBBA with copper(II) is studied. The results show that a red complex of BHPADTBBA and copper(II) is formed in the buffer solution of $Na_2B_4O_7$-NaOH at pH 10.0 in the presence of Triton X-100. The complex shows a peak of maximum absorption at 570 nm with an apparent molar absorptivity of 2.18×10^5 L mol^{-1} cm^{-1}. Beer's law is obeyed in the range of 0–18 g/25 mL for copper(II), as reported.

7.17 7-Iodo-8-hydroxyquinoline-5-sulfonic acid

Wu Lan-Ju et al. [17] have reported the color reaction between Cu(II) and 7-iodo-8-hydroxyquinoline-5-sulfonic acid that takes place and forms a complex at pH = 5.0 in Clark-Lubs buffer solution. This chelate shows molar absorptivity 7.35×10^3 L mol^{-1} cm^{-1} at 380 nm and obeys Beer's law in the range of 0.15–4.5 mg mL^{-1} for Cu(II). The method is applied to the determination of Cu(II) in water with satisfactory results, as described.

7.18 Losartan potassium

Ul Hassan et al. [18] have used spectrophotometric method for analysis of losartan potassium in pharmaceutical formulation. Losartan forms a colored complex with cupric acetate. This complex shows absorption maximum at 530 nm and obeys Beer's law in the range of 10–50 µg mL^{-1} with a correlation coefficient (r2) of 0.9989. Mean analysis results from the calibration curve and absorption ratio methods are 99.42 and 99.16% with relative standard deviation (RSD) of 0.97 and 0.82%, respectively. Mean recovery is between 98.61 and 101.35%, and precision expressed as relative standard deviation (RSD) is 0.91%, as described.

7.19 Cefixime

Ramadan Abdul Aziz et al. [19] have used spectrophotometry for determination of cefixime in pure and pharmaceutical dosage forms. In acetate-acetic acid acidic buffer at pH 4.8 cefixime-copper(II) gives three different complexes by reacting in stoichiometry ratio of 2:1, 1:1, 1:2. These complexes have molecular formula $[(CEFI)_2(Cu)\cdot 2HCl]$, $[(CEFI)(Cu)\cdot HCl]$ and $[(CEFI)(Cu)_2\cdot 2HCl]$. The complexes formed show maximum absorbance at 510, 500 and 450 nm respectively. The molar absorptivity is 1.52×10^3, 1.06×10^3 and 3.42×10^3 L mol^{-1} cm^{-1}, respectively. It is further stated that under optimum conditions Beer's law is obeyed at concentrations ranging from 0.4535 to 18.138 µg mL^{-1} with correlation coefficients ≥0.9980 in all cases with RSD generally less than 4.8%. The limit of detection (LOD) and limit of quantification (LOQ) are 0.036 µg mL^{-1} and 0.109 µg mL^{-1}, respectively.

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Section B

Chapter 8
Analytical reagents having oxygen (O) as donor atom

8.1 Phenol class

8.1.1 2,6-Dithiol-4-methylphenol (DTMP)

Kerim, A. Kuliev et al. [1] have presented 2,6-dithiol-4-methylphenol (DTMP) as a photometric reagent for the extractive spectrophotometric determination of iron(III). The reagent DTMP in the presence of amino phenols (AP) gives instantaneous and stable red color with iron(III) in the pH range 4.2 to 5.3. Beer's law is applicable in the range of 0.4–20 μg mL^{-1} at 550–556 nm. The limit of detection (LOD) is found to be 9.3–9.7 ng mL^{-1}. The stoichiometry of the complex is established as 1:2:2 (Fe:DTMP:AP) by equilibrium shift, relative yield, Asmus straight line and the intersection curves method. The standard deviation and the coefficient of variance are presented. The proposed method has been successfully applied for determination of Fe(III) in pharmaceutical, food and plant samples.

8.1.2 Polyphenol from green tea

Martinovic Bevanda, A. et al. [2] have described a batch spectrophotometric method for determination of Fe(II) and Fe(III) using green tea extract as reagent. The method is based on complex formation reaction between Fe and polyphenol compounds from green tea in buffered medium (pH = 4.8). Absorbance of Fe-polyphenol complex formed during the reaction is measured at 570 nm wavelength. The linear dynamic ranges are obtained from 1.0×10^{-5} to 5.0×10^{-4} mol L^{-1}. The applicability of the proposed method is demonstrated by determination of Fe ions in pharmaceutical dosage forms, orange juice, degassed mineral water and candy.

8.1.3 5-Bromo salicylidene-2-aminothiophenol (BSATP)

Patil, S. K.; Kulkarni, S. W. et al. [3] have developed a spectrophotometric method for the determination of Fe(III) using 5-bromo salicylidene-2-aminothiophenol (BSATP) as an extractive reagent. The reagent forms a colored complex that is extracted into chloroform at pH 8.2. The method obeys Beer's law over a range of 1 to 10 ppm. The molar absorptivity is 16,460 L $mol^{-1}cm^{-1}$ and Sandell's sensitivity is 0.01639 μg cm^2 respectively. The proposed method is very sensitive and

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selective. This method has been successfully applied to synthetic and commercial samples.

8.1.4 Green tea polyphenols

Martinovic, Bevanda A. et al. [4] have proposed an interesting, simple and an inexpensive experiment that can be successfully applied in student laboratory. Optimization procedures of SIA system are suggested and the achieved results presented. The proposed method, based on reaction between green tea polyphenols and Fe ions, can be allowed to the determination of Fe ions in the concentration range of 4×10^{-5} to 4×10^{-4} mol L^{-1} with sample throughput 122 h^{-1}. The formed stable complex has the absorption maximum at $\lambda = 570$ nm. This optimized method is successfully applied to the determination of Fe ions in laboratory samples and pharmaceuticals.

8.1.5 2,21-Ethylenebis(nitrilo-methylidene)diphenol(H2EBNMDP)

Nworie F.S. et al. [5] have investigated solvent extraction using 2,21-ethylenebis (nitrilo-methylidene)diphenol(H_2EBNMDP) as ligand for the spectrophotometric determination of Fe(II), Fe(III), Mn(II) and Cr(III). The complexes formed by H_2EBNMDP with the Fe(II), Fe(III), Mn(II) and Cr(III) ions are stable in water for pH 8, 4, 6 and 6 respectively with a maximum of absorption at 366 nm, 383 nm, 415 nm 405 nm and molar absorptivity (ε) 1.84×10^4, 2.29×10^4, 2.96×10^4 and 3.85×10^4, respectively. Using the logarithmic method the combination ratio is established that is to be 1:2, 1:1, 1:2 and 1:1 for Fe(II), Fe(III), Mn(II) and Cr(III) respectively. The proposed method has also been applied successfully in the determination of Fe(II), Fe(III), Mn(II) and Cr(III) from tap water and synthetic samples, as stated by the authors.

8.1.6 5-[(Phenyliminoethyl)]-3-hydroxyphenol [PIEHP]

Sawant Shulmith M. et al. [6] have proposed a new analytical reagent 5-[(phenylimino ethyl)]-3-hydroxyphenol [PIEHP], a Schiff base, as a sensitive spectrophotometric reagent for Fe(III). The reagent PIEHP is selective and free from interference from most of the ions. The PIEHP and Fe(III) form a 1:2 violet colored complex showing ($\lambda_{max} = 430$ nm) in acidic aqueous solution (pH = 3.0). Beer's law is obeyed in the concentration range from 1 to 5 ppm. The Sandell's sensitivity is 0.07692 mg cm^{-2} with molar absorptivity 0.726×10^4 L mol^{-1} cm^{-1}. The proposed method has been successfully applied for the determination of vanadium in alloy as proposed by the authors.

8.1.7 Ion pair reagent potassium salt of tetrabromophenolphthaleinethylester (TPBE-K)

Gavrilenko N. A. et al. [7] have studied the interaction of Fe(II) with 2,2′-dipyridyl and 1,10-phenanthroline immobilized in a polymethacrylate matrix. The authors have determined the optimum conditions of the complexation of Fe(II) with the immobilized reagents and the chemical analysis properties of the complexes in the polymethacrylate matrix. A sorption-spectrophotometric procedure is developed for the determination of Fe(II) and the total of Fe(II, III) after the reduction of Fe(III) by ascorbic acid. The procedure with 2,2′-dipyridyl is used for the analysis of samples of tap, well and mineral water and a solution of glucose.

8.1.8 Tetrabromophenolphthalein Et.ester (TBPE)

Shiki Masaharu et al. [8] have examined trace Fe(II) with 1,10-phenanthroline (phen) and tetrabromophenolphthalein Et.ester (TBPE) using chitosan co-precipitation in spectrophotometric method. Fe(II) reacts with phen to a stable chelating complex, $[Fe(phen)_3]^{2+}$. $[Fe(phen)_3]^{2+}$ associated with TBPE- buffered at about pH 6.5 to form the ion associated $[Fe(phen)_3]^{2+}\cdot(TBPE^-)_2$. A chitosan solution dissolved with HOAc is added to this solution and chitosan precipitated from the solution immediately. The ion associated $[Fe(phen)_3]^{2+}$-$(TBPE^-)_2$ is adsorbed onto the chitosan precipitate. After centrifugation, the supernatant solution is discarded. The chitosan precipitate is dissolved with HOAc and NaOAc, and Fe(II) which is determined by measuring the absorbance of the solution at 606 nm, that is, the maximum absorption wavelength of TBPE without any pre-treatment. As mentioned by the authors the detection limit (S/N = 3) is ~8 ppb. The relative standard deviations (n = 3) for 60 ppb Fe(II) is 3.9%. The authors report that this method is simple for the determination of Fe(II) at <60 ppb, and there is no use of toxic organic solvents.

8.2 Phenylfluorone

8.2.1 *p*-Aminophenylfluorone (APF)

Ma Weixing et al. [9] have established a spectrophotometric determination method for iron that is based on the color reaction between Fe(III) and chromotropic acid and emulsifier OP in alkaline medium. It is found that Fe(III) could form a green quaternary blending micellar complex with APF, chromotropic acid (CA) and OP. The λ_{max} of this complex is observed at 620 nm. The molar ratio of Fe(III), APE, and CA is 1:2:1. Beer's law is obeyed for iron in 1–10 μg/10 mL with the correlation coefficient of 0.9995. As reported by the authors, the proposed method was applied to the determination of trace iron in aluminum alloy samples.

8.2.2 9-(4-Carboxyphenyl)-2,3,7-trihydroxyl-6-fluorone

Li Zaijun et al. [10] have developed a spectrophotometric method for the determination of iron(III)-dimethyldithiocarbamate (ferbam) by converting it into an iron(III)-9-(4-carboxyphenyl)-2,3,7-trihydroxyl-6-fluorone complex. The reagent reacts with ferbam to form a blue complex with a maximum absorption peak at 640 nm, in NH_3-HAc buffer solution (pH 6.5). The reaction can be completed rapidly at room temperature and the absorbance is stable for at least 24 h. As the authors describe, the apparent molar absorption coefficient, Sandell’s sensitivity of the complex, the detection limit and the relative standard deviation are 1.06×10^5 L mol^{-1} cm^{-1}, 3.9 ng cm^{-2}, 2.2 ng mL^{-1} and 1.06%, respectively. From 0 to 75 µg of ferbam in 25 mL solution the absorbance obeys Beer’s law. The effect of foreign ions and other dithiocarbamates were also studied by the authors in detail. The results indicate that all coexisting ions examined can be tolerated in considerable amounts, especially other dithiocarbamates such as ziram and zineb, which always interfere with the determination of ferbam in the literature. The proposed method is very sensitive, selective and simple. It has been applied to determine ferbam in commercial samples.

8.2.3 Phenylfluorone

Ma Wei-xing et al. [11] have studied the chromogenic reaction of iron(III) with phenylfluorone in the presence of Tween-20 by the Spectrophotometric method. Results show that in the basic medium, iron(III) reacts with the phenylfluorone forming a stable blue chelate(III). The maximum absorption of this chelate is observed at 620 nm with an apparent molar absorptivity of 9.355×10^4 L mol^{-1}cm^{-1}). Beer’s law is obeyed at the iron(III) concentration range of 0–16 µg/25 mL. The proposed method has been applied to the direct determination of amounts of iron in polyolefin resin samples with satisfactory results, as described.

8.3 Morin (3,5,7,2′,4′-pentahydroxyflavone)

Rohani Moghadam, Masoud et al. [12] A solidified floating orgame drop microextn. (SFODME) procedure is developed for the simultaneous extraction and preconcentration of Fe(III) and Al(III) from water samples. The method is based on the formation of cationic complexes between Fe(III) and Al(III) and 3,5,7,2′,4′-pentahydroxyflavone (morin) which is extracted into 1-undecanol as ion pairs with perchlorate ions. The absorbance of the extracted complexes is then measured in the wavelength range of 300–450 nm. Finally, the concentration of each metal ion is determination by the use of the orthogonal signal correction-partial least squares (OSC-PLS) calibration method. Several experimental parameters that may be affected on the extraction process such as the type and volume of extraction solvent, pH of the aqueous solution, morin and perchlorate concentration and extraction time are optimized. Under the optimum conditions, Fe(III) and Al(III) are determination in the ranges of 0.83–27.00 µg L^{-1} ($R^2 = 0.9985$) and 1.00–32.00 µg L^{-1} ($R^2 = 0.9979$) of Fe(III) and Al(III), respectively. The relative standard deviations (n = 6) at 12.80 µg L^{-1} of Fe(III) and 17.00 µg L^{-1} of Al(III) were 3.2% and 3.5%, respectively. Enhancement factors of 102 and 96 are obtained for Fe(III) and Al(III) ions, respectively. The procedure was successfully applied to determination of iron and aluminum in steam and water samples of thermal power plant; and the accuracy was assessed through the recovery experiments and by independent analytical electrothermal atomic absorption spectroscopy (ETAAS).

Safavi Afsaneh et al. [13] have carried out simultaneous spectrophotometric determination of iron, titanium and aluminum using their morin (3,5,7,2′,4′-pentahydroxy flavone) complexes in Triton X-100 micellar medium. Partial least squares regression is employed for the resolution of ternary mixtures of Fe, Ti and Al. The presence of Triton X-100 micellar system avoids the solvent extraction step necessary for the formation of soluble morin complexes. The limits of detection obtained for Fe(III), Ti(IV), and for Al (III) are 0.03, 0.04 and 0.02 µg mL^{-1}, respectively. The relative standard error for applying the method to the analysis of 20 synthetic samples in the concentration ranges of 0.03 to 1.0 µg mL^{-1}Al(III), 0.06 to 1.6 µg mL^{-1}Ti(IV) and 0.04 to 1.5 µg mL^{-1}Fe(III) is 5%. Analysis of synthetic and artificial mixtures of solutions of several alloys is successfully performed by the method, as described by the authors.

8.4 5-Sulfosalicylic acid

Mahadevaiah and Nagendrappa G [14] have described sensitive spectrophotometric methods for the determination of iron as iron(III) in sugarcane leaves and sugarhouse products. The proposed methods involve the complexation of iron(III) in weakly acidic conditions with 5-sulfosalicylic acid and tiron having respective maximum absorbances at 490 nm and 670 nm. Both the systems obey Lambert and Beer’s law in the concentration range 0.5–23 µg mL^{-1}. Molar absorptivity, correlation coefficient and Sandell’s sensitivity values are found to be of 1.7141×10^3 mol^{-1} cm^{-1} dm^{-3}, 0.9998 and 32.5845 ng cm^{-2} respectively for iron(III)-5-sulfosalicylic acid, whereas the corresponding values are found to be 1.870×10^3 mol^{-1} cm^{-1} dm^{-3}, 0.99903, 29.8553 ng cm^{-2} for iron(III)-tiron system. Iron present in sugarcane leaves, sugarcane juice, press mud, bagasse and also iron in pharmaceutical sample, plant leaves of *Murraya koenigii* and *Moringa oleifera* was determined by the authors as iron(III) by both the methods following the principles of calibration graph method. The results obtained from iron(III)-5-sulfosalicylic acid are reproducible with acceptable standard deviation 0.021–0.0319 and coefficient of variation 0.2414–1.5978%. Whereas the results of iron(III)-tiron system are also reproducible with standard deviation 0.0192–0.033 and coefficient of variation 0.351–1.756% as described.

Bao Gui-lan et al. [15] have determined different contents of iron by using sulfosalicylic acid. Iron and sulfosalicylic acid can form purplish red complexes in the pH 1.80–3.00 buffer solution, and its apparent molar absorptivity is 1.70×10^3 L mol^{-1} cm^{-1}. The content of iron obeys Beer's law at 4.00–28.00 mg L^{-1} (or 16.00–40.00 mg L^{-1}). The method is suitable for macro-iron, especially high content iron determination in the geological sample and steel sample as described.

8.5 Catechol class

Bhaskar C. Vijaya et al. [16] have developed a simple, rapid and a sensitive spectrophotometric method for the determination of iron(III) through nucleophilic coupling reaction between catechol and *p*-nitro aniline, system 1 or catechol and *m*-nitroaniline, system 2 mediated by iron(III). As reported by the authors this method is based on catechol oxidation by iron(III) followed by its nucleophilic coupling with *m*-nitro aniline or *p*-nitroaniline in 0.1 M hydrochloric acid medium forming a dye with λ_{max} 540 nm. Both the systems obey Beer's law in the range, 0.8–20 mg mL^{-1}. The molar absorptivity values for system 1 and system 2 are found to be 9.379×10^2 L mol^{-1} cm^{-1} and 8.8032×10^2 L mol^{-1} cm^{-1}, respectively, and their corresponding Sandell's sensitivity values are 0.0595 mg cm^{-2} and 0.0634 mg cm^{-2}. The composition of the dye product is determined and found to be 1:2 for both systems. The results obtained by both the systems are reproducible and comparable with the results of iron determined separated by phenanthroline method, as described by the authors.

Abdul Galil et al. [17] have carried out a comprehensive study on the nucleophilic coupling reaction between catechol and *p*-anisidine, system 1 or *p*-chloroaniline, system 2, with iron(III). Both systems were exploited for the spectrophotometric determination of iron present as iron(III) and iron(II) after its oxidation to iron(III). As described by the authors this system works on the principle of catechol oxidation by iron(III) followed by its nucleophilic coupling with *p*-anisidine, λ_{max} 565 nm or *p*-chloroaniline, λ_{max}, 545 nm in 0.1 M hydrochloric acid medium. Under the optimized experimental conditions, Beer's law is obeyed by both systems for the determination of iron as iron(III) in the concentration range 0.4–48, system 1 and 0.4–40 mg mL^{-1}, system 2. The molar absorptivity values for system 1 and 2 are found to be 1.7×10^3 L mol^{-1} cm^{-1} and 1.6×10^3 L mol^{-1} cm^{-1}, with the corresponding Sandell's sensitivity values, 0.033 mg mL^{-1} and 0.035 mg mL^{-1}, respectively. The composition of the dye product of both systems are detected by Job's method of continuous variation as well as mole ratio method and found to be 1:1. The method involving both systems are successfully applied for the determination of iron(III) and iron(II) present in pharmaceutical preparations, sugarcane juice, laboratory chemicals and also in standard solutions. The results of iron obtained from both systems are comparable with those of the iron results determined separately following the procedure of the reported tiron-iron(III) method.

8.6 Miscellaneous Class

8.6.1 2-Thenoyltrifluoroacetone (TTA)

Moghadam Masoud Rohani et al. [18] have developed a dispersive liquid-liquid microextraction based on solidification of floating organic drop (DLLME-SFO) and artificial neural networks method for the simultaneous separation/preconcentration and speciation of iron in water samples. An appropriate mixture of ethanol (as the disperser solvent) and 1-undecanol (as the extracting solvent) containing appropriate amount of 2-thenoyltrifluoroacetone (TTA) (as the complexing agent) is injected rapidly into the water sample containing Fe(II) and Fe(III) species. At this step, the iron species interacts with the TTA and extracted into the 1-undecanol. The absorbance of the extracted iron is measured in the wavelength region of 450–600 nm after the phase separation. The artificial neutral networks are then applied for simultaneous determination of individual iron species. Under optimum conditions, the calibration graphs are linear in the range of 95–1,070 mg L^{-1} and 31–350 mg L^{-1} with detection limits of 25 and 8 mg L^{-1} for Fe(II) and Fe(III), respectively. The RSDs (R.S.D., $n = 6$) were <4.2%. The enhancement factor of 162 and 125 are obtained for Fe^{3+} and Fe^{2+} ions, respectively. As reported by the authors, the procedure has been applied to power plant drum water and several potable water samples.

8.6.2 2,6-Dihydroxy benzoic acid (2,6-DHB)

Hosseini Mohammad Saeid et al. [19] have presented a study on the basis of affinity of Fe(III) ions toward functional groups of 2,6-dihydroxy benzoic acid (2,6-DHB), a charge transfer complex (CT) is formed between Fe(III) ion and 2,6-DHB in acidic media. The stoichiometry and stability constant of the complex are determined using both mole ratio and Job's methods. The stability constant of 1:1 complex formed in acidic media is $2.55 \pm 0.14 \times 10^5$ (mole ratio) or $2.70 \pm 0.12 \times 10^5$ (Job), in which the quantities are in agreement with together. This method has been used for spectrophotometric determination of Fe(III) in aqueous media. The dynamic range and detection limit (DL) were 1.2×10^{-5} to 3.6×10^{-4} M and 1.5×10^{-6} M, respectively. As reported by the authors the relative standard deviation (RSD) is found to be 0.76% in the replicate treatments ($n = 7$) with 1.6×10^{-4} M Fe(III). The practical applicability of the method is confirmed using a synthetic certificated reference material (CRM) and spiked natural water samples.

8.6.3 Chlortetracycline

Ruengsitagoon Wirat [20] developed a simple reversed flow injection colorimetric method to determine Fe^{3+}, based on the reaction between Fe^{3+} and chlortetracycline. It forms an intense yellow-colored complex showing maximum absorption at 435 nm. A 200 µL chlortetracycline reagent solution is injected into a phosphate buffer stream (flow rate, 2.0 mL min^{-1}), which is then merged with Fe^{3+} standard or sample in dilute HNO_3 stream (flow rate, 1.5 mL min^{-1}). Optimum conditions to determined Fe^{3+} are examined using a univariate method. A linear calibration graph is obtained over a 0.5–20.0 µg mL^{-1} range under optimum conditions. Detection (3σ) and quantification limits (10σ) are 0.10 and 0.82 µg mL^{-1}, respectively. Relative standard deviation of the proposed method calculated by the authors from 12 replicate injections of 2.0 and 10.0 µg mL^{-1} Fe^{3+} were 0.43 and 0.59%, respectively; sample through-put was 60 h^{-1}. The proposed method is satisfactorily used to determine Fe^{3+} in natural water as reported by author.

8.6.4 1,2-Dimethyl-3-hydroxypyrid-4-one (Hdmp)

Hua Nan-Ping et al. [21] have studied a new highly selective spectrophotometric method for determination of Fe(III) with 1,2-dimethyl-3-hydroxypyrid-4-one (Hdmp) in the $NH_4{\cdot}H_2O\text{-}NH_4Cl$ buffer solution (pH 8.5). As described by the authors, Beer's law is obeyed at 0.1–2.0 with molar absorptivity being 4.4 L mol^{-1} cm^{-1} at 450 nm. The interference resulted from most of metal ions is masked by EDTA. The method has also been applied to determination of Fe in samples with satisfactory results as mentioned by the authors.

8.6.5 Gallic acid

Abdollahi H. et al. [22] have described simultaneous determination of total Fe and V by H-point standard addition method (HPSAM) and partial least squares (PLS). Gallic acid (GA) in a cationic micellar solution of CTAB has been used for determination of Fe and V in different oxidation states at pH 5. The presence of a micellar system enables total Fe and V to be determined with improved sensitivities. The total relative standard error for applying the PLS method to 15 synthetic samples in the ranges 0.20–15.00 µg mL^{-1} Fe and 0.20–8.00 µg mL^{-1} V is 2.2%. The results of applying the H-point standard addition method show that Fe and V can be determined simultaneously with the concentration ratios of Fe to V from 10:1 to 1:20 in the mixed sample. Both HPSAM and PLS methods show suitable abilities to resolve accurately overlapped absorption spectra of the compounds. Both proposed methods have been successfully applied by the authors to the determination of Fe and V in several synthetic alloy solutions.

8.6.6 Pyrogallol red

Yuan Xia and He Bin [23] have studied the color reaction of Fe(III) with pyrogallol red. In a buffer solution of HAc-NaAc(pH 5.0) and the presence of CPB, Fe(III) reacts with pyrogallol red to form a stable green complex. The molar absorptivity is 3.24×10^4 L (mol cm)$^{-1}$ at 648 nm. Beer's law is obeyed in the range of 0 ~ 25 μg (25 mL)$^{-1}$ for Fe(III). In the presence of sodium potassium tartrate and sodium fluoride, the method is highly selective. It has been applied to the determination of Fe in grains, plant materials and environmental water samples with satisfactory results.

8.6.7 Rutin

Li Zhong et al. [24] have proposed a method for the determination of Fe in tobacco. For this Rutin has been used as a chromogenic reagent. It reacts with Fe(III) in a weakly acidic solution (0.014–0.032 mol L^{-1} HCl) in the presence of CTMAB to form a stable bluish-violet complex (mole ratio of Fe: R = 1:2) that has an absorption maximum at 620 nm. Beer's law is obeyed in the range of 0–20 μg Fe(III) per 25 mL of solution with its apparent molar absorptivity of 4.40×10^4. The RSD is 2.2–3.1%, the recovery is 95–98% and the results are consistent with those obtained by AAS.

8.6.8 Piperonal fluorine (PIF)

Zhong Ming-hua and Mo Chun-sheng [25] have developed a new method for the silica gel H phase-diffuse reflectance spectrophotometric determination of iron(III) with piperonal fluorine (PIF). In the presence of cetyltrimethyl ammonium bromide and in a NH_4Cl-NH_3. H_2O medium at pH 9.6–10.3, iron(III) reacts with PIF to form a stable blue complex which is absorbed by silica gel H with a diffuse reflectance absorption peak at 640 nm. The calibration curve is linear over the concentration range 0–25 ng of iron(III) in 1 mL. The linear regression equation is AR = 0.022 1 c–0.005,5(r = 0.999,7), where c is expressed as ng per 1 mL. The method has high analytical speed and sensitivity. The effect of a number of foreign ions is studied by carrying out determining of 200 ng (10 mL)$^{-1}$ of iron(III), 1 mg K^+, Na^+, F^-, Cl^-, NO_3^-, PO_4^{3-}, 0.6 mg Ca^{2+}, Mg^{2+}, 35 micrograms Sr^{2+}, 20 micrograms Cr(III), 6 micrograms Mn^{2+}, 4 micrograms Pb^{2+}, 3.5 micrograms Cd^{2+}, 2.5 micrograms Cu^{2+}, Ag^{+}, 1.5 micrograms Cr(VI), 1 microgram Ni^{2+}, 0.75 microgram Zn^{2+}, Sn^{4+} etc., do not interfere with the measurement. The method has been applied to the determination of micro amount iron in magnesium oxide with satisfactory results.

8.6.9 Quercetin (Qu)

Zhang Shu-Min et al. [26] have studied that Quercetin(Qu) reacted with Fe(III) to form a complex ($\lambda_{max} = 430$ nm) in the buffer solution of HAc-NH_4Ac(pH = 4.05). A linear relationship holds between the absorbance and the concentration of Fe(III) in the range of 2.0×10^{-5} to 1.2×10^{-4} mol L^{-1}. The detection limit is 2.0×10^{-5} mol L^{-1}. The complex ratio of Fe(III): Qu is 1:2 and the stability constant is 1.0×10^{8}.

8.6.10 Resorcylic acid (2,4-dihydroxybenzoic acid, DHB)

Hashem Elham Y [27] studied the complexation equilibrium of Fe(III) with resorcylic acid (2,4-dihydroxybenzoic acid, DHB) spectrophotometrically in ethanol-water (4 + 6, vol./vol.) at an ionic strength of 0.1 M $NaClO_4$. The complexation reactions have been demonstrated and characterized. A simple, rapid and sensitive method that is based on the formation of the Fe(III)-DHB complex at pH 2.5 (λmax = 520 nm, $\varepsilon = 0.8 \times 10^{4}$ L mol^{-1} cm^{-1}) has been developed for the spectrophotometric determination of Fe(III). The authors isolated the Fe-DHB complex and characterized by both elemental analysis and IR spectroscopy. The proposed method has been tested by determinations of iron in various synthetic samples and Portland cement materials as described.

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Chapter 9
Analytical reagents having nitrogen (N) as donor atoms

9.1 Triazine class

9.1.1 2,4,6-Tri(2'-pyridyl)-l,3,5-triazine (TPTZ)

Yousefi Dareh Door et al. [1] have developed quick and disperser-solvent-free analytical method based on ultrasound-assisted temperature-control deep eutectic solvent dispersive liquid phase microextraction (UA-TC-DES-DLPME) in combination with spectrophotometry for the separation/preconcentration and determination of iron species. In this method, Fe(II) is complexed with 2,4,6-tri(2'-pyridyl)-l,3,5-triazine (TPTZ), and extracted into a hydrophobic deep eutectic solvent (DES) consisting of choline chloride and 4-chlorophenol (ChCl/4-Chph). The dispersion of DES in aq. phase is speeded up by ultrasound waves and temperature control process without using any organic dispersive solvent. Total iron concentration is obtained after reduction of Fe(III) to Fe(II) with hydroxylamine hydrochloride, and the amount of Fe(III) was calculate according to the difference between the concentration of total iron and Fe(II). At optimum conditions that obtained using multisimplex method, the calibration curve is linear over the range of 5.0–100.0 mg L^{-1} with the detection limit of 1.2 mg L^{-1}. The intra- and inter-day relative standard deviations (RSDs) at 20 g L^{-1} level of Fe(II) (n = 5) were 3.6 and 4.5.%, respectively. The proposed method was successfully applied to the determination of iron species in water samples, as reported.

Teixeira Leonardo S. G. et al. [2] have reported three ferroin reagents for the simultaneous spectrophotometric determination of iron and copper: 1,10-phenanthroline, 2,2'-bipyridine and 2,4,6-tri(2-pyridyl)-1,3,5-triazine. Effect of pH conditions, order of reagent addition, interferences, amount of reagents, linear range, sensitivity and stability of each system are also compared. As described by the authors the 2,4,6-tri(2-pyridyl)-1,3,5-triazine can be used for determination of iron in the presence of copper with a detection limit of 5 µg/L and coefficient of variation of 2.0%; however, it was not possible to determine directly copper in the presence of iron with this reagent. 1,10-phenanthroline can be used for simultaneous determination of the metallic ions with detection limits of 7 and 8 µg/L and coefficients of variation of 1.8 and 2.3% in the determination of iron and copper, respectively. In addition, 2,2'-bipyridine can be used for simultaneous determination of the metallic ions with detection limits of 11 and 32 µg/L and coefficients of variation of 1.9 and 2.5% in the determination of iron and copper, respectively. It is mentioned that the reagents have also been used for spectrophotometric determination of iron and copper in ethanol fuel.

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9.1.2 Ferrospectral; 3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine (FST)

Toral M. Ines et al. [3] have proposed spectrophotometric determination of iron and cobalt by batch and continuous flow modes. As solid phase the authors have used Ferrospectral; 3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine (FST) sorbed on DEAE Sephadex A-25. In batch simultaneous determination, the second derivatives for iron and cobalt determination are used at 536.0 and 601.4 nm, respectively. In this modality, the detection limits (3 s criterions), for iron and cobalt are 1.3, 9.1 mg L^{-1} and the determination ranges are: 4.3 to 220 and 30.3 to 800 mg L^{-1}. The method by FIA mode is carried out by stopped flow and then the analytical signal is evaluated by 2 nd derivative at 560.9 and 482.3 nm for iron and cobalt determination, respectively. In FIA modality, the detection limits for iron and cobalt were 6.4, 31 mg L^{-1}, and the determination ranges 21 to 200 and 106 to 1000 mg L^{-1} iron and cobalt, respectively, as mentioned by the authors. These methods are applied successfully in drinking water and soil samples.

9.1.3 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT)

Zhu Wei-huang et al. [4] have studied organic extraction spectrophotometry to determine iron. As deriving reagent, 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT) is used and the potassium salt of tetrabromophenolphthaleinethyl ester (TPBE-K) is used as an ion-pair reagent. It is found that the sensitivity of the method is enhanced with the addition of the ion pair, TPBE-K, because TPBE- and Fe(II)-PDT can form a ternary chelate of ionic association. The maximum absorbance wavelength is red shifted, which leads to an increase in molar absorption coefficient from 2.4×10^4 L mol^{-1} cm^{-1} to 1.9×10^5 L mol^{-1} cm^{-1}. The calibration graph is constructed in a concentration range of 0–0.3 mg/L, the linear regression equation is $A = 0.3582\ C + 0.002$ ($r^2 = 0.9974$) and the limit of the detection (LOD) is 0.96 ng/mL (S/N = 3). As mentioned by the authors organic extraction ion-pair spectrophotometry can be satisfactorily applied to determining the concentrations of Fe(II) and total iron in the fountain and surface lake water samples.

9.2 1,10-Phenanthroline

Kumar, K. Ravi et al. [5] have proposed new cloud point extraction (CPE) procedure with spectrophotometry for the pre-concentration and determination of iron(II). In this method, Fe^{2+} is complexed with 1,10-phenanthroline at a pH of 4.2. Fe^{2+}-1, 10-phenanthroline complex is then extracted into mixed micelles of Triton X-114 (TX-114) and docusate sodium salt (DOSS). Various parameters such as pH, concentration of

1,10-phenanthroline, concentrations of the surfactants (TX-114 and DOSS), concentration of salt (Na_2SOp_4), equilibration temperature and equilibration time are optimized. Under optimum conditions the linear range of Fe^{2+} is found to be 0.14–2.23 mg mL^{-1}. The corresponding detection limit is found to be 5.1 ng mL^{-1}. The proposed method has been successfully applied to the determination of Fe^{2+} in tap water and sea water samples. The recoveries are found to be in the range of 80–95% and the effect of sodium nitroprusside on the recovery is studied.

Veerabhadraswamy, M. et al. [6] have proposed simple and sensitive derivative spectrophotometric method for the determination of Fe(II) and Ru(III) using the baseline to peak measurement techniques. In the present method 1,10-phenanthroline (o-phen) is used as a complexing agent. Fe(II) and Ru(III) form a complex with o-phen at pH 5 and 4, respectively. Based on baseline-to-peak measurement techniques deep red Fe(II)-o-phen complex shows the maximum peak at 535 nm, while the yellow product of Ru(II)-o-phen complex at 466 nm. Beer's law is obeyed in the range of 0.1–2.0 mg mL^{-1} for Fe(II) and 5.0–20.0 mg mL^{-1} for Ru(III) which is supported by correlation coefficient 0.99853 and 0.99914, respectively. The present method has been applied successfully for the determination of Fe(II) in pharmaceutical formulations and Ru(III) in some synthetic mixtures.

Metarwiwinit, S. et al. [7] report a simplified dispersive micro-solid phase extraction (d-m-SPE) using silica sol as the sorbent for the preconcentration of ferrous ions. Ferrous ions are prederivatized via complexation with 1,10-phenanthroline (Phen) before being adsorbed by the silica sol. The adsorption of the [Fe^{2+}-Phen] complex simultaneously occurs with aggregation of the silica sol with the assistance of the phase transfer catalyst (PTC) tetrabutylammonium bromide. The enriched [Fe^{2+}-Phen] complex on the silica sol is directly detected using a spectrophotometer at 510 nm. Several experimental parameters including the amount of silica sol, pH, PTC, extraction and centrifugation times are investigated. Under the optimal conditions, the enrichment factor is 7.3 and the linear range is from 0.07 mg L^{-1} to 1.43 mg L^{-1}. The limit of detection and the limit of quantitation are 16 mg L^{-1} and 54 mg L^{-1}, respectively. Furthermore, the precision, expressed as the relative standard deviation, is lower than 4% from ten replicates. The extraction recoveries of Fe^{2+} in cereal and vegetable samples are 71.0–107.5%. In addition, a camera in combination with Image J program is used as an alternative tool for the detection of the adsorbed [Fe^{2+}-Phen] complex.

Abdel Ghafar, Hany H. et al. [8] have developed sensitive and selective spectrophotometric procedures for the determination of Fe(III) and Cu(II) using simple chromogenic reagents. The procedure of iron determination is based on the formation of ternary complex between Fe(III) and 4,7-diphenyl-1,10-bathophenanthroline (DPBP)-eosin in acid medium. On the other hand, the procedure of copper(II) determination is based on the formation of ternary complex between Cu(II) and 4,7-diphenyl-1,10-bathophenanthroline (DPBP)-Eriochrome Black-T (EBT) in alkaline medium. The ternary complexes are extracted in the presence of cetyltrimethyl ammonium bromide with chloroform. The molar absorptivities of the Fe(III)-DPBP-eosin and Cu(II)-DPBP-EBT ternary complexes were $2.23 \cdot 10^5$ and $9.35 \cdot 10^4$ L mol^{-1} cm^{-1} at 542 and 565 nm, respectively. Beer's law is valid over the concentration ranges from 0.280 to 7.814 and from 0.320 to 8.260 mg mL^{-1} for Fe(III) and Cu(II), respectively. Sandell sensitivity (0.0025 and 0.0679 ng cm^{-2}), relative standard deviation (0.257–1.94 and 0.305–1.85), limits of detection (0.076 and 0.045 mg mL^{-1}) and quantification (0.253 and 0.150 mg mL^{-1}) for Fe(III) and Cu(II) ions, respectively, are calculated. The procedures are applied for the determination of Fe(III) and Cu(II) in different polluted water sources, drinking water, river water as well as cooling water and boiler scales. The results obtained are compared with those obtained using atomic absorption spectroscopy. The effects of different tolerances are studied in the presence of masking agents.

Chen, Shujuan et al. [9] have reported a simple and new low pressure ion chromatog. combined with flow injection spectrophotometric procedure for determining Fe (II) and Fe(III). It is based on the selective adsorption of low pressure ion chromatography column to Fe(II) and Fe(III), the online reduction reaction of Fe(III) and the reaction of Fe(II) in sodium acetate with phenanthroline, resulting in an intense orange complex with a suitable absorption at 515 nm. Various chemicals (such as the concentration of color reagent, eluant and reductive agent) and instrumental parameters (reaction coil length, reductive coil length and wavelength) are studied and are optimized. Under the optimum conditions calibration graph of Fe(II)/Fe(III) is linear in the Fe(II)/Fe(III) range of 0.040–1.0 mg/L. The detection limit of Fe(III) and Fe(II) is respectively 3.09 and 1.55 mg/L, the relative standard deviation ($n = 10$) of Fe(II) and Fe(III) 1.89% and 1.90% for 0.5 mg/L of Fe(II) and Fe(III), respectively. About 2.5 samples in 1 h can be analyzed. The interfering effects of various chemical species studied. The method can be successfully applied in the determination of water samples.

Gavrilenko N. A. et al. [10] have studied the interaction of Fe(II) with 2,2'-dipyridyl and 1,10-phenanthroline immobilized in a polymethacrylate matrix. The authors determined the optimum conditions of the complexation of Fe(II) with the immobilized reagents and the chemical analysis properties of the complexes in the polymethacrylate matrix. A sorption-spectrophotometric procedure is developed for the determination of Fe(II) and the total of Fe(II, III) after the reduction of Fe(III) by ascorbic acid. The procedure with 2,2'-dipyridyl is used for the analysis of samples of tap, well and mineral H_2O and a solution of glucose.

Nadzhafova O. Yu. et al. [11] have optimized conditions for preparing sol-gel modified composite films based on silicon oxide and poly vinylsulfonicacid in the presence of the Tween 20 non-ionic surfactant as a template for the adsorption of Fe(II) and Zn(II) phenanthrolinates. The adsorption of Zn(II), Cu(II), Mn(II), Co(II) and Ni(II) phenanthrolinates followed by their development on the surface with Rose

Bengal oxyxanthene dye was studied by spectrophotometry. The variation of the pH of the solution pH and the addition of 0.01 M of EDTA enhanced the selectivity of detecting Zn(II) using a film obtained under optimum conditions. The applicability of the proposed thin-film coatings to the adsorption-spectrophotometric determination of Fe(II) and Zn(II) in the ranges of 0.2–5.6 and 0.3–5.0 mg/L, respectively, is shown by the authors.

Shiki Masaharu et al. [12] have examined trace Fe(II) with 1,10-phenanthroline (phen) and tetrabromophenolphthalein Et ester (TBPE) using chitosan co-precipitation in spectrophotometric method. Fe(II) reacts with phen to a stable chelating complex, $[Fe(phen)_3]^{2+}$.$[Fe(phen)_3]^{2+}$ associated with TBPE- buffered at about pH 6.5 to form the ion associated $[Fe(phen)_3]^{2+}\cdot(TBPE^-)_2$. A chitosan solution dissolved with HOAc is added to this solution and chitosan precipitated from the solution immediately. The ion associated $[Fe(phen)_3]^{2+}$-$(TBPE^-)_2$ is adsorbed onto the chitosan precipitate. After centrifugation, the supernatant solution is discarded. The chitosan precipitate is dissolved with HOAc and NaOAc, and Fe(II) can be determined by measuring the absorbance of the solution at 606 nm, i.e., the maximum absorption wavelength of TBPE without any pre-treatment. As mentioned by the authors the detection limit (S/N = 3) is 8 ppb. The relative standard deviations (n = 3) for 60 ppb Fe(II) was 3.9%. The authors report that this method is simple for the determination of Fe(II) at <60 ppb, and there is no use of toxic organic solvents.

Teixeira Leonardo S. G. et al. [2] have reported three ferroin reagents for the simultaneous spectrophotometric determination of iron and copper: 1,10-phenanthroline, 2,2'-bipyridine and 2,4,6-tri(2-pyridyl)-1,3,5-triazine. Effect of pH conditions, order reagent addition, interferences, amount of reagents, linear range, sensitivity and stability of each system are also compared. As described by the authors the 2,4,6-tri(2-pyridyl)-1,3,5-triazine can be used for determination of iron in the presence of copper with a detection limit of 5 µg/L and coefficient of variation of 2.0%; however, it is not possible to determine directly copper in the presence of iron with this reagent. 1,10-phenanthroline can be used for simultaneous determination of the metallic ions with detection limits of 7 and 8 µg/L and coefficients of variation of 1.8 and 2.3% in the determination of iron and copper, respectively. In addition, 2,2'-bipyridine can be used for simultaneous determination of the metallic ions with detection limits of 11 and 32 µg/L and coefficients of variation of 1.9 and 2.5% in the determination of iron and copper, respectively. It is mentioned that the reagents have also been used for spectrophotometric determination of iron and copper in ethanol fuel.

Safavi Afsaneh et al. [13] have described simultaneous determination of total iron and copper using either a partial least squares (PLS) or an H-point standard addition method (HPSAM). The authors used mixed reagents of 1,10-phenanthroline and neocuproine for the determination of iron and copper. For applying the method on 15 synthetic samples in the concentration ranges of 0.10–8.00 µg mL^{-1} Fe and

0.12–8.75 μg mL^{-1} Cu, the total relative standard error is 2.02%. Both PLS and HPSAM show suitable abilities to accurately determine iron and copper from overlapped absorption spectra of their complexes. These methods have been successfully applied to the determination of iron and copper in blood serum and river water. The results for several analyzed samples are in satisfactory agreement with those acquired by using the FAAS technique as described.

Tesfaldet Zeriet O. et al. [14] have proposed a sequential injection analysis (SIA) system for the determination of iron(II). Fe(II) is determined by SIA based on the reaction between 1,10-phenanthroline and iron(II), yielding an orange-red color complex with absorption maximum at 512 nm. The method involves aspiration of 187 L sample/standard zone followed by a zone of a reagent solution containing 140 L of 7.8×10^{-4} mol L^{-1} 1,10-phenanthroline into a carrier stream to be stacked inside a holding coil and flow reversed through a reaction coil to a detector. The optimum condition is evaluated and the calibration curve obtained is linear over a range of 0.25 to 5.0 mg L^{-1} of Fe(II) with detection limit of 18 μg L^{-1}. A sample throughput of 40 h^{-1} is established. The proposed method was successfully applied for the determination of total iron as Fe(II) in pharmaceutical products (multivitamin tablets) and has been especially useful for the determination of iron(II) in tablets with lower iron(II) contents, as the authors mention.

Wang Li-min et al. [15] have reported a method for the spectrophotometric determination of Fe after extraction of its ternary complex with 4,7-diphenyl-1,10-phenanthroline and tetraphenylborate into molten naphthalene. Fe(II) reacts with 4,7-diphenyl-1,10-phenanthroline and tetraphenylborate to form a stable red ternary complex, at pH 4 that is easily extracted by the authors into molten naphthalene. The solid naphthalene containing the ternary complex is separated by filtration and dissolved in acetone. Against a reagent blank, the absorbance is measured at 534 nm. Beer's law is obeyed in the concentration range of 0–50 μg/25 mL acetone solution of Fe. The molar absorptivity and Sandell's sensitivity at 534 nm is 2×10^4 L mol^{-1} cm^{-1} and 0.0025 μg/cm^2, respectively. The interference of various ions has also been studied by the authors. The method can be applied to determine micro amounts of Fe in natural H_2O samples with satisfactory results.

Demirhan Nebahat et al. [16] have developed a new spectrophotometric method for the determination of Fe(II) with 5-nitro-6-amino-1,10-phenanthroline (NAF). The effect of factors such as pH, amount of reagent (NAF), reaction time and temperature are studied. The method is based on the formation of a colored product between Fe(II) and NAF. The reaction proceeds quantitatively at 20° for 210 min in acidic medium. The absorption maximum is at 520 nm. A linear relation exist between absorbance and Fe(II) concentration over the range 0.1 μg/mL and 0.4 μg/mL. The molar ratio of Fe(II) to the reagent has been determined as 1: 3. The limiting concentration for interference by Co(II), Ni(II), Cu(II), Zn(II), Mn(II), Al(III), Ca(II) and Mg(II) cations is reported by the authors.

Lin Xinhua et al. [17] have studied the spectrophotometric determination of iron with phen in the presence of CTMAB and potassium hydrogen tartrate. The resulting complex has a maximum absorption at 515 nm. Beer's law is obeyed in the concentration range of 0.5–8.0 μg/mL, having correlation coefficient 0.9995. Its apparent molar absorptivity is 1.23×10^4 L mol^{-1} cm^{-1}. The method has also been applied to determine iron in Aloe with satisfactory results. The relative standard deviations are less than 0.54% ($n = 6$), and the recovery rate of iron from three samples (whole leaf, outer skin and mesophyll) is from 98.1% to 101.5%, as described by the authors.

H. Abdollahi [18] has reported simultaneous determination of Cr(VI) and Fe(III) by PLS calibration and H-point standard addition method (HPSAM). As a selective chromogenic system mixed reagents of diphenylcarbazide and 1,10-phenanthroline in a non-ionic micellar solution of Triton X-100 are used for determination of Cr(VI) and Fe(III). This micellar system is beneficial for elimination of the previous solvent extraction step that is necessary for the determination of slightly soluble metal complexes in the absence of micelles. The total relative standard error for applying the PLS method to 15 synthetic samples lies in the range of 0.20–6.00 μg mL^{-1} Cr(VI) and 0.20–8.00 μg mL^{-1} is 1.5%. By applying H-point standard addition method the results obtained show that Cr(VI) and Fe(III) can be determined simultaneously with weight concentration ratios of Cr(VI) to Fe(III) varying from 15: 1 to 1: 30 in the mixed sample. Author mention that both methods (PLS and HPSAM) could also be applied successfully to the determination of Cr and Fe in several synthetic alloy solutions.

Fan Zhefeng et al. [19] have presented a new spectrophotometric method for the determination of Fe with polyethylene glycol-$(NH_4)_2SO_4$-1,10-phenanthroline system. A stable complex with the ratio of 1: 3 is formed by Fe(II) and 1,10-phenanthroline in pH 5.8 buffer solution and extracted by polyethylene glycol. The complex shows maximum absorption at 508 nm, the molar absorptivity 1.1×10^4, and Beer's law is obeyed at 0–50 μg. As the authors describe the method has been used in the determination of Fe in serum and hair samples.

9.3 2, 2'-Bipyridine

Samadi, A., Amjadi, M [20] have introduced halloysite nanotubes (HNTs) as a new solid phase extraction adsorbent for preconcentration of iron(II) as a complex with 2,2-bipyridine. The cationic complex is effectively adsorbed on the sorbent in the pH range of 3.5–6.0 and efficiently desorbed by trichloroacetic acid. The eluted complex has a strong absorption around 520 nm, which is used for determination of Fe(II). After optimizing extraction conditions, the linear range of the calibration graph is 5.0–500 mg/L with a detection limit of 1.3 mg/L. The proposed method is successfully applied for the determination of trace iron in various water and food samples, and the accuracy is assessed through the recovery experimental and analyses of a certified reference material (NIST 1643e).

Pourreza Nahid et al. [21] have developed preconcentration of iron(II) using silica gel-polyethylene glycol (silica-PEG) as an adsorbent by solid phase extraction. The method is based on retention of iron(II) as 2,2'-bipyridine complex on silica-PEG. The retained complex is eluted by 1.0 mol L^{-1} of H_2SO_4-acetone mixtures (1:2) and its absorbance is measured at 518 nm, spectrophoto-metrically. The calibration graph was linear in the range of 1–60 ng mL^{-1} of iron(II). The method has been successfully applied to the determination of iron(II) in water, multivitamin tablet, and spinach samples as reported.

Gavrilenko N. A. et al. [10] have studied the interaction of Fe(II) with 2,2'-dipyridyl and 1,10-phenanthroline immobilized in a polymethacrylate matrix. The authors determined the optimum conditions of the complexation of Fe(II) with the immobilized reagents and the chemical analysis properties of the complexes in the polymethacrylate matrix. A sorption-spectrophotometric procedure is developed for the determination of Fe(II) and the total of Fe(II, III) after the reduction of Fe(III) by ascorbic acid. The procedure with 2,2'-dipyridyl is used for the analysis of samples of tap, well and mineral H_2O and a solution of glucose.

Teixeira Leonardo, S. G. et al. [2] have reported three ferroin reagents for the simultaneous spectrophotometric determination of iron and copper: 1,10-phenanthroline, 2,2'-bipyridine and 2,4,6-tri(2-pyridyl)-1,3,5-triazine. Effect of pH conditions, order reagent addition, interferences, amount of reagents, linear range, sensitivity and stability of each system are also compared. As described by the authors 2,4,6-tri(2-pyridyl)-1,3,5-triazine can be used for determination of iron in the presence of copper with a detection limit of 5 µg/L and coefficient of variation of 2.0%; however, it is not possible to determine directly copper in the presence of iron with this reagent. 1,10-phenanthroline can be used for simultaneous determination of the metallic ions with detection limits of 7 and 8 µg/L and coefficients of variation of 1.8% and 2.3% in the determination of iron and copper, respectively. In addition, 2,2'-bipyridine can be used for simultaneous determination of the metallic ions with detection limits of 11 and 32 µg/L and coefficients of variation of 1.9% and 2.5% in the determination of iron and copper, respectively. It is mentioned that the reagents have also been used for spectrophotometric determination of iron and copper in ethanol fuel.

Malik Ashok Kumar et al. [22] have developed a procedure for the direct fourth-derivative spectrophotometric determination of iron(III) dimethyldithiocarbamate by converting it into an iron(II) 2,2'-bipyridyl complex, which is then dissolved in Triton X-100. Beer's law is obeyed over the concentration range 0.5–20 µg mL^{-1} in the final solution. Various parameters such as the effect of pH and interference of large number of ions on the determination of ferbam have been studied by the authors in detail. The method is sensitive, highly selective and can be used for the determination of ferbam in a commercial sample and in mixtures with various dithiocarbamates (ziram, zineb, maneb, etc.) and from wheat grains.

Jankiewicz B. et al. [23] have determined bioavailable and total iron in the soil collected in two allotment gardens in the city. Iron is been determined spectrophotometrically in the form of red-pink complex of Fe(II) and 2,2'-dipyridine. The method of determination recommended by the Polish Standards has been modified by the authors using hydroxylamine instead of glycine to reduce Fe(III) to Fe(II).

9.4 Miscellaneous class

9.4.1 Methyl green

Fan Xue-mei et al. [24] have proposed a method that is applicable for the determination of iron content in local iron tailings. Iron(III) has inhibitory effect in hydrochloric acid-potassium acid phthalate medium, on the fading reaction of methyl green oxidized by potassium per-iodate. In the present method, absorbance difference between the inhibitory reaction and non-inhibitory reaction at 458 nm shows good linearity to the mass concentration of iron in certain range. On the basis of result obtained, a new determination method of trace iron by inhibitory kinetic spectrophotometry is established and kinetic parameters of inhibitory fading reaction are also measured. The apparent activation energy of inhibitory reaction is $Ea = 0.85$ kJ/mol, and the reaction rate constant is $K' = 6.0{*}10^{-4}/s$. The linear range of method is in range of 20–120 mg/L, and the detection limit was 8.39 mg/L as described.

9.4.2 Ferrozine

Kamaya Minori et al. [25] have investigated iron and zinc as contaminant metals in chromium(III) platting bath by spectrophotometry. The reagents used are ferrozine and 4-(2-Pyridylazo) resorcinol (PAR) for iron and zinc respectively. The iron contents in the prepared chromium(III) plating bath contained cobalt, copper and zinc is detected successfully by addition of EDTA as masking agent. However, in the case of zinc in the prepared plating bath, it is difficult to determine without interference with chromium (Ni). Therefore, it was necessary to detect the zinc by addition method as mentioned.

9.4.3 *N*,*N*-Dimethyl-*p*-phenylenediaminedihydro chloride (DPD)

Huang Yongming et al. [26] have developed a method for determining iron in seawater by coupling reverse flow injection analysis (rFIA) and catalytic spectrophotometric detection with *N*,*N*-dimethyl-p-phenylenediaminedihydro chloride (DPD). With a seawater sample or a standard solution as the carrier, the mixture of DPD and buffer is injected into the carrier stream quantitatively and discretely. After mixing with H_2O_2, the DPD is oxidized to form two pink semiquinone derivatives that are monitored at 514 nm wavelength with a reference at 700 nm. As reported by the authors detection limit of the method is 0.40 nmol L^{-1} lower than half of that of normal flow injection analytical (nFIA) method. The analytical results of the certified seawaters CASS-4 (12.33 ± 0.18 nmol L^{-1}) and NASS-5 (3.47 ± 0.23 nmol L^{-1}) well agree with the certified values (12.77 ± 1.04 and 3.71 ± 0.63 nmol L^{-1}, respectively). The typical precision of the method for a 2.97 nmol L^{-1} iron sample is 4.49% (n = 8). An instrument is assembled based on the proposed method and applied successfully to analyze total dissolvable iron (TDFe) in surface seawater samples collected from the Pearl River Estuary, the results of which revealed non-conservative behavior of TDFe during the estuarine mixing.

9.4.4 *p*-Nitro aniline and *m*-nitro aniline

Bhaskar C. Vijaya et al. [27] have developed a simple, rapid and a sensitive spectrophotometric method for the determination of iron(III) is through nucleophilic coupling reaction between catechol and p-nitro aniline, system 1 or catechol and m-nitroaniline, system 2 mediated by iron(III). As reported by the authors this method is based on catechol oxidation by iron(III) followed by its nucleophilic coupling with m-nitro aniline or *p*-nitroaniline in 0.1 M hydrochloric acid medium forming a dye with λ_{max} 540 nm. Both the systems obey Beer's law in the range, 0.8–20 mg mL^{-1}. The molar absorptivity values for system 1 and system 2 are found to be 9.379×10^2 L mol^{-1} cm^{-1} and 8.8032×10^2 L mol^{-1} cm^{-1} respectively and their corresponding Sandell's sensitivity values, 0.0595 mg cm^{-2} and 0.0634 mg cm^{-2}. The composition of the dye product is determined and found to be 1: 2 for both systems. The results obtained by both the systems are reproducible and comparable with the results of iron determined separated by phenanthroline method, as described by the authors.

9.4.5 *p*-Anisidine and *p*-chloroaniline

Abdul Galil et al. [28] have carried out a comprehensive study on the nucleophilic coupling reaction between catechol and p-anisidine, system 1 or *p*-chloroaniline, system 2, with iron(III). Both systems are exploited for the spectrophotometric determination of iron present as iron(III) and iron(II) after its oxidation to iron(III). As described by the authors this system works on the principle of catechol oxidation by iron(III) followed by its nucleophilic coupling with *p*-anisidine, λ_{max} 565 nm or p-chloroaniline, λ_{max}, 545 nm in 0.1 M hydrochloric acid medium. Under the optimized experimental conditions, Beer's law is obeyed by both systems for the determination of iron as iron(III) in the concentration range 0.4–48, system 1 and 0.4–40 mg mL^{-1}, system 2. The molar absorptivity values for system 1 and 2 are found to be 1.7×10^3 L mol^{-1} cm^{-1} and 1.6×10^3 L mol^{-1} cm^{-1}, with the corresponding Sandell's sensitivity values, 0.033 mg mL^{-1} and 0.035 mg mL^{-1}, respectively. The composition of the dye product of both systems are detected by Job's method of continuous variation as well as mole ratio method and found to be 1: 1. The method involving both systems have been successfully applied for the determination of iron(III) and iron(II) present in pharmaceutical preparations, sugarcane juice, laboratory chemicals and also in standard solutions. The results of iron obtained from both systems are comparable with those of the iron results determined separately following the procedure of the reported tiron-iron(III) method.

9.4.6 Diphenylamine-4-sulfonic acid sodium salt (DPA-4-SA)

Asan Adem et al. [29] have presented a highly sensitive and very simple spectrophotometric flow-injection analysis (FIA) method for the determination of iron(III) at low concentration levels using the color developing reagent DPA-4-SA in acetate buffer at pH 5.50. The complex formed by iron(III) and diphenylamine-4-sulfonic acid sodium salt (DPA-4-SA) shows absorbance intensity at 410 nm. The flow rate was 1 mL min^{-1} with the sample. The method provides a linear determination range between 5 µg L^{-1} and 200 µg L^{-1} with the detection limit (3S) of 1 µg L^{-1} of iron(III) using the injection volume of 20 µL. The amount of iron(III) and total iron in river and seawater samples can be successfully determined. Repeatability of the measurements is satisfactory at the RSD of 3.5% for 5 determinations of 10 µg L^{-1} iron(III) as reported by the authors. The accuracy of the method is evaluated using the standard addition method and checked by the analysis of the certified material Std Zn/Al/Cu 43 XZ3F, as described by the authors.

9.4.7 Variamine blue

Khaled Elmorsy et al. [30] have developed a simple, rapid and sensitive kinetic spectrophotometric method for the determination of trace amounts of iron(II). It is based on its catalytic effect on the oxidation of variamine blue with hydrogen peroxide in the presence of triethanolamine as activator to form a deep violet blue-colored species with an absorption maximum at 560 nm. The reaction is monitored using FIA and batch methods. The calibration graphs are linear in the concentration range 5.4–130 and 4.5–50 ng of iron for the FIA and batch, respectively. The FIA technique shows good average recoveries with lower detection limit compared with the batch technique. As reported by the authors the method is highly selective to iron (the tolerance limit for 20 ions was listed) and successfully applied for iron determination in pharmaceutical preparation, polluted air and tap water with average recoveries agreeing with the official method.

9.4.8 Iminodibenzyl (IDB)

Manjula Subbanaika et al. [31] have proposed a novel, rapid, sensitive and selective spectrophotometric method using 4-aminoantipyrine (AAP) as an electrophilic coupling reagent and iminodibenzyl (IDB) as a chromogen, for the determination of trace amounts of Fe(III) in H_2O, industrial effluent and soil samples. The method is based on the reduction of Fe(III) by AAP, which subsequently couples with IDB in a mild HCl medium to form a blue-colored product having λ_{max} at 620 nm. The color is stable up to 24 h and obeys Beer's law that is followed in the concentration range of 0.2–4.8 mg mL^{-1}. The optimum reactions conditions and other important analytical parameters are established to enhance the sensitivity of the proposed method. The interference due to various non-target ions is also studied. The proposed method can be applied to the analysis of Fe(III) in H_2O, industrial effluent and soil samples. The performance of the proposed method is also evaluated in terms of student's t-test and variance ratio F-test that indicated the significance of the proposed method over reference spectrophotometric method.

9.4.9 *N*,*N*-dodecyltrimethylammoniumbromide (DTAB)

Shokrollahi Ardeshir et al. [32] have described a simple, selective and sensitized spectrophotometric method for determination of trace amounts of Fe^{3+} ion in tap and waste water solutions. In the presence of *N*,*N*-dodecyltrimethylammoniumbromide (DTAB), the spectrophotometric determination of Fe^{3+} ion using Ferron is carried out. Beer's law is obeyed over the concentration range of 0.05–2.6 μg mL^{-1} of Fe^{3+} ion with the relative standard deviation (relative standard deviation %) <0.2% and the molar absorptivity of complexes at pH 3.5 is 3.8×10^3 L mol^{-1} cm^{-1}. Potentiometric pH titration is used for prediction of protonation constants of ferron and evaluating its stoichiometry and respective stability constants with Fe^{3+} ion. As it is obvious the most likely species of Ferron alone and its complexes are LH (log = 7.64), LH_2 (logK = 10.52), LH_3 (logK = 11.74) and ML_2 (log = 23.68), ML_3 (log = 23.68), ML_3H (log = 23.68), ML_3H_2 (log = 23.68) and $ML(OH)_2$ (log = 23.68) respectively.

9.4.10 Desipramine hydrochloride (DPH) and trimipramine maleate (TPM)

Syed A. A. et al. [33] have proposed novel spectrophotometric reactions for determination of iron(III), using desipramine hydrochloride (DPH) and trimipramine maleate

(TPM) as chromogenic reagents. In aqueous neutral medium and subsequent coupling with DPH or TPM the reduction of iron(III) by an electrophilic coupling reagent, 3-methyl-2-benzothiazoline hydrazono hydrochloride hydrate (MBTH) occurs. The blue color formed in the reaction shows maximum absorbance at 630 nm and obeys Beer's law over the range 0.4–4.4 µg mL^{-1} and 0.4–6.0 µg mL^{-1}. The molar absorptivity values with DPH and TPM were 3.288×10^3 and 3.374×10^3 L mol^{-1} cm^{-1} and Sandell's sensitivity values are 0.0130 and 0.0331 µg cm^{-2} respectively. As proposed by the authors this methods can be successfully applied in the determination of iron(III) in polluted lake water, sewage water and industrial effluent samples. Student t-test and variance ratio F-test indicated the significance of proposed methods over the standard spectrophotometric method.

9.4.11 Cetylpyridinium chloride (CPC)

Stoyanova A [34] has described a new catalytic kinetic method for the determination of trace iron(III) over the concentration range 1–100 ng mL^{-1}. In the presence of cetylpyridinium chloride (CPC), the detection limit is 0.52 ng mL^{-1} and the sensitivity of the determination is increased. The reaction rate is monitored spectrophotometrically by measuring the absorbance of the reaction product at 580 nm. The variables that affected the reaction rate are also investigated and the reaction conditions were established as mentioned.

9.4.12 8-Aminoquinaldine (AQ)

Dong Xuechang et al. [35] have developed a novel method for the determination of trace Fe^{3+} in water samples. The method is based on that 8-aminoquinaldine (AQ) reacts with Fe^{3+} in HAc-NaAc buffer (pH 5.5) to form a stable 3:1 color complex. The complex shows an absorption maximum at 600 nm and apparent absorptivity 1.157×10^4 L mol^{-1} cm^{-1}. The complex is extracted with Waters Porapak SepPak C18 cartridge and eluted with ethanol containing 1% HAc. The eluted complex is then detected by spectrophotometer at 600 nm. Beer's law is obeyed at 0–7 µg/mL for Fe^{3+}. The proposed method was successfully used for the determination of trace Fe^{3+} in water samples as described by the authors.

9.4.13 Neocuproine

Safavi Afsaneh et al. [13] have described simultaneous determination of total iron and copper using either a PLS or an H-point standard addition method (HPSAM). The authors use mixed reagents of 1,10-phenanthroline and neocuproine for the determination of iron and copper. For applying the method on 15 synthetic samples in the concentration ranges of 0.10–8.00 μg mL^{-1} Fe and 0.12–8.75 μg mL^{-1} Cu, the total relative standard error is 2.02%. Both PLS and HPSAM show suitable abilities to accurately determine iron and copper from overlapped absorption spectra of their complexes. These methods have been successfully applied to the determination of iron and copper in blood serum and river water. The results for several analyzed samples are in satisfactory agreement with those acquired by using the FAAS technique as described.

9.4.14 Meso-tetra(4-methoxy-4-sulfonophenyl)porphyrin (p-OCH_3TPPS_4)

Zhao Ye et al. [36] have developed a highly sensitive spectrophotometric method for the determination of trace iron. This method is based on the color reaction of iron(III) with meso-tetra(4-methoxy-4-sulfonophenyl)porphyrin (p-OCH_3TPPS_4) in the pH range 3.5–5.5. At 446 nm, the apparent molar absorptivity of the complex is 2.0×10^4 L mol^{-1} cm^{-1} which obeys Beer's law in the range of 0–10 μg/25 mL. The method has been used for the determination of iron in the peanut shell with satisfactory results, as mentioned by the authors.

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Chapter 10
Analytical reagents having nitrogen (N) and oxygen (O) as donor atoms

10.1 Naphthol class methyl Ph. thiazolyl azo]-3-methyl-4-methoxy-2-naphthol (MPTAN)

Jawad, Shawket Kadhim et al. [1] have developed new coupled cloud point extraction (CPE) method as prompt, easy and economical preconcentration technique for spectrophotometric determination of tiny quantities of Fe^{3+} and Hg^{2+} in real samples. New thiazolylazo ligand [methyl Ph thiazolyl azo]-3-methyl-4-methoxy-2-naphthol (MPTAN) is used for the CPE method in the preconcentration of Fe^{3+} and Hg^{2+} as an earlier step to its characterization by UV-VIS spectrophotometry. The analytical method includes the formation of complex with new ligand and quantitative extraction to the cloud point layer (CPL) of TritonX-100 after heating. The concentration of MPTAN, metals, pH, thermodynamic data and volume of surfactant were optimized. The investigation of stoichiometry has the ratio of metal to ligand of 1:1. Under finest settings and conditions, the calibration curve was found to be linear in the concentration range of two ions (0.05–10) ppm and the limit of detection for Fe^{3+} and Hg^{2+} are (0.016 and 0.041) ppm resp. The suggested CPE is an excellent methodol for characterization of trace metal ions in surrounding samples with a complex matrix as in soils, water, vegetable, meats and fruits.

10.1.1 3-5-(3-Methyl-1-phenylpyrazolazo)-1-nitroso-2-naphthol

Khazaal, Fatma A. et al. [2] have proposed an azo reagent 3-5-(3-methyl-1-phenylpyrazolazo)-1-nitroso-2-naphthol that has been synthesized and characterized by FT-IR, ^{1}H-NMR and ^{13}C NMR spectral techniques. The electrochemical behavior of the azo reagent and its complex with Fe(III) has been studied at glassy carbon disk GCE electrode in different supporting electrolyte at concentration (1 M) and scan rate (100 m v s^{-1}). Spectrophotometric determination of iron(III) is based on the formation of a 2:1 complex with above reagent. The complex has max at (454) nm and max of (1.7982×10^4) L mol^{-1} cm^{-1}. A linear correlation (0.1–3.0 g mL^{-1}) is found between absorbance at max and concentration. The effect of diverse ions on the determination of copper(II) to investigate the selectivity of the method are also studied. The stability constant of the product is (2.869×10^8). The proposed method can be successfully applied to the analysis of honey samples.

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10.1.2 1-Nitroso-2-naphthol

Shar Ghulam Abbas et al. [3] have developed a simple rapid new spectrophotometric method for the determination of iron(II) at trace level using 1-nitroso-2-naphthol as complexing agent in presence of anionic aqueous 1% sodium dodecyl sulfate micellar surfactant solution. This analytical reagent reacts with iron(II) to form tris(1-nitroso-2-naphtholato) iron(II) complex. It is mentioned that by using micellar system the previous solvent extraction steps could be replaced while enhancing the sensitivity, selectivity and the molar absorptivity that reduces the cost and toxicity. At λ_{max} 443.6 nm, the average molar absorption coefficients and Sandell's sensitivity are 1.6×10^4 L mol^{-1} cm^{-1}, 5.8 ng cm^{-2} and Beer's law is obeyed over the concentration range 0.12–4.0 g mL^{-1}. The stoichiometric composition of the chelate is 1:3 (Fe:$[NNPh]_3$). The developed method can be successfully applied for the determination of iron(II) from pharmaceutical samples as mentioned by the authors.

10.1.3 Disodium-1-nitroso-2-naphthol-3,6-disulfonate (nitroso-*R* salt)

Kruanetr Senee et al. [4] have used flow injection (FI) spectrophotometric method for iron(III) determination using disodium-1-nitroso-2-naphthol-3,6-disulfonate (nitroso-*R* salt). The reaction between Fe(III) and nitroso-*R* salt in an acetate buffer solution at pH 5, Fe(III)-nitroso-*R* salt complex is formed which shows absorption maximum at 720 nm. The FI parameters that affect the signal response have been optimized by the authors in order to get the better sensitivity and low standard deviation. The linear range for determination of iron in water samples is over the range of 0.05–4.0 g mL^{-1} with a correlation coefficient (r^2) of 0.9997. The limit of detection (3) is 0.011 g mL^{-1} with sample throughput of 110 samples h^{-1}. The repeatability measured from three standard Fe(III) (0.1, 2.0 and 4.0 g mL^{-1}) are 1.42, 1.29 and 1.01% ($n = 11$), respectively. The proposed method can be successfully applied to determination of Fe(III) in water samples as reported by the authors.

10.1.4 1-(2-Pyridyl-azo)-2-naphthol (PAN)

Guo Yibing et al. [5] have studied a phase-separation spectrophotometry for the determination of iron(II) in gasoline. In HAc-NaAc buffer solution at pH 6.0, using microemulsion (Tween-80/n-C_4H_9OH/n-C_5H_{12}/water) as extractant and 1-(2-pyridyl-azo)-2-naphthol (PAN) as color reagent, the microemulsion phase can completely be separated from water solution by heating for 20 min in water bath at 75° and can be directly used for spectrophotometric analysis. The apparent molar absorptivity is 8.936×10^4 L mol^{-1} cm^{-1} at 768 nm. Beer's law is obeyed in the range of 0.014–0.48 g mL^{-1} for iron(II). The detection limit is 0.004 g mL^{-1}. The proposed method is applied for direct determination of iron(II) in gasoline with RSD of less than 2% and recovery of 97.3–101.4%, as described.

Nekoei Mehdi et al. [6] have established a simple and reliable method for simultaneous spectrophotometric determination of Fe(II) and Co(II). The method is based on complex formation with 1-(2-pyridylazo)-2-naphthol (PAN) in a micellar medium. Despite a spectral overlap, Fe^{2+} and Co^{2+} are simultaneously determined with chemometric approaches involving principal component artificial neural network (PC-ANN), principal component regression (PCR) and partial least squares (PLS). Various synthetic mixtures of Fe and Co were assessed by the authors and the results obtained by the applications of these chemometric approaches were evaluated and compared. The PC-ANN method affords relatively better precision than that of PCR or PLS. The proposed method permits detection limits of 0.05 and 0.07 ng mL^{-1} for Co and Fe, respectively. The influences of pH, ligand amount, solvent percentage and time on the absorbance are also studied. The proposed method is also applied satisfactorily for the determination of Fe(II) and Co(II) in real and synthetic samples.

Liu Shu-juan et al. [7] have developed a novel method for separation and speciation of iron species using solvent extraction. At pH 1.0, the complex Fe^{2+}-1-(2-pyridylazo)-2-naphthol (PAN) is formed. Me iso-Bu ketone (MIBK) is employed to extract the complex from aqueous solution, which separates Fe^{2+} from Fe^{3+} and reduces speciation transformation between the two oxidation states. In this method optimal conditions for reaction and extraction are studied. Fe^{2+}-PAN is extracted with 5 mL MIBK after 10 min color developing reaction. Iron is detected in organic phase. The total iron is estimated after introducing reducing reagent into the system. The linear range is 0–20 g/5 mL with the molar absorptivity of 1.51×10^4 L mol^{-1} cm^{-1}. As reported by the authors good results are obtained for tea infusion samples.

Zarei K. et al. [8] have described a very simple and selective spectrophotometric method for simultaneous determination of iron(II), nickel(II) and cobalt(II) based on formation of their complexes with 1-(2-pyridylazo)-2-naphthol (PAN) in micellar media. Although the complexes of Fe(II), Ni(II) and Co(II) with reagent show a spectral overlap, they were simultaneously determined by PLS with and without preprocessing step using direct orthogonal signal correction (DOSC). As the authors mentioned the linear range was 0.30–4.50 g mL^{-1} for Co(II), 0.20–3.00 g mL^{-1} for Ni(II) and 0.30–5.00 g mL^{-1} for Fe(II). Interference effects of common anions and cations are studied and the proposed method can be applied satisfactorily to the determination of Fe(II), Ni(II) and Co(II) in synthetic samples as reported by the authors.

Abdollahi H. et al. [9] have developed a classical univariate micellar calorimetric method for determination of Fe, Co and Cu metal ions, which appear together in many real samples. The organized molecule assemblies such as micelles have been used by the authors in spectroscopic measurements due to their possible effects on the systems of interest. The ability of micellar systems to solubilize slightly insoluble or even very insoluble complexes and/or ligands is used to enhance the analytical merit of the given methods. The ability of micelles to solubilize complexes in aqueous solutions can eliminate the need for nonaqueous extraction step in a given analysis. The simultaneous determination of Fe, Co and Cu is carried out as 1-nitroso-2-naphthol complexes in the presence of aqueous solution of non-ionic surfactant of Triton-X100. A partial least square multivariate calibration method for the analysis of ternary mixtures of Fe, Co and Cu is developed. For individual determinations, molar absorptivities and the limit of detection are obtained, respectively. The total relative standard error for applying the method on synthetic samples is 2.02%. The proposed method can also be successfully applied to the determination of Fe, Co and Cu in several synthetic alloy solutions.

10.2 Phenol class

Nworie, F. S. et al. [10] have used solvent extraction using 2,2' -ethylenebis (nitrilomethylidene) diphenol as ligand for the spectrophotometric determination of Fe(II), Fe(III), Mn(II) and Cr(III). The complex formed by H2EBNMDP with the Fe(II), Fe(III), Mn(II) and Cr(III) ions were stable in water for pH 8, 4, 6 and 6, respectively, with a maximum of absorption at 366 nm, 383 nm, 415 nm, 405 nm and molar absorptivity is 1.84×10^4, 2.29×10^4, 2.96×10^4 and 3.85×10^4 respectively. The combination ratio has been established using the logarithmic method to be 1:2, 1:1, 1:2 and 1:1 for Fe(II), Fe(III), Mn(II) and Cr(III) resp. The proposed method can be applied successfully in the determination of Fe(II), Fe(III), Mn(II) and Cr(III) from tap water and synthetic samples.

Ahmed M. Jamaluddin et al. [11] have presented a very simple, ultra-sensitive and highly selective non-extractive spectrophotometric method for the rapid determination of iron(III) at trace levels using 2-aminophenol (OAP) as a new spectrophotometric reagent. This reagent shows reaction with Fe(III) instantaneously at $\lambda_{max} = 402$ nm in slightly acidic (0.0005–0.0015 M H_2SO_4) aqueous solution and this absorbance remains stable for over 24 h. The average molar absorption coefficients and Sandell's sensitivity have been found to be 6.65×10^5 L mol^{-1} cm^{-1} and 5 ng cm^{-2}, respectively. Linear calibration graphs are obtained for 0.01–6.0 mg L^{-1} of iron with a correlation coefficient value 0.9998 for Fe-OAP complex. The stoichiometric composition of the chelate is 1:3 (Fe:OAP). The detection limit and quantification of limit of the reaction system i.e. found 1 g L^{-1} and 10 g L^{-1} respectively. In the determination, excesses of over 50 cations, anions and complexing agents (e.g. tartrate, oxalate, citrate, phosphate, thio-urea, SCN-) do not interfere. The developed method has been successfully used in the determination of iron in several standard reference materials (alloys and steels) as well as in some environmental waters (portable and polluted), biological samples (human blood and urine), food samples (bean, meat, banana, tomato, egg, etc.), soil samples, pharmaceutical samples (tablets, capsules, etc.), and some solution containing both iron(II) and iron(III) and complex synthetic mixtures. The method described by the authors has high precision and accuracy (s = ± 0.01 for 0.5 mg L^{-1}).

Makhijani Ritika M. et al. [12] have developed a spectrophotometric method that is simple, rapid and sensitive for the determination of Fe(II) by using N-(omethoxybenzaldehyde)-2-aminophenol (NOMBAP) as an analytical reagent. NOMBAP extracts Fe(II) quantitatively (99.67%) into Et acetate from an aqueous solution in the pH range 5.6–6.8. The Et acetate extract shows an intense peak at 470 nm (λ_{max}). Beer's law is obeyed over the Fe(II) concentration range of 1–7 mg mL^{-1}. The Sandell's sensitivity and molar absorptivity for FeNOMBAP system are found to be 0.0176 mg cm^{-2} and 3,166 L mol^{-1} cm^{-1}, respectively. The composition of extracted species is found to be 1:2 (Fe:NOMBAP) by Job's continuous variation and mole ratio method. Interference by various ions was also studied. The proposed method is successfully applied for determination of Fe(II) in ore and pharmaceutical samples as mentioned.

Yu Ping et al. [13] have studied the phase separation spectrophotometric determination of Fe^{2+}. In HOAc-NaOAc buffer (pH 5.0), Fe^{2+} reacts with 2-5-bromo-pyridylazo5-diethylaminophenol (5-Br-PADAP) to form a coordination complex. OP-BuOH-n-heptaneH_2O micro emulsion has been used by the authors as extractant for phase separation of Fe^{2+}-5-Br-PADAP-micro emulsion system. The micro emulsion phase can be separated from H_2O phase completely and on the H_2O phase when bathed at 72° for 5 min, thus the micro emulsion phase can be directly used for spectrophotometric determination of Fe^{2+}. The complex shows an absorption maximum at 744 nm and apparent molar absorptivity 3.09×10^5 L mol^{-1} cm^{-1}. Beer's law is obeyed at 0–0.32 g mL^{-1} for Fe^{2+}. The method was used for the determination of Fe^{2+} in pond H_2O and tap H_2O, and the results were satisfactory. The method is simple, rapid, sensitive and selective as reported.

Wu Lixiang and Guo Jincun [14] have determined the level of Fe(III) in crude oil by spectrophotometry with the developing system of 5-Br-PADAP and Triton X-100 after extraction with polyethylene glycol-$(NH_4)_2SO_4$-aluminon. The authors studied both separation and determination conditions. Beer's law is obeyed in the concentration range of 0–10 g/25 mL for Fe(III). The apparent molar absorptivity is 4.48×10^4 L mol^{-1} cm^{-1}. When the amounts of them were at least as much as five times of Fe(III), Al^{3+}, Pb^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+}, etc. did not interfere in the determination of Fe (III), respectively, after extraction with polyethylene glycol. This method was applied by the authors to the determination of Fe(III) in Liaohe crude oil and Saudi Arabia residual oil with RSD of 3.82% and 3.08%, respectively, and recoveries of 95.6–103.8%.

Guo Hang-Ming et al. [15] have presented method using color reaction of iron(II) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) in the presence of cationic surfactant CTMAB. Iron(II) reacts with this reagent at pH 3.6–6.4 to form a stable 1:3 complex in aqueous solution. The apparent molar absorptivity of the complex formed is 3.1×10^4 L mol^{-1} cm^{-1} (at 749 nm). The complex solution obeys Beer's law in the concentration range 0–50 g/25 mL for iron (at 749 nm). As the authors mentioned the proposed method could also be applied to the determination of trace iron in water with satisfactory results.

Hou Jin et al. [16] have studied the simultaneous determination of trace Mn, Fe, Cu and Zn by iterative target transformation factor analysis algorithm assisted spectrophotometry. In pH 9.5 borax-NaOH buffer solution, four stable ternary micellar complexes are formed by Mn(II), Fe(III), Cu(II), Zn(II) and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and OP. The λ_{max} of the complexes of Mn(II), Fe(III), Cu(II), Zn(II) were 566, 560, 562 and 559 nm, and the apparent molar absorptivities are 1.13×10^5, 7.32×10^4, 1.02×10^5 and 1.04×10^5 respectively and the observed linear range is 0–0.4 mg L^{-1}. Ni^{2+} shows serious interference on the determination. The method has been used in the direct determination of trace Mn, Fe, Cu and Zn in simulated samples, grain and soil samples.

10.3 Hydrazone class

Devi, V. S. Anusuya et al. [17] have proposed a simple and sensitive derivatives spectro-photometric method for simultaneous determination of iron and gallium using 2-hydroxy-3-methoxy-benzaldehydeisonicotinoylhydrazone (HMBAINH) as a selective analytical reagent. The complexes of metal ions with HMBAINH are formed immediately in acidic media at pH 5.0 in the presence of aqueous solution of nonionic surfactant Triton-X100. The zero-crossing measurement technique is found suitable for the direct measurement of the second derivative value of [Fe(II)-HMBAINH] and [Ga(III)-HMBAINH] at 442 nm and 412 nm respectively. The concentration ranges applicable for the determination of Fe(II) and Ga(III) are 0.14–1.396 g mL^{-1} and 0.266–2.661 g mL^{-1} with detection limits 0.013 g mL^{-1} and 0.085 g mL^{-1} respectively. Analysis of synthetic samples of magnetic garnets showed that this method can be successfully used for simultaneous determination of iron and gallium in real samples.

Lopez-Lopez Jose A. et al. [18] have developed a simple direct spectrophotometric method for the analysis of Fe(II) and total Fe in wine samples. This method is based on the formation of an Fe(II) complex with 2,2'-dipyridylketone picolinoylhydrazone (DPKPH), which shows a maximum green-blue absorption ($\lambda = 700$ nm) at pH 4.9. Operative conditions for the batch procedure, the tolerance limits of foreign ions and sample matrix have been also evaluated. Limits of detection and quantification observed are 0.005 and 0.017 mg L^{-1} of Fe(II), respectively, which allows its determination in real wine samples. As mentioned by the authors the proposed method has been used in the analysis of white, rose, and red wines.

Govindu G. et al. [19] have used a novel chromogenic reagent 2-hydroxy-3-methoxy benzaldehyde-*p*-hydroxy benzoic hydrazone (HMBAHBH) for the direct spectrophotometric determination of Iron(III) in acidic surfactant of Triton X-100. This chromogenic reagent reacts with Fe(III) to form brown colored [Fe(III)-HMBAHBH] water-soluble complex. The maximum absorbance is observed at 390 nm at pH 3.0. Beer's law is obeyed in the concentration range of 0.14–4.19 g mL^{-1}. The molar absorptivity and Sandell's sensitivity of the colored complex is found to be 1.87×10^4 L mol^{-1} cm^{-1} and 2.9×10^{-3} g cm^{-2}. The stoichiometric study of the Fe(III) complex is determined as 1:2 with formation of stability constant 1.02×10^{11}. The proposed method is successfully employed in the analysis of various surface soil samples, biological, food materials and pharmaceutical samples for the determination of iron(III) content as reported.

Anusuya Devi V. S. et al. [20] have optimized and validated spectrophotometric methods for determination of Fe and Co individually and simultaneously. 2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone (HNAHBH) reacts with Fe(II) and Co(II) to form reddish-brown and yellow-colored [Fe(II)-HNAHBH] and [Co(II)-HNAHBH] complexes, respectively. The maximum absorbance of these complexes is at 405 nm and 425 nm, respectively. For [Fe(II)-HNAHBH], Beer's law is obeyed over the concentration range of 0.055–1.373 mg mL^{-1} with a detection limit of 0.095 mg mL^{-1} and molar absorptivity = 5.6×10^4 L mol^{-1} cm^{-1}. [Co(II)-HNAHBH] complex obeys Beer's law in 0.118–3.534 mg mL^{-1} range with a detection limit of 0.04 mg mL^{-1} and molar absorptivity, of 2.3×10^4 L mol^{-1} cm^{-1}. All the proposed methods are successfully employed in the analysis of various biological, water and alloy samples for the determination of Fe and Co content, as described by the authors.

Devanna N. et al. [21] have used diacetylmonoximebenzoyl hydrazone as a chromogenic reagent for the determination of Fe(II) that is a yellow-colored water-soluble complex with Fe(II) in acidic buffer medium (pH 6.25). The molar absorptivity and Sandell's sensitivity of the complex at λ_{max} 360 nm are found to be 1.25×10^4 L mol^{-1} cm^{-1} and 0.0045 g cm^{-2} of Fe(II) respectively. Beer's law validity range is from 0.11 to 2.24 g mL^{-1}. Fe(II) gives 1:1 complex with diacetylmonoxime benzoyl hydrazone and stability constant of the complex is 1.1×10^4. The developed direct and first-order derivative spectrophotometric method was employed for the determination of Fe in alloy samples and effect of various diverse ions have also been studied by the authors.

Babaiah O. et al. [22] have developed a simple, sensitive and selective spectrophotometric method for the determination of iron(III) in aqueous solution. The metal ion forms yellowish-brown colored, soluble complex with 2,4-dihydroxybenzaldehydeisonicotinoylhydrazone (2,4-DHBINH) at pH 3.0 with λ_{max} at 400 nm. Beer's law is obeyed in the range 0.07–2.20 g mL^{-1} of Fe(III). The molar absorptivity and the Sandell's sensitivity of the method are $1.75 \pm 0.025 \times 10^4$ L mol^{-1} cm^{-1} and 0.0034 g cm^{-2}, respectively. The interference of various ions has been studied. The complex has a 1:1

[Fe III:2,4-DHBINH] stoichiometry. A method for the determination of Fe(III) by first-order derivative spectrophotometry has also been proposed.

Madalena C. da Cunha Areias et al. [23] have proposed a new analytical method by using di-2-pyridyl ketone salicyloylhydrazone(DPKSH) as a colorimetric chelating agent for simultaneous spectrophotometric determination of iron(II) and iron(III) in natural waters. Absorption maximum of both of the complex ions is at 375 nm, and the molar absorptivity is 4.21×10^4 and 1.26×10^4 L mol^{-1} cm^{-1} respectively, for Fe(II) and Fe(III). DPKSH complexes with Fe(II) show another absorbance maximum at 644 nm and a molar absorptivity equal to 1.27×10^4 L mol^{-1} cm^{-1}. The detection limits are 0.09 μM for Fe(II) and 0.22 μM for Fe(II + III). This analytical method has been used to determine Fe(II) and Fe(III) in natural waters and compared to the 2,2’-bipyridyl and atomic absorption spectroscopy (AAS) methods.

Reddy V. Krishna et al. [24] have proposed a first derivative spectrophotometric method that is very simple, highly sensitive and selective for the determination of copper(II) and iron(III) in microgram quantities. Copper(II) and iron(III) react with 2-hydroxy-1-naphthaldehyde benzoylhydrazone (OHNABH) in the pH range 3–7 forming greenish–yellow and yellowish brown–colored solutions, respectively. The first-order derivative spectra of these complexes show maximum derivative amplitude at 443 nm for Cu(II) and at 450 nm and 540 nm for Fe(III). Beer’s law is obeyed in the range 0.16–4.80 g mL^{-1} of Cu(II) at 443 nm and 0.14–4.20 g mL^{-1} of Fe(III) at 540 nm. As described by the authors this method is applied for the determination of copper in some copper-based alloys and iron in some food materials. This method has also been employed for the selective simultaneous determination of copper and iron in some plant samples.

10.4 Oxime class

Bazmandegan-Shamili, Alireza et al. [25] have proposed a vortex-assisted dispersive liquid–liquid microextraction method in combination with UV-VIS spectrophotometry for the simultaneous extraction and determination of iron species. In this method, Fe^{2+} and Fe^{3+} are complexed with pyridine-2-amidoxime, neutralized through ion pair formation with sodium dodecyl sulfate, and extracted into the fine droplets of chloroform. After centrifugation, the absorbance of the extracted complexes is recorded in the wavelength range of 360–700 nm. The parameters affecting the extraction efficiency such as the pH, the type and volume of the extraction solvent, ligand concentration and sample volume are optimized. The individual iron species is then determined by means of the orthogonal signal correction-generalized partial least squares method. Under the optimized conditions, the calibration curves are linear over the range of 2.0–100 and 3.0–200 g L^{-1} with detection limits of 0.4 g L^{-1} for Fe^{2+} and 0.8 g L^{-1} for Fe^{3+}, respectively. The relative standard deviations for intra- and inter-day assays (n = 5) were 2.3 and 4.0 for Fe^{2+} at 50 g L^{-1} and 2.7 and 4.3 for Fe^{3+} at 30 g L^{-1}, respectively. The enhancement factors of 77 and 69 were achieved for Fe^{2+} and Fe^{3+}, respectively. The proposed method was successfully applied to the determination of iron species in water samples.

Khanam Rehana et al. [26] have proposed spectrophotometric determination of iron(III) using p-bromophenylazo-bis-acetoxime as coloring agent. This reagent form complex with Fe(III) at 370 nm, in the pH range 3.5–4.5. Beer's law is obeyed in the range (1 to 6) × 10^{-5} M, and the molar absorptivity and Sandell's sensitivity values are 1,030 $dm^3\ mol^{-1}\ cm^{-1}$ and 54.22 ng cm^{-2}, respectively.

Khan Saba et al. [27] have proposed o-carboxy phenylazo-bis-acetoxime as chromogenic reagent for spectrophotometric determination of iron(III) at 376 nm, keeping the pH at 2.8–4.0. Beer's law is obeyed in the range (4 to 24) × 10^{-5} M. The molar absorptivity and Sandell's sensitivity values are 2.446 $dm^3\ mol^{-1}\ cm^{-1}$ and 22.83 ng cm^{-2}, respectively, as described by the authors.

Khan Saba et al. [28] have used phenylazo-bis-acetoxime for spectrophotometric determination of iron(III) at 362 nm, keeping the pH at 3.5–4.0. Beer's law is obeyed in the range (4 to 24) × 10^{-5} M. The molar absorptivity and Sandell's sensitivity values are found to be 1,852 $dm^3\ mol^{-1}\ cm^{-1}$ and 30.15 ng cm^{-2}, respectively.

Lokhande R. S. et al. [29] have synthesized the reagent 5-bromosalicylaldoxime (5-BSO) and its characterization has been carried out by FTIR and NMR techniques. The reagent is used by the authors for the development of a new analytical method for the extractive spectrophotometric determination of Fe(III). The reagent reacts with Fe(III) to produce reddish orange–colored complex. The complex can be extracted in BuOH at pH 7.2 at 460 nm. Beer's law is obeyed at 10–100 g. The molar absorptivity and Sandell's sensitivity are 0.018 × 10^4 L $mol^{-1}\ cm^{-1}$ and 3.2 × 10^{-6} g cm^{-2}, respectively. The stoichiometric ratio of the complex is 1:2. The method was successfully applied for the determination of Fe in pharmaceutical samples.

Khan Saba et al. [30] have used p-sulfonamidophenylazo-bisacetoxime for spectrophoto-metric determination of iron(III) at 405 nm, keeping the pH at 2.5–3.0. As the authors reported, Beer's law is obeyed in the range (4 to 24) × 10^{-5} M. The molar absorptivity and Sandell's sensitivity values are 1,853 $dm^3\ mol^{-1}\ cm^{-1}$ and 30.14 ng cm^{-2}, respectively.

10.5 Hydroxyquinoline class

Adebayo Basheer K. et al. [31] have used 8-hydroxyquinoline as chromogenic reagent for the determination of trace amounts of iron(III) by spectrophotometric method which is a simple, rapid and sensitive method. This method is based on the reaction of iron(III) with 8-hydroxyquinoline in chloroform solution to form a metal-oxine complex showing absorption maximum at 359 nm. Beer's law is obeyed in the range of 1 to 14 mg mL^{-1} Fe^{3+}. The recovery is between 98.60% and 103.30% with a coefficient of variation of 1.209%. The method can be successfully applied to tap water samples, as described by the authors.

Li Yong zhong and Liu Shujuan [32] have studied the color reaction of 5-(4-carboxyphenylazo)-8-hydroxyquinoline (5-CPAHQ) with Fe(III) and optimum condition for it. In the presence of CTMAB 5-CPAHQ reacts with Fe(III) to form a red complex in a buffer medium of pH 4.2–5.6, with a mole ratio of Fe:R = 1:6. This complex shows absorption maximum at 448 nm, the apparent molar absorptivity 4.14×10^4 L mol^{-1} cm^{-1}, and Beer's law obeyed at 0–14 g/25 mL. In this reaction KF, thiourea and Na citrate are used as mixed masking agent. As mentioned by the authors this reaction has also been used in the spectrophotometric determination of Fe in ammonium ferric citrate tablets and rheum with the relative standard deviation 0.364–2.117%, the recovery being 98.1–103.5%.

10.6 Miscellaneous

Chauhan, Jayprakash S. et al. [33] have developed new spectrophotometric method for the determination of Fe(II) in an aqueous solution. The metal ion forms a red-colored complex with pyridine 2, 5 dicarboxylic acid in the pH 4.0 to 7.0. The complex shows maximum absorbance at 492 nm. Job's method for continuous variation and mole ratio method show metal ligand ratio in the complex to be 1:2. The complex is stable for days. The red-colored complex obeys Beer's law in the concentration range of 225 to 500 g of iron. The molar absorptivity is found to be 1.55×10^2 $lmole^{-1}$ cm^{-1}. The method has been used for the determination of Fe^{+2} in synthetic samples. The complex has been synthesized and FTIR studies have been carried out.

Kiaie Seyed Hossein et al. [34] have developed a novel method for extractive spectrophoto-metric determination of Fe(II) and Fe(III) using PAR, that is, 4-(2-pyriclylazo) resorcinol as analytical reagent that forms the colored complexes. At pH 8.1, these complexes show instantaneous ion-pairing with 1-hexadecylpyridinium counter ion (HDP+) in aqueous solution. These complexes subsequently extracted onto the organic phase of Me isobutyl ketone (MIBK), where both ion-associations can sensitively be detected spectrophotometrically. To define a model between calibration spectra and the corresponding concentrations a statistical method based on the PLS is then used in the range 350–750 nm. Their concentration in the calibration matrix was 0.3–1.1 ppm for both Fe(II) and Fe(III); the detection limits being estimated to be 0.09 and 0.13 ppm, respectively. The performance of the model proposed has been confirmed by the determination/speciation of Fe(II) and Fe(III) in model solutions and real samples of pharmaceutical formulations, as reported by the authors.

Yadav D. K. et al. [35] have proposed a new analytical reagent acetophenone-2’,4’-dihydroxy semicarbazone [A24DHS], as a sensitive spectrophotometric reagent for Fe(III). A24DHS forms a 1:2 violet colored complex at ($\lambda_{max} = 350$ nm) in acidic aqueous solution (pH = 3.4). Beer’s law is obeyed in the concentration range from 1 to 5 ppm. The Sandell’s sensitivity is 0.0288 g cm^{-2} with molar absorptivity 3,899.2 L mol^{-1} cm^{-1} as reported by the authors. It is described that the proposed method has been successfully applied to the determination of iron in various real and synthetic samples.

Asadollahi Tahereh et al. [36] have implemented solid phase extraction spectrophotometry in this work. An octadecyl silica membrane disk modified with N-benzoyl-Nphenylhydroxylamine (BPHA) in combination with PLS regression is used by the authors for simultaneous preconcentration and spectrophotometric determination of iron and vanadium in water samples. The method is based on the retention of V(V) and Fe(III) on the disks modified by BPHA in the pH range of 2.0–4.5. The retained ions are eluted with 3 mL of Me iso-Bu ketone and are measured spectrophotometrically. The data obtained from the experiments are processed by partial least squares chemometric method. PLS is applied for multivariate calibration and noise reduction through elimination of the less important latent variables. Under the optimum conditions, for preconcentrating the analytes from 100 mL sample, the linear dynamic ranges are 14–320 mg L^{-1} and 10–530 mg L^{-1} and the detection limits are 4.2 mg L^{-1} and 2.5 mg L^{-1} for V(V) and Fe(III), respectively. This method was successfully applied to the determination of analytes in several categories of water samples as described.

Dong Wen-li et al. [37] have explored a micro-emulsion spectrophotometric method for determination of iron in aluminum alloy. Fe(III) reacts with KSCN solution and Et rhodamine B in H_2SO_4 solution in the presence of gum arabic and micro-emulsion solution. An association complex is formed between the anionic complex of $[Fe(CN)_6]^{3-}$ and the cation of Et rhodamine B (ERB^+), which is solubilized by solutions of gum arabic and micro-emulsion. Linear relationship between values of absorbance and mass concentration of Fe(III) was found in the range of 0.026–0.36 mg L^{-1}. Apparent molar absorptivity of the associated system found was 1.08×10^5 L mol^{-1} cm^{-1} at the wavelength of its absorption maximum 620 nm. The proposed method was applied to the determination of Fe in samples of aluminum alloy, giving values of RSD’s (77 = 5) less than 2% as mentioned.

Kiran K [38] has used 3-Hydroxy benzyl amino benzoic acid successfully to estimate the amount of iron present in the water samples. This complex of reagent-iron shows absorption maximum at 480 nm. N-butanol is used as the solvent, a pH of 5.0 was maintained, the reagent concentration is chosen as 6.0×10^{-3} M and there is no interference of foreign ions. By these standardized parameters, more than 90% recovery of added iron was found in the samples as described by author.

Ombaka O. et al. [39] have reported spectrophotometry as highly sensitive and selective method for the determination of iron(III) in aqueous solution with hydroxytriazenes. Hydroxytriazenes react with the Fe^{3+} and form colored complexes with Fe(III) showing λ_{max} at 410 nm and pH range 3–4 for reagent no(i), 530 nm and 4–5 for reagent no (ii), 410 nm and 4.5–5.5 for reagent (iii), 396 nm and 3.5–5.0 for reagent (iv), 467 nm and 2.5–3.5 for reagent no. (vi). Beer-Lambert's law is obeyed in the concentration range $(1.0–5.0) \times 10^{-5}$ M, $(1.5–9.0) \times 10^{-5}$ M, $(0.5–4.0) \times 10^{-5}$ M, $(0.3–1.8) \times 10^{-5}$ M, $(0.6–3.6) \times 10^{-5}$ M, $(2–12) \times 10^{-5}$ M for nos. (i), (ii), (iii), (iv), (v) and (vi) respectively. The molar ratio of Fe(III) to the hydroxytriazene was found as 1:3. The standard deviation ranges in between 0.019 and 0.088. The Sandell's sensitivity in ng cm^{-3} ranges between 2.5.579 and 4.189. Reagent nos. (iii), (iv), (v), which are very sensitive and used to determine the level of iron in vegetable samples as reported.

Gupta Anand kumar S. et al. [40] have developed spectrophotometric method for the determination of Fe(II) that is a simple, rapid and sensitive method. The authors propose *N*-(o-hydroxybenzylidene) pyridine-2-amine (NOHBPA) as an analytical reagent to extracts Fe(II) quantitatively (99.60%) into benzene from an aqueous solution of pH range 5.6–6.5. The benzene extract shows an intense peak at 530 nm (λ_{max}). Beer's law is obeyed over the Fe(II) concentration range of 0.1–12 mg mL^{-1}. The Sandell's sensitivity and molar absorptivity for FeNOHBPA system is 0.0125 mg cm^{-2} and 4,469.27 L mol^{-1} cm^{-1} respectively. Using Job's continuous variation and mole ratio method the composition of extracted species is found to be 1:2 (Fe:NOHBPA). The proposed method was successfully applied for determination of Fe(II) in pharmaceutical samples, as reported.

Hashem E. Y. et al. [41] have presented a highly stable ternary complex of iron(III) with 5-(4-nitrophenyl azo) salicylic acid (NPAS) and eosin (Es) in acidic medium. At room temperature this ternary complex shows maximum absorption at 545 nm with a molar absorptivity 2.81×10^{4} L mol^{-1} cm^{-1}. The linear range for iron(III) determination is 0.18–6.0 mg L^{-1}. The proposed method was easy to perform for the determination of iron in pharmaceutical and water samples as described.

Zhong Guoxiu et al. [42] have presented the color reaction between dibromo-p-nitro-chlorophosphonazo and iron in acidic medium, forming a complex (2:1) that shows maximum absorption at 610 nm. Beer's law is obeyed for iron in the range of 0.14–0.80 m mL^{-1} and molar absorptivity of the complex is 1.63×10^{4} L mol^{-1} cm^{-1}. The proposed method was applied to the determination of iron in standard silicon iron sample, and the results were consistent with the certified values, giving RSD ($n = 6$) of 1.4–2.1% as described.

Abdul Galil et al. [43] have carried out a comprehensive study on the nucleophilic coupling reaction between catechol and p-anisidine, system 1 or p-chloroaniline, system 2, with iron(III). Both systems were exploited for the spectrophotometric determination of iron present as iron(III) and iron(II) after its oxidation to iron(III). As described by the authors this system works on the principle of catechol oxidation by iron(III) followed by its nucleophilic coupling with panisidine, λ_{max} 565 nm or p-chloroaniline, λ_{max}, 545 nm in 0.1 M hydrochloric acid medium. Under the optimized experimental conditions, Beer's law is obeyed by both systems for the determination of iron as iron(III) in the concentration range 0.4–48, system 1 and 0.4–40 mg mL^{-1}, system 2. The molar absorptivity values for system 1 and 2 are found to be 1.7×10^3 L mol^{-1} cm^{-1} and 1.6×10^3 L mol^{-1} cm^{-1}, with the corresponding Sandell's sensitivity values, 0.033 mg mL^{-1} and 0.035 mg mL^{-1}, respectively. The composition of the dye product of both systems are detected by Job's method of continuous variation as well as mole ratio method and found to be 1:1. The method involving both systems have been successfully applied for the determination of iron(III) and iron(II) present in pharmaceutical preparations, sugarcane juice, laboratory chemicals and also in standard solutions. The results of iron obtained from both systems are comparable with those of the iron results determined separately following the procedure of the reported tiron-iron(III) method.

Fathi M. R. et al. [44] have described a kinetic spectrophotometric method for the determination of iron(III). The method is based on the catalytic effect of iron(III) on the reduction reaction of methyl red by pyrosulfite. Using a fixed time method (2.5 min), the reaction is followed spectrophotometrically by measuring the change in absorbance at 522 nm. The effect of different parameters on the reaction is studied to obtained optimum conditions. The calibration curve is linear at 0.4–2.0 g mL^{-1} of iron(III) and the detection limit is 0.07 g mL^{-1}. The method was successfully applied to the determination of iron(III) in an iron oral drop and clover plant, as stated by the authors.

Syed A. A. et al. [45] have proposed a novel and newer spectrophotometric reactions for determination of iron(III), using desipramine hydrochloride (DPH) and trimipramine maleate (TPM) as chromogenic reagents. In aqueous neutral medium and subsequent coupling with DPH or TPM the reduction of iron(III) by an electrophilic coupling reagent, 3-methyl-2-benzothiazoline hydrazono hydrochloride hydrate (MBTH) occurs. The blue color formed in the reaction shows maximum absorbance at 630 nm and obeys Beer's law over the range 0.4–4.4 g mL^{-1} and 0.4–6.0 g mL^{-1}. The molar absorptivity values with DPH and TPM are 3.288×10^3 and 3.374×10^3 L mol^{-1} cm^{-1} and Sandell's sensitivity values are 0.0130 and 0.0331 g cm^{-2} respectively. As proposed by the authors this method can be successfully applied in the determination of iron(III) in polluted lake water, sewage water and industrial effluent samples. Student t-test and variance ratio F-test indicated the significance of proposed methods over the standard spectrophotometric method.

Sato Kenji et al. [46] have prepared 1-Phenyl-3-methyl-4-stearoyl-5-pyrazolone (HC18) loaded on a silica gel (SG) and used it to determine the diffusion reflectance/spectrophotometric of iron(III) ion. As the authors mentioned iron(III) ion is quantitatively retained on the absorbent, HC18/SG, from an aqueous solution of pH >2.0 in the batch experiment. The calibration curve for iron is linear over 0.5–10 g. The relative standard deviation ($n = 7$) is less than 3% and the detection limit (1% absorption) was 0.1 µg. The absorbance of the Fe(III)-HC18/SG, which turned red and has stability for at least one month, and no change in the absorbance have also been confirmed. The recovery from 1,000 mL of sample solution containing 8 µg of iron was about 100%. In the column experiment, iron(III) was quantitatively retained with 0.5 g of HC18/SG when the flow rate of the sample solution was lower than 8 mL min. On the determination of iron(III), alkali, alkaline earth metal ions and other metal ions such as cobalt(II) or nickel(II) had no effect. The method was applied to the determination of iron(III) in a salt sample and environmental samples such as sea water. The recovery of iron(III) added to these samples was approximately 100%, as described.

Ghazy S. E. and Mostafa G. A. E [47] have reported that Diphenylcarbazone (HDcO) reacts with Fe(II) and Hg(II) to form water-soluble colored 1:2 (M:Reagent) complexes. The colored complexes of Fe(II) and Hg(II) are quantitatively floated with oleic acid (HOL) surfactant at pH 6.0 and 3.5, respectively. These complexes show maximum absorbances (in the surfactant layer) at 500 and 550 nm. Beer's law is obeyed in the ranges 2.0 to 200 mg mL^{-1} of Fe(II) and over 8–40 mg mL^{-1} of Hg(II). Their molar absorptivities are 0.4×10^4 and 1.4×10^4 L mol^{-1} cm^{-1}, respectively. The different analytical parameters affecting the flotation process and spectrophotometric determination have also been studied by the authors. The method can be applied to the determination of Fe(II) in various samples such as synthetic mixtures, pyrolusite ores, tap and river waters.

Melwanki M. B. et al. [48] have proposed Piroxicam (PR) as a sensitive and selective reagent for the spectrophotometric determination of Fe(III) in ore, pharmaceutical formulations, plant material and foodstuff. The method is based on the formation of a chloroform-soluble red-colored 1:1 complex by the reaction of Fe(III) with PR in Walpole buffer. Beer's law is valid over the concentration range of 0.4–6.4 ppm. The colored complex exhibits an absorption maximum at 510 nm with molar absorptivity of 1.82×10^4 L mol^{-1} cm^{-1} and Sandell's sensitivity of 17.32 ng cm^{-2}. The absorbances increase linearly with increase in concentration of iron, which are corroborated by the calculated correlation coefficient value (0.9992). The effects of foreign ions in the determination of Fe(III) have also been studied by the authors. Statistical comparison of the results with those of direct AAS method shows good agreement and indicates no significant difference in precision.

Lokhande R. S. et al. [49] proposed that p-methylisonitrosoacetophenone (MINAP) extracts Fe(II) quantitatively (99.5%) into $CHCl_3$ from an aqueous solution of pH 7.5–8.5. The $CHCl_3$ extract shows an intense peak at 650 nm (λ_{max}). Beer's law is obeyed over the Fe(II) concentration range 0.1–10 µg mL^{-1}. The molar absorptivity is 6,515 L $mole^{-1}$ cm^{-1} at 650 nm. The composition of extracted species is 1:2 (Fe:MINAP) by Job's continuous variation and mole ratio methods. The interference by various ions has been studied. The proposed method has been applied to determination of Fe(II) in pharmaceutical sample (Capsule Dexorange).

Nagabhushana B. M. et al. [50] have reported diformylhydrazine (OHC-HN-NHCHO) DFH, the bidentate ligand that combines with Fe(II) and Fe(III) in alkaline media in the pH range 7.3–9.3 to form an intensely colored red-purple Fe(III) complex with an absorption maximum at 470 nm. Beer's law is obeyed for Fe concentrations from 0.25 to 13 g mL^{-1}. The molar absorptivity is in the range 0.3258×10^4–0.3351×10^4 L mol^{-1} cm^{-1}, and Sandell's sensitivity is 0.0168 µg cm^{-2}. The method was applied to the determination of Fe in industrial waste, ground H_2O and pharmaceutical samples.

H. Abdollahi [51] has reported simultaneous determination of Cr(VI) and Fe(III) by PLS calibration and H-point standard addition method (HPSAM). As a selective chromogenic system mixed reagents of diphenylcarbazide and 1,10-phenanthroline in a non-ionic micellar solution of Triton X-100 have been used for determination of Cr(VI) and Fe(III). This micellar system is beneficial for elimination of the previous solvent extraction step that is necessary for the determination of slightly soluble metal complexes in the absence of micelles. The total relative standard error for applying the PLS method to 15 synthetic samples lies in the range of 0.20–6.00 µg mL^{-1} Cr(VI) and 0.20–8.00 µg mL^{-1} would be 1.5%. By applying H-point standard addition method the results obtained show that Cr(VI) and Fe(III) can be determined simultaneously with weight concentration ratios of Cr(VI) to Fe(III) varying from 15:1 to 1:30 in the mixed sample. The authors mentioned that both methods (PLS and HPSAM) could also be applied successfully to the determination of Cr and Fe in several synthetic alloy solutions.

Derya Kara and Mahir Alkan [52] have reported the synthesis and analytical applications of *N*,*N*'-bis(2-hydroxy-5-bromo-benzyl)1,2 diaminopropane (HBDAP). Fe(III) reacts with this compound in the range of pH 3–6 and produces a red complex (2:3 mol ratio of Fe(III)/HBDAP) that is soluble in chloroform. As mentioned by the authors spectrophotometric method is a highly sensitive, selective and rapid method for the determination of trace amounts of iron(III) by HBDAP. The complex obeys Beer's law from 0.056 to 1.68 mg L^{-1} with an optimum range. The detection limit (taken as three times the standard deviation of the reagent blank) is ~1.23×10^{-7} M Fe(III) and the limit of quantitation (taken as ten times the standard deviation of the reagent blank) is about 4.11×10^{-7} M Fe(III). Good separation of Fe(III) from Ni(II), Fe(II), Co(II), Cd(II), Mn(II), Zn(II), Pb(II) has also been achieved at pH 3–5.

Lu Guoren [53] presented a method for the rapid determination of Fe in ferroaluminum alloy by spectrophotometry. In hexamine buffer solution at pH 5–6, a stable complex is formed by Fe^{3+} and EDTA that shows maximum absorbance at 420 nm having molar absorptivity 87.4 L mol^{-1} cm^{-1}. This complex obeys Beer's law at 0–4.5 mg/50 mL as reported.

Du Licheng et al. [54] have reported that in the presence of diluted HCl and Mn(II), Fe(III) reacts with diantipyrylphenylethylenemethane in 100° water bath to form a red complex. The complex has a molar absorptivity of 1.44×10^6 L mol^{-1} cm^{-1} at 540 nm and obeys Beer's law in the range of 0.04–0.8 g Fe(III) 25 mL^{-1}. The method could be applied to the determination of trace Fe(III) in natural water.

Zhang Liping et al. [55] have presented a method for the simultaneous photometric determination of Cu and Fe in tea using chrome azurol S and 8-quinolinol. The determination wavelengths of Cu and Fe are 524 and 520 nm, the linear ranges 0–2.0 and 0–5.0 g mL^{-1}, and the molar absorptivities are 2.832×10^5 (524 nm) and 2.777×10^5 (520 nm), respectively.

Long Jianlin and Heng Linsen [56] have reported a method for the spectrophotometric determination of Fe that is based on its color reaction with *N*-2-hydroxyphenylamino-*N*-2-hydroxy-1-cyclobutene-3,4-dione. A yellowish brown solution compound is formed by Fe^{3+} and the reagent in a pH = 1 HCl buffer medium. The absorption maximum of the compound is at 455 nm, and the molar absorptivity 1.7×10^3. Ag^+, Cu^{2+}, EDTA, citric acid, tartaric acid, PO_4^{3-}, and some oxidants, such as H_2O_2 and $NaNO_2$, show interferences on the determination. As the authors described the method has been used for the determination of Fe in $Fe(NO_3)_3$ and electroplating waste water samples.

Qiu Feng-xian and Yao Cheng [57] have studied the chromogenic reaction of a new organic reagent 4-(2-pyridylazo)pyrocatechol (PAPC) with Fe(II). In the presence of reductants such as ascorbic acid and polyethylene glycol *p*-octylphenyl ether (OP), Fe(II) has the capability of reacting with PAPC to form a stable, negative charged, orange complex in the pH range 6.0 to 7.5. The complex has 1:3 ratio for Fe(II) and PAPC with the apparent stability constant of 3.89×10^{14}. At the maximum absorption wavelength of 494 nm, the apparent molar absorptivity is 4.96×10^4 L mol^{-1} cm^{-1}. Beer's law is obeyed in the range of 0 to 0.8 g mL^{-1} Fe(II). As the authors mentioned, in applying the method for the determination of trace iron in aluminum alloys, satisfactory results have been obtained.

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Chapter 11
Analytical reagent having miscellaneous combinations of donor atoms

11.1 2,2′-Azinobis(3-ethylbenzothiazoline-6-sulfonate) (ABTS)

Elsuccary S. A. A. and Salem Alaa A [1] have described a rapid, sensitive and highly precise method for the determination of total iron in blood serum and water samples, using batch, normal flow injection analysis (nFIA) and reverse flow injection analysis (rFIA) techniques. The proposed methods are based on the selective oxidation of 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) by iron(III). The absorbance of the resultant green solution of radical cation ($ABTS^{\cdot +}$) has been monitored spectrophotometrically at $\lambda_{max} = 415$ nm. As determined by Job's and molar ratio methods, the reaction is stoichiometric with a ratio of 1:1 (Fe(III):ABTS). The proposed methods allow for the determination of Fe(III) in the ranges 0–4.5 mg L^{-1} (limit of detection (LOD) 25.5 μg L^{-1}, %RSD 0.97%, $n = 7$); 0–4.5 mg L^{-1} (LOD 370 μg L^{-1}, %RSD 1.28%, $n = 7$) and 0–2.7 mg L^{-1} (81.6 μg L^{-1}, %RSD 0.76%, $n = 6$) for batch, nFIA and rFIA techniques, respectively. The proposed methods show high selectivity to Fe(III), as indicated by the high tolerance limits for common interfering ions. The nFIA method has been applied in total iron assay in camel blood serum, whereas batch and rFIA methods have been successful in the determination of total iron in municipal pipeline water and spiked ground water.

11.2 4,7-Diphenyl-1,10-bathophenanthroline (DPBP)

Abdel Ghafar Hany H. et al. [2] have proposed a sensitive and selective spectrophotometric procedures for the determination of Fe(III) and Cu(II) using 4,7-diphenyl-1,10-bathophenanthroline (DPBP)-eosin as chromogenic reagents. The formation of ternary complex between Fe(III) and 4,7-diphenyl-1,10-bathophenanthroline (DPBP)–eosin in acid medium and the formation of ternary complex between Cu(II) and 4,7-diphenyl-1,10-bathophenanthroline (DPBP)-Eriochrome Black-T (EBT) in alkaline medium are reported. The ternary complexes are extracted in the presence of cetyltrimethyl ammonium bromide with chloroform. The molar absorptivities of the Fe(III)–DPBP–eosin and Cu(II)–DPBP–EBT ternary complexes are 2.23×10^5 and 9.35×10^4 L mol^{-1} cm^{-1} at 542 and 565 nm, respectively. Beer's law is valid over the concentration ranges from 0.280 to 7.814 and from 0.320 to 8.260 μg mL^{-1} for Fe(III) and Cu(II), respectively. Sandell's sensitivity (0.0025 and 0.0679 ng cm^{-2}), relative standard deviation (0.257–1.94 and 0.305–1.85), LOD (0.076 and 0.045 μg mL^{-1}), and quantification (0.253 and 0.150 μg mL^{-1}) for Fe(III) and Cu(II) ions, respectively, have been

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calculated. As reported by the authors the procedures have also been applied for the determination of Fe(III) and Cu(II) in different polluted water sources, drinking water, river water as well as cooling water and boiler scales.

11.3 Solid phase extraction

Kassem Mohammed A. et al. [3] have reported spectrophotometric method for the determination of iron(II) after solid phase extraction which is a simple, selective and highly sensitive extraction method. The absorption maximum is measured at 644 nm. Beer's law is obeyed up to 450 ng mL^{-1} of iron. The molar absorptivity, Sandell's sensitivity, detection and quantification limits are calculated and found to be 1.09×10^5 L mol^{-1} cm^{-1}, 0.51 ng cm^{-2}, 1.98 and 6.0 ng mL^{-1}, respectively, which were compared with parameters obtained without using solid phase extraction method. After reduction of Fe(III) by addition of hydroxylamine HCl, the system was applied to the total iron. The proposed method is successfully applied for the determination of trace amount of iron in environment water, soil and botanical reference materials as mentioned.

11.4 2-Amino-2′,5-dichlorobenzophenone (MCB) or 2-amino-5-chloro-2′-fluorobenzophenone (MFB)

Al Okab Riyad Ahmed et al. [4] have exploited 2-amino-2′,5-dichlorobenzophenone (MCB) or 2-amino-5-chloro-2′-fluorobenzophenone (MFB) reagents for the determination of trace concentrations of iron(III) in environmental water and soil samples. This method is based on oxidation of the electrophilic coupling reagents, 2-amino-2′,5-dichloro benzophenone (MCB) or 2-amino-5-chloro-2′-fluorobenzophenone (MFB) by iron(III) and coupling with phenoxazine (PNZ) in acidic medium which yield a red color derivative. This derivative shows an absorbance maximum at 520 nm, having stability up to 12 h. Beer's law is obeyed for iron in the concentration ranges 0.31–1.2121 mg mL^{-1} and 0.42–1.41 mg mL^{-1}, respectively. These methods have also been applied to the analysis of iron(III) in various matrixes and the performance of developed methods were evaluated in terms of Student's *t*-test and variance ratio *F*-test that indicate the significance of developed methods over reported method.

11.5 SCN (I) and Rhodamine B

Wang Xiao-ling et al. [5] have presented spectrophotometry as a highly sensitive method for determination of trace iron. This method is based on the reaction of Fe(III) with SCN (I) and Rhodamine B, which forms a stable blue ternary ion complex system in sulfuric acid medium in the presence of polyvinyl alcohol and gelatin. The maximum absorption wavelength is observed at 620 nm, and apparent molar absorptivity is 3.38×10^6 L mol^{-1} cm^{-1}, with detection limit of 0.025 mg L^{-1}, the linear range is 0–0.8 mg/25 mL. As reported by the authors, samples of mineral water, grape wine and beer were also analyzed by this method for their Fe(III) contents. The relative standard deviations (RSD) of determinations were 1.3–3.1% and recoveries were 98–101%.

11.6 Acetophenone 2′,5′-dihydroxy thiosemicarbazone (ADHTS)

Navarkar Prabhakar S. et al. [6] have proposed acetophenone 2′,5′-dihydroxy thiosemicarbazone (ADHTS) as a new sensitive and selective analytical reagent for the spectrophotometric determination of trace amount of Fe. The reagent reacts with Fe to form a yellow colored 1:2 chelate, at the pH 3.6. The complex is extracted in n-butanol. The absorption spectrum shows λ_{max} at 430 nm. Beer's law is obeyed in the concentration range 1–8 ppm for Fe. The molar absorptivity is 646.06 L mol^{-1} cm^{-1} and Sandell's sensitivity is 0.0869 mg cm^{-2}. The LOD for the proposed method is found to be 0.561 ppm. This method is highly sensitive, selective, simple, rapid, accurate and satisfactorily applied for the determination of Fe in the synthetic mixtures, and real samples as reported.

11.7 Chrom Azurol S (CAS) in the presence of tetradecyltrimethylammonium bromide (TTA)/ octadecyltrimethyl ammonium chloride (ODTA) and Triton X-100 (TX100)

Pytlakowska K. et al. [7] have reported simple and sensitive method for the spectrophoto-metric determination of iron(III) in food, based on the formation of colored complexes of Fe(III) with Chrom Azurol S (CAS) in the presence of tetradecyltrimethylammonium bromide (TTA) or octadecyltrimethyl ammonium chloride (ODTA) and Triton X-100 (TX100). For the Fe-CAS-TTA-TX100 system the molar absorptivity is 1.12×10^5 L mol^{-1} cm^{-1} at 650 nm; for Fe-CAS-ODTA-TX100 it is 1.35×10^5 L mol^{-1} cm^{-1} at 659.5 nm. Beer's law is obeyed for iron concentration in the range 0.08–0.56 mg mL^{-1} for the complex Fe-CAS-TTA-TX100 and 0.08–0.64 mg mL^{-1} for Fe-CAS-ODTA-TX100. The stoichiometry of the complexes is established by applying Job's method. The more sensitive method, based on the Fe-CAS-ODTA-TX100 system, has been applied to the determination of iron in cereals as described by the authors.

11.8 Phenanthroline

Zhong Yu Jun [8] has developed, a new method for spectrophotometric determination of iron in soil using phenanthroline. The results show that when phenanthroline used as chromogenic reagent, the amount of Fe can be determined at 510 nm in soil sample. Beer's law is obeyed in the range of 0–4 mg L^{-1} for iron(III), and the apparent molar absorption coefficient is found as 2.10×10^4 L mol^{-1} cm^{-1}. It is used for the determination of iron in soil, and the results obtained agreed with those achieved by sulfosalicylic acid method, with RSD 0.50–1.0% ($n = 6$), as described by the authors.

11.9 Dibromo-*p*-sulfonic acid-arsenazo (DBS-arsenazo, DBS-ASA)

Zou Ming-Qiang et al. [9] have developed a method for the determination of traces of iron. This method is based on its catalytic effect on the oxidation reaction of dibromo-*p*-sulfonic acid-arsenazo (DBS-arsenazo, DBS-ASA) by KBrO in a 5.0×10^{-3} M H_2SO_4. The optimum experimental conditions for the determination of iron using iron(III)-DBS-ASA-$KBrO_3$-ascorbic acid system and its kinetic spectrophotometric properties have also been studied. The absorbance difference (DA) is linearly related with the concentration of Fe(III) over the range of 0.20–6.0 ng mL^{-1} at the maximum absorption wavelength of 520 nm and described by the equation: DA = 0.133 c (ng mL^{-1}) − 0.0133 with a regression coefficient of 0.9966. The detection limit of the method is 0.17 ng mL^{-1}. As described by the authors, the method could successfully be used in the determination of traces of iron in potato samples.

11.10 *p*-Acetylarsenazo(ASApA)

Zhai Qing-Zhou [10] proposes a novel catalytic kinetic spectrophotometric method for the iron determination that is based on the catalytic effect of Fe(III) on the oxidation reaction of *p*-acetylarsenazo(ASApA) by potassium periodate. Maximum absorbance of the Fe(III)-ASApA-KIO_4 system in 8.0×10^{-3} M sulfuric acid is observed at the wavelength of 540 nm. The change in absorbance (DA) is linearly related with the concentration of iron(III) in the range of 0.10–4.0 ng mL^{-1} and fitted the equation: $DA = 4.91 \times 10^{-2}$ C (C: ng mL^{-1}) + 0.017, with a regression coefficient of 0.9966 at the wavelength, as described by the authors. The detection limit of the method is 0.031 ng mL^{-1}. The reported method has also been used to determine iron in the black gingili paste, oat slice, sleeve-fish silk food samples.

11.11 Dibromo-*p*-chloroarsenazo

Zhan Xiaoxia et al. [11] have proposed a novel catalytic kinetic spectrophotometric method for the determination of iron on the basis of catalytic effect of Fe(III) on dibromo-*p*-chloroarsenazo in 5.0×10^{-3} mol L^{-1} H_2SO_4 medium. The absorbance difference (DA) showed good linearity with Fe(III) in the range of 0.2–6.0 ng mL^{-1} at 518 nm. The regression equation was $DA = 0.032\,r\ (\text{ng mL}^{-1}) + 0.0161$ with correlation coefficient of $r = 0.9980$. The detection limit of method is 0.025 ng mL^{-1}. This method has been applied to the determination of iron in tap water and rain water with the relative standard deviations (RSD) of 0.37–1.4% ($n = 13$) and the recoveries of standard addition of 101–103%, as mentioned by the authors.

11.12 Picolinaldehyde-4-phenyl-3-thiosemi-carbazone (PAPT)

Balouch Aamna et al. [12] have applied partial least squares regression for the simultaneous determination of iron, vanadium, and cobalt after complexation with picolinaldehyde-4-phenyl-3-thiosemicarbazone (PAPT) in the presence of anionic sodium dodecylsulfate (SDS) micelles. These three complexed metal ions exhibit overlapping spectra in the 390–510 nm regions with a maximum absorbance at 415 nm at pH 3.0 and enhanced absorbance in the presence of SDS. For the simultaneous determination of these metal ions the data were analyzed using a simple partial least squares algorithm. Formation constants ($\log K_f$) were found to be 4.65, 3.29 and 4.85 for PAPT complexes of Fe, V and Co, respectively, and the detection limits for Fe, V and Co were 0.013, 0.002 and 0.010 µg mL^{-1}, respectively. With the proposed method common anions and cations did not interfere. The method was validated by the authors by calculating root mean square error of cross-validation, root mean square error of calibration and root mean square error of prediction and was applied to determine these three metal ions in real crude oil samples.

11.13 Methylthymol blue

Pouretedal Hamid Reza et al. [13] have described a simple and sensitive kinetic-spectrophotometric method for the determination of trace amounts of Fe(II). The method proposed by the authors is based on the inhibitory effect of Fe(II) on the oxidation of methylthymol blue by bromate in the H_2SO_4 media and at 35°, which is monitored at 440 nm. The variables affecting the rate of the reaction were studied and the optimum conditions were established. Fe(II) can be measured at 1.0–200.0 ng mL^{-1} with a detection limit of 0.6 ng mL^{-1}. The relative standard deviations for 10 replicate analyses of 50 and 160 ng mL^{-1} of Fe(II) were obtained 1.2% and 2.0%, respectively. The authors mentioned that the method is relatively selective in the presence of foreign ions and can be successfully applied to the determination of Fe(II) in pharmaceutical products and real H_2O samples.

11.14 4-(2-Thiazolylazo) resorcinol

Wu Lan-Ju et al. [14]have studied the reaction of Fe(II) with 4-(2-thiazolylazo) resorcinol in pH = 10.0 NH_3–NH_4Cl buffer solution. The results show that Fe(II) reacts with 4-(2-thiazolylazo) resorcinol to form a red chelate. The apparent molar absorptivity of this chelate is 6.98×10^4 L mol^{-1} cm^{-1} at 733 nm. Beer's law is obeyed in range of 0–25 µg/25 mL for Fe(II) as described by the authors.

11.15 1,2-Dihydroxybenzene-3,5-disulfonic acid (Tiron)

Watanabe Kunihiro et al. [15] have studied a precision determination method of Fe based on the formation of a stable Fe complex by flow injection analysis. Four significant figures on the Fe content (%) could be obtained as the result of analysis by the present method, which is applied to the determination of Fe in Fe ores. Besides high precision, the results of Fe determination in standard, Fe-ores samples show good agreement with certified values. The precision of the present method is equal to that of titration as the conventional method. The Fe complex formed in a line reaction tube with 1,2-dihydroxybenzene-3,5-disulfonic acid (Tiron) is detected by spectrophotometry at 667 nm. Tiron as the optimum detection reagent has been selected by the authors based on the complex stability examined by using a stopped flowmeter, which could measure the absorbance with 6 significant figures, from among four kinds of conventional detective reagents. The absorbance obtained by UV-visible spectrophotometry is recorded with six significant figures by Chromatomonitor with a personal computer. As a result, a single flow system is selected as the optimum manifold. A calibration curve is constructed by measuring the peak height of the absorbance signal. The optimum conditions of Fe determination by the present method are as follows: sample solution (29.4 µL), pH 1.0; Tiron, 8.0×10^{-3} M, pH 5.0; flow rate, 0.5 mL min^{-1}; reaction coil length, 10 m; pump, double-plunger pump. The Fe is detected at 10–300 ppm by measuring a 1:1 complex of Fe–Tiron. The authors observed the relative standard deviation was 0.07% at 150–300 ppm and the present method could also be applied to Fe ores containing >55% Fe. The throughput per hour was 6 for the sample solution.

11.16 Thiocyanate (SCN-)

Achar B. N. and Bellappa S [16] have carried out a systematic study of the color reaction between Fe(III) and thiocyanate reagent by micro-scale spectrophotometric method. The optimized data resulted conditions in obtaining unusual highest sensitivity with molar absorption of 2.9565×10^4 L mol^{-1} cm^{-1} at wavelength of maximum absorption 480 nm in 0.2–1.4 N nitric acid medium containing 60% acetone and 25,000 fold molar excess of the thiocyanate reagent. Beer's law is valid for 0.1–4.0 ppm of Fe(III) and Sandell's sensitivity is 0.002 μg cm^{-2}. Effects of reagent concentration, order of addition, stability, acidity, types of solvents and diverse ions are reported. It was found to give accurate results of Fe estimations in pharmaceutical preparations and mustard seeds. As the authors mentioned the proposed optimized method has highest sensitivity, unusual stability and simplicity in operation, without involving cumbersome extractive procedure.

Patel K. S. et al. [17] have presented A new, simple, selective and sensitive spectrophotometric procedure for the on-site quantification of Fe at nanogram levels in atmospheric precipitations, that is, rain as sample source. This method is based on the color reaction of Fe^{3+} with SCN^- ions in the presence of a cationic surfactant, that is, cetylpyridinium chloride (CPC), in strong HCl solution. The subsequent extraction of the complex is done with *N*-octylacetamide into toluene or chloroform. The apparent molar absorptivity of the complex is 2.60×10^5 L mol^{-1} cm^{-1} at $\lambda_{max} = 480$ nm. The detection limit (causing higher absorbance than the sum of the blank absorbance (0.009) and 3 SD) is 5 ng mL^{-1} Fe. Ions commonly associated with Fe did not interfere in the present method as described by the authors. The presented method has also been applied to the determination of Fe at the ppb level in rainwater samples.

11.17 8-Hydroxyquinadine

Tai Xi [18] has studied the color reaction of Fe(III) with 8-hydroxyquinadine. In the presence of pH 8.0 $NH_4Cl\text{-}NH_3 \cdot H_2O$ buffer solution and emulsifier of OP. 8-hydroxyquinadine can react with Fe(III) to form a stable 3:1 complex. This complex can be extracted and enriched by Water plus-C18 cartridge, and can be eluted by EtOH. In EtOH medium, the molar absorptivity of the chelate is 7.82×10^3 L mol^{-1} cm^{-1} at 595 nm. Beer's law is obeyed at 0.1–5.0 μg mL^{-1}. This method can be applied to the determination of Fe in biological sample with satisfactory results as reported by the authors.

11.18 Potassium iso-Bu xanthate (KIBX)

Rao B. Sreenivasa et al. [19] have developed a simple and selective spectrophotometric method for the determination of iron(III) based on the reaction of iron(III) with potassium iso-Bu xanthate (KIBX). The absorbance of the complex is measured spectrophotometrically at λ_{max} 378 nm at pH 5.0. The molar absorptivity of the complex is 2.58×10^3 dm^3 mol^{-1} cm^{-1} that obeyed Beer's law in the concentration range

2.5–35.0 mg of iron(III). The method is sensitive and selective and has been applied to the determination of iron(III) in the selected food and pharmaceutical samples.

11.19 Thiocyanate with cetyltrimethylammonium (CTMA)/ thiocyanate with tetraphenylphosphonium (TPP)

Ivsic Astrid Gojmerac et al. [20] have investigated extraction of Fe(III) from sulfuric and hydrochloric acid solutions containing an excess of thiocyanate ions with tetraphenylphosphonium chloride(I) and cetyltrimethyl-ammonium bromide(II) in chloroform. Optimum conditions for extraction by both extractants are determined. The extraction behavior of II has been found to be more efficacious than that of TPP because less thiocyanate and extractant has been required. Better extraction efficiency of II can be attributed to surface active properties of this substance. Formation of an extractable Fe(III) thiocyanate complex with CTMA or TPP has also been determined spectrophotometrically by measuring the absorbance of the organic phase at 473 nm or 506 nm, respectively. The composition of the extracted iron(3+) complexes is determined by distribution and spectrophotometric methods. The molar ratio Fe:SCN:I of the extracted complex is 1:4:1; accordingly, its composition is [I][Fe(SCN)4]. The molar ratio Fe:II of the extracted complex is found to be 1:3. The molar ratio Fe:SCN in the complex extracted with II could not be determined because of the turbidity in solutions containing less than 0.01 mol dm^{-3} thiocyanate ion, but it was concluded that the composition of the extracted complex was $[II]_3[Fe(SCN)_6]$.

11.20 PPT (pyridoxal-4-phenyl-3-thiosemicarbazone)

Singh Kaman et al. [21] have proposed a selective and sensitive method for the extractive spectrophotometric determination of iron(II/III), employing PPT (pyridoxal-4-phenyl-3-thiosemicarbazone) and n-butanol as spectrophotometric reagent and extractive solvent, respectively. It shows a wavelength of maximum absorption (λ_{max}) at 440 and 420 nm, for Fe(II) and Fe(III), respectively. The extraction behavior of the complex of iron(III) with the reagent in the pH range 2.5–6.5 and the effect of various metal ions on the extraction are critically examined. Beer's law is obeyed from 0.5 to 8.0 mg Fe mL^{-1}. The proposed method has been compared by the authors with other existing spectrophotometric methods and found to be more sensitive and selective. It offers advantages such as reliability and reproducibility in addition to its simplicity, instant color formation and less interference. A relative standard deviation about 0.5% for sample analysis underlines the versatility of the proposed method. This method makes it feasible to determine Fe down to 0.5 mg Fe mL^{-1}.

11.21 8-Hydroxyquinadine

Chen Jianghong et al. [22] have studied the color reaction of Fe(III) with 8-hydroxyquinaldine. In pH 8.0 $NH_4Cl–NH_3·H_2O$ buffer solution and cetyltrimethylammonium bromide (CTMAB) medium, 8-hydroxyquindine reacts with Fe(III) to form a stable 3:1 complex. This complex can be extracted by Waters Sep-Park C18 cartridge and eluted by EtOH. The molar absorptivity of the complex is 7.17×10^3 L mol^{-1} cm^{-1} at 600 nm. Beer's law is obeyed at 0–5.0 mg L^{-1} for Fe(III). This method has also been applied to the determination of Fe in H_2O with satisfactory results.

11.22 5,5-Dimethylcyclohexane-1,2,3-trione 1,2-dioxime 3-thiosemicarbazone (DCDT)

Galeano Diaz T et al. [23] have developed two methods for the determination of iron olive oil by spectrophotometry and by adsorptive stripping square wave voltammetry (Ad-SSWV). These two methods are based on the formation of a 5,5-dimethylcyclohexane-1,2,3-trione 1,2-dioxime 3-thiosemi-carbazone (DCDT)-iron(II) complex in strongly acid media. In both, iron is extracted from the olive oil by using HCl. Spectrophotometric determination of iron with DCDT is based on the feature that the DCDT–Fe complex shows an absorbance maximum at 550 nm. A calibration graph has been constructed from 0 to 4,000 ng mL^{-1}, and the detection limit was 115 ng mL^{-1} (57 ng g^{-1} in olive oil). On the other hand, the voltammetric determination of the metal is based on the appearance of a peak due to an adsorptive reductive process of the complex that it is observed when the Ad-SSWV technique is used. A calibration graph is constructed from 0 to 30 ng mL^{-1}, and the detection limit is 0.55 ng mL^{-1} (13.75 ng g^{-1} in olive oil) according to the proposed procedure.

11.23 Norfloxacin (NRF)

Pojanagaroon Teraboon et al. [24] have proposed a reversed flow injection colorimetric procedure for determining Fe(III) at the µg level. It is based on the reaction of Fe(III) with norfloxacin (NRF) in 0.07 mol L^{-1} ammonium sulfate solution, resulting in an intense yellow complex with a suitable absorption at 435 nm. Optimum conditions for determining Fe(III) have been studied by univariate method. The method involved injection of a 150 µL of 0.04% wt./vol. colorimetric reagent solution into a merged streams of sample and/or standard solution containing Fe(III) and 0.07 mol L^{-1} ammonium sulfate in H_2SO_4 (pH 3.5) solution, which was then passed through a single bead string reactor. Subsequently the absorbance as peak height is monitored at 435 nm. Beer's law is obeyed at 0.2–1.4 µg mL^{-1} Fe(III). The method has been applied to the determination of total Fe in H_2O samples digested with $HNO_3–H_2O_2$ (1:9 vol./vol.).

Detection limit (3) was 0.01 μg mL^{-1} the sample through of 86 h^{-1} and the coefficient of variation of 1.77% ($n = 12$) for 1 μg mL^{-1} Fe(III) were achieved with the recovery of the spiked Fe(III) of 92.6–99.8%.

11.24 Tiron

Kass M. and Ivaska A [25] have described a procedure for determination of concentrations of Fe(III) and total Fe by sequential injection analysis. This method is based on the strong blue-colored complexes formed between Fe(III) and Tiron. The absorbance of the complexes is measured spectrophotometrically at 635 nm. Oxidation of Fe(II) and masking of interfering fluoride are simultaneously done by injecting one zone of H_2O_2 and one of Th(IV) between the sample and reagent zones. Concentration of Fe(III) and total Fe, in the range 0.002–0.026 M, in diluted samples from a pickle bath have also been determined by the authors. The relative standard deviation was 0.4% ($n = 7$). The method is also used in a pilot plant of a Zn process for determination of Fe(III) in the range 0.2–3.0 g L^{-1}. The sample throughput is 17 samples per hour, including three repetitive determinations of each sample.

11.25 5-Bromo salicylaldehyde thiosemicarbazone (5-BSAT)

Ramanjaneyulu G. et al. [26] have developed a simple, sensitive and specific spectrophotometric method for the determination of iron(II) in aqueous DMF. The metal ion reacts with 5-bromo salicylaldehyde thiosemicarbazone (5-BSAT) forming a green-colored complex in the pH range 5.0–6.0. The complex shows maximum absorption at 385 nm. Beer's law is obeyed in the range 0.28–5.60 μg mL^{-1}. The molar absorptivity and Sandell's sensitivity are 1.72×10^4 L mol^{-1} cm^{-1} and 0.032 μg cm^{-2}, respectively. The method has been employed successfully for the determination of Fe(II) in grape leaves, multivitamin capsules and blood.

11.26 *N*-(*o*-methyl)phenyl-*N*-hydroxy-*N′*-(*o*-methyl)phenylbenzamidine hydrochloride

Mishra Alok and Mohabey Hemlata [27] have proposed *N*-(*o*-methyl)phenyl-*N*-hydroxy-*N′*-(*o*-methyl)phenylbenzamidine hydrochloride as a new reagent for selective extraction and spectrophotometric determination of Fe(III) in presence of thiocyanate. The orange-red mixed complex is formed that is extractable into benzene. The optimum acidity range for the extraction and spectrophotometric determination of the complex is 0.25 M to 0.6 M. Molar absorptivity and Sandell's sensitivity of the complex at its λ_{max} (470 nm) are 11,480 L mol^{-1} cm^{-1} and 0.0047 cm^{-2}, respectively. The system obeys Beer's law in the range 0.4 ppm to 4 ppm and interference due to the presence of a number of cations and anions have been studied and the method is successfully applied to determine Fe content in a number of Fe drugs, soil samples and Fe ores.

11.27 PAN-S

Lian Guojun and Pan Liqin [28] have developed a new spectrophotometric method for selective determination of Fe(II) in finger blood with PAN-S at pH 4.5 by using HOAc–NaOAc buffer. A red complex is formed by Fe(II) and PAN-S, and the absorbance of system's increases with increase in the concentration of Fe. The observed absorption maximum is 756 nm, the linear range is 0–1.5 × 10^4 μmol L^{-1} and the apparent molar absorptivity 1.72 × 10^4 L mol^{-1} cm^{-1}. The average recovery is 99.5%; the CV of within-run and between-day were 0.027 and 0.039, respectively.

11.28 2-Aminocyclo-1-pentenedithiocarboxylic acid (ACDA)

Safavi and H. Abdollahi [29] have demonstrated the simultaneous determination of Fe, Co and Ni using 2-aminocyclo-1-pentenedithiocarboxylic acid (ACDA) as ligand in the presence of an aqueous solution of cationic surfactant of cetyl trimethylammonium bromide (CTAB). The presence of micellar systems allows the elimination of the previous solvent extraction step that is necessary for the determination of metal-ACDA complexes in the absence of micelles. For the analysis of ternary mixtures of Fe, Co and Ni a partial least squares multivariate calibration method has been developed by the authors. For individual determinations, molar absorptivities of 8.46 × 10^3 (Fe, 650 nm), 4.76 × 10 × (Co, 458 nm) and 2.61 × 10^4 (Ni, 538 nm), are obtained, the LOD being 0.11, 0.04 and 0.04 μg mL^{-1}, for Fe, Co and Ni, respectively. The total relative standard error for applying the method on 15 synthetic samples in the concentration ranges of 0.2–3.0 μg mL^{-1} Fe, 0.05–2 μg mL^{-1} Co and 0.05–2.5 μg mL^{-1} was 2.02%. The proposed method could also be successfully applied to the determination of Fe, Co and Ni in several synthetic alloy solutions as described by the authors.

11.29 Zincon

Liu Chang-Zeng [30] has developed a catalytic spectrophotometry for the determination of ultra-trace iron(III). The basis of this method is the catalytic effect of iron(III) on the oxidation of Zincon with hydrogen peroxide in HAc–NaAc buffer solution (pH = 4.74) when 1,10-phenanthroline is present. The detection limit for iron(III) is

2.2×10^{-11} g mL^{-1}, and the linear range of determination is 0.0–2.0 ng mL^{-1}. The method has been used by the authors for determination of trace iron(III) in distilled water, analysis of pure sodium chloride and analysis of pure hydrochloric acid with satisfactory results.

11.30 *N*,*N′*-Bis(2-hydroxy-5-bromo-benzyl)-1,2-diamino-propane (HBDAP)

Kara D. and Alkan M [31] have described the synthesis and analytical applications of *N*,*N′*-bis(2-hydroxy-5-bromo-benzyl)-1,2-diamino-propane (HBDAP). In $CHCl_3$ the synthesized compound reacts with Fe(III) in the range of pH 3–6 to produce a red complex (2:3 mol ratio of Fe(III)/HBDAP) solution. The authors report a highly sensitive, selective and rapid spectrophotometric method for the determination of trace amounts of Fe(III). The complex obeys Beer's law in the concentration range 0.056–1.68 mg L^{-1} with an optimum range. The detection limit (taken as three times the standard deviation of the reagent blank) is 1.23×10^{-7} M Fe(III), and the limit of quantitation (taken as ten times the standard deviation of the reagent blank) is 4.11×10^{-7} M Fe(III). A single extraction gives a good separation of Fe(III) from Fe(II). Good separation of Fe(III) from Ni(II), Fe(II), Co(II), Cd(II), Mn(II), Zn(II) and Pb(II) has also been achieved at pH 3–5.

11.31 Sulfosalicylic acid

Bao Gui-lan et al. [32] have determined different content of iron by using sulfosalicylic acid. Iron and sulfosalicylic acid form purplish red complexes in the pH 1.80–3.00 buffer solution, and its apparent molar absorptivity is 1.70×10^3 L mol^{-1} cm^{-1}. The content of iron obeys Beer's law at 4.00–28.00 mg L^{-1} (or 16.00–40.00 mg L^{-1}). The method is suitable for macro-iron, especially high content iron determination in the geological samples and steel samples as described.

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