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CHAPTER I

REVIEW OF LITERATURE

PART –A: REVIEW ON SPECTROPHOTOMETRIC DETERMINATION OF IRON (III)

Spectrophotometry has been serving as an excellent tool for determination of transition metals. The method offers sensitivity, selectivity and ease of handling along with minimum investment in terms of money. Although there are better methods for metal estimation no single method offers this kind of versatility. Reviews on spectrophotometric method for various metals have been published by our group but a review on Iron on the work reported for spectrophotometric determination has not been published during last ten years. In view of this the present review has been written on the basis of survey of literature from 2001 to till now.

The review has been written in text form and various parameters of spectrophotometric determination as reported by the authors have been included. Thus, this review will be extremely useful for researchers of both for coordination chemistry as well as analytical chemistry domain.

Further the last part of the review has been presented in form of a table in which the information on used analytical reagent, molar absorptivity and Sandell’s sensitivity with reference has been compiled so that it can as act as a index as per the application of the reagent.

Kiaie Seyed Hossein et.al.¹ (2015) have developed A novel method for extractive spectrophotometric determination of Fe(II) and Fe(III) using PAR, i.e., 4-(2-pyriclylazo) resorcinol as analytical reagent which forms the colored complexes. At pH 8.1, these complexes showed 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 partial least squares (PLS) has then been 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 authors.

**Shar Ghulam Abbas et.al.** (2015) 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 which reduces the cost and toxicity. At $\lambda_{\text{max}}$ 443.6 nm, the average molar absorption coefficients and Sandell's sensitivity have been found to be $1.6 \times 10^4$ 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 was 1:3 (Fe:[NNPh]$^3$). The developed method could be successfully applied for the determination of iron(II) from pharmaceutical samples as mentioned by authors.

**Yadav D. K.** (2015) 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 ($\lambda_{\text{max}}$ = 350 nm) in acidic aqueous solution (pH = 3.4). The Beer's law is obeyed in the concentration range from 1 to 5 ppm. The Sandell's Sensitivity is 0.0288 µg.cm$^{-2}$ with molar absorptivity 3899.2 L.mol$^{-1}$.cm$^{-1}$as reported by authors. It is described that the proposed method has been successfully applied to the determination of Iron in various real and synthetic samples.

**Nworie F. S. et.al.** (2015) have investigated Solvent extraction using 2,2$^1$-ethylenedioxy(nitrilo-methylidene)diphenol(H$_2$EBNMDP) as ligand for the spectrophotometric determination of Fe(II), Fe(III), Mn(II) and Cr(III). The
complex formed by H$_2$EBNMDP 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 366nm, 383nm, 415nm 405nm and molar absorptivity ($\varepsilon$) 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 has been established which 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 authors.

Ahmed M. Jamaluddin et.al. (2015) 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 $\lambda_{\text{max}} = 402$ nm in slightly acidic (0.0005- 0.0015 M H$_2$SO$_4$) 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 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 were found 1 µg.L$^{-1}$ and 10 µg.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.), some solution containing both iron (II) and iron (III) and complex synthetic mixtures. The method described by authors has high precision and accuracy (s = ±0.01 for 0.5 mg.L$^{-1}$).

Lopez-Lopez Jose A. et.al. (2015) 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 allowing its determination in real wine samples. As mentioned by authors the proposed method has been used in the analysis of white, rose, and red wines.

Govindu G. et.al.\textsuperscript{7} (2015) 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 react with Fe(III) to form brown colored [Fe(III)-HMBAHBH] water soluble complex. The maximum absorbance has been observed at 390 nm at pH 3.0. Beer's law is obeyed in the concentration range of 0.14-4.19 μg.mL$^{-1}$. The molar absorptivity and Sandell's sensitivity of the colored complex has been found to be $1.87 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$ and $2.9 \times 10^3$ μg.cm$^{-2}$. The stoichiometric study of the Fe (III) complex is determined as 1:2 with formation of stability constant $1.02 \times 10^{11}$. The proposed method is successively employed in the analysis of various surface soil samples, biological, food materials and pharmaceutical samples for the determination of Iron (III) content as reported.

Elsuccary S. A. A. and Salem Alaa A.\textsuperscript{8} (2015) have described A rapid, sensitive and highly precise methods for the determination of total iron in blood serum and water samples, using batch, nFIA and 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$^+$) has been monitored spectrophotometrically at $\lambda_{\text{max}} = 415$ 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$^{-1}$ (LOD 25.5 μg.L$^{-1}$, %RSD 0.97%, n = 7); 0 to 4.5 mg.L$^{-1}$ (LOD 370 μg.L$^{-1}$, %RSD 1.28%, n = 7) and 0 to 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.

Abdel Ghafar Hany H. et al. 9 (2015) 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 whereas the formation of ternary complex between Cu(II) and 4,7-diphenyl-1,10-bathophenanthroline (DPBP)- Eriochrome Black-T (EBT) in alkaline medium is reported. The ternary complexes have been 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 $2.23 \times 10^5$ 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 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), limits of detection (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 calculated. As reported by 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.

Sawant Shulmith M. et al. 10 (2014) have proposed a new analytical reagent 5-[(Phenyliminoethyl)]-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 $0.726 \times 10^4$
L.mol\(^{-1}\).cm\(^{-1}\). The proposed method has been successfully applied for the determination of vanadium in alloy as proposed by authors.

Asadollahi Tahereh et.al.\(^{11}\) (2014) have implemented solid phase extraction spectrophotometry in this work. An octadecyl silica membrane disk modified with N-benzoyl-N-phenylhydroxylamine (BPHA) in combination with partial least squares regression (PLS) was used by authors for simultaneous preconcentration and spectrophotometric determination of iron and vanadium in water samples. The method was 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 were eluted with 3 mL of Me iso-Bu ketone and were measured spectrophotometrically. The data obtained from the experiments were processed by partial least squares chemometric method. PLS was 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 were 14-320 mg.L\(^{-1}\) and 10-530 mg.L\(^{-1}\) and the detection limits were 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.

Khanam Rehana et.al.\(^{12}\) (2014) 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. The Beer's law is obeyed in the range (1 to 6) \(\times 10^{-5}\) M and the molar absorptivity, Sandell's sensitivity values are 1030 dm\(^3\).mol\(^{-1}\).cm\(^{-1}\) and 54.22 ng.cm\(^{-2}\), respectively.

Fan Xue-mei et.al.\(^{13}\) (2013) have proposed a method which is applicable for the determination of iron content in local iron tailings. Iron (III) had inhibitory effect in hydrochloric acid-potassium acid phthalate medium, on the fading reaction of methyl green oxidized by potassium per-iodate. In present work, absorbance difference between the inhibitory reaction and non-inhibitory reaction at 458 nm has shown 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 has been established and kinetic parameters of inhibitory fading reaction were also measured by authors. The apparent activation energy of inhibitory reaction was \( E_a = 0.85 \text{ kJ/mol} \), and the reaction rate constant was \( K' = 6.0 \times 10^{-4} \text{s} \). The linear range of method was in range of 20-120 mg/L, and the detection limit was 8.39 mg/L as described.

**Dong Wen-li et.al.** (2013) have explored a micro-emulsion spectrophotometric method for determination of iron in aluminium alloy. Fe (III) reacted with KSCN solution and Et rhodamine B in \( \text{H}_2\text{SO}_4 \) solution in the presence of gum arabic and micro-emulsion solution. An assocn. complex was formed between the anionic complex of \([\text{Fe(CN)}_6]^{3-}\) and the cation of Et rhodamine B (ERB\(^+\)), which was 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 \( 1.08 \times 10^5 \text{L.mol}^{-1}.\text{cm}^{-1} \) at the wavelength of its absorption maximum 620 nm. The proposed method was applied to the determination of Fe in samples of aluminium alloy, giving values of RSD's (77=5) less than 2% as mentioned.

**Kassem Mohammed A. et.al.** (2013) 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 has been measured at 644 nm. Beer's law was obeyed up to 450 ng.mL\(^{-1}\) of iron. The molar absorptivity, Sandell's sensitivity, detection and quantification limits were calculated and found to be \( 1.09 \times 10^5 \text{L.mol}^{-1}.\text{cm}^{-1} \), 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.

**Makhijani Ritika M. et.al.** (2013) have developed a spectrophotometric method which is simple, rapid, and sensitive for the determination of Fe (II) by using \( \text{N-}(\text{o}-\text{methoxybenzaldehyde})-2\)-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 ($\lambda_{\text{max}}$). Beer's law is obeyed over the Fe (II) concentration range of 1-7 mg/mL. The Sandell's sensitivity and molar absorptivity for Fe-NOMBAP system are found to be 0.0176 mg.cm$^{-2}$ and 3166 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 was successfully applied for determination of Fe (II) in ore and pharmaceutical samples as explained.

**Pourreza Nahid et.al.** (2013) 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 was eluted by 1.0 mol.L$^{-1}$ of $\text{H}_2\text{SO}_4$-acetone mixtures (1:2) and its absorbance is measured at 518 nm, spectrophotometrically. 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.

**Al Okab Riyad Ahmed et.al.** (2012) 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 which indicate the significance of developed methods over reported method.
Wang Xiao-ling et al.\textsuperscript{19} (2012) 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 was observed at 620 nm, and apparent molar absorptivity is $3.38 \times 10^6$ L.mol\(^{-1}\).cm\(^{-1}\), with detection limit of 0.025 mg/L, the linear range was 0-0.8 mg/25mL. As reported by 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%.

Kamaya Minori et al.\textsuperscript{20} (2012) have investigated iron and zinc as contaminant metals in chromium (III) plating bath by spectrophotometry. The reagents used were 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 was detected successfully by addition of EDTA as masking agent. However, in the case of zinc in the prepared plating bath, it was difficult to determine without interference with chromium (Ni). Therefore, it was necessary to detect the zinc by addition method as mentioned.

Navarkar Prabhakar S. et al.\textsuperscript{21} (2012) 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 $\lambda_{\text{max}}$ at 430 nm. Beer's law is obeyed in the concentration range 1 to 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 Limit of detection for the proposed method was found to be 0.561ppm. 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.

Kiran K.\textsuperscript{22} (2012) 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 was used as the solvent, a pH of 5.0 was maintained, the reagent concentration was chosen as $6.0 \times 10^{-3}$ M and there was 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.

Huang Yongming et al.\(^{23}\) (2012) 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 was injected into the carrier stream quantitatively and discretely. After mixing with H\(_2\)O\(_2\), the DPD was oxidized to form two pink semiquinone derivatives that were monitored at 514 nm wavelength with a reference at 700 nm. As reported by authors detection limit of the method was 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 nmolL\(^{-1}\)) well agreed 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 was 4.49% ($n = 8$). An instrument was 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.

Anusuya Devi V. S. et al.\(^ {24}\) (2012) 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 was found 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 = $5.6 \times 10^4$ 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 \(\times\) 10\(^4\) L.mol\(^{-1}\).cm\(^{-1}\). All the proposed methods were successfully employed in the analysis of various biological, water, and alloy samples for the determination of Fe and Co content, as described by authors.

**Ombaka O. et.al.**\(^{25}\) (2012) have reported spectrophotometry as highly sensitive and selective method for the determination of iron (III) in aqueous solution with hydroxytriazenes. Hydroxytriazenes reacts with the Fe\(^{3+}\) and form colored complexes with Fe(III) showing \(\lambda_{\text{max}}\) 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), (vi) respectively. The molar ratio of Fe (III) to the hydroxytriazenes was found as 1:3. The standard deviation ranges in between 0.019 to 0.088. The Sandell's sensitivity in ng/cm\(^3\) ranges between 2.5.579 to 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.**\(^{26}\) (2012) have developed spectrophotometric method for the determination of Fe (II) which is a simple, rapidand sensitive method. Authors proposed, 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 (\(\lambda_{\text{max}}\)). Beer's law is obeyed over the Fe (II) concentration range of 0.1-12 mg/mL. The Sandell's sensitivity and molar absorptivity for Fe-NOHBPA system is 0.0125 mg.cm\(^{-2}\) and 4469.27 L.mol\(^{-1}\).cm\(^{-1}\) respectively. 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.

**Aliyeva R.A. et.al.**\(^{27}\) (2011) have reported photometric determination of iron (III) as a Fe(III)-R-Ox different ligand complex. In this study 1-phenyl-2,3-
dimethylpyrazolone-5-azopyrogallol form complex with Fe(III). Spectrophotometric method and effect of 8-hydroxyquinoline to the complex formation was also studied. Formation of different ligand complex Fe(III)-R-Ox with 1:1:1 ratio in the presence of 8-hydroxyquinoline was determined. There is bathochromic shift and hyperchromic effect is observed in the absorption spectrum by formation of this complex. As reported by authors the maximum yield shift towards acidic medium, which is applicable for its determination in aluminium alloy A386-1.

Xie Jianying et.al.\textsuperscript{28} (2011) have established a new catalytic kinetic spectrophotometric method for trace iron. This experiment is based on the fact that trace iron could catalyze the fading reaction of phenosafranine oxidized by potassium bromate under the sensitivity enhancing function of poly vinyl alcohol(PVA) surfactant in HAc-NaAc buffer solution medium at pH 4.0. The effect of other ions on the determination was also investigated by authors. Under the optimal experimental conditions, the apparent activation energy of catalytic fading reaction was 84.03 kJ/mol, the linear range of method was 0.02-0.32 mg/mL, and the detection limit of iron(III) was $6.6 \times 10^{-7}$ g/L. The presented method could be applied to the determination of iron in glass and ceramic sample, as reported. The relative standard Deviations (RSD) have been found 2.6-4.1\%, and the recoveries of standard addition were 94-102\%.

Adebayo Basheer K. et.al.\textsuperscript{29} (2011) 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 was 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 was obeyed in the range of 1 to 14 mg/mL Fe$^{3+}$. The recovery was between 98.60 and 103.30\% with a coefficient of variation of 1.209\%. The method was successfully applied to tap water samples, as described by authors.

Moghadam Masoud Rohani et.al.\textsuperscript{30} (2011) 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) was injected rapidly into the water sample containing Fe (II) and Fe (III) species. At this step, the iron species interacted with the TTA and extracted into the 1-undecanol. The absorbance of the extracted iron was measured in the wavelength region of 450-600 nm after the phase separation. The artificial neutral networks were then applied for simultaneous determination of individual iron species. Under optimum conditions, the calibration graphs were linear in the range of 95-1070 mg.L$^{-1}$ and 31-350 mg.L$^{-1}$ with detection limits of 25 and 8mg.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 were obtained for Fe$^{3+}$ and Fe$^{2+}$ ions, respectively. As reported by authors, the procedure has been applied to power plant drum water and several potable water samples.

Toral M. Ines et.al.\textsuperscript{31} (2011) have proposed spectrophotometric determination of iron and cobalt by batch and continuous flow modes. As solid phase Authors 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 2nd derivatives for iron and cobalt determination have been used at 536.0 and 601.4 nm, respectively. In this modality, the detection limits (3s criterions), for iron and cobalt were 1.3, 9.1, mg.L$^{-1}$ and the determination ranges were: 4.3 to 220 and 30.3 to 800 mg.L$^{-1}$. The method by FIA mode was carried out by stopped flow and then the analytical signal was 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 authors. These methods were applied successfully in drinking water and soil samples.

Labhade S. R. et.al.\textsuperscript{32} (2011) have proposed new analytical method for spectrophotometric determination of iron through measurement of permittance of
the copper (II)-ethylenediaminetetraacetate, \([\text{Cu(II)-EDTA}]^2\) absorbing system. In this method, Fe\(^{3+}\) solution buffered at pH 1.15 and excess of EDTA and the surplus EDTA was used for generation of \([\text{Cu(II)-EDTA}]^2\) system. Permittance of the absorbing system measured at 722 nm has been observed which is directly proportional to the concentration of iron. At pH 1.15, the average value of the permitance coefficient was investigated as 0.5168 L.g\(^{-1}\).m\(^{-1}\) for quantitative determination of iron in the range of 1.0 mg to 10.0 mg. Efficacy of this method was further tested for determination of iron in Livogen-Z, Ferium-xt, and Orofer-xT tablets. The metal cations such as aluminium, barium, calcium, cadmium, lead, magnesium, manganese, zine, and copper do not interfere in determination of iron as reported by authors.

**Hashem E. Y. et.al.**\(^{33}\) (2011) 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 \(2.81 \times 10^4\) 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.

**Pytlakowska K. et.al.**\(^{34}\) (2011) have reported simple and sensitive method for the spectrophotometric 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 \(1.12 \times 10^5\) L.mol\(^{-1}\).cm\(^{-1}\) at 650 nm; for Fe-CAS-ODTA-TX100 it is \(1.35 \times 10^5\) L.mol\(^{-1}\).cm\(^{-1}\) at 659.5 nm. Beer's law was obeyed for iron concentration in the range 0.08-0.56 mg/mL for the complex Fe-CAS-TTA-TX100 and 0.08-0.64 mg/mL for Fe-CAS-ODTA-TX100. The stoichiometry of the complexes has been 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 authors.
**Alula Melisew Tadele et.al.**\(^{35}\) (2010) have developed chemometric assisted method for simultaneous analysis of iron(II) and copper(II) ions in the pharmaceutical mixtures. The significant spectral overlap \((Di)_{0.5} = 0.5667\) which is about 75.3% overlapping of the UV/Visible absorption spectra of iron (II) and copper (II) complexes. For this investigation 8-hydroxyquinoline has been used as a chromogenic reagent. The absorption spectra were recorded in the wavelength range of 350-600 nm digitized at 1 nm. Four chemo-metrics methods such as first derivative spectrophotometry (1D zero crossing), first derivative ratio (1D ratio), classical least squares (CLS) and principal component regression (PCR) have been used by authors to predict the concentrations of the metal ions. The calibration curves have been found to be linear in the range of 2-12 mg/mL for both ions. For classical least squares and principal component regression, the calibration model was obtained and predictions of the unknown concentrations of the ions in the synthetic mixtures and in the dosage form were done. The methods were successfully applied for analyzing synthetic mixtures and common pharmaceutical preparation as reported.

**Watanabe Kunihiro et.al.**\(^{36}\) (2010) have studied a precision determination method for Fe based on rapid complex formation using stopped-flow spectrometric method. For this \(\text{NH}_4\text{SCN}\) has been selected as a detection reagent. It is mentioned that the sample solution was prepared with HCl solution after alkali fusion with a mixtures of Na carbonate and Na peroxide. The concentration of chloride ion was adjusted to under 0.1 mol/L in the final solution. The average of fifty points at 0-0.2 was obtained as 1 measurement result. The optimum conditions of Fe determination reported by authors are: pH of sample solution (250 mL), 1.6; pH of 6.2 mol/L \(\text{NH}_4\text{SCN}\) (250 mL), 5.0; measurement time, 0-0.2 s; results. The Fe in a sample cell was detected at 7-10 ppm by measuring a complex of Fe at 480 nm. The analysis time for 1 sample solution was 1 min including cleaning time of the reaction line. The results of Fe determination in standard Fe ores showed good agreements with certified values as mentioned.
Zhong Guoxiu et.al.\textsuperscript{37} (2010) have presented the color reaction between dibromo-p-nitro-chlorophosphonazo and iron in acidic medium, forming a complex (2:1) which showed maximum absorption at 610 nm. Beer's law was obeyed for iron in the range of 0.14-0.80 mg/mL and molar absorptivity of the complex was $1.63 \times 10^4$ 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.

Ma Weixing et.al.\textsuperscript{38} (2010) have established a spectrophotometric determination method for iron which is based on the color reaction between Fe (III) and p-aminophenyl fluorine (APF), chromotropic acid and emulsifier OP in alkaline medium. It was found, that Fe (III) could form a green quaternary blending micellar complex with APF, chromotropic acid (CA), and OP. The $\lambda_{max}$ of this complex was observed at 620 nm. The molar ratio of Fe (III), APF, and CA was 1:2:1. Beer's law was obeyed for iron in 1-10 mg/10 mL with the correlation coefficient of 0.9995. As reported by authors, the proposed method was applied to the determination of trace iron in aluminium alloy samples.

Zhong Yu jun\textsuperscript{39} (2010) has developed, a new method for spectrophotometric determination of iron in soil using phenanthroline. The results showed that when phenanthroline used as chromogenic reagent, the amount of Fe was determined at 510 nm in soil sample. Beer's law was obeyed in the range of 0-4 mg/L for iron (III), and the apparent molar absorption coefficient was found as $2.10 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$. It had been used for the determination of iron in soil, and the results obtained agreed with those achieved by sulphosalicylic acid method, with RSD 0.50%-1.0% (n=6), as described by author.

Zou Ming-Qiang et.al.\textsuperscript{40} (2010) 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$_3$ in a $5.0 \times 10^{-3}$ M H$_2$SO$_4$. 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 at the maximum absorption wavelength of 20
nm and described by the equation: \( DA = 0.133c \) (ng/mL) - 0.0133 with a
regression coefficient of 0.9966. The detection limit of the method is 0.17 ng/mL.
As described by authors, the method could successfully be used in the
determination of traces of iron in potato samples.

Bhaskar C. Vijaya et al.\(^\text{41}\) (2009) 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
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 \( \lambda_{\text{max}} \) 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 were found to be \( 9.379 \times 10^2 \) L.mol\(^{-1}\).cm\(^{-1}\) and \( 8.8032 \times 10^2 \) 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 was determined and
found to be 1:2 for both systems. The results obtained by both the systems were
reproducible and comparable with the results of iron determined separated by
phenanthroline method, as described by authors.

Zhai Qing-Zhou\(^\text{42}\) (2009) has reported A novel catalytic kinetic
spectrophotometric method for the iron determination which 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 \times 10^{-3} \) M sulfuric acid 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 and fitted the equation: \( DA = 4.91 \times 10^2 \) C (C: ng/mL) + 0.017, with a regression coefficient of 0.9966 at the wavelength, as
described by author. The detection limit of the method is 0.031ng/mL. The
reported method has also been used to determine iron in the black gingili paste,
oat slice, sleeve-fish silk food samples.
Zhan Xiaoxia et al. (2009) 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 $5.0 \times 10^{-3}$ mol/L $\text{H}_2\text{SO}_4$ medium. The absorbance difference (DA) showed good linearity with Fe (III) in the range of 0.2-6.0 ng/mL at 518 nm. The regression equation was $\text{DA}=0.032r \text{ (ng/mL)} + 0.0161$ with correlation coefficient of $r=0.9980$. The detection limit of method was 0.025 ng/mL. 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 authors.

Hosseini Mohammad Saeid et al. (2009) 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 was 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 $1.2 \times 10^{-5}$ to $3.6 \times 10^{-4}$ M and $1.5 \times 10^{-6}$ M, respectively. As reported by authors the relative standard deviation (RSD) was found to be 0.76% in the replicate treatments (n = 7) with $1.6 \times 10^{-4}$ M Fe (III). The practical applicability of the method was confirmed using a synthetic certificated reference material (CRM) and spiked natural water samples.

Khan Saba et al. (2009) 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) $\times 10^{-5}$ M. The molar absorptivity and Sandell's sensitivity values are 2.446 $\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and 22.83 ng.cm$^{-2}$, respectively as described by authors.

Shen Ming-jin (2009) has proposed simultaneous spectrophotometric determination an aliquot of the sample solution and 5-Br-PADAP as color reagent
for Fe$^{3+}$, Ni$^{2+}$, V, and Co$^{2+}$. Sample of petroleum products was burned and ignited to eliminate hydrocarbons, and the residue was dissolved in dilute HCl. Values of absorbance were taken in the range of wavelengths between 540-620 nm at 2 nm intervals, using reagent blank as reference data of absorption spectra were treated by wavelet-transform to filter the noise from the analytical signals. As shown by the results, the algorithm of LSSVM showed its special features of speedy calculation, high accuracy and good generalization. In pretesting of LSSVM with some simulated samples, values of recovery for the 4 elements were found in the range of 96.0-103.5%. Values of RSD's ($n = 8$) for all the 4 elements were less than 4% as mentioned by authors.

Abdul Galil et al. 47 (2009) 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 authors this system works on the principle of catechol oxidation by iron(III) followed by its nucleophilic coupling with p-anisidine, $\lambda_{\text{max}}$ 565 nm or p-chloroaniline, $\lambda_{\text{max}}$, 545 nm in 0.1 M hydrochloric acid medium. Under the optimized experimental conditions, the 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 were found to be $1.7 \times 10^3$ L.mol$^{-1}$.cm$^{-1}$ and $1.6 \times 10^3$ L.mol$^{-1}$.cm$^{-1}$, with the corresponding Sandell's sensitivity values, 0.033 mg.mL$^{-1}$ and 0.035mg.mL$^{-1}$, respectively. The composition of the dye product of both systems were detected by Jobs 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 were comparable with those of the iron results determined separately following the procedure of the reported tiron-iron (III) method.
Prasad Rajendra and Prasad Surendra\textsuperscript{48} (2009) have presented a simple and convenient spectrophotometric method for the laboratory determination of the iron(III)-glycine formation constant via competitive ligand binding. Solver, Excel's suite of analytical tools, was used for the dynamic optimization of the molar absorption coefficient and the equilibrium constant. The program finds a requested optimal value in the target cell, by adjusting the values in the adjustable cells, as specified by the user, while subjecting the model to a number of restrictions or constraints. This method was tested by authors in the class and was found to work satisfactorily. It can easily be extended to determination of formation constants of other non-phenolic amino acids and organic bases with iron (III) and gives good quantitative comparisons, as mentioned.

Puzanowska-Tarasiewicz Helena \textit{et.al.}\textsuperscript{49} (2009) have presented a review which is devoted to analytical applications of reactions of Fe(III) and K$_3$[Fe(CN)$_6$] with 2,10-disubstituted phenothiazines (PT). It was found that iron(III) and hexacyanoferrate(III) ions in acidic media easily oxidized PT with the formation of colored oxidation products. This property has been exploited by authors for spectrophotometric determination of iron(III) ions and phenothiazines. Some flow-injection procedures of the determination of PT based on the oxidation reaction by means of the above-mentioned oxidants have also been proposed and the application of 2,10-disubstituted phenothiazines as indicators in complexometric titration of iron(III) as well as procedures of PT determination based on generation of ternary compound in the system Fe(III)-SCN(-)- PT was also described.

Balouch Aamna \textit{et.al.}\textsuperscript{50} (2009) have applied partial least-squares regression for the simultaneous determination of iron, vanadium, and cobalt after complexation with picolinaldehyde-4-phenyl-3-thiosemi -carbazone (PAPT) in the presence of anionic sodium dodecylsulfate (SDS) micelles. These 3 complexed metal ions exhibited 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 (SIMPLS) 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 microg/mL, respectively. With the proposed method common anions and cations did not interfere. The method was validated by 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 3 metal ions in real crude oil samples.

**Khan Saba et al.** (2008) 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) $\times 10^{-5}$ M. The molar absorptivity and Sandell's sensitivity values are found to be 1852 dm$^3$.mol$^{-1}$.cm$^{-1}$ and 30.15 ng. cm$^{-2}$, respectively.

**Zhu Wei-huang et al.** (2008) have studied organic extraction spectrophotometry to determine iron. As deriving reagent, 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT) was used and the potassium salt of tetrabromophenolphthaleinethyl ester (TPBE-K) was used as an ion-pair reagent. It was found that the sensitivity of the method was 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 was red shifted, which would lead to an increase in molar absorption coefficient from $2.4 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$ to $1.9 \times 10^5$ L.mol$^{-1}$.cm$^{-1}$. The calibration graph was constructed in a concentration range of 0-0.3 mg/L, the linear regression equation was $A = 0.3582C + 0.002$ ($r^2 = 0.9974$), and the limit of the detection (LOD) is 0.96 ng/mL ($S/N = 3$). As mentioned by 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.

**Gavrilenko N. A. et al.** (2008) have studied the interaction of Fe(II) with 2,2'-dipyridyl and 1,10-phenanthroline immobilized in a polymethacrylate matrix. 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 was 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 was used for the analysis of samples of tap, well, and mineral H₂O and a solution of glucose.

**Asan Adem et.al.** (2008) 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 of 1 mL.min⁻¹ with the sample throughput of 60 h⁻¹. The method provided 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 was successfully determined. Repeatability of the measurements was satisfactory at the RSD of 3.5% for 5 determinations of 10 μg.L⁻¹ iron(III) as reported by authors. The accuracy of the method was 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.

**Ma Wei-xing et.al.** (2008) 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 phenyl-fluorone forming a stable blue chelate (III). The maximum absorption of this chelate was observed at 620 nm with an apparent molar absorptivity of 9.355 × 10⁴ L/(mol/cm). 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.

**Ruengsitagoon Wirat** (2008) has proposed a simple reversed flow injection colorimetric method to determine Fe³⁺, based on the reaction between Fe³⁺ and chlortetracycline. It forms an intense yellow colored complex shown
maximum absorption at 435 nm. A 200 μL chlortetracycline reagent solution was
injected into a phosphate buffer stream (flow rate, 2.0 mL/min) which was then
merged with Fe$^{3+}$ standard or sample in dilute HNO$_3$ stream (flow rate, 1.5
mL/min). Optimum conditions to determined Fe$^{3+}$ were examined using a
univariate method. A linear calibration graph was obtained over a 0.5-20.0 μg/mL
range under optimum conditions. Detection (3σ) and quantification limits (10σ)
were 0.10 and 0.82 μg/mL, respectively. Relative standard deviation of the
proposed method calculated by the authors from 12 replicate injections of 2.0 and
10.0 μg/mL Fe$^{3+}$ were 0.43 and 0.59%, respectively; sample through-put was
60/h. The proposed method was satisfactorily used to determine Fe$^{3+}$ in natural
water as reported by author.

Kruanetr Senee et al.$^{57}$ (2007) 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 pH 5, Fe(III)-nitroso-R salt complex is
formed which showed absorption maximum at 720 nm. The FI parameters that
affect the signal response have been optimized by authors in order to get the better
sensitivity and low standard deviation. The linear range for determination of iron
in water samples was over the range of 0.05-4.0 μg.mL$^{-1}$ with a correlation
coefficient ($r^2$) of 0.9997. The limit of detection (3σ) was 0.011 μg 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 μg.mL$^{-1}$) were 1.42, 1.29, and 1.01% (n = 11),
respectively. The proposed method was successfully applied to determination of
Fe(III) in water samples as reported by authors.

Khaled Elmorsy et al.$^{58}$ (2007) 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 was monitored by authors using FIA and batch methods. The
calibration graphs were linear in the concentration range 5.4-130 and 4.5-50 ng of
iron for the FIA and batch, respectively. The FIA technique showed good average recoveries with lower detection limit compared with the batch technique. As reported by authors the method was 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 agreed with the official method.

Guo Yibing et.al.\textsuperscript{59} (2007) 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\textsubscript{4}H\textsubscript{9}OH/n-C\textsubscript{5}H\textsubscript{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°C and can be directly used for spectrophotometric analysis. The apparent molar absorptivity is \(8.936 \times 10^4\) L.mol\(^{-1}\).cm\(^{-1}\) at 768 nm. Beer's law is obeyed in the range of 0.014-0.48 \(\mu\)g/mL for iron(II). The detection limit is 0.004 \(\mu\)g/mL. 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.

Manjula Subbanaika et.al.\textsuperscript{60} (2007) 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\textsubscript{2}O, 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 \(\lambda_{\text{max}}\) at 620 nm. The color is stable up to 24 h and obeys Beer's law in the concentration range of 0.2-4.8 mg.mL\(^{-1}\). The optimum reactions conditions and other important analytical parameters were established by authors to enhance the sensitivity of the proposed method. The interference due to various non-target ions was also studied. The proposed method was applied to the analysis of Fe(III) in H\textsubscript{2}O, industrial effluent and soil samples. The performance of the proposed method was 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.

Chitra K. et.al.\(^6\) (2007) have observed that iron reacts with meloxicam in buffer to form a chloroform soluble red colored complex which exhibits an absorption maximum at 510 nm. Complex formation was not observed in sulfuric and phosphoric acid media. The absorbance remains constant over a pH range of 4.5-5.2. However 1.5 mL meloxicam was found to be sufficient for maximum color intensity. Hence 2.0 mL of meloxicam was used to ensure complete reaction. Out of the several organic solvents, authors found chloroform to be most suitable solvent. The absorbance of the complex was found to be stable for more than 6 h as mentioned by the authors.

Zhang Yingqi et.al.\(^6\) (2007) have studied a new kinetic spectrophotometric method for the determination of trace Fe(III). It is based on the catalytic effect of Fe(III) on the decoloring reaction of MB by H\(_2\)O\(_2\) in the presence of microemulsion n-C\(_7\)H\(_{16}\)/n-C\(_4\)H\(_9\)OH/CPC/H\(_2\)O and 1,10-phenanthroline (Phen) as activator. The optimum conditions are 0.6 mL 1.0 \(\times\) 10\(^{-3}\) mol/L MB, 0.2 mL 20% H\(_2\)O\(_2\), 1.4 mL 1.0 \(\times\) 10\(^{-3}\) mol/L Phen, 1.8 mL microemulsion, 2.0 mL HAc- NaAc (pH = 4). The linear calibration curve from 1.0 to 40 \(\mu\)g/L of Fe(III) and the detection limit of 8.4 \(\times\) 10\(^{-7}\) g/L are reported. The speed constant of the reaction at 100\(^\circ\) is 0.028 min\(^{-1}\) and the apparent activation energy is 36.22 kJ/mol. The method has been used to determine Fe(III) in water samples with satisfactory results.

Pour etedal Hamid Reza et.al.\(^6\) (2007) have described a simple and sensitive kinetic-spectrophotometric method for the determination of trace amounts of Fe(II). The method proposed by authors is based on the inhibitory effect of Fe(II) on the oxidation of methylthymol blue by bromate in the H\(_2\)SO\(_4\) media and at 35\(^\circ\), which was 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 with a detection limit of 0.6 ng/mL. The relative standard deviations for ten replicate analysis of 50 and 160 ng/mL of Fe(II) were obtained 1.2% and 2.0%, respectively. 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 H₂O samples.

Nadzhafova O. Yu. *et al.* (2007) 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) phenanthrolineates. The adsorption of Zn(II), Cu(II), Mn(II), Co(II), and Ni(II) phenanthrolineates 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 was shown by authors. The procedure was used to determine zinc in vitamin preparations, a food supplement, and an insulin preparation, as described by the authors.

Shokrollahi Ardeshir *et al.* (2007) have described a simple, selective and sensitized spectrophotometric method for determination of trace amounts of Fe³⁺ ion in tap and waste water solutions. In the presence of N,N-dodecyltrimethylammoniumbromide (DTAB), the spectrophotometric determination of Fe³⁺ ion using Ferron was carried out. The Beer's law is obeyed over the concentration range of 0.05-2.6 μg.mL⁻¹ of Fe³⁺ ion with the relative standard deviation (relative standard deviation %) <0.2% and the molar absorptivity of complexes in pH 3.5 is 3.8 × 10³ L.mol⁻¹.cm⁻¹. Potentiometric pH titration has been used for prediction of protonation constants of ferron and evaluating its stoichiometry and respective stability constants with Fe³⁺ ion. As it is obvious the most likely species of ferron alone and its complexes are LH (log = 7.64), LH₂ (logK = 10.52), LH₃ (logK = 11.74) and ML₂ (logβ = 23.68), ML₃ (logβ = 23.68), ML₃H (logβ = 23.68), ML₃H₂ (logβ = 23.68) and ML(OH)₂ (logβ = 23.68) respectively.
Fathi M. R. et al. (2007) 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 was studied to obtained optimum conditions. The calibration curve was linear at 0.4-2.0 μg.mL⁻¹ of iron(III) and the 3Sb detection limit was 0.07 μg.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.

Stauffer Mark T. (2007) has reported an analytical chemical laboratory project to use and evaluate pyridyl- and triazine-containing chelators for spectrophotometric determination of iron. The "Iron Project" introduces students to UV-visible spectrophotometry and Beer's law via hands-on development and use of spectrophotometric methods for iron. Nine chelators are currently available for use and values of molar absorptivities (εmax) and λmax for ligands 1-9 agree with published values to within ±15% (εmax) and ±3 nm (λmax) for 75% of results obtained so far. Stoichiometries for Fe(II) chelates of ligands 1-5 are within ±1 mol of ligand of the published ratios as described by authors.

Nekoei Mehdi et al. (2007) 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, Fe²⁺ and Co²⁺ were 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 authors and the results obtained by the applications of these chemometric approaches were evaluated and compared. The PC-ANN method afforded 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 were also studied. The proposed method was also applied...
satisfactorily for the determination of Fe(II) and Co(II) in real and synthetic samples.

Liu Shu-juan *et al.*69 (2006) 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. Meso-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 article 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 μg/5 mL with the molar absorptivity of $1.51 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$. As reported by authors good results are obtained for tea infusion samples.

Syed A.A. *et al.*70 (2006) 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 showed maximum absorbance at 630 nm and obeyed 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 $3.288 \times 10^3$ and $3.374 \times 10^3$ L.mol$^{-1}$.cm$^{-1}$ and Sandell's sensitivity values were 0.0130 and 0.0331 μg.cm$^{-2}$ respectively. As proposed by 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.

Patel A. L. and Patel I. J.71 (2006) have described a rapid, accurate and simple spectrophotometric method for the determination of iron in pharmaceutical samples based on the formation of colored complexes with 1-(3'-sulfo-phenyl)-3-methyl-4-azo-(4''-sulfonamidophenyl)-5-pyrazolone (mSMASP) reagent. The
method is free from the interference of a large no. of foreign ions and applicable for the routine determination of iron in pharmaceutical samples.

Cheng Zheng-jun *et al.* 72 (2006) have proposed a new orthogonal signal correction-linear interpolation-RBF (radial basis function) neural networks (OSC-Interp-RBF) approach to deal with the data obtained by spectrophotometry. With this method, noises in visible spectra were eliminated by authors by orthogonal signal correction, and linear interpolation to make specimen of training samples cover recognizable room better. As a result, RBF could collect characteristic information more efficiently, and the accuracy of the prediction was improved. The contents of Fe, Ni and V in synthetic samples and raw oil samples were determined simultaneously by this method. Relative error (RE) of synthetic samples and raw oil samples were less than 10% as described by authors.

Shiki Masaharu *et al.* 73 (2006) have examined trace Fe(II) with 1,10-phenanthroline (phen) and tetrabromophenolphthalein Et ester (TBPE) using chitosan co-precipitation in spectrophotometric method. Fe(II) reacted with phen to a stable chelating complex, \([\text{Fe(phen)}_3]^{2+} \cdot [\text{Fe(phen)}_3]^{2+}\) associated with TBPE-buffered at about pH 6.5 to form the ion associated \([\text{Fe(phen)}_3]^{2+} \cdot (\text{TBPE})_2\). A chitosan solution dissolved with HOAc was added to this solution and chitosan precipitated from the solution immediately. The ion associated \([\text{Fe(phen)}_3]^{2+} \cdot (\text{TBPE})_2\) was adsorbed onto the chitosan precipitated. After centrifugation, the supernatant solution was discarded. The chitosan precipitate was dissolved with HOAc and NaOAc, and Fe(II) could 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 authors the detection limit (S/N = 3) was ~8 ppb. The relative standard deviations (n = 3) for 60 ppb Fe(II) was 3.9%. 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.

Wu Lan-Ju *et al.* 74 (2006) have studied the reaction of Fe (II) with 4-(2-thiazolylazo) resorcinol in pH = 10.0 NH$_3$-NH$_4$Cl 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 $6.98 \times 10^4$ 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 authors.

**Teixeira Leonardo S. G. et.al.** (2006) 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 were also compared. As described by 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.

**Zarei K. et.al.** (2006) 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 partial least squares (PLS) with and without pre-processing step using direct orthogonal signal correction (DOSC). As authors mentioned the linear range was 0.30-4.50 µg.ml⁻¹ for Co(II), 0.20-3.00 µg.ml⁻¹ for Ni(II) and 0.30-5.00 µg.ml⁻¹ for Fe(II). Interference effects of common anions and cations were studied and the proposed method was also applied satisfactorily to the determination of Fe(II), Ni(II) and Co(II) in synthetic samples as reported by authors.

**Stoyanova A.** (2005) 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 was 0.52 ng.mL\(^{-1}\) and the sensitivity of the determination was increased. The reaction rate was monitored spectrophotometrically by measuring the absorbance of the reaction product at 580 nm. The variables that affected the reaction rate were investigated and the reaction conditions were established.

**Dong Xuechang et.al.**\(^{78}\) (2005) have developed a novel method for the determination of trace Fe\(^{3+}\) in water samples. The method was 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 showed an absorption maximum at 600 nm and apparent absorptivity 1.157 \(\times\) 10\(^4\) L.mol\(^{-1}\).cm\(^{-1}\). The complex was extracted with Waters Porapak SepPak C18 cartridge and eluted with ethanol containing 1% HAc. The eluted complex was then detected by spectrophotometer at 600 nm. Beer's law was obeyed at 0-7 \(\mu\)g/mL for Fe\(^{3+}\). The proposed method was successfully used for the determination of trace Fe\(^{3+}\) in water samples as described by authors.

**Xiang Lunqiang and Zhang Jinjie**\(^{79}\) (2005) have presented an improved method for determining Fe in Ti alloys by spectrophotometry with 1,10-phenanthroline to overcome the disadvantage of conventional method (setting the chromogenic solution over night for eliminating the interference of >4 mg of V). As authors reported a sample is dissolved rapidly with HF solution and complexed with saturated \(\mathrm{H}_3\mathrm{BO}_3\), and Fe in the sample solution is determined by 1,10-phenanthroline spectrophotometry with HOAc-NH4Ac as buffer and ternary organic ammonium salts (ammonium tartrate, ammonium citrate, and ammonium oxalate) as masking agents. The method shortened determination time and showed satisfactory results as claimed by the authors.

**Yu Ping et.al.**\(^{80}\) (2005) have studied the phase separation spectrophotometric determination of Fe\(^{2+}\). In HOAc-NaOAc buffer (pH 5.0), Fe\(^{2+}\) reacts with 2-5-bromo-pyridylazo-5-diethylaminophenol (5-Br-PADAP) to form a coordination complex. OP-BuOH-n-heptane-H\(_2\)O micro emulsion has been used by authors as extractant for phase separation of Fe\(^{2+}\)-5-Br-PADAP- micro emulsion system. The micro emulsion phase can be separated from H\(_2\)O phase
completely and on the H$_2$O phase when bathed at 72° for 5 min, thus the microemulsion phase can be directly used for spectrophotometric determination of Fe$^{2+}$. The complex showed an absorption maximum at 744 nm and apparent molar absorptivity $3.09 \times 10^{5}$ L/mol-cm. Beer's law was obeyed at 0-0.32 µg/mL for Fe$^{2+}$. The method was used for the determination of Fe$^{2+}$ in pond H$_2$O and tap H$_2$O, and the results were satisfactory. The method is simple, rapid, sensitive, and selective as reported.

Lokhande R.S. et.al.$^{81}$ (2005) have synthesized the reagent 5-bromosalicylaldoxime (5-BSO) and its characterization has been carried out by FTIR and NMR techniques. The reagent was then used by 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 µg. The molar absorptivity and Sandell’s sensitivity are $0.018 \times 10^{4}$ L.mol$^{-1}$.cm$^{-1}$ and $3.2 \times 10^{6}$ µg.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.

Mahadevaiah and Nagendrappa G.$^{82}$ (2005) 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. Molar absorptivity, correlation coefficient and Sandell’s sensitivity values were found to be of $1.7141 \times 10^{3}$ 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 were found to be $1.870 \times 10^{3}$ 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, pressmud, bagasse and also iron in pharmaceutical sample, plant leaves of Murrya coyingi and Moringaoliera was determined by authors as iron(III) by both the methods following the principles of calibration graph method. The results
obtained from iron(III)-5-sulfosalicylic acid were 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 have also been reproducible with standard deviation 0.0192-0.033 and coefficient of variation 0.351-1.756% as described.

Lembrikov V. M. et.al.\textsuperscript{83} (2005) have determined iron in phosphoric acid, obtained by sulfuric acid-assisted decomposition of phosphate ores and subsequent purification with tri-Bu phosphate, is determined by photometry of complexed iron in solution at 200-270 nm. Phosphoric acid formed in the process of phosphate ore digestion is diluted with an aqueous solution of ortho-phosphoric acid containing 10-40\% of P\textsubscript{2}O\textsubscript{5} at a volume ratio of diluents to the solution being analyzed of 1:(0.002-1).

Devanna N. et.al.\textsuperscript{84} (2005) have used diacetylmonoximebenzoyl hydrazone as a chromogenic reagent for the determination of Fe(II) and gives 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 $\lambda_{\text{max}}$ 360 nm is found to be $1.25 \times 10^4$ L.mol\textsuperscript{-1}.cm\textsuperscript{-1} and 0.0045 $\mu$g/cm\textsuperscript{2} of Fe(II) respectively. Beer's law validity range is from 0.11-2.24 $\mu$g/mL. Fe (II) gives 1:1 complex with diacetylmonoxime benzoyl hydrazone and stability constant of the complex is $1.1 \times 10^4$. 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 authors.

Watanabe Kunihiro et.al.\textsuperscript{85} (2005) have studied a precision determination method of Fe based on the formation of a stable Fe complex was studied by flow injection analysis (FIA). Four significant figures on the Fe content (%) could be obtained as the result of analysis by the present method, which was applied to the determination of Fe in Fe ores. Besides high precision, the results of Fe determination in standard, Fe-ores samples showed good agreement with certified values. The precision of the present method was 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) was detected by spectrophoto-
metry at 667 nm. Tiron as the optimum detection reagent has been selected by authors based on the complex stability examined by using a stopped flow-meter, which could measure the absorbance with 6 significant figures, from among 4 kinds of conventional detective reagents. The absorbance obtained by UV-visible spectrophotometry was recorded with 6 significant figures by Chroma-to-monitor with a personal computer. As a result, a single flow system was selected as the optimum manifold. A calibration curve was constructed by measuring the peak height of the absorbance signal. The optimum conditions of Fe determination by the present method were 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; reaction coil length, 10 m; pump, double-plunger pump. The Fe was detected at 10-300 ppm by measuring a 1:1 complex of Fe-Tiron. 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 h was 6 for the sample solution.

Gomes D. M. C. et al.⁸⁶ (2005) have proposed computer-controlled multi-syringe flow injection systems to perform the spectrophotometric determination of available iron and boron in soil extracts. The methodologies were based on the formation of ferroin complex (determination of iron) and azomethine-H reaction (determination of boron). Both determinations were performed in manifolds with similar configurations by changing the reagents present in the different syringes. In the determination of iron, elimination of Schlieren effect in the detection system was achieved through the binary sampling approach, where a three-way valve was actuated to intercalate small slugs of sample and reagent, promoting better mixing conditions for solutions with different values of refractive index. As authors reported, in the determination of boron, in-line sample blank measurement was attained by omitting the introduction of reagent through software control, without manifold reconfiguration. Linear calibration curves were established between 0.50 and 10.0 mg Fe⁻¹ and between 0.20 and 4.0 mg Bi⁻¹. No systematic difference has been found when soil extracts have analyzed by the proposed methodologies and compared to the respective reference procedures.
Babaiah O. et al. (2005) 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 \( \lambda_{\text{max}} \) at 400 nm. Beer's law is obeyed in the range 0.07-2.20 \( \mu g.mL^{-1} \) 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 \( \mu g/cm^{2} \), 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.

Achar B. N. and Bellappa S. (2005) 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 \( 2.9565 \times 10^{4} \) L/mol.cm 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 \( \mu g/cm^{2} \). 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 authors mentioned the proposed optimized method has highest sensitivity, unusual stability and simplicity in operation, without involving cumbersome extractive procedure.

Wu Lixiang and Guo Jincun (2004) 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\(_4\))\(_2\)SO\(_4\)-aluminon. Authors studied both separation and determination conditions. Beer's law was obeyed in the concentration range of 0-10 \( \mu g/25 \) mL for Fe(III). The apparent molar absorptivity is \( 4.48 \times 10^{4} \) L.mol\(^{-1}\).cm\(^{-1}\). When the amounts of them were at least as much as 5 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 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%.

Ion Ion et.al.\(^\text{90}\) (2004) have developed a method for the speciation of Fe
in natural waters. As authors reported, this method is based on a mathematical
modification of the ferrozine that overcomes the interference of Fe (III) on the
spectrophotometric determination of Fe(II). The detection limit of the method is
estimated to 0.3 μmol/L with 1 cm cell. Tests carried on a 25 μmol/L Fe (III)
solution lead to 25.2 ± 0.2 μmol/L Fe (III). The average molar absorption
coefficients calculated were 39500(± 30) L.mol\(^{-1}\).cm\(^{-1}\) for Fe (III) and 1000 (±30)
L.mol\(^{-1}\).cm\(^{-1}\) for Fe (III). This work demonstrated the feasibility for the speciation
analysis of dissolved Fe (II) and Fe (III) at low levels in H\(_2\)O samples.

Safavi Afsaneh et.al.\(^\text{91}\) (2004) have described simultaneous determination
of total iron and copper using either a partial least squares (PLS) or an H-point
standard addition method (HPSAM). 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 was
2.02%. Both PLS and HPSAM showed 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.

Hua Nan-Ping et.al.\(^\text{92}\) (2004) 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\(_4\)H\(_2\)O-NH\(_4\)Cl buffer solution (pH 8.5). As
described by authors, Beer's law was obeyed at 0.1-2.0 with molar absorptivity
being 4.4 L.mol\(^{-1}\).cm\(^{-1}\) at 450nm. The interference resulted from most of metal
ions was masked by EDTA. The method has also been applied to determination of
Fe in samples with satisfactory results as mentioned by the authors.
Tesfaldet Zeriet O. et al.\textsuperscript{93} (2004) have proposed a sequential injection analysis (SIA) system for the determination of iron (II). Fe(II) has 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 involved aspiration of 187 µL sample/standard zone followed by a zone of a reagent solution containing 140 µL of $7.8 \times 10^{-4}$ 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 has evaluated by authors 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$^{-1}$ was established. The proposed method was successfully applied for the determination of total iron as Fe(II) in pharmaceutical products (multi-vitamin tablets) and has especially useful for the determination of iron (II) in tablets with lower iron (II) contents, as authors mentioned.

Wang Li-min et al.\textsuperscript{94} (2004) have studied the 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) reacted with 4,7-diphenyl-1,10-phenanthroline and tetraphenylborate to form a stable red ternary complex, at pH 4 which has been easily extracted by authors into molten naphthalene. The solid naphthalene containing the ternary complex has separated by filtration and dissolved in acetone. Against a reagent blank, the absorbance was measured at 534 nm. Beer's law was 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 was $2 \times 10^{4}$ L.mol$^{-1}$.cm$^{-1}$ and 0.0025 µg/cm$^{2}$, respectively. The interference of various ions has also been studied by authors. The method can be applied to determine micro amounts of Fe in natural H$_2$O samples with satisfactory results.

Sato Kenji et al.\textsuperscript{95} (2004) have prepared 1-Phenyl-3-methyl-4-stearoyl-5-pyrazolone (HC18) loaded on a silica gel (SG) and used to determine the diffusion reflectance/ spectrophotometric of iron(III) ion. As authors mentioned iron(III) ion was quantitatively retained on the absorbent, HC18/SG, from an aqueous
solution of pH >2.0 in the batch experiment. The calibration curve for iron was linear over 0.5-10 μg. The relative standard deviation (n = 7) was 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 have stability for at least one month, and no change in the absorbance has also been confirmed. The recovery from 1000 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 approx. 100%, as described.

Afshar-Ebrahimi Arash et al. (2004) have proposed a partial least-squares multivariate calibration method for simultaneous spectrophotometric determination of iron, nickel and vanadium as their complexes with 8-hydroxyquinoline (oxine). Experimental calibration and validation matrices have also been designed by authors with 15 and 8 samples, respectively. The upper limit of the concentration range was 288 μmol.L⁻¹ for iron, and 96 μmol.L⁻¹ for nickel and vanadium. The average relative error of determination was 2.5%, 5.9% and <7.0% for Fe, Ni, and V, respectively. This method was applied to the analysis of some synthetic and real alloy samples, as mentioned.

Tai Xi (2004) has studied the color reaction of Fe (III) with 8-hydroxyquinadine. In the presence of pH 8.0 NH₄Cl-NH₃·H₂O 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 waters plus-C18 cartridge, and can be eluted by EtOH. In EtOH medium, the molar absorptivity of the chelate is 7.82 × 10³ L.mol⁻¹.cm⁻¹ at 595 nm. Beer's law is obeyed at 0.1-5.0 μg/mL. This method can be applied to the determination of Fe in biological sample with satisfactory results as reported by author.

Li Zaijun et al. (2004) 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 authors described, the apparent molar absorption coefficient, Sandell's sensitivity of the complex, the detection limit and the relative standard deviation were $1.06 \times 10^5$ 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 obeyed Beer's law. The effect of foreign ions and other dithiocarbamates were also studied by authors in detail. The results indicated 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 com. samples.

Ensafi Ali A et al. (2004) have described a flow injection procedure for the sequential spectrophotometric determination of iron(II) and iron(III) in pharmaceutical products. Authors mentioned that this method is based on the catalytic effect of iron(II) on the oxidation of iodide by bromate at pH = 4.0. The reaction was monitored spectrophotometrically by measuring the absorbance of produced tri-iodide ion at 352 nm. The activating effect for the catalysis of iron(II) was extremely exhibited in the presence of oxalate ions, while oxalate acted as a masking agent for iron(III). The iron(III) in a sample solution could be determined by authors by passing through a Cd-Hg reductor column introduced in the FIA system to reduce iron(III) to iron(II), which allows total iron determination. Under the optimum conditions, iron(II) and iron(III) could be determined over the range of 0.05 - 5.0 and 0.10 - 5.0 microg.ml$^{-1}$, respectively, with a sampling rate of 17 +/- 5 h$^{-1}$. The experimental limits of detection were 0.03 and 0.04 microg ml$^{-1}$ for iron(II) and iron(III), respectively. The proposed method has been successfully applied to the speciation of iron in pharmaceutical products.
Abdollahi H. et.al.\textsuperscript{100} (2003) 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 authors in spectroscopic measurements due to their possible effects on the systems of interest. The ability of micellar systems to solubilise slightly insoluble or even very insoluble complexes and/or ligands has been used to enhance the analytical merit of the given methods. The ability of micelles to solubilise complexes in aqueous solutions can eliminate the need for nonaqueous extraction step in a given analysis. The simultaneous determination of Fe, Co and Cu has been carried out as 1-nitroso-2-naphthol complexes in 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 have also been developed. For individual determinations, molar absorptivities and the limit of detection have obtained, respectively. The total relative standard error for applying the method on synthetic samples was 2.02\%. The proposed method has also been successfully applied to the determination of Fe, Co and Cu in several synthetic alloy solutions.

Rao B. Sreenivasa et.al.\textsuperscript{101} (2003) 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 has measured by authors spectrophotometrically at $\lambda_{\text{max}}$ 378 nm at pH 5.0. The molar absorptivity of the complex is $2.58 \times 10^3$ dm$^3$.mol$^{-1}$.cm$^{-1}$ which 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.

Khan Saba et.al.\textsuperscript{102} (2003) have used p-sulfonamido phenylazo-bisacetoxime for spectrophotometric determination of iron(III) at 405 nm, keeping the pH at 2.5-3.0. As authors reported, Beer's law is obeyed in the range (4 to 24) $\times 10^{-5}$ M. The molar absorptivity and Sandell's sensitivity values are 1853 dm$^3$.mol$^{-1}$.cm$^{-1}$ and 30.14 ng.cm$^{-2}$, respectively.
Ghazy S. E. and Mostafa G. A. E.\textsuperscript{103} (2003) 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 of Fe (II) and over 8–40 mg/mL of Hg (II). Their molar absorptivities are $0.4 \times 10^4$ and $1.4 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$, respectively. The different analytical parameters affecting the flotation process and spectrophotometric determination have also been studied by 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.

Ivsic Astrid Gojmerac\textit{ et al.}\textsuperscript{104} (2003) have investigated extraction of iron(3+) from sulfuric and hydrochloric acid solutions containing an excess of thiocyanate ions with tetraphenylphosphonium chloride (I) and cetyltrimethylammonium bromide (II) in chloroform. Optimum conditions for extraction by both extractants have determined. The extraction behaviour 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 iron(3+) 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 has been determined by distribution and spectrophotometric methods. The molar ratio Fe:SCN:I of the extracted complex was 1:4:1; accordingly, its composition was [I][Fe(SCN)4]. The molar ratio Fe:II of the extracted complex has been found 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)$_6$].
Singh Kaman et.al.\textsuperscript{105} (2003) 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 showed a wavelength of maximum absorption ($\lambda_{\text{max}}$) at 440 and 420 nm, for Fe(II) and Fe (III), respectively. The extraction behaviour 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. The proposed method has been compared by 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 determined Fe down to 0.5 mg Fe/mL.

Chen Jianghong et.al.\textsuperscript{106} (2003) have studied the color reaction of Fe(III) with 8-hydroxyquinaldine. In pH 8.0 NH$_4$Cl-NH$_3$.H$_2$O buffer solution and cetyltrimethylammonium bromide (CTMAB) medium, 8-hydroxyquinldine 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 $7.17 \times 10^3$ L.mol$^{-1}$.cm$^{-1}$ at 600 nm. Beer's law has been obeyed at 0-5.0 mg/L for Fe(III). This method has also been applied to the determination of Fe in H$_2$O with satisfactory results.

Demirhan Nebahat et.al.\textsuperscript{107} (2003) 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 have 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 was at 520 nm. A linear relation existed between absorbance and Fe(II) concentration over the range 0.1 mg/mL and 0.4 mg/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 have reported by authors.
Safavi Afsaneh et al.\textsuperscript{108} (2003) have carried out simultaneous spectrophotometric determination of iron, titanium and aluminium using their Morin (3,5,7,2',4'-pentahydroxy flavone) complexes in Triton X-100 micellar medium. Partial least-squares regression has been 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) have 0.03, 0.04, and 0.02 mg.mL\textsuperscript{-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 mg.mL\textsuperscript{-1} Al(III), 0.06 to 1.6 mg.mL\textsuperscript{-1} Ti(IV), and 0.04 to 1.5 mg.mL\textsuperscript{-1} Fe(III) was 5%. Analysis of synthetic and artificial mixtures of solutions of several alloys has successfully performed by the method, as described by authors.

Abdollahi H. et al.\textsuperscript{109} (2003) 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 mg.mL\textsuperscript{-1} Fe and 0.20-8.00 mg.mL\textsuperscript{-1} V was 2.2\%. The results of applying the H-point standard addition method showed 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 showed suitable abilities to resolve accurately overlapped absorption spectra of the compounds. Both proposed methods have successfully applied by authors to the determination of Fe and V in several synthetic alloy solutions.

Melwanki M. B. et al.\textsuperscript{110} (2003) 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 $1.82 \times 10^4$ 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 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.\textsuperscript{111} (2003) have 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 ($\lambda_{max}$). Beer's law is obeyed over the Fe(II) concentration range 0.1-10 mg/mL. The molar absorptivity is 6515 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 (Cap. Dexorange).

Galeano Diaz T et.al.\textsuperscript{112} (2003) have developed two methods for the determination of iron in olive oil by spectrophotometry and by adsorptive stripping square wave voltammetry (Ad-SSWV) have been developed. These two methods are based on the formation of a 5,5-dimethylcyclohexane-1,2,3-trione 1,2-dioxime 3-thiosemicarbazone (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 4000 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 has been constructed from 0 to 30
ng.mL$^{-1}$, and the detection limit was 0.55 ng.mL$^{-1}$ (13.75 ng.g$^{-1}$ in olive oil according to the proposed procedure).

**Malik Ashok Kumar et.al.**$^{113}$ (2003) 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 microg.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 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.

**Lin Xinhua et.al.**$^{114}$ (2002) have studied the spectrophotometric determination of iron with phen in the presence of CTMAB and potassium hydrogen tartrate. The resulting complex had a maximum absorption at 515 nm. Beer's law has been obeyed in the concentration range of 0.5-8 µg/mL, having correlation coefficient 0.9995. Its apparent molar absorptivity is $1.23 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$. The method has also been applied to determine iron in Aloe with satisfactory results. The relative standard deviations have 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 authors.

**Yuan Xia and He Bin**$^{115}$ (2002) 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 $3.24 \times 10^4$ L.(mol.cm)$^{-1}$ at 648 nm. Beer's law has been 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.
Jankiewicz B. et al.\textsuperscript{116} (2002) have determined bioavailable and total iron in the soil collected in two allotment gardens in the city. Iron has 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 authors using hydroxylamine instead of glycine to reduce Fe(III) to Fe(II).

Pojanagaroon Teraboon \textit{et al.}\textsuperscript{117} (2002) have proposed a reversed flow injection colorimetric procedure for determining Fe(III) at the \(\mu g\) level. It is based on the reaction between 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 \(\mu L\) 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 has monitored at 435 nm. Beer's law obeyed at 0.2-1.4 \(\mu g.mL^{-1}\) 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\(\sigma\)) was 0.01 \(\mu g.mL^{-1}\) the sample through of 86 h\(^{-1}\) and the coefficient of variation of 1.77\% (\(n = 12\)) for 1 \(\mu g.mL^{-1}\) Fe(III) were achieved with the recovery of the spiked Fe(III) of 92.6-99.8\%.

Kass M. and Ivaska A.\textsuperscript{118} (2002) 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 is 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 authors. The relative standard deviation was 0.4\% (\(n = 7\)). The method has 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 h, including three repetitive determinations of each sample.

Shu Yude et.al.\(^{119}\) (2002) have determined Fe of Zn-Fe coatings and in bath solutions by spectrophotometry at pH 1.5-3 with sulfosalicylic acid as chromogenic agent and H\(_2\)O\(_2\) as oxidizing agent. The coating samples have been dissolved with diluted HCl, the absorbance has been measured at the iso-absorption point, and the Fe content has been calculated by authors according to Beer's law.

Li Zhong et.al.\(^{120}\) (2002) have proposed a method for the determination of Fe in tobacco. For this Rutin has been used as a chromogenic reagent. It reacted with Fe(III) in a weakly acidic solution (0.014-0.032 mol/L HCl) in the presence of CTMAB to form a stable bluish-violet complex (mole ratio of Fe:R = 1:2) which has an absorption maxima at 620 nm. Beer's law was obeyed in the range of 0-20 \(\mu\)g Fe(III) per 25 mL of solution with its apparent molar absorptivity of 4.40 \(\times\) 10\(^4\). The RSD has 2.2-3.1\%, the recovery has 95-98\%, and the results have consistent with those obtained by AAS.

Cassella Ricardo J.\(^{121}\) (2002) has reported the development of a simple and accurate online procedure for preconcentration and determination of dissolved Fe in waters and biological materials using unloaded polyether-type polyurethane foam as solid extractor. In the developed flow injection system, the analyte has been pre-concentrated from acidic aqueous medium as Fe-thiocyanate complex with post-elution with ascorbic acid solution and spectrophotometric measurement with 1,10-phenanthroline as colorimetric reagent. In order to improve the performance of the system several chemical and flow variables have been studied as well as the effect caused by the presence of possible interferents. The method has validated by the analysis of two certified reference materials. Application of the methodology has been carried out by the determination of dissolved Fe content in eight natural H\(_2\)O samples with different characteristics. The results have been compared with those obtained by electro-thermal atomic absorption spectrometry (ETAAS) and no statistical difference has observed. The detection limit was 0.75 \(\mu\)g.L\(^{-1}\) and the relative standard deviation was 1.2\% for 2 min.
preconcentration time. At this condition, a productivity of 20 samples h\(^{-1}\) has been achieved. Increasing the preconcentration time up to 3 min, a detection limit of 0.45 \(\mu g.L^{-1}\), a relative standard deviation of 1.5\% and an analysis throughput of 15 h\(^{-1}\) have also been verified by authors.

**Ramanjaneyulu G. et.al.**\(^{122}\) (2002) 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 \(\mu g/mL\). The molar absorptivity and Sandell's sensitivity are 1.72 \(\times\) 10\(^4\) L.mol\(^{-1}\).cm\(^{-1}\) and 0.032 \(\mu g.cm^{-2}\), respectively. The method has been employed successfully for the determination of Fe(II) in grape leaves, multivitamin capsules and blood.

**Nagabhushana B. M. et.al.**\(^{123}\) (2002) have reported diformylhydrazine (OHC-HN-NH-CHO) DFH, the bidentate ligand which 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 \(\mu g.mL^{-1}\). The molar absorptivity has been observed in the range 0.3258 \(\times\) 10\(^4\)-0.3351 \(\times\) 10\(^4\) L.mol\(^{-1}\).cm\(^{-1}\) and Sandell's sensitivity is 0.0168 \(\mu g.cm^{-2}\). The method was applied to the determination of Fe in industrial waste, ground \(H_2O\), and pharmaceutical samples.

**Mishra Alok and Mohabey Hemlata**\(^{124}\) (2002) 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 which is extractable into benzene. The optimum acidity range for the extraction and spectrophotometric determination of the complex is 0.25M to 0.6M. Molar absorptivity and Sandell's sensitivity of the complex at its \(\lambda_{max}\) (470nm) are 11480 L.mole\(^{-1}\).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 no. of
cations and anions have been studied and the method is successfully applied to determine Fe content in a no. of Fe drugs, soil samples and Fe ores.

Zhong Ming-hua and Mo Chun-sheng (2002) have developed a new method for the silica gel H phase-diffuse reflectance spectrophotometric determination of iron(III) with piperonal fluorine (PIF) has been developed. In the presence of cetyltrimethyl ammonium bromide and in a NH₄Cl-NH₃-H₂O 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 1c-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 has been studied by carrying out determining of 200 ng.(10 mL)⁻¹ of iron (III), 1 mg K⁺, Na⁺, F⁻, Cl⁻, NO₃⁻, PO₄³⁻, 0.6 mg Ca²⁺, Mg²⁺, 35 micrograms Sn²⁺, 20 micrograms Cr(III), 6 micrograms Mn²⁺, 4 micrograms Pb²⁺, 3.5 micrograms Cd²⁺, 2.5 micrograms Cu²⁺, Ag⁺, 1.5 micrograms Cr(VI), 1 microgram Ni²⁺, 0.75 microgram Zn²⁺, Sn⁴⁺ et al don't interfere with the measurement. The method has been applied to the determination of micro amount iron in magnesium oxide with satisfactory results.

H. Abdollahi (2001) has reported Simultaneous determination of Cr(VI) and Fe(III) by partial least squares (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 has been used for determination of Cr(VI) and Fe(III). This micellar system is beneficial for elimination of the previous solvent extraction step which 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 0.20–8.00µg.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. Author mentioned that both methods (PLS and HPSAM) could
also be applied successfully to the determination of Cr and Fe in several synthetic alloy solutions.

**Madalena C. da Cunha Areias et al.** (2001) 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 $4.21 \times 10^4$ and $1.26 \times 10^4$ 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 $1.27 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$. The detection limits are 0.09 $\mu$M for Fe(II) and 0.22 $\mu$M 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 methods.

**Hyungphil Chun et al.** (2001) have studied the coordination chemistry of the ligands 2-anilino-4,6-di-tert-butylphenol, H[L$^{AP}$], and $N,N$-cyclic-bis{2-(4,6-di-tert-butylphenol)}diethylenetriamine, $H_2[(L^{AP})N(L^{AP})]$, with the first-row transition metal ions V, Cr, Fe, and Co. The ligands are non innocent in the sense that the aminophenolato parts, [L$^{AP}$] - and [L$^{AP}$H] $^{2-}$, can be readily oxidized to their o-iminobenzosemiquinonato, [L$^{ISO}$], and o-iminobenzoquinone, [L$^{SB}$], forms. The isolated neutral octahedral complexes have been obtained as crystalline materials,$[Cr^{III}(L^{ISO})_3]$ (1), $[Fe^{III}(L^{ISO})_3]$ (2), $[Co^{III}-(L^{ISO})_3]$ (3), $[V^V(L^{ISO})(L^{AP}H)_2]$ (4), $[V^V(L^{AP}H)_2(L^{AP})]$ (5), and $[V^VO{(L^{AP})N(L^{AP}-H)}]$ (6) and their crystal structures have been determined by X-ray crystallography at 100 K. From variable temperature magnetic susceptibility measurements and X-band EPR spectroscopy it has been established which shows that these complexes possess ground states: 1, $S = 0$; 2, $S = 1$; 3, $S = 3/2$; 4, $S = 1/2$; 5, $S = 0$; 6, $S = 0$. The o-iminobenzosemiquinonato radicals ($S_{rad} = 1/2$) couple strongly intramolecularly antiferromagnetically to singly occupied orbitals of the $t_{2g}$ subshell at the respective metal ion but ferromagnetically to each other in 3 containing a Co$^{III}$ ion with a filled $t_{2g}$ subshell. The oxidation level of the ligands and metal ions could be unequivocally determined by high-quality X-ray
crystallography in conjunction with EPR, UV-vis, and Mössbauer spectroscopies. The molecular and electronic structures have also been compared by authors with those of their o-semiquinonato analogues.

**Derya Kara and Mahir Alkan** (2001) have reported the synthesis and analytical applications of \( \text{N}_2 \text{N} \text{'-bis(2-hydroxy-5-bromo-benzyl)} \text{1,2 diaminopropane (HBDAP). Fe(III) reacts with this compound in the range of pH 3–6 and produce a red complex (2:3 mol ratio of Fe(III)/HBDAP) which is soluble in chloroform. As mentioned by 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 \( \sim 1.23 \times 10^{-7} \text{ M Fe(III)} \) and the limit of quantitation (taken as ten times the standard deviation of the reagent blank) is about \( 4.11 \times 10^{-7} \text{ M Fe(III)} \). Good separation of Fe(III) from Ni(II), Fe(II), Co(II), Cd(II), Mn(II), Zn(II), Pb(II) have also been achieved at pH 3–5.

**Shuji Kimura et al.** (2001) have synthesized three hexadentate, asymmetric pendent arm macrocycles containing a 1,4,7-triazacyclononane-1,4-diacetate backbone and a third, N-bound phenolate or thiophenolate arm. In \([L^1]_3\)
the third arm is 3,5-di-tert-butyl-2-hydroxybenzyl, in \([L^2]_3\) it is 2-mercaptobenzyl, and in \([L^3]_3\) it is 3,5-di-tertbutyl-2-mercaptobenzyl. With trivalent metal ions these ligands form very stable neutral mononuclear complexes \([\text{M}^{\text{III}} L^1] \text{ (M ) Ga, Fe, Co)}, [\text{M}^{\text{III}} L^2] \text{ (M ) Ga, Fe, Co)}, \text{ and [M}^{\text{III}} L^3] \text{ (M ) Ga, Co})\) where the gallium and cobalt complexes possess an \( S = 0 \) and the iron complexes an \( S = 5/2 \) ground state. Some of synthesized complexes have been characterized by X-ray crystallography. Cyclic voltammetry shows that all three \([\text{M}^{\text{III}} L^1] \) complexes undergo a reversible, ligand-based, one-electron oxidation generating the mono-cations \([\text{M}^{\text{III}} L^1]^+ \) which contain a coordinated phenoxy radical which has also been established by their electronic absorption, EPR, and Mössbauer spectra. In contrast, \([\text{M}^{\text{III}} L^2] \) complexes in \( \text{CH}_3\text{CN} \) solution undergo an irreversible one-electron oxidation where the putative thyl radical mono-cationic intermediates dimerize with S-S bond formation yielding dinuclear disulfide.
species \([M^{\text{III}} L^2-L^3M^{\text{III}}]^{2+}\). \([\text{GaL}^3]\) behaves similarly despite the steric bulk of two tertiary butyl groups at the 3,5-positions of the thiophenolate, but \([\text{Co}^{\text{III}} L^3]\) in \(\text{CH}_2\text{Cl}_2\) at -20 to -61 °C displays a reversible one-electron oxidation yielding a relatively stable monocation \([\text{Co}^{\text{III}} L^3]^+\). Its electronic spectrum displays intense transitions in the visible region at 509 nm \((\varepsilon) 2.6 \times 10^3 \text{M}^{-1}\cdot\text{cm}^{-1})\) and 670sh, 784 (1.03 \times 10^3) typical of a phenylthiyl radical. The EPR spectrum of this species at 90 K proves the thyl radical to be coordinated to a diamagnetic cobalt(III) ion \((g_{\text{iso}}) 2.0226; A_{\text{iso}}(^{59}\text{Co}) 10.7 \text{G})\).

Safavi and H. Abdollahi\(^{131}\) (2001) 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 which 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 authors. For individual determinations, molar absorptivities of 8.46 \times 10^3 (Fe, 650nm), 4.76 \times 10^4 (Co, 458 nm) and 2.61 \times 10^4 (Ni, 538 nm), have been obtained, the limit of detection being 0.11, 0.04 and 0.04 mg/ml, 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 mg/ml Fe, 0.05–2 mg/ml Co and 0.05–2.5 mg/mL 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 authors.

Lian Guojun and Pan Liqin\(^{132}\) (2001) 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 has been 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 \times 10^4 \text{µmol.L}^{-1}, and the apparent molar absorptivity 1.72
x $10^4$ 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.

Lu Guoren\textsuperscript{133} (2001) have presented a method for the rapid determination of Fe in ferro-aluminium alloy by spectrophotometry. In hexamine buffer solution at pH 5-6, a stable complex has been formed by Fe$^{3+}$ and EDTA which show maximum absorbance at 420 nm having molar absorptivity 87.4 L.mol$^{-1}$.cm$^{-1}$. This complex obeyed Beer’s law at 0-4.5 mg/50 mL as reported.

Ahmed A. T. M. Tanvir\textsuperscript{134} (2001) have studied the comparative absorptiometric characteristics of the iron(II) complexes of 3-(2-pyridyl)-5,6-diphenyl-as-triazine (PDT), 3-(2-pyridyl)-5, 6-bis(p-methoxyphenyl)-as-triazine (PBMPT), and 3-(4-phenyl-2-pyridyl)-5, 6-bis(p-methoxyphenyl)-as-triazine (PPBMPT) together with the compound available 1,10-phenanthroline, 4,7-diphenyl-1, 10-phenanthroline, and 2,4,6-tripyridyl-s-triazine (TPTZ) have been studied. Among these chromogenic reagents PPBMPT ($\varepsilon$569 = 37,500 dm$^3$/mol-cm) shows the highest sensitivity and 1, 10-phenanthroline ($\varepsilon$510 = 11,250 dm$^3$/mol-cm) is the least sensitive towards iron (II). The reagents forms tris complex with iron (II) and act as bidentate ligands except TPTZ, which forms a bis-complex and acting as a tridentate ligand. Since A sensitive spectrophotometric method which is based on the formation of the CHCl$_3$-extractable PBMPT Fe(II) complex with the potential of detecting $1.7\times10^{-3}$ µg/mL (1.7 ppb) of iron in water samples has been described by authors.

Li Yong zhong and Liu Shujuan\textsuperscript{135} (2001) have studied the color reaction of 5-(4- carboxy-phenylazo)-8-hydroxyquinoline (5-CPAHQ) with Fe(III) and optimum condition for it. In the presence of CTMAB 5-CPAHQ reacted 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 $4.14 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$, and Beer's law obeyed at 0-14 µg/25 mL. In this reaction KF, thiourea and Na citrate has been used as mixed masking agent. As mentioned by 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 98.1-
103.5%.

Zhao Ye et.al.\textsuperscript{136} (2001) 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\textsubscript{3}
TPPS\textsubscript{4}) in the pH range 3.5-5.5. At 446nm, the
apparent molar absorptivity of the complex is \(2.0 \times 10^4\) L.mol\textsuperscript{-1}.cm\textsuperscript{-1}
which obeys Beer's law in the range of 0-10 μg/25mL. The method has been used for the
determination of iron in the peanut shell with satisfactory results, as mentioned by
authors.

Du Licheng et.al.\textsuperscript{137} (2001) have reported that in the presence of diluted
HCl and Mn(II), Fe(III) reacted with diantipyrylphenylethylene methane in 100°
water bath to form a red complex. The complex has a molar absorptivity of \(1.44 \times 10^6\)
L.mol\textsuperscript{-1} cm\textsuperscript{-1} at 540 nm and obeys Beer's law in the range of 0.04-0.8 μg
Fe(III) 25 mL\textsuperscript{-1}. The method could be applied to the determination of trace Fe(III)
in natural water.

Reddy V. Krishna et.al.\textsuperscript{138} (2001) have proposed A 1st derivative
spectrophotometric method which 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 1st 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
μg.mL\textsuperscript{-1} of Cu(II) at 443 nm and 0.14-4.20 μg.mL\textsuperscript{-1} of Fe(III) at 540 nm. As
described by 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.
Guo Hang-Ming et al.\textsuperscript{139} (2001) have presented 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 $3.1 \times 10^4 \text{ L.mol}^{-1}\cdot\text{cm}^{-1}$ (at 749 nm). The complex solution obeys Beer's law in the concentration range 0-50 $\mu$g/25 mL for iron (at 749 nm). As authors mentioned the proposed method could also be applied to the determination of trace iron in water with satisfactory results.

Liu Chang-Zeng\textsuperscript{140} (2001) 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 $2.2 \times 10^{-11}$ g/mL and the linear range of determination is 0.0-2.0 ng/mL. The method has been used by author for determination of trace iron (II) in distilled water, analysis pure sodium chloride and analysis pure hydrochloric acid with satisfactory results.

Zhang Liping et al.\textsuperscript{141} (2001) 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 $\mu$g/mL, and the molar absorptivities 2.832 x $10^5$ (524 nm) and 2.777 x $10^5$ (520 nm), respectively.

Long Jianlin and Heng Linsen\textsuperscript{142} (2001) have reported A method for the spectrophotometric determination of Fe which is based on its color reaction with N-2-hydroxyphenylamino-N-2-hydroxy-1-cyclobutene-3,4-dione. A yellowish brown solution compound has been formed by Fe$^{3+}$ and the reagent in a pH = 1 HCl buffer medium. The absorption maximum of the compound was at 455 nm, and the molar absorptivity 1.7 x $10^3$. Ag$^+$, Cu$^{2+}$, EDTA, citric acid, tartaric acid, PO$_4^{3-}$, and some oxidants, such as H$_2$O$_2$, NaNO$_2$, etc., shows interferences on the determination. As authors described the method has been used for the determination of Fe in Fe(NO$_3$)$_3$ and electroplating wastewater samples.
Hou Jin et al.\cite{143} (2001) 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 have been formed by Mn(II), Fe(III), Cu(II), Zn(II) and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and OP. The $\lambda_{\text{max}}$ 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 $1.13 \times 10^5$, $7.32 \times 10^4$, $1.02 \times 10^5$ and $1.04 \times 10^5$ respectively and the observed linear range is 0-0.4 mg/L. 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.

Fan Zhefeng et al.\cite{144} (2001) have presented a new spectrophotometric method for the determination of Fe with polyethylene glycol-(NH$_4$)$_2$SO$_4$-1,10-phenanthroline system. A stable complex with the ratio of 1:3 has been 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 $1.1 \times 10^4$, and Beer's law is obeyed at 0-50 $\mu$g. As authors described the method has been used in the determination of Fe in serum and hair samples.

Kara D. and Alkan M.\cite{145} (2001) 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. Authors reported 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 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 $\sim 1.23 \times 10^{-7}$ M Fe(III) and the limit of quantitation (taken as ten times the standard deviation of the reagent blank) is $\sim 4.11 \times 10^{-7}$ M Fe(III). A single extraction gave 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), Pb(II) has also been achieved at pH 3-5.
Wu Daiun and Wu Shaozu\textsuperscript{146} (2001) have studied the determination of iron by centrifugation-photometry. The results revealed an apparent molar absorptivity \( = 3.08 \times 10^6 \text{ L.(mol.cm)}^{-1} \), and a linearity of \( \text{Fe}^{3+} \) content 0.4-6.0 mg.L\(^{-1} \). The method has also been applied by authors to the analysis of trace iron in pure chemical reagent.

Bao Gui-lan et.al.\textsuperscript{147} (2001) have determined Different content 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 \( 1.70 \times 10^3 \text{ L.mol}^{-1}.\text{cm}^{-1} \). 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.

Zhang Shu-Min et.al.\textsuperscript{148} (2001) have studied that Quercetin(Qu) reacted with Fe(III) to form a complex (\( \lambda_{\text{max}} = 430 \text{ nm} \)) in the buffer solution of HAc-NH\(_4\)Ac(pH = 4.05). A linear relationship holds between the absorbance and the concentration of Fe(III) in the range of \( 2.0 \times 10^{-5} \) to \( 1.2 \times 10^{-4} \) mol/L. The detection limit is \( 2.0 \times 10^{-5} \) mol/L. The complex ratio of Fe(III):Qu is 1:2 and the stability constant is \( 1.0 \times 10^8 \).

Hashem Elham Y.\textsuperscript{149} (2001) have 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 0.1M NaClO\(_4\). The complexation reactions have been demonstrated and characterized. A simple, rapid, and sensitive method which is based on the formation of the Fe(III)-DHB complex at pH 2.5 (\( \lambda_{\text{max}} = 520 \text{ nm}, \varepsilon = 0.8 \times 10^4 \text{ L/mol·cm} \)) has been developed for the spectrophotometric determination of Fe(III). 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.
Patel K. S. et al.\textsuperscript{150} (2001) have presented a new, simple, selective, and sensitive spectrophotometric procedure for the on-site quantification of Fe at nano-gram levels in atmospheric precipitations, i.e. rain as sample source. This method is based on the color reaction of Fe\textsuperscript{3+} with SCN\textsuperscript{-} ions in the presence of a cationic surfactant, i.e. cetylpyridinium chloride (CPC), in strong HCl solution. The subsequent extraction of the complex has been done with N-octylacetamide into toluene or chloroform. The apparent molar absorptivity of the complex is $2.60 \times 10^5$ L.mol\textsuperscript{-1}.cm\textsuperscript{-1} at $\lambda_{\text{max}} = 480$ nm. The detection limit (causing higher absorbance than the sum of the blank absorbance (0.009) and 3 SD) is 5 ng.mL\textsuperscript{-1} Fe. Ions commonly associated with Fe did not interfere in the present method as described by authors. The presented method has also been applied to the determination of Fe at the ppb level in rainwater samples.

Qiu Feng-xian and Yao Cheng\textsuperscript{151} (2001) have studied the chromogenic reaction of a new organic reagent 4-(2-pyridylazo)pyrocatechol (PAPC) with Fe(II). In the presence of reductant such as ascorbic acid and polyethylene glycol p-octylphenyl ether (OP), Fe(II) has 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 $3.89 \times 10^{14}$. At the maximum absorption wavelength of 494 nm, the apparent molar absorptivity is $4.96 \times 10^4$ L/mol/cm. Beer's law is obeyed in the range of 0 to 0.8 $\mu$g/mL Fe(II). As authors mentioned in applying the method to determination of trace iron in aluminium alloys the satisfactory results have been obtained.
2. Summary of analytical reagent available for iron determination and details their off

<table>
<thead>
<tr>
<th>S.No</th>
<th>Name of analytical reagent</th>
<th>λmax</th>
<th>Molar absorptivity</th>
<th>Sandell’s sensitivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1-nitroso-2-naphthol</td>
<td>443.6 nm</td>
<td>$1.6 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
<td>5.8 ng.cm$^{-2}$</td>
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<tr>
<td>2.</td>
<td>Acetophenone 2',4'-dihydroxy semicarbazone [A24DHS]</td>
<td>350 nm</td>
<td>3899.2 L.mol$^{-1}$.cm$^{-1}$</td>
<td>0.0288 µg.cm$^{-2}$</td>
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</tr>
<tr>
<td>3.</td>
<td>2,2'-ethylenebis(nitrilo-methylidene)diphenol(H$_2$EBNMDP)</td>
<td>383 nm</td>
<td>$2.29 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
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<tr>
<td>4.</td>
<td>2-aminophenol (OAP)</td>
<td>402 nm</td>
<td>$6.65 \times 10^5$ L.mol$^{-1}$.cm$^{-1}$</td>
<td>5 ng.cm$^{-2}$</td>
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<tr>
<td>5.</td>
<td>2-hydroxy-3-methoxy benzaldehyde-p-hydroxy benzoic hydrazone (HMBAHBH)</td>
<td>390 nm</td>
<td>$1.87 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
<td>$2.9 \times 10^3$ µg.cm$^{-2}$</td>
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<tr>
<td>6.</td>
<td>4,7-diphenyl-1,10-bathophenanthroline (DPBP)-eosin</td>
<td>542 nm</td>
<td>$2.23 \times 10^5$ L.mol$^{-1}$.cm$^{-1}$</td>
<td>0.0025 ng.cm$^{-2}$</td>
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<tr>
<td>7.</td>
<td>5-[(Phenyliminoethyl)]-3-hydroxyphenol [PIEHP]</td>
<td>430 nm</td>
<td>$0.726 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
<td>0.07692 mg.cm$^{-2}$</td>
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<tr>
<td>8.</td>
<td>p-bromophenylazo-bis-acetoxime</td>
<td>370 nm</td>
<td>$1030$ dm$^3$.mol$^{-1}$.cm$^{-1}$</td>
<td>54.22 ng.cm$^{-2}$</td>
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<td>9.</td>
<td>KSCN solution and Et rhodamine B</td>
<td>620 nm</td>
<td>$1.08 \times 10^5$ L.mol$^{-1}$.cm$^{-1}$</td>
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<tr>
<td>10.</td>
<td>solid phase extraction</td>
<td>644 nm</td>
<td>$1.09 \times 10^5$ L.mol$^{-1}$.cm$^{-1}$</td>
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<td>S.No</td>
<td>Name of analytical reagent</td>
<td>λmax</td>
<td>Molar absorptivity</td>
<td>Sandell’s sensitivity</td>
<td>Reference</td>
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<tr>
<td>11</td>
<td>N-(o-methoxybenzaldehyde)-2-aminophenol (NOMBAP)</td>
<td>470 nm</td>
<td>3166 L.mol⁻¹.cm⁻¹</td>
<td>0.0176 mg.cm⁻²</td>
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<tr>
<td>12</td>
<td>SCN (I) and Rhodamine B</td>
<td>620 nm</td>
<td>3.38 × 10⁶ L.mol⁻¹.cm⁻¹</td>
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<td>13</td>
<td>Acetophenone 2',5'-dihydroxy thiosemicarbazone (ADHTS)</td>
<td>430 nm</td>
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<td>14</td>
<td>2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone (HNAHBH)</td>
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<td>15</td>
<td>N-(o-hydroxybenzylidene)pyridine-2-amine (NOHBPA)</td>
<td>530 nm</td>
<td>4469.27 L.mol⁻¹.cm⁻¹</td>
<td>0.0125 mg.cm⁻²</td>
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<td>16</td>
<td>5-(4-nitrophenyl azo) salicylic acid (NPAS)</td>
<td>545 nm</td>
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<td>17</td>
<td>Chromazurol S (CAS) in the presence of tetradecyltrimethylammonium bromide (TTA) and Triton X-100 (TX100)</td>
<td>650 nm</td>
<td>1.12 × 10⁵ L.mol⁻¹.cm⁻¹</td>
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<td>Chromazurol S (CAS) in the presence of octadecyltrimethyl ammonium chloride (ODTA) and Triton X-100 (TX100)</td>
<td>659.5</td>
<td>1.35 × 10⁵ L.mol⁻¹.cm⁻¹</td>
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<td>18</td>
<td>dibromo-p-nitro-chlorophosphonazo</td>
<td>610 nm</td>
<td>1.63 × 10⁴ L.mol⁻¹.cm⁻¹</td>
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<td>S.No</td>
<td>Name of analytical reagent</td>
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<tr>
<td>19</td>
<td>Phenanthroline</td>
<td>510 nm</td>
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<td>20</td>
<td>Catechol and p-nitro aniline</td>
<td>540 nm</td>
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<td>Catechol and m-nitroaniline</td>
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<td>0.0634 mg.cm^{-2}</td>
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<td>21</td>
<td>o-carboxy phenylazo-bis-acetoxime</td>
<td>376 nm</td>
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<td>22</td>
<td>catechol and p-anisidine</td>
<td>565 nm</td>
<td>1.7 × 10^3 L.mol^{-1}.cm^{-1}</td>
<td>0.033 mg.ml^{-1}</td>
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<td></td>
<td>catechol and p-chloroaniline</td>
<td>545 nm</td>
<td>1.6 × 10^3 L.mol^{-1}.cm^{-1}</td>
<td>0.035 mg.ml^{-1}</td>
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<tr>
<td>23</td>
<td>Phenylazo-bis-acetoxime</td>
<td>362 nm</td>
<td>1.852 × 10^3 dm^3.mol^{-1}.cm^{-1}</td>
<td>30.15 ng. cm^{-2}</td>
<td>51</td>
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<tr>
<td>24</td>
<td>3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT)</td>
<td></td>
<td>2.4 × 10^4 L.mol^{-1}.cm^{-1}</td>
<td></td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT) with ion pair reagent potassium salt of tetrabromophenol phthaleinethylester (TPBE-K)</td>
<td></td>
<td>1.9 × 10^5 L.mol^{-1}.cm^{-1}</td>
<td></td>
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<tr>
<td>25</td>
<td>Phenylfluorone in the presence of Tween-20</td>
<td>620 nm</td>
<td>9.355 × 10^4 L.mol^{-1}.cm^{-1}</td>
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<td>55</td>
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<tr>
<td>26</td>
<td>1-(2-pyridyl-azo)-2-naphthol (PAN)</td>
<td>768 nm</td>
<td>8.936 × 10^4 L.mol^{-1}.cm^{-1}</td>
<td></td>
<td>59</td>
</tr>
<tr>
<td>27</td>
<td>N,N-dodecyltrimethylammoniumbromide (DTAB)</td>
<td></td>
<td>3.8 × 10^3 L.mol^{-1}.cm^{-1}</td>
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<td>S.No</td>
<td>Name of analytical reagent</td>
<td>$\lambda_{\text{max}}$</td>
<td>Molar absorptivity</td>
<td>Sandell’s sensitivity</td>
<td>Reference</td>
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<tr>
<td>28</td>
<td>1-(2-pyridylazo)-2-naphthol (PAN)</td>
<td></td>
<td>$1.51 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
<td></td>
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<tr>
<td>29</td>
<td>Desipramine hydrochloride (DPH)</td>
<td>630 nm</td>
<td>$3.288 \times 10^3$ L.mol$^{-1}$.cm$^{-1}$</td>
<td>0.0130 $\mu$g.cm$^{-2}$</td>
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<td></td>
<td>Trimipramine maleate (TPM)</td>
<td></td>
<td>$3.374 \times 10^3$ L.mol$^{-1}$.cm$^{-1}$</td>
<td>0.0331 $\mu$g.cm$^{-2}$</td>
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<td>30</td>
<td>4-(2-thiazolylazo) resorcinol</td>
<td>733 nm</td>
<td>$6.98 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
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<td></td>
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<tr>
<td>31</td>
<td>8-aminoquinidine (AQ)</td>
<td>600 nm</td>
<td>$1.157 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
<td></td>
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<tr>
<td>32</td>
<td>2-5-bromo-pyridylazo-5-diethylaminophenol (5-Br-PADAP)</td>
<td>744 nm</td>
<td>$3.09 \times 10^5$ L.mol$^{-1}$.cm$^{-1}$</td>
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<tr>
<td>33</td>
<td>5-bromosalicylaldoxime (5-BSO)</td>
<td>460 nm</td>
<td>$0.018 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
<td>$3.2 \times 10^6$ $\mu$g.cm$^{-2}$</td>
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<tr>
<td>34</td>
<td>5-sulfosalicylic acid</td>
<td>490 nm</td>
<td>$1.7141 \times 10^3$ dm$^3$.mol$^{-1}$.cm$^{-1}$</td>
<td>32.5845 ng/cm$^2$</td>
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<td></td>
<td>Tiron</td>
<td>670 nm</td>
<td>$1.870 \times 10^3$ dm$^3$.mol$^{-1}$.cm$^{-1}$</td>
<td>29.8553 ng/cm$^2$</td>
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<tr>
<td>35</td>
<td>Diacetylmonoximebenzoyl hydrazone</td>
<td>360 nm</td>
<td>$1.25 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
<td>0.0045 $\mu$g/cm$^2$</td>
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<td>36</td>
<td>2,4-dihydroxybenzaldehydeiso nicotinoylhydrazone (2,4-DHBINH)</td>
<td>400 nm</td>
<td>$1.75 \pm 0.025 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
<td>0.0034 $\mu$g/cm$^2$</td>
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<td>37</td>
<td>Thiocyanate</td>
<td>480 nm</td>
<td>$2.9565 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
<td>0.002 $\mu$g/cm$^2$</td>
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</tr>
<tr>
<td>38</td>
<td>5-Br-PADAP and Triton X-100</td>
<td></td>
<td>$4.48 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$</td>
<td></td>
<td>89</td>
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<tr>
<td>39</td>
<td>1,2-dimethyl-3-hydroxypyrid-4-one (Hdmp)</td>
<td>450 nm</td>
<td>$4.4 \text{ L.mol}^{-1}.\text{cm}^{-1}$</td>
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<td>40</td>
<td>4,7-diphenyl-1,10-phenanthroline and tetraphenylborate</td>
<td>534 nm</td>
<td>$2 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$</td>
<td>0.0025 $\mu$g/cm²</td>
<td>94</td>
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<tr>
<td>41</td>
<td>8-hydroxyquinadine</td>
<td>595 nm</td>
<td>$7.82 \times 10^3 \text{ L.mol}^{-1}.\text{cm}^{-1}$</td>
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<td>97</td>
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<tr>
<td>42</td>
<td>9-(4-carboxyphenyl)-2,3,7-trihydroxyl-6-fluorone</td>
<td>640 nm</td>
<td>$1.06 \times 10^5 \text{ L.mol}^{-1}.\text{cm}^{-1}$</td>
<td>3.9 ng.cm²</td>
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<td>43</td>
<td>Potassium iso-Bu xanthate (KIBX)</td>
<td>378 nm</td>
<td>$2.58 \times 10^3 \text{ dm}^3.\text{mol}^{-1}.\text{cm}^{-1}$</td>
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<tr>
<td>44</td>
<td>p-sulfonamidophenylazobisacetoxime</td>
<td>405 nm</td>
<td>$1.853 \times 10^3 \text{ dm}^3.\text{mol}^{-1}.\text{cm}^{-1}$</td>
<td>30.14 ng.cm²</td>
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<td>45</td>
<td>Diphenylcarbazone (HDCO)</td>
<td>500 nm</td>
<td>$0.4 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$</td>
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<td>46</td>
<td>8-hydroxyquinaldine</td>
<td>600 nm</td>
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<td>47</td>
<td>Piroxicam (PR)</td>
<td>510 nm</td>
<td>$1.82 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$</td>
<td>17.32 ng.cm²</td>
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<td>48</td>
<td>p-methylisonitrosoacetophenone (MINAP)</td>
<td>650 nm</td>
<td>$6.515 \times 10^3 \text{ L.mole}^{-1}.\text{cm}^{-1}$</td>
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<td>49</td>
<td>Phenenthroline(phen)</td>
<td>515 nm</td>
<td>$1.23 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$</td>
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<td>114</td>
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<tr>
<td>50</td>
<td>pyrogallol red</td>
<td>648 nm</td>
<td>$3.24 \times 10^3 \text{ L.mol}^{-1}.\text{cm}^{-1}$</td>
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<td>51</td>
<td>Rutin</td>
<td>620 nm</td>
<td>$4.40 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$</td>
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<td>Sandell’s sensitivity</td>
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<tr>
<td>52</td>
<td>5-bromo salicylaldehyde thiosemicarbazone (5-BSAT)</td>
<td>385 nm</td>
<td>$1.72 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
<td>0.032 μg.cm$^{-2}$</td>
<td>122</td>
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<tr>
<td>53</td>
<td>Diformylhydrazine (DFH)</td>
<td>470 nm</td>
<td>0.3258 - 0.3351 $\times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
<td>0.0168 μg.cm$^{-2}$</td>
<td>123</td>
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<tr>
<td>54</td>
<td>N-(o-methyl)phenyl-N-hydroxy-N'(o-methyl)phenylbenzamidine hydrochloride</td>
<td>470 nm</td>
<td>1.1480 $\times 10^4$ L.mole$^{-1}$.cm$^{-1}$</td>
<td>0.0047 cm$^{-2}$</td>
<td>124</td>
</tr>
<tr>
<td>55</td>
<td>di-2-pyridyl ketone salicyloylhydrazone(DPKSH)</td>
<td>375 nm</td>
<td>4.21 $\times 10^4$ L.mol$^{-1}$.cm$^{-1}$ [Fe (II)] &amp; 1.26 $\times 10^4$ L.mol$^{-1}$.cm$^{-1}$ [Fe(III)] &amp; 1.27 $\times 10^4$ L.mol$^{-1}$.cm$^{-1}$ [Fe(II)]</td>
<td>127</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>2-aminocyclo-1-pentenedithiocarboxylic acid (ACDA)</td>
<td>650 nm</td>
<td>$8.46 \times 10^3$ L.mol$^{-1}$.cm$^{-1}$</td>
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<td>57</td>
<td>PAN-S</td>
<td>756 nm</td>
<td>$1.72 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
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<td>58</td>
<td>EDTA</td>
<td>420 nm</td>
<td>87.4 L.mol$^{-1}$.cm$^{-1}$</td>
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<td>59</td>
<td>5-(4- carboxy-phenylazo)-8-hydroxyquinoline (5-CPAHQ)</td>
<td>448 nm</td>
<td>$4.14 \times 10^4$ L.mol$^{-1}$.cm$^{-1}$</td>
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<td>135</td>
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<tr>
<td>S.No</td>
<td>Name of analytical reagent</td>
<td>λ\text{max}</td>
<td>Molar absorptivity</td>
<td>Sandell’s sensitivity</td>
<td>Reference</td>
</tr>
<tr>
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</tr>
<tr>
<td>60</td>
<td>meso-tetra(4-methoxy-4-sulfonophenyl)porphyrin (p-OCH\textsubscript{3}TPPS\textsubscript{4})</td>
<td>2.0 × 10\textsuperscript{4} L.mol\textsuperscript{-1}.cm\textsuperscript{-1}</td>
<td></td>
<td></td>
<td>136</td>
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<tr>
<td>61</td>
<td>Diantipyrylphenylethlenemthane</td>
<td>540 nm</td>
<td>1.44 x 10\textsuperscript{6} L.mol\textsuperscript{-1}·cm\textsuperscript{-1}</td>
<td></td>
<td>137</td>
</tr>
<tr>
<td>62</td>
<td>2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP)</td>
<td>749 nm</td>
<td>3.1 × 10\textsuperscript{4} L.mol\textsuperscript{-1}·cm\textsuperscript{-1}</td>
<td></td>
<td>139</td>
</tr>
<tr>
<td>63</td>
<td>chrome azurol S and 8-quinolinol</td>
<td>520 nm</td>
<td>2.777 x 10\textsuperscript{5} L.mol\textsuperscript{-1}·cm\textsuperscript{-1}</td>
<td></td>
<td>141</td>
</tr>
<tr>
<td>64</td>
<td>N-2-hydroxyphenylamino-N-2-hydroxy-1-cyclobutene-3,4-dione</td>
<td>455 nm</td>
<td>1.7 × 10\textsuperscript{3} L.mol\textsuperscript{-1}·cm\textsuperscript{-1}</td>
<td></td>
<td>142</td>
</tr>
<tr>
<td>65</td>
<td>2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and OP</td>
<td>560 nm</td>
<td>7.32 x 10\textsuperscript{4} L.mol\textsuperscript{-1}·cm\textsuperscript{-1}</td>
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<td>143</td>
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<tr>
<td>66</td>
<td>1,10-phenanthroline</td>
<td>508 nm</td>
<td>1.1 × 10\textsuperscript{4} L.mol\textsuperscript{-1}·cm\textsuperscript{-1}</td>
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<tr>
<td>67</td>
<td>sulfosalicylic acid</td>
<td></td>
<td>1.70 × 10\textsuperscript{3} L.mol\textsuperscript{-1}·cm\textsuperscript{-1}</td>
<td></td>
<td>147</td>
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<tr>
<td>68</td>
<td>resorcylic acid (2,4-dihydroxybenzoic acid, DHB)</td>
<td>520 nm</td>
<td>0.8 × 10\textsuperscript{4} L.mol\textsuperscript{-1}·cm\textsuperscript{-1}</td>
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<td>149</td>
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<td>69</td>
<td>SCN\textsuperscript{-}</td>
<td>480 nm</td>
<td>2.60 × 10\textsuperscript{5} L.mol\textsuperscript{-1}·cm\textsuperscript{-1}</td>
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<td>150</td>
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<tr>
<td>70</td>
<td>4-(2-pyridylazo)pyrocatechol (PAPC)</td>
<td>494 nm</td>
<td>4.96 × 10\textsuperscript{4} L.mol\textsuperscript{-1}·cm\textsuperscript{-1}</td>
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3. References


PART-B : REVIEW ON MECHANOCHEMICAL SYNTHESIS OF METAL COMPLEXES

The present review survey brings out an up to date compilation on mechanochemical synthesis of metal complexes. The review includes work done on mechanochemical synthesis of complexes using various ligands and their application. Recent research on nanomaterial as well as solvent free synthesis is catching attraction of chemists due to important applications of such materials including bioactivity. So the work will be of utmost importance for drug development as well as synthesis of nano material using simple synthetic routes. The literature since 2004 has been surveyed and up to date information on the mechanochemical synthesis of metal complexes or related compound has been compiled. It is being presented in form of text and the citations i.e. references have been reported as per standard format.

Brede Franziska A. et.al. (2016) have reported that Liquid assisted grinding (LAG) reactions can successfully applied to formation of a series of complexes and coordination polymers which are based on divalent 3d-transition metal chlorides (TM chlorides) and the aromatic ligand 1H-benzotriazole (BtzH, 2). These substances were studied by single crystal X-ray, powder X-ray determination and simultaneous DTA/TGA as model compounds for structural and chemical influences on their dielectric properties. Different constitutions and structures are observed, depending on the synthesis method. When mechanochemical LAG route were used for synthesis, two polymorphous forms of the 1D polymer \( \approx [\text{MnCl}_2(\text{BtzH})_2] \) (1) as well as the complexes \([\text{ZnCl}_2(\text{BtzH})_2] \text{BtzH} \) (3) and \([\text{CoCl}_2(\text{BtzH})_2] \text{BtzH} \) (4) were obtained as phase-pure bulk substances and even single crystals are also available. Simultaneously thermal reactions were carried out which gave the neutral complexes: \([\text{CoCl}_2(\text{BtzH})_2] \) (5) and \([\text{CoCl}_2(\text{BtzH})_4] \text{4BtzH} \) (6), \([\text{ZnCl}_2(\text{BtzH})_2] \) (7) and the anionic complex \( \text{BtzH}_2[\text{CoCl}_3\text{BtzH}] \) (8). In addition, thermal treatment of complex 3 yields the benzotriazolium salt \{(BtzH)\text{BtzH}}\text{Cl} \) (9). By frequency-dependent as well as temperature-dependent permittivity studies the transition metal compounds were additional analyzed regarding their dielectric properties.
Compounds 1 and 3 show remarkably low dielectric constants and loss factors up to 50° named as potential "low-k materials".

Cao Hujun et.al. \(^2\) (2016) have synthesized K\(_2\)[Mn(NH\(_2\))\(_4\)] and K\(_2\)[Zn(NH\(_2\))\(_4\)] successfully via mechanochemical method. The mixture of K\(_2\)[Mn(NH\(_2\))\(_4\)] and LiH showed excellent rehydrogenation properties. Fully rehydrogenation of K\(_2\)[Mn(NH\(_2\))\(_4\)]-8LiH occurs after dehydrogenation within 60 s at ca. 230 °C and 5 MPa of H\(_2\). which is one of the fastest rehydrogenation rates in amidehydride systems known. This process also shows a strategy for the synthesis of transition metal nitrides by decomposition of the mixtures of M[M'(NH\(_2\))\(_n\)] (where M is an alkali or alkaline earth metal and M' is a transition metal) and metal hydrides.

Brede Franziska A. et.al. \(^3\)(2016) have synthesized complexes of [MCl\(_2\)(TzH)\(_4\)] (M = Mn (1), Fe (2); TzH = 1,2,4-1H-triazole) and [ZnCl\(_2\)(TzH)\(_2\)] (3) type by mechanochemical reactions of the corresponding divalent metal chloride and 1,2,4-1H-triazole. Either by a microwave-assisted reaction or by thermal conversion, these were successfully used as precursors for the formation of coordination polymers. The conversion yielded directly for Mn, 1 \(\propto\)[MnCl\(_2\)TzH] (4), whereas the Fe-containing precursor, 1 \(\propto\)[FeCl\(_2\)TzH] (6), was formed via the intermediate coordination polymer 1 \(\propto\)[FeCl(TzH)\(_2\)]Cl (5). But by a microwave-induced reaction directly from CoCl\(_2\) form the isotypic polymer of Co, 1 \(\propto\)[CoCl(TzH)\(_2\)]Cl (7) was obtained. The crystal structures were resolved from single crystals and powders and the dielectric properties were determined which revealed large differences in permittivity between the precursor complexes and the rigid chain-like coordination polymers. Whereas, the monomeric complexes exhibit very different dielectric behavior, depending on the transition metal, from low-k to high-k with the permittivity ranging from 4.3 to >100 for frequencies of up to 1000 Hz. The coordination polymers and complexes having strong intermolecular interactions are all close to low-k materials with very low dielectric constants up to 50°. Therefore, the presented conversion procedures can be beneficial to deliberately influence the dielectric properties from complex to polymer and for different 3d transition-metal ions.
Michael Philipp and Binder Wolfgang H.\textsuperscript{4} (2015) have reported "Click" chemistry which is the most powerful approach for linking molecules in chemistry and materials science. This reaction was triggered by mechanical force which enables site- and stress-specific "click" reactions - a hitherto unreported observation. Authors introduced the design and realization of a homogeneous Cu catalyst which is able to activate through mechanical force when attached to suitable polymer chains, acting as a lever to transmit the force to the central catalytic system. Activation of the subsequent copper-catalyzed "click" reaction (CuAAC) is achieved either by ultrasonication or mechanical pressing of a polymeric material, using a fluorogenic dye to detect the activation of the catalyst. Based on an N-heterocyclic copper(I) carbene with attached polymeric chains of different flexibility, the force is transmitted to the central catalyst, thereby activating a CuAAC in solution and in the solid state.

Adams Christopher J. \textit{et.al.}\textsuperscript{5} (2015) have presented the two-step mechanochemical preparation of carbene-pyridine complexes of palladium and platinum. The organometallic products are rapidly formed in excellent yield proving solvent-free synthesis to be a viable synthetic alternative even in the case of NHC-containing compounds.

Wang Xiao-Feng \textit{et.al.}\textsuperscript{6} (2015) have synthesized a series of methotrexatum intercalated layered double hydroxide (MTX/LDH for short) hybrids by a mechanochemical-hydrothermal method. To play as the examined factors in the orthogonal design four variables, i.e., addition of NaOH solution, grinding duration, hydrothermal temperature and time, were chosen by authors. Furthermore, three respective levels, i.e., high, medium and low levels, are conducted. The resulting hybrids were characterized by X-ray diffraction (XRD) patterns, transmission electron microscope (TEM) graphs and Zeta potentials. XRD diffractions indicate that MTX anions have been successfully intercalated into LDH interlayers and the gallery height can change greatly by the amount of NaOH solution. The TEM graphs and Zeta potentials states that the increase of alkali solution gives rise to regular morphology and the increase of Zeta potentials. As a result of the statistical analysis, addition of alkali solution is the
major factor affecting the morphology and drug-loading capacity. At last, the mechanism of particle growth is explored emphatically, and the anticancer efficacy of some MTX/LDH hybrids is estimated by MTT assay on A549 cells as well.

Hyatt Michael G. and Allenbaugh Rachel J. (2015) have reported mechanochemical synthesis of dialkyl 2,2'-bipyridyl-4,4'-dicarboxylate (Lβn, where βn refers to the no. of carbons in β-substituted alkyl chain) complexes including PtLβ16Cl2, CdLβ16Cl2, [AgLβnNO3] and the dodecylsulfate salt [AgLβn 2](DOS), at reduced cost and in shorter times, compared to traditional solvent-based methods. Thie reaction occurs in the absence of solvent. PtLβ16Cl2 and the [AgLβn 2](DOS) complexes are the first mesogenic transition metal complexes to be produced via ball milling. For increasing the stable temperature range of a variety of metallomesogens and for producing sub-room-temperature liquid crystals the effectiveness of a simple ligand modification, β- vs. α-attachment of the alkyl functionalities to the ligand, was presented by authors.

Hernandez Jose G. et.al. (2014) have demonstrated the mechanochemical oxidative addition and ligand substitution on organometallic centers which can be mutually orthogonal, permitting the rational design of multi-component mechanochemical reaction procedures for assembling complex or solution-sensitive organometallic species from three, four or even five components in one pot. This represents a new level of complexity in mechanochemical reactions by milling and is the first to combine redox and ligand substitution reactions into mechanochemical procedure for either one-pot sequential ("telescoping") or one-pot multi-component syntheses. This method has been explained mechanochemical transformations solvent-free, room-temperature syntheses of relatively complex organometallics directly for simple zero valent metal carbonyls as the simplest precursors and also demonstrate the efficiency of mechanochemical oxidative addition by targeting selected pentacarbonyl halides of rhenium(I) and manganese(I), and illustrate the potential of multi-step organometallic mechanochemistry in the syntheses of selected fac-tricarbonyl complexes of these metals.
**Rightmire Nicholar R. et al.** (2014) have reported a solid-state mechanochemical synthesis as solvent-free synthetic route for metal allyl complexes of electropositive metals with sterically demanding allyl ligands. Compounds of the form $A'xM$ ($A' = [1,3-(SiMe_3)_2C_3H_3]$) are traditionally synthesized by salt metathesis in ethereal solvents (e.g., Et$_2$O, THF). The use of such ethers can often lead to products containing coordinated solvent molecules that are not always subsequently removable, either in whole or in part. The presence of such solvents control product reactivity, influence binding modes of the bulky allyls, or even redirect reaction pathways, so that desired products do not form. In this paper authors described synthesis and characterization of $A'xM$ complexes formed in the absence of reaction solvent.

**Scholz Gudrun et al.** (2014) have reported the mechanochemical synthesis as easy process to obtain alkaline earth metal terephthalates $M(C_8H_4O_4)\cdot nH_2O$. In presented paper the authors describe the mechanochemical synthesis of powders of $Ca(C_8H_4O_4)\cdot 3H_2O$, $Ca(C_8H_4O_4)$, $Sr(C_8H_4O_4)\cdot H_2O$, and $Ba(C_8H_4O_4)$, which were only synthesized as single crystals from aqueous solutions or by reactions in an autoclave. In this paper a new hydrate $Ba(C_8H_4O_4)\cdot 2(1.5)H_2O$ was prepared which is not described so far in the literature. All compounds were characterized by x-ray powder diffraction, thermal analysis, elemental analysis, FTIR, and MAS NMR spectroscopic measurements.

**Gomes Clara S. B. et al.** (2014) have reported the preparation of Ni(II) and Co(II) complexes containing $\alpha$-diimine ligands using a mechanochemical approach. The solvent-free reaction of $[NiBr_2(DME)]$ (DME = 1,2-dimethoxyethane) with the appropriate $\alpha$-diimine ligand gave the expected Ni(II) complexes in very short reaction times and with quantitative yields. The same compounds were also synthesized when NiBr$_2$ was employed. This methodology was extended to the preparation of $[Co(\alpha$-diimine)Cl$_2$] complexes through the reaction of CoCl$_2$ with different $\alpha$-diimine ligands. These compounds were characterized by XRPD and SCXRD, when possible Mechanochemistry has an enormous potential and is an effective technique for the synthesis of coordination and organometallic compounds.
Tell a A. C. et al. 12 (2014) have studied solid-state mechanochemical synthesis of [Cu(CAF)2(H2O)(OAc)]OAc complex 1a and [Cu(COD)2(H2O)(OAc)]OAc complex 2a by grinding stoichiometric amounts of Cu(CH3COO)2·H2O and corresponding non-steroidal anti-inflammatory drugs[caffeine (CAF) and codeine (COD)], respectively, in a mortar with pestle. Solvent-based synthesis of 1b and 2b was also carried out by reaction of metal acetate salt and each drug by solution based method. The complexes formed were characterized by comparison of elemental analysis, FT-IR, UV-Vis and 1H NMR spectra with those of the free ligand and solvent-based products. The analytical and spectroscopic data of the complexes prepared via both two different methods are almost identical. X-ray diffraction patterns of the complexes prepared by mechanochemical method were different from that of the starting material reveals formation of new metal complexes. In vitro inhibitory activities of both mechanochemical and solvent-based complexes were found to be higher than parent ligands, indicating that the antimicrobial effect of these drugs could be enhanced when they are chelated to the metal. The mechanochemical synthesis was carried out without the use of solvent or external heating. The solid state reaction presented higher efficiency in terms of materials, energy and time compared to solvent-based synthesis.

Mandal Haridas et al. 13 (2014) have synthesized three new structurally diverse zinc(II) complexes of formula [H3O][ZnL2]ClO4 (1), [Zn2(μ-L)2(NCS)2] (2) and [Zn3(μ-L)2(μ-N3)4]n (3) using the same furan-based tridentate ONO-donor Schiff base ligand HL (2-hydroxybenzyl-2-tetrahydrofurylmethyl)imine and characterized by x-ray structural anal. Complex 1 is mononuclear, whereas complex 2 is a double phenoxido-bridged dinuclear compound and compound 3 was the novel polymeric from azido coordination driven aggregation possesses a very rare 1D structure in which the dinuclear ligand-bound Zn3L2 fragments are bridged by four ligand-free μ1,1-azido bridging Zn(N3)4 2- units resulting in a zigzag arrangement of repeating triangular Zn3 motifs with structural similarity to the P1 nuclease.
Solid state mixing and grinding processes were applied for the ligand exchange reaction and core conversion. In mechanochemical solvent free synthetic routes 1 reacts with isothiocyanato and azido ions to provide 2 and 3 in pure form. In MeOH medium, the ligand HL serves as sensitive fluorescent probe for Zn\(^{2+}\), and complex 1 for SCN\(^-\) and N\(_3\) \(^-\) ions. Coordination induced fluorescence enhancement due to intraligand \(\pi \rightarrow \pi^*\) transition in the presence of Zn\(^{2+}\) of HL and quenching of emission intensities of 1 with SCN\(^-\) and N\(_3\) \(^-\) anions are accounted for by the formation of hitherto unknown complexes [Zn(L)(X)] (X = ClO\(_4\) \(^-\), SCN\(^-\) and N\(_3\) \(^-\)). HL shows chelation-enhanced fluorescence response from strong metal ion coordination and binding of isothiocyanato and azido anions with an appreciable lifetime of the fluorophore signals. Excitation at 380 nm of MeOH solutionns of all three complexes in air exhibit excited state lifet ime spanning from 2.5-4.8 ns.

**Fekri Ahmed and Zaky Rania**\(^{14}\) (2014) have prepared, 2-(2,4-Dichlorophenoxy)-N′-(2-hydroxybenzylidene)acetohydrazide (H\(_2\)L) complexes by ball milling involving the reaction of ligand with Ni(II), Co(II), Cu(II) and VO(II) salts (mechanochemical synthesis). The compounds were characterized by elemental analysis, \(^1\)H NMR, IR, UV-visible, MS spectroscopy and by physical measurements i.e. magnetic susceptibility and molar conductance. IR spectra suggested that the H\(_2\)L behaved as a monodentate and/or bidentate ligand coordinating via azomethine N and/or deprotonated enolized carbonyl O. The electronic spectra of the complexes and their magnetic moments provided information about geometries. The biological activities of synthesized compounds have also been evaluated by authors.

**Ferguson Michael et.al.**\(^{15}\) (2014) have reported the use of ball milling to induce reactions between solids (mechanochemical synthesis) to provide lower-waste routes to chemical products by avoiding solvent during the reaction. Further, authors reported their potential advantages in one-pot multistep synthesis to avoid the use of bulk solvents for the purification of intermediates. In present paper two-step synthesis involving formation of salen-type ligands from diamines and hydroxaldehydes followed directly by reactions with metal salts to provide
the corresponding metal complexes have been presented. Five salen-type ligands namely (2,2'-[1,2-ethanediylbis[(E)-nitrilomethylidyne]]bis-phenol, 'salenH2', 1; 2,2'-[(±)-1,2-cyclohexanediylbis[(E)-nitrilomethylidyne]]bis-phenol, 2; 2,2'-[1,2-phenylenebis(nitrilomethylidyne)]bis-phenol, 'salphenH2' 3; 2-[(2 aminophenyl) imino]methyl]phenol, 4; 2,2'-[(±)-1,2-cyclohexanediylbis[(E) nitrilomethylidyne]]bis[4,6-bis(1,1-dimethylethyl)phenol, 'Jacobsen ligand', 5) form readily in a shaker-type ball mill. The only ligand which required the addition of solvent was the Jacobsen ligand 5. The one-armed salphen ligand 4 could also be obtained selectively by changing the reaction stoichiometry to 1:1. SalenH2 (1) was explored for the one-pot two-step synthesis of metal complexes. After in situ formation of the ligand by ball milling, metal salts (ZnO, Ni(OAc)2·4H2O or Cu(OAc)2·H2O) were added directly to the jar and milling continued for a further 30 min. Small amts. of methanol were needed for these reactions to run to completion. The corresponding metal complexes [M(salen)] (M = Zn, 6; Ni, 7; or Cu, 8) in hydrated form were thus obtained quantitatively after 30min, and could be heated to give analytical pure dehydrated products. The all-at-once 'tandem' synthesis of [Zn(salen)] 6 was also explored by milling ZnO, ethylenediamine and salicylaldehyde together in the appropriate mole ratio for 60 min. This approach also gave the target complex selectively with no solvent needed. Overall, these syntheses are highly efficient in terms of time and the avoidance of bulk solvent both. Thus the present work demonstrates the applicability of mechanochemical synthesis to one-pot multi-step strategies.

Mac Donald Neil A. et.al. 16 (2013) have presented solid-state synthesis of organometallic complexes and relatively compared with previous work focusing on either thermally-induced transformations or the creation of coordination and supramolecular complexes. Mechanochemical ball-milling have expanded the technique to synthesize a wide variety of compound which has hardly been explored for the synthesis of organometallic complexes. Authors reported the use of ball milling to carry out ligand substitution of group (VI) metal(0) hexacarbonyls with a halide ion (Cl, Br, I). Compounds of this nature have become of interest for their therapeutic applications as CO releasing molecules.
(CORMs). Authors discussed comparisons between the conventional solution-phase synthesis, solid-state thermal reactions and mechanochemical ball milling.

Lu Lingbin et.al.\textsuperscript{17} (2013) have reported green mechanochemical technique which is grinding-based method, was applied for synthesis of multi-metal cyanide (MMC) complexes. In order to discover the effect of metal element on structure and catalyst efficiency, the obtained three MMCs were made from different three metal salts groups, and three MMCs were further used for copolymerization of CO\textsubscript{2} and propylene oxide. FTIR and \textsuperscript{1}H NMR results shown, the alternating copolymerization obtained anticipated poly(propylene carbonate) with high catalytic activity. Comparing to the conventional solvent-based synthesis reveals that grinding-based method has merits for syntheses of MMC complexes.

Ni Jun et.al.\textsuperscript{18} (2013) have reported discrete metal complexes, \([\text{MCl}_{2} (\text{CEAP})_2]\) \(\{\text{M} = \text{Zn} (1), \text{Co} (2) \text{and Hg} (3), \text{CEAP} = 4-[,]^{N,N}\text{-bis}(2\text{-cyanoethyl})\text{amino}\}\text{pyridine}\}) and their hydrogen-bonded salts \([\text{CEAPH}]_2[\text{MCl}_4]\) \(\{\text{M} = \text{Zn} (4), \text{Co} (5) \text{and Hg} (6), \text{CEAPH} = 4-[,]^{N,N}\text{-bis}(2\text{-cyanoethyl})\text{amino}\}\text{pyridinium}\}) were prepared using CEAP or CEAP·HCl ligands and metal chlorides (molar ratio = 2:1) by both solvent-thermal synthesis method and solvent-free method. The crystal structure and powder x-ray diffraction (PXDR) studies revealed that the discrete metal complexes 1-3 could be converted into their hydrogen-bonded salts 4-6 respectively by absorbing HCl vapor in solid-gas station and these salts except for 6 could be converted back to their corresponding discrete metal complexes by grinding with KOH in solid station.

Yun Jin-Shik et.al.\textsuperscript{19} (2013) have reported carbon-coated Li\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}-LiMnPO\textsubscript{4} composite cathode materials prepared by the mechanochemical process with a complex metal oxide as the precursor and sucrose as the carbon source. X-ray diffraction pattern of the composite material indicates that both olivine LiMnPO\textsubscript{4} and monoclinic Li\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} co-exist. In present paper the electrochemical properties of our Li\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}-LiMnPO\textsubscript{4} composite cathode materials using galvanostatic charging/discharging tests were determined. The composites display unique electrochemical performances in terms of overvoltage.
and cycle stability, displaying a reduced gap between charge and discharge voltage and have more capacity, efficiency after 15th cycles.

Ramhold Dietmar et al. (2012) have reported metal chelates with amino acids LnM (1, HL = glycine, lysine, methionine; M = Cu, Zn, Mn, Fe, Ca, Mg, Co, V, Se, Ni), useful as bio available forms of microelements for animal nutrition, were prepared by solid-state process, comprising reaction of dry, having less amount of humidity, mechanical preactivated in a mill device metal oxides, carbonates, sulfates, chlorides or hydroxides with amino acids HL at >100° with concomitant separation of the reaction water, which precludes baking of the reaction product.

R.B. Nasir Baig et al. (2012) have presented mechanochemical, microwave and ultrasound-assisted organic synthesis as alternative energy input. By applying these alternative methods a number of chemical transformations have been achieved by many existing protocols with superior results as compared to results obtained under traditional conditions.

James Stuart L et al. (2012) have reported mechanochemistry as opportunity for new and cleaner synthesis. In this critical review authors reported the reactions conducted by grinding solid reactant together with no or minimal solvent. As opportunity it provides more sustainable methods. This review covers industrial aspects, inorganic materials, organic synthesis, co-crystallization, pharmaceutical aspects, metal complexes (including metal-organic frameworks) supramolecular aspects and characterization methods and discussed historical developments, mechanistic aspects, limitations and opportunities.

Wang pipi et al. (2012) have reported mechanochemical interconversion between discrete complexes and coordination networks – formal hydration/dehydration by liquid assisted grinding (LAG). As reported by the authors (LAG) of metal salts or oxides (ZnO, CdO, CdCO3, Cu(OAc)2·H2O, Co(OAc)2·4H2O, Mn(OAc)2·4H2O, Ni(OAc)2·4H2O, FeSO4·7H2O) with two equivalent of isonicotinic acid (HINA) and small amounts of water gave discrete aquo complexes trans-[M(INA)2(OH)24] (M = Zn, Cd, Cu, Fe, Co, Ni, Mn)
efficiently within 30 minutes by using small planetary ball mill. The complexes formed by M = Zn, Cd and Cu readily undergo reversible formal dehydration to the extended network structures [M(INA)_2] (M = Zn, Cu) whereas in case of M= Cd further LAG of [Cd(INA)_2(OH)_2]-DMF with non-aqueous liquids such as methanol or DMF is required for the same. So, the mechanochemical dehydrations are more effective than heating or immersion in bulk solvents. This article demonstrated two step mechanochemical synthesis of coordination networks via discrete aquo complexes which may be preferable to single step reactions or grinding-annealing procedures. Mechanochemically [Cd(INA)_2(OH)_2]-DMF can be prepared by only two step method and the porous network Cu(INA)_2 could not be obtained from the aqua complex by heating.

Friscic tomslav (2012) has reported supramolecular concepts and new techniques in mechanochemistry to prepare co-crystals, cages, rotaxanes, open metal organic frameworks and interlocked architectures. Author suggested that in milling mechanochemistry and supramolecular chemistry the basic relationship is the ability to avoid bulk solvent which avoids limitations of solution based chemistry like solubility, solvent complexation, and solvolysis which makes the process highly environmentally friendly. In this article author systematically explored different modes of molecular self assembly and chemical reactions dependent on molecular recognition can be conducted by mechanochemical methods which can effected by milling or grinding. This review highlights on synthesis of supramolecular targets in solid state like molecular hydrogen of halogen-bonded complexes. It has been also demonstrated that molecular self-assembly phenomena which already established in solution chemistry like reversible binding through covalent or non-covalent bonds, thermodynamic equilibration and structure templating can also be accessible in milling mechanochemistry by using LAG or ion-liquid assisted grinding (ILAG). In this article the new opportunities by using both supramolecular and mechanochemical synthesis combinely including organocatalysis, deracemisation and discovery of new molecular recognition motifs has also been explored.
Jobbágy csaba et al. (2011) have reported a versatile solvent free mechanochemical route to the synthesis of heterometallic dicyanoaurate based coordination polymers. As authors reported that this mechanochemical method is fast, simple and efficient route to synthesis of heterometallic [Au(CN)\(_2\)]-based coordination polymers. By using this method authors prepared, pure dicyanoaurate based compounds by grinding stoichiometric amounts of K[Au(CN)\(_2\)] and transition metal(II) chlorides whereas aqueous solution synthesis leads to an unseparable mixture of products. This method can also be applied to main group metals to obtain various cyanoaurate based heterometallic coordination polymers. Authors also explained the reaction rate of 2:1 mixture of K[Au(CN)\(_2\)] and Me\(_2\)SnCl\(_2\) dramatic enhanced by presence of minor amount of water. The bonding pattern of Ph\(_3\)Sn[Au(CN)\(_2\)] was explained by using single crystal X-ray diffraction. By heating or grinding of moderate pink Co(H\(_2\)O)\(_2\)[Au(CN)\(_2\)]\(_2\) complex dehydrated blue Co[Au(CN)\(_2\)]\(_2\) complex was obtained.

Sun Jie et al. (2011) have reported dimerization of a metal complex through thermally induced single-crystal to single crystal transformation or mechanochemical reaction. In this article it was explained that the mononuclear copper complex [Cu(NH\(_3\))\(_3\)](L\(_6\))·(H\(_2\)O)\(_{0.66}\) having flexible dicarboxylate ligand H\(_2\)L\(_6\)2,2'-{(1,2-phenylenebis(methylene))bis(sulfanediyl)-dibenzoic acid, possesses a 3D +6 supramolecular architecture containing 1D tubular subunits composed of double helical chain, could be dimerized through thermal SCSC (single-crystal-to-single crystal) transformation or solid state reaction under dry grinding condition form the binuclear complex. This binuclear complex of copper has different coordination geometry but no change in symmetry was observed. The color change (blue to green) indicated the transformation has potential application in sensing devices. So the results represented that thermally induced dimerization of a metal complex by SCSC transformation involves change in coordination geometry of the metal ion.

Zhang Wuyuan et al. (2011) have presented clean and rapid synthesis of double metal cyanide complexes using mechanochemistry. Authors explained
that it is green chemical technique and demonstrated the synthesis of double metal cyanide complexes \( \text{Zn}_3\text{[M(CN)\textsubscript{6}]_2} \) where [M= Fe,Co] which can be used for the copolymerization of CO\(_2\) and propylene oxide. This is practically applicable and efficient method to improve catalytic activity and selectivity.

**Pribytkova et al.**\(^{28}\) (2011) have reported mechanochemical preparation of water soluble composites based on quercetin. As authors explained, solid composites of the bioflavonoid quercetin with metal carbonates and carbohydrate compounds formed by mechanochemical method have more solvolysis and antioxidant activity.

**Lu Jian et al.**\(^{29}\) (2011) have reported formation of C-N bond in metal free solvothermal condition and organic complexes built by halogenated molecules. In this article, by combinational use of solvothermal and mechanochemical method reactions of two halogenated derivatives of bis(4-hydroxyphenyl)sulfone (BPS, 1), tetrabromobisphenol-S (TBBPS, 2), and tetrachlorobisphenol-S (TCBPS, 3), with piperazine (PZ, 4), were investigated. The organic complexes formed were fully characterized by single crystal and powder x-ray diffractions.

**Bowmaker Graham A. et al.**\(^{30}\) (2011) have presented single x-ray diffraction and IR spectroscopic studies of Cu(II)halide /pyridine systems synthesized by mechanochemical method. Authors reported, that complexes of divalent metal halides (X = Cl, Br, I) with/from pyridine commonly crystallize as trans-\([\text{M(py)}_4\text{X_2}] \cdot 2\text{py}\), M on a site of 222 symmetry in space group Ccca, true for CuCl\(_2\) and CuBr\(_2\) in particular, the Cu(II) iodide adduct is \([\text{Cu(py)}_4\text{I}] \cdot 2\text{py}\). In this article the space group arrangement of cation and anion present in the complex were mentioned. It has also been explained that in the solvated salt unbound iodide ion may be substituted by bromide and N-thiocyanate which gives disorder in both anion and metal atom arrangement in space group. The \([\text{CuII(py)}_4]\) entity can be stabilized in an unexpectedly diverse range of mononuclear and multinuclear complexes through the presence of lattice pyridine molecules, the bulky tri-iodide ion, or a combination of both.
Willans Charlotte E. et.al.\textsuperscript{31} (2011) have reported reversible vapor sorption with and without significant structural changes in tripodal imidazole frameworks (TIFs) which is based on a tripodal, cavity-containing 1,3,5-tris(imidazolyl methyl)-1,2,6-triethylbenzene. Authors also explained their framework structures, characteristics and demonstrated, preparation of some materials by mechanochemical as well as solution based method.

Tella Adedibu Clement et.al.\textsuperscript{32} (2011) have reported four metal-organic coordination compounds were synthesized from 2,4-dinitrophenylhydrazine in the absence of solvent. The complexes were characterized by AAS, conductivity, TLC, IR, UV-Vis spectroscopy, and x-ray powder diffraction. In all complexes formed, the ligand coordinated with the metal ion through the nitrogen of the amino group (NH\textsubscript{2}), nitrogen of hydrazinic band and oxygen atom from each of the two acetate ions to complete octahedral geometry. The m.p., color, and x-ray diffraction patterns of the complexes were different from that of the ligand suggested formation of coordination compounds.

Ramaswamy padmini et.al.\textsuperscript{33} (2010) have reported studies of synthesis, structure and solid state transformation of phosphonoacetate based hybrid compounds of uranium and thorium. In the present paper authors synthesized three new phosphonoacetate hybrid frameworks. These are built up from the connectivity between the metal polyhedra and the phosphonoacetate/oxalate units. These compounds can be prepared by using solvent free solid-state reaction at various temperatures and characterized by powder x-ray diffraction, IR spectroscopy, TGA and fluorescence studies.

Strobridge Fiona C et.al.\textsuperscript{34} (2010) have studied role of water in liquid assisted grinding in synthesis of metal-organic frameworks. The mechanism of synthesis of co-ordination polymers by liquid assisted grinding at room temperatures by using catalytic amount of water has also been demonstrated. In this article mechanochemical synthesis of zinc fumarate and copper (II) acetate proceeds through a stepwise mechanism and the intermediate formation of solvates with water and acetic acid involved as kinetic product. The zinc fumarate
LAG synthesis using three different natured solvent has been performed and detail of synthesis by grinding have also given.

Adams Christopher J. et.al.\textsuperscript{35} (2010) have reported synthesis of imidazole and pyrazole complexes with platinum and palladium in the solid state. Authors illustrated solid state reaction of $K_2[MCl_4]$ or $MCl_2$ with imidazole (Him) and pyrazole (Hpz) or their hydrochloride salts to produce imidazolium and pyrazolium tetrachlorometallates and co-ordination compounds. To produce the co-ordination compound $K_2[MCl_4]$ or $MCl_2$ can further grind with imidazolium chloride which produce their respective salt. These salts further dehydrochlorinated in the solid state. They may have cis or trans-geometry. The single crystal structure of product was reported by XRPD data.

Zhang Qiwu et.al.\textsuperscript{36} (2010) have reported mechanochemical reaction and its intrinsic nature to form complex oxide. In this article authors introduced the rule of reaction to form complex oxide. Trivalent and pentavalent metals have been used for reaction and found that the reactivity of trivalent oxide depends on the product formed. Authors also focused on decomposition of halogen containing organic polymer when co-grinding with oxide additives. The decomposition of polymers depends on the materials and its mechanism is classified into dechlorination and dehydrochlorination. The radicals on the product created during the grinding have been detected by ESR analysis which is useful to understanding the mechanochemical decomposition of the polymers.

Adams Christopher J. et.al.\textsuperscript{37} (2010) have reported the synthesis and interconversion of pyrazolium salts pyrazole complexes and pyrazolate metal organic frameworks in the solid state. Solid pyrazole react with HCl gas to form pyrazolium chloride which reacts in the solid state, under grinding with metal chlorides $MCl_2$ to form the pyrazolium tetrachlorometallate salts. Upon standing at room temperatures or ground together with bases, they emit HCl to give their respective co-ordination compound. These compounds can also be synthesized in the solid state by direct reaction of the appropriate metal chloride with pyrazole or by reaction of a basic metal salt with pyrazolium chloride and they can be further grind with two equivalent of base to make the known polymeric metal...
pyrazolates. The imidazolate complexes were similarly prepared by grinding the appropriate precursor with KOH.

Adams Christopher J. et.al.\textsuperscript{38} (2010) have studied reactivity of manganese and cadmium chlorides with imidazole, pyrazole and their hydrochlorides in the solid state. Authors demonstrated that crystal co-ordination compounds can be synthesized in solid state reactions by grinding the appropriate metal chloride and 2 equivalent of the neutral ligand. By grinding together the metal chlorides with the ligand hydrochloride salts gives the halometalate salts, whereas reaction of the metal salts with ligand in concentrated HCl solution gives a different set of salts. Some of them can be partly dehydrochlorinated by grinding with KOH to form an impure sample of the pyrazolate compound. They can be recrystallized from ethanol, yielded crystals of solvated co-ordination compound.

Yuan Wenbing et.al.\textsuperscript{39} (2010) have reported synthesis of homo and hetero-rare-earth (III) metal-organic frameworks by ball milling. Authors explained that they can be produced by liquid assisted grinding in a ball mill for 20 minute by reaction between metal carbonates and benzene-1,3,5-tricarboxylic acid in the presence of small amounts of DMF or water.

Chow Ernest H.H. et.al.\textsuperscript{40} (2010) have revisited mechanochemistry of magnesium oxide and facile derivatization of pharmaceuticals using co-ordination and supramolecular chemistry. Authors explored that liquid assisted grinding is rapid, waste free and one pot synthesis of a variety of magnesium drug derivatives directly from the MgO.

Ono Taisuke et.al.\textsuperscript{41} (2010) have presented structural and thermal gas desorption properties of metal aluminium amides. Authors synthesized various metal aluminium amides by ball milling under liquid NH\textsubscript{3}. The data of synchrotron radiation x-ray diffraction suggested that the metal aluminium amide formed were indexed with single phases. Combination of both FTIR and $^{27}$Al MAS/3QMAS NMR shows that all product formed have anion complex unit as basic component indicated synthesis of metal aluminium amides. During thermal decomposition release of NH\textsubscript{3} below 140° shown by TG-DTA coupled with mass
spectroscopy. The NH$_3$ desorption peak temperature decreased with increase in atomic number. This article gives information about the thermal stability of anion complex [Al(NH$_2$)$_4$]$^-$ can be controlled by a cation M.

**Srinivasan Sesha S. et.al.**\(^{42}\) (2010) have reported the effects of nano additives on hydrogen storage behavior of the multinary complex hydride. These multinary complex hydrides contain borohydrides, amides, metal hydrides and synthesized by solid state mechanochemical process. Some LiBH$_4$/LiNH$_2$/MgH$_2$ shown reversible hydrogen storage behavior at temperature of 125-175°C. To improve the hydrogen performance of the system various nano additives were used and observed that some of these additives lowered the hydrogen release temperature upto 75-100°C in major hydrogen decomposition step and some additives behaves as catalyst and increased the rate of hydrogen released. By combinational addition of some selected material found that they shown both positional effect on kinetics and reduction in hydrogen desorption temperature.

**Berchmans L.J. et.al.**\(^{43}\) (2010) have studied one step mechano synthesis and characterization of nanocrystalline CaFe$_2$O$_4$ with orthorhombic structure. In this article characterization of material have been done by using $^{57}$Fe Mössbauer spectroscopy, XRD, HR-TEM and has also been cleared that synthesis of complex oxide is almost completed if this process starting from the metal/oxide system, for 1h mechanochemical treatment at room temperature. The mechano synthesized nanoparticles of CaFe$_2$O$_4$ have average size about 15 nm possess the core-shell structure consisting of an ordered inner core surrounded by a disordered surface shell with the thickness of about 1.9 nm. The main structural features of the surface shell of nanoparticles were distorted oxygen octahedral.

**Frisicic Tomislav et.al.**\(^{44}\) (2009) have reported one pot mechano synthesis with co-ordination bonds, hydrogen bonds and host guest inclusion of molecular self-assembly. To mechano synthesis liquid-assisted grinding (LAG) were used. The one pot process may consists of i) The coordination-driven binding of addends to the equatorially-protected metal ion, resulting in "wheel-and-axle"-shaped complexes; ii) self-assembly of resulting complexes by way of hydrogen-bonded synthons to form metal-organic inclusion hosts; iii) in situ inclusion of the
grinding liquid in the resulting host. By the help of this method inclusion compound obtained in single synthetic step within 20 minutes quantitatively, by changing the liquid phase in LAG the inclusion behavior of new wheel-and-axel adducts. Overall one-pot LAG is more convenient to solution synthesis in screening for metal-organic inclusion compounds. The basic difference could be explained in terms of reactant solubility and solvent competition. The difference in the inclusion properties of two adducts by structural information obtained from single crystal and powder X-ray diffraction has also been reported by authors.

Balch Alan L.45 (2009) has reported mechanochemical changes in the luminescence of gold and other transition-metal complexes which can be visually detected dynamic crystals. Author explained certain crystal complexes of Au, Pt and V which undergoes exciting changes in their luminescence or their color upon grinding. It has also been demonstrated that this process is reversible.

Kuroda Reiko et.al.46 (2009) have focused on heating or annealing process to mechanochemical preparation of co-ordination compounds in the solid state. Heating of metal complexes promotes the liberation of weakly coordinated ligands and remains co-ordination geometry unsaturated in the complex. These unsaturated co-ordination geometry having complexes are activated complexes which can be used as the building blocks of co-ordination polymers in the solid state. Authors further reported co-grinding and annealing treatments of an enantiomeric pair of chiral crystals afford diffusion and rearrangement of transition metal complex ions to form co-crystal phases of racemic or quasi-racemic compounds to recognizing chirality. Formation of co-crystal via chirality transfer between optically stable and labile metal complexes has also been explored.

Bowmaker Graham A. et.al.47 (2009) have reported synthesis and IR spectroscopic studies of two different polymorphs of Cu(I) thiocyanate, adducts of Cu(I)thiocyanate with thiourea (tu) and ethylene thiourea. A mechanochemical /IR study of the complex shown that no 1:2 complexes exists in this case, the product being mixture of a 1:3 complex and a novel 1:0.5 complex. They prepared
complex by using both mechanochemical and solution based method and characterized by IR and solid state $^{65}$Cu broad line NMR spectroscopy.

Zhang Jing et al.\textsuperscript{48} (2009) have reported mechanochemical synthesis of Mg-Li-Al-H complex hydride. For preparation Mg-Li-Al-H complex hydride ingot casting has been used and then undergoes to reactive ball milling. The evolution of various species of the reaction during milling and effect of Li/Al ratio in the raw materials on desorption properties of hydride formed were studied by x-ray diffraction and simultaneous TG and DSC techniques. Milling increases the solvolysis of Li in Mg and leading to the transformation. As authors mentioned a lower Li/Al ratio resulted in faster hydrogen desorption rate and a greater amount of hydrogen released at a low temperature range, but sacrificing total hydrogen storage capacity.

Bowmaker Graham A. et al.\textsuperscript{49} (2009) have prepared 1:1 complexes of Ag(I) thiocyanate with (substituted) thiourea ligands and recorded their single crystal X-ray structural characterization together with IR spectroscopic studies. A mechanochemical/IR study of AgSCN:etu (1:1) system shown that in this case no 1:1 complex exists. The product formed is a mixture of the 1:2 complexes and 1:0.5 complexes. So latter complex was prepared by using both mechanochemical and solution based method and characterized by IR spectroscopy. Authors studied IR spectra of diagnostic ligand and metal-ligand bands. For AgSCN and the entire complex formed they studied far IR spectra and discussed the relation to the structures of the complexes. The double degeneracy of the $\delta$(SCN) mode of the coordinated thiocyanate is lifted and the 1st overtone of this band at gains intensity in the IR in the 1:1 complexes, behavior that is not observed for the terminal bonding mode that is present in the 1:2 complexes.

Braga Dario et al.\textsuperscript{50} (2008) have reported simple and quantitative mechanochemical preparation of complexes of the neuroleptic drug gabapentin with Zn and Cu. Structures of the complexes were detected by single crystal X-ray diffraction and X-ray powder diffraction. The copper complex have trans-square planar geometry whereas zinc complex have tetrahedral co-ordination geometry.
Komarov Yu M et.al.\textsuperscript{51} (2008) have presented mechanochemical synthesis of copper zinc double salts in chemically active gaseous media. In this article it has been reported that mechanochemical activation of Cu and Zn under oxidative condition gives mixed basic carbonate. The composition of reaction product was analyzed by powder x-ray diffraction by using this method, amine and carbonate salts of Cu, Zn and their double salts in solvent free conditions could be obtained. The effect of gas phase components on the aurichalcite yields and kinetics of its formation have also been studied by authors.

Bowmaker Graham A. et.al.\textsuperscript{52} (2008) have reported solvent assisted mechanochemical synthesis of metal complex by using silver halides with ethylenethiourea.

Yoshida Jun et.al.\textsuperscript{53} (2008) have reported formation of 1D and 3D coordination polymers of Bis(3-cyano-pentane-2,4-dionato) (CNacac) metal complexes in solid state which is induced by mechanochemical and annealing treatments. These complexes act as a metal-ion-like and a ligand-like building unit, forms supramolecular structures by self-assembly. Co-grinding of metal acetates Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with CNacacH gives a CNacac complex in all cases: in case of Mn(II), Cu(II) and Zn(II) mononuclear complex was formed whereas in case of Fe(II), Co(II) and Ni(II) polymeric complexes were formed. Subsequent annealing converted the mononuclear complexes of above reported metals, to their corresponding polymers as a result of dehydration of the mononuclear complexes. The resultant polymeric complexes had a common 3-dimensional structure with high thermal stability. In case of Cu(II) 1D-polymer had obtained. On exposure to H\textsubscript{2}O vapor polymeric complexes returned to their original mononuclear complexes but by re-annealing they reverted to the polymeric complexes. Co-grinding of metal chlorides with CNacacH and annealing of the mononuclear CNacac complexes prepared from solution reactions were also examined for comparison. The new compounds obtained clearly indicated the power of the combined mechanochemical/annealing method for the synthesis of varied metal coordination complexes.
Myakishev K.G. et.al.\textsuperscript{54} (2008) have reported mechanochemical synthesis of N,N',N''-trimethylborazine from solvent free mixture of MeNH\textsubscript{2}.HCl and MBH\textsubscript{4} in an evacuated vibrational ball mill and condition for pyrolysis and intermediate formed during reaction.

Bowmaker Graham A. et.al.\textsuperscript{55} (2008) have presented the role of short range diffusion in solvent assisted mechanochemical synthesis of metal complex. Authors studied the polymorphic transition and a ligand dissociation reaction involving Cu(I)thiocyanate complexes.

Manivannan V. et.al.\textsuperscript{56} (2008) have reported mechanochemical activation of complex metal fluoride KMF\textsubscript{3} (M = Mg, Zn, Mn, Ni, Cu and Co) , their metathesis synthesis and characterization. Authors demonstrated the high lattice energy of KCl which is obtained as the byproduct helps the reaction towards product formation within 20 minutes. This proposed method is very rapid, economical and results in products with controled morphology. The structural, optical and chemical properties of synthesized powders were detected by powder X-ray diffraction, SEM, XPS, magnetization measurements and diffused reflectance spectra in the UV-VIS range.

Pichon Anne et.al.\textsuperscript{57} (2008) have reported an array-based approach to obtain insight into reactivity under mechanochemical solvent free conditions. In this paper sixty potential reactions between twelve metal salts MX\textsubscript{2} and five bridging organic ligands have also been described. Reactions proceed via grinding ball mill without external heating. The product obtained from reaction examined by XRPD, which further compared with patterns simulated from single crystal X-ray diffraction data in the Cambridge structural database allowed structural identification. Some products formed by using this method were micro porous or 1-D connectivity. Overall array based approach is a useful way to reveal underlying trends in reactivity under solvent free mechanochemical condition.

Adams Christopher J \textsuperscript{58} (2008) has reported synthesis of co-ordination compounds from basic metal salts by solid state method. Author explored
preparation of the complex salts and co-ordination compounds by a range of solid state and solid gas reaction.

**Srinivasan Sesha et.al.**\(^59\) (2008) have reported effects of catalysts doping on the thermal decomposition behavior of Zn(BH\(_4\))\(_2\). For this authors synthesized Zn(BH\(_4\))\(_2\) by solid state mechanochemical process.

**Santhanam Ranganathan et.al.**\(^60\) (2008) have studied a novel preparation method of hexahydroaluminate complexes M\(_3\)AlH\(_6\) (M = Li, Na or K) from the corresponding alkali metal hydride and tetrahydroaluminate. In this preparation dimethyl ether (Me\(_2\)O) was used as solvent at near-ambient temperatures. The results were compared with established mechanochemical approach. Powder x-ray diffraction revealed M\(_3\)AlH\(_6\) to be formed in high yield for M = Li and Na, but not for M = K. By using this method Li\(_2\)NaAlH\(_6\) and Li\(_2\)KAlH\(_6\) was not prepared.

**Garay Ana Lazuen et.al.**\(^61\) (2007) have reported solvent free synthesis can reduce environmental contamination and even be more convenient than using solvent-based synthesis. In present review authors focused on use of mechanochemistry (grinding) to synthesize metal complexes in the absence of solvent and synthesis of mononuclear complexes, coordination clusters, spacious coordination cages, and 1-, 2- and 3-dimensional coordination polymers (metal organic frameworks) were also included which can even exhibit micro porosity. In many cases, mechanochemical synthesis is faster and more convenient than the original solvent-based methods. In this review some examples of solvent-free methods other than grinding were also discussed briefly.

**Pichon A et.al.**\(^62\) (2006) have reported solvent-free mechanochemical synthesis of a micro porous metal-organic framework [Cu(INA)\(_2\)] (INA = isonicotinic acid); the product has robust 3-dimensional connectivity and was obtained quantitatively by grinding Cu acetate and isonicotinic acid together for 10 minutes without any applied heating. The high efficiency of the synthesis revealed that mechanochemical synthesis works as convenient method for the preparation of micro porous metal-organic frameworks (MOFs).
Fernandez-Bertran J. F. et.al. (2006) have reported synthesis of Ag, Zn, Cd, and Hg imidazolates mechanochemically by milling imidazole and metal oxides in an agate mortar. The reaction products were characterized by FTIR and XRPD techniques. The results obtained for the mechanochemical imidazolates were compared with those obtained by precipitation. The mechanochemical Ag imidazolate has the same orthorhombic crystal structure as the precipitated one. The mechanochemical Zn imidazolate has a tetragonal structure with similar crystal parameters to those of Zn(Imz)$_2$H$_2$O, but no H$_2$O molecules were present in the structure. This new anhydrous form was a polymorph of the one obtained by precipitation. The mechanochemical Cd imidazolate has a monoclinic structure which was the polymorph of the precipitated orthorhombic form. The mechanochemical Hg imidazolate presents a hexagonal structure which is a polymorph of the orthorhombic structure obtained by precipitation. Authors also discussed the influence of the nd electronic configuration of the cations on the mechanochemical reaction.

Miyazaki Y et.al. (2005) have studied heat capacity measurements of the two-dimensional metal-assembled complex, (NEt$_4$) [{MnIII(salen)}$_2$FeIII(CN)$_6$] [Et = Et, salen = N,N'-ethylene bis (salicylideneaminato) dianion], were performed at 0.2-300 K by adiabatic calorimetry. A ferrimagnetic phase transition was observed at T$_{c1}$ = 7.51 K also, another small magnetic phase transition appeared at T$_{c2}$ = 0.78 K above T$_{c1}$, a heat capacity tail arising from the short-range ordering of the spins characteristic of two-dimensional magnets were found. The magnetic enthalpy and entropy were evaluated. The experimental magnetic entropy agreed roughly with $\Delta S = R\ln(5\cdot5\cdot2)$ where R being the gas constant), which is expected for the metal complex with two Mn(III) ions in high-spin state (spin quantum no. S = 2) and one Fe(III) ion in low-spin state (S = 1/2). The heat capacity tail above T$_{c1}$ became small by grinding and pressing the crystal. This mechanochemical effect would be attributed to the increase of lattice defects and imperfections in the crystal lattice, leading not only to formation of the crystal with a different magnetic phase transition temperature but also to decrease of the magnetic heat capacity and thus the magnetic enthalpy and entropy.
Moran M E et al. (2005) have reported a process for preparation of oxalates and their use as precursors in the synthesis of oxides. Authors disclosed preparation of metal oxalates by solid-state mechanochemical reaction of oxalic acid with metal nitrates at temperatures close to ambient. The mixture of oxalic acid and metal nitrates were grind in a mortar and lightly heated, producing a redox reaction between nitrate and oxalate anions (giving NO and CO$_2$), the oxalate also serving to complex the remaining metal ions to give metal oxalates. The metal oxalates can then be thermally treated at appropriate temperatures to give corresponding oxides. Advantages of the process include: (1) a preparation time of only minutes; (2) a small no. of factors affecting reproducibility of results; (3) 100% yield, given that all reaction steps occur in the same mortar; (4) provides a highly generalized preparation of metal oxalates from metal nitrates; (5) allows preparation of oxalates on an industrial scale; and (6) does not require a special atmosphere and avoids the disadvantages of the sol-gel method. For instance, a mixture of polycrystalline powder Cu(NO$_3$)$_2$.3H$_2$O and H$_2$C$_2$O$_4$.2H$_2$O was grind at approx. 70°. Reaction began in several minutes with emanation of gases. After cessation of reaction, a small amount of solvent (H$_2$O, alc., or acetone) was added, and the product dried under grinding and recovered. The purity of the Cu oxalate product was demonstrated by powder X-ray diffraction. Heating of the oxalate in an O$_2$ atmosphere at 400° for 4 h gave CuO, also with an appropriate powder X-ray diffraction spectrum. Similarly La$_2$(C$_2$O$_4$)$_3$ (as the decahydrate) was prepared. This compound was likewise oxidized under heating at 850° to give La$_2$O$_3$. Alternatively, a mixture of Cu and La nitrates were converted to mixed oxalates, which were heated together under O$_2$ at 850° for 4 h to give La$_2$CuO$_4$. In present paper X-ray powder diffraction spectra for various oxalates and oxides have also been attached.

Sokolov Maxim N. et al. (2005) have studied mechanochemical reaction of cluster coordination polymers 1:2[M$_3$Q$_7$Br$_4$] (M = Mo, W; Q = S, Se) with solid K$_2$C$_2$O$_4$ leads to cluster core excision with the formation of anionic complexes [M$_3$Q$_7$(C$_2$O$_4$)$_3$]$^{2-}$. All synthesized compounds were characterized by x-ray structure analysis, IR, Raman, electronic, and $^{77}$Se NMR spectra were also reported. Thermal decomposition of complexes prepared were studied by TG.
Zhang Q et al.\textsuperscript{67} (2004) have reported mechanochemical reactions applicable to syntheses of perovskite-type compounds, LaMO\textsubscript{3}, where M is trivalent metals, were taken as examples to investigate effects of crystal structures of starting materials, M\textsubscript{2}O\textsubscript{3}, on the reactions. The investigated oxides M\textsubscript{2}O\textsubscript{3} were categorized into two groups: one was the corundum structure and the other was the non-corundum structure. Under the experimental conditions, it has been found that the oxides with non-corundum structure react easily with La\textsubscript{2}O\textsubscript{3} by their co-grinding at room temperature to form the corresponding compounds. On the other hand, no such reactions can occur for the oxides with corundum structure. This difference has been discussed on the basis of grinding-induced phase transformation from loose packing of atoms to close packing of atoms. Based on the results, the extension to the synthesis of other compounds such as CrO\textsubscript{2} was presented.

Hihara Goro et al.\textsuperscript{68} (2004) have reported solvent-free solid-solid reactions of dimethylglyoxime (H\textsubscript{2}dmg) with Ni(II) salts or Cu(OAc)\textsubscript{2} were conducted Mechanochemically. Complexes prepared were identified by powder x-ray diffractometry (XRD) and elemental analysis. The progress of some of the solid-solid reactions was followed by the measurement of weight change of the reaction mixture revealed that mechanical energy was used as a driving force for the reactions.

Alacova A. et al.\textsuperscript{69} (2004) have reported application of mechanochemical processing in extractive metallurgy and material science. The selected examples included surface oxidation of mechanical activated sulphides, sorption properties of CaCO\textsubscript{3} after mechanical activation, Au leaching from mechanochemical pretreated Cu-Pb-Zn complex ore concentration, and pilot plant tests of mechanochemical technology. The mechanical reduction of Cu\textsubscript{2}S to prepare nanocrystalline Cu is an example of a novel process for preparation of advanced materials, as authors mentioned.

Braga Dario et al.\textsuperscript{70} (2004) studied the organometallic zwitterions [CoIII(\eta\textsuperscript{5}-C\textsubscript{5}H\textsubscript{4}COOH)(\eta\textsuperscript{5}-C\textsubscript{5}H\textsubscript{4}COO)] reacts quantitatively as a solid polycrystalline phase with a number of crystalline alkali salts MX (M = K\textsuperscript{+}, Rb\textsuperscript{+},
Cs\(^{+}\), NH\(_4\)^{+}; X = Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), PF\(_6\)^{-}, although not in all cation/anion permutations) to afford supramolecular complexes of the formula [CoIII(\(\eta^5\)-C\(_5\)H\(_4\)COOH)(\(\eta^5\)-C\(_5\)H\(_4\)COO)]\(_2\)·M\(^{+}\)X\(^{-}\). In some cases, the mechanochemical complexation requires kneading of the two solids with a catalytic amount of water. The solid-state products were characterized by a combination of x-ray single-crystal and powder-diffraction data. The existence of hydrogen bonding interactions was confirmed by solid-state NMR spectroscopy. The mechanochemical reactions imply a profound solid-state rearrangement accompanied by breaking and forming of O-H...O hydrogen-bonding interactions between the organometallic molecules. All compounds could also be obtained by solution crystallization of the inorganic salts in presence of the organometallic unit. The solid-state complexation of alkali cations by the organometallic zwitter ions was rationalized as a special kind of solvation process taking place in the solid state.

Kolotilov SV et.al.\(^{71}\) (2004) have reported a mechanochemical synthesis of Mn(II), Co(II) and Ni(II) tris(pyrazolyl)borates (Tp-), which enabled preparation of metal complexes TpMCl and TpMCl·Hpz type (Hpz is the substituted pyrazole generated by hydrolysis of the corresponding Tp- ligand). The x-ray structure of a new Co(II) tris(pyrazolyl)borate [TpPh,MeCoCl (HpzPh,Me)], and the electronic spectra of these coordination compounds have also been discussed.
2. REFERENCES


