

## APPLICATIONS OF SCHIFF'S BASES CHELATES IN QUANTITATIVE ANALYSIS : A REVIEW

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### ABSTRACT

Applications of Schiff's bases chelates in quantitative analysis and sample preparation for chemical analysis have been reviewed. The stability of Schiff's bases chelates has been discussed. The uses of Schiff's bases as an analytical chemical reagents and/or separation reagents have been also listed and discussed.

**Keywords:** Schiff's base, Chelates, Quantitative analysis.

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### INTRODUCTION

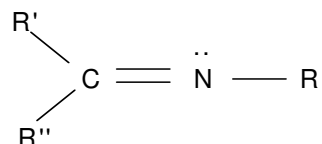
Schiff-bases are considered as a very important class of organic compounds, having wide applications in many biological aspects, proteins, visual pigments, enzymic aldolization and decarboxylation reactions. Moreover, some Schiff's bases and their metal complexes exhibit antibiotic, antiviral and antitumor agents, biological activity.<sup>1,2</sup> They are also used as catalysts in polymer and dyes industry, beside some uses as antifertility and enzymatic agents.<sup>3</sup>

An interesting application of Schiff's bases is their use as an effective corrosion inhibitor, which is based on their ability to spontaneously form a monolayer on the surface to be protected.<sup>4</sup>

In this review we will focus on the application of Schiff's bases in quantitative analytical chemistry.

#### Schiff's bases

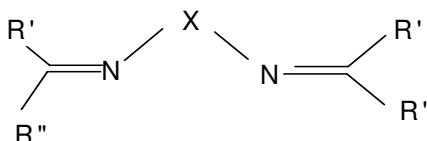
A *Schiff base* or Schiff's base is a type of chemical compounds containing a carbon-nitrogen double bond as functional group, where the nitrogen atom connected to aryl group or alkyl group (R) but not hydrogen. The Schiff base is synonymous with an azomethine. These compounds were named after Hugo Schiff and has the following general structure:



Where R stands for a phenyl or alkyl group which makes the Schiff base a stable imine.

This kind of ligands is able to coordinate metal ions through the imine nitrogen and another group, usually linked to the aldehyde. The chemists still prepare Schiff bases and nowadays active and well-designed Schiff base ligands are considered "privileged ligands".<sup>5</sup>

The bridged Schiff's bases have the following structure which contains many functional groups able to change according to the purpose required.



Where R' = H or alkyl group

R'' = phenyl or substituted phenyl, X = alkyl or aryl group

In fact, Schiff bases are able to stabilize many different metals in various oxidation states controlling the performance of metals in a large variety of useful catalytic transformations.<sup>6</sup>

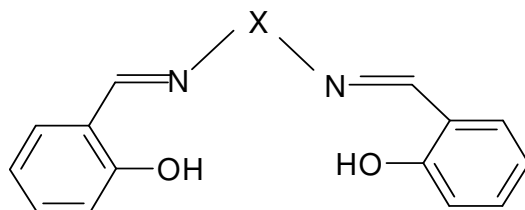
Most commonly Schiff bases have NO or N<sub>2</sub>O<sub>2</sub>-donor groups but the oxygen atoms can be replaced by sulphur, nitrogen, or selenium atoms.<sup>4</sup>

Although the Schiff bases are known to be good chelating agents, and easily prepared and characterized, little interest has been given to their uses for analytical purposes because of two serious drawbacks, they are insoluble in aqueous solutions and they decompose easily in acidic solutions, limiting their use to basic conditions.<sup>7</sup>

This family can be divided into two groups of symmetric and asymmetric Schiff's base. Salens and salophen can be symmetric or asymmetric but hydrazones are the members of the asymmetric Schiff's bases.

### **Salen**

When two equivalents of salicylaldehyde are combined with a diamine, a particular chelating Schiff base is produced. The so-called Salen ligands with four coordinating sites and two axial sites open to ancillary ligands. Although the term Salen was used originally only to describe the tetradentate Schiff bases derived from ethylenediamine, the more general term Salen-type is used in literature to describe the class of [O,N,N,O] tetradentate Schiff base ligands.<sup>5</sup>



Salen compounds are insoluble in aqueous solutions and they decompose easily in acidic solutions, limiting their use to basic condition.

### **Salophen**

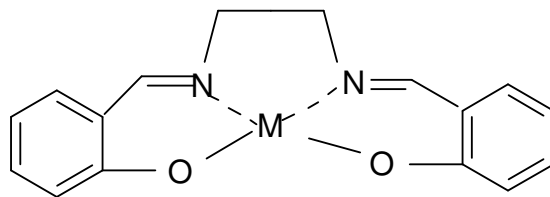
Salophen or acetylparamidophenyl salicylate is a Schiff's base with non-toxic properties, which is an effective substitute for salicylic acid.

### **Hydrazones**

Hydrazones are a class of organic compounds with the general structure of R<sub>2</sub>C=N-NR<sub>2</sub> which are related to ketones and aldehydes by the replacement of the oxygen with the NNR<sub>2</sub> functional group. These compounds are commonly formed through the reaction of hydrazine with ketones or aldehydes.

Schiff's bases are able to coordinate metals through imine nitrogen, and there is a wide use of these metal complexes as catalysts.<sup>5</sup> In the last few years, various Schiff's base complexes of transition metals including Mn(III), Fe(II), Ni(II), Cr(III), Ru(III) etc. have been used as the catalysts for epoxidation of olefins and as mono oxygen sources for catalyst to carry out oxygen transfer to the olefins.<sup>6,7</sup>

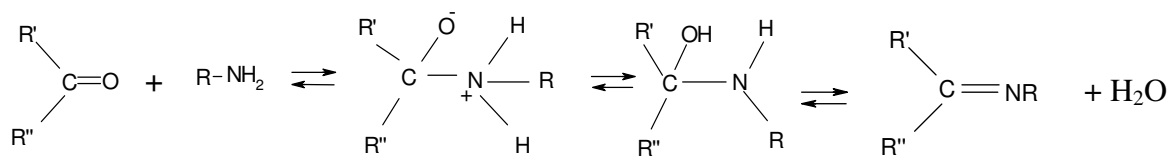
They are easy to synthesize (simply and cheaply) and multidentate. Substitution at the aromatic ring can modify the electronic and steric properties of the resulting complexes (fine-tuning) as it can form metal complexes of various sizes because of its open structure, as shown in the following structure.



Metal chelate of N,N'-Bis(salicylidene)ethylenediamine

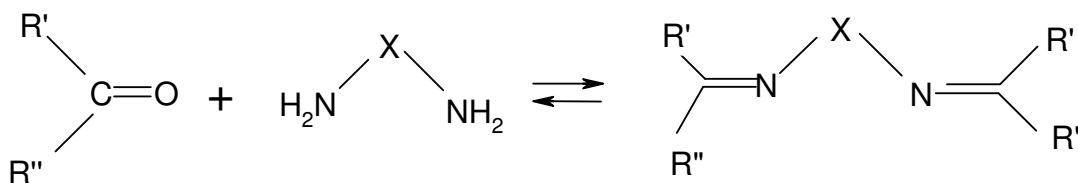
### Synthesis

There are several reaction pathways to synthesise Schiff bases.<sup>5</sup><sup>Error! Bookmark not defined.,8,9</sup> The most common is an acid catalysed condensation reaction of amine with an aldehyde or ketone under refluxing conditions (Scheme -1). The first step in this reaction is an attack of nucleophilic nitrogen atom of amine on the carbonyl carbon, resulting in a normally unstable carbinolamine intermediate. The reaction can reverse to the starting materials, or when the hydroxyl group is eliminated and a C=N bond is formed and the product is called imine. Many factors affect the condensation reaction, for example the pH of the solution as well as the steric and electronic effects of the carbonyl compound and amine. In acidic solutions the amine is protonated, thus cannot function as a nucleophile and the reaction cannot proceed. Furthermore, in very basic reaction conditions the reaction is hindered as sufficiently protons are not available to catalyse the elimination of the carbinolamine hydroxyl group. In general, aldehydes react faster than ketones in Schiff base condensation reactions as the reaction centre of aldehyde is sterically less hindered than that of ketone. Furthermore, the extra carbon of ketone donates electron density and thus makes the ketone less electrophilic compared to aldehyde.<sup>4</sup>



Scheme -1: Preparation of Schiff's bases.

For preparation of the bridged Schiff's bases a diamine compound is required with two molecules of aldehyde or ketone according to the structure of the product of interest as in the following reaction.



Scheme -2

Where R' = H or alkyl group  
 R'' = phenyl or substituted phenyl  
 X = alkyl or aryl group

### Metal salen complexes

Metal salen complexes have a tendency for square-planar geometry as the bridge between the imine moieties forces the *cis*-configuration around the metal centre, although in some cases a slightly distorted geometry towards tetrahedral form exists. When the metal complex has square-planar geometry, the metal ion is in the plane formed by the  $N_2O_2$ -donor atoms and the two axial positions are free for coordination with solvent or other molecules.<sup>10,11</sup>

Metal salen complexes can have an umbrella, stepped, or planar molecular conformation (Figure- 1) due to folding of the six-membered metallocycles and the metal center may deviate from the plane defined by the  $N_2O_2$ -donor atoms. The umbrella and stepped forms are the most common for salen complexes and the strictly planar conformation has been reported only for few complexes.<sup>5</sup>

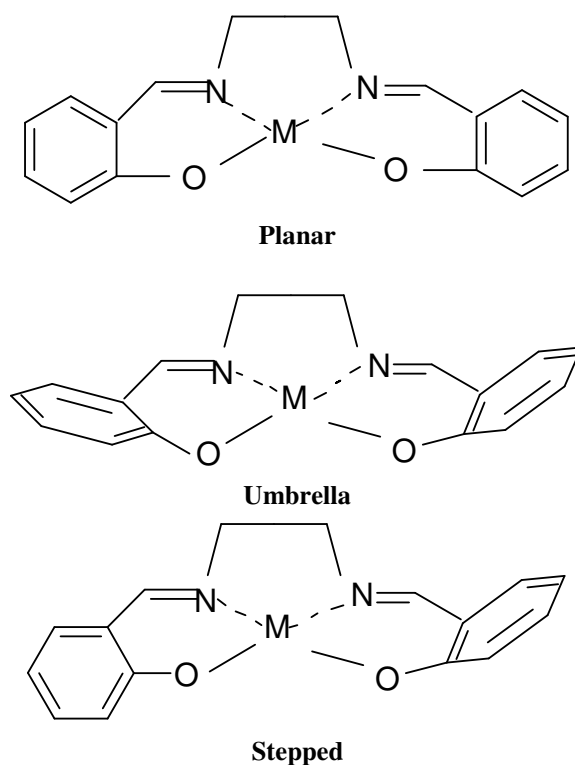


Fig.-1: Schematic presentations of planar, umbrella, and stepped molecular conformation of salen complexes.

Conformation of the ethylene-bridge is closely related to the overall conformation of the salen compound. Fully planar complexes might have an eclipsed conformation ( $N(1)-CH_2-CH_2-N(2)$  torsion angle *ca.*  $0^\circ$ ) but usually the conformation is *gauche*. In *gauche* conformation the carbon atoms of the ethylene-bridge are on the opposite sides of the  $MN_2O_2$ -plane. The geometry around the metal centre in  $N,N'$ -bridged Schiff base complexes may be tuned by altering the length of the bridge, the molecular structure becomes more flexible as the number of methylene groups in the bridge increases.<sup>12</sup> In the salen complexes, which prefer square-planar geometry, dioxygen is coordinated in one axial position and the other axial position is occupied by a base or solvent molecule.<sup>13</sup>

### Applications of Schiff's bases chelates in quantitative analysis

Jungreis and Thabet<sup>14</sup> have reported several applications for Schiff' bases in qualitative and quantitative classical analyses. All these applications did not cover a wide area in analytical chemistry.

Advances in analytical techniques and the development and application of new analytical reagents are as important in trace analyses as the development of analytical instruments

A number of Schiff's base chelating agents used for the detection of metal ions can also be applied for their quantitative determination. The procedures in most cases remain similar.

The main step in the above applications is the complex formation which depends mainly on pH, temperature, cation size, and the structure of the ligand. Optimisation of these factors to enhance the stability of the complex leads to high selectivity of the developed analytical method.

### A. Photometric methods

Developments in photometric methods have been extensive, particularly for the determination of trace amount of metals. A number of these procedures are based on color formation resulting from the reaction between Schiff's base and the metal ion. For example, *o*-[N-(*o*-hydroxyphenyl)formimidoyl]phenol, known as Manganon, forms with manganese(II) at pH 9.1 to 11.6 a brown complex, the absorbance of which is measured at 428nm.

2,2'-(2,6-Pyridinediyl BIS (Methylidene Nitrilo) Phenol has been used by Abdennabi and Anter for spectrophotometric determination of Uranium (VI). The red color developed is measured at 500nm and the molar absorptivity is  $1.19 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>. It was found that a 100- fold excess of Barium, Strontium, Calcium, Lead, Cadmium, Chloride, Nitrate, Sulphate, and Phosphate did not interfere. The interference of some elements such as Fe(III), Cr(III), Hg(II), V(V), and Ti(V) could be eliminated by applying the ion exchange technique using the resine Dowex 1x 8 in the chloride form.<sup>15</sup>

N,N'-Bis(salicylidene)ethylenediamine forms with iron(III) a complex, which is red-violet at a pH less than 5 and yellow at a pH higher than 6, with maximum wavelength 495 and 470nm respectively.<sup>14</sup>

G. Tantar et al. have prepared Salen-type Schiff's base, 1-ethyl-salicylidene-bis-ethylene diamine by condensing ethyl-*o*-hydroxyphenyl ketone with ethylene diamine. These Schiff's bases present a good capacity of complexing Mn(II) ions, resulting brown complexes. The Schiff base forms a brown complex with Mn(II) cation, with maximum absorbance at 460 nm. The complex showed a maximum stability at pH 6.0. Spectrophotometric determination of Mn(II) using this Schiff base as reagent were successfully applied to pharmaceutical products containing Mn(II) cation.<sup>16</sup>

N,N'-bis(3-methylsalicylidene)-ortho-phenylene diamine (MSOPD), has been synthesized and used in the spectrophotometric determination of nickel. At pH 8, MSOPD can react with nickel ion at room temperature to form a 1:1 complex. The apparent molar absorptivity is  $9.5 \times 10^4$  l mol<sup>-1</sup> cm<sup>-1</sup> at 430 nm. With a detection limit of  $1.36 \times 10^{-8}$  M. Nickel in some natural food samples has been determined.<sup>17</sup>

N-N'-bis(pyridinylmethylene)ethylenediamine was studied by Leyva and Palma. The optimum experimental conditions for the spectrophotometric determination of copper were established. Beer's law is obeyed between 1 and 10 ppm of copper. The precision of the procedure, expressed in terms of relative standard deviation, was 0.31%.<sup>18</sup>

A.G. Asuero has reviewed Schiff's bases derived from biacetyl as analytical reagent, more than 50 reagents and their related cation, method used, and medium have been reported.<sup>19</sup>

Number of spectrophotometric determinations have been carried out, for biacetyl bis(4-phenyl-3-thiosemicarbazone) (BBPT). It has been used as a reagent for the extractive spectrophotometric determination of cadmium and bismuth. Analytical applications of biacetyl bis(4-phenyl-3-thiosemicarbazone) and bipyridylglyoxal bis(4-phenyl-3-thiosemicarbazone) has been reported.<sup>20</sup>

Trace levels of palladium(II) has been determined by Asuero et al. The method relies upon the extraction of palladium(II)-biacetylmonoxime 2-pyridylhydrazone (BMPH) from aqueous acidic solution into chloroform to form a purple-reddish complex. The molar absorptivity of the Pd-BMPH complex is about 7500 L mol<sup>-1</sup> cm<sup>-1</sup> at 560 nm in the chloroform extract.<sup>21</sup>

### B. Fluorometry

Fluorometric methods often provide excellent means for the detection and determination of inorganic ions. The reagents employed to produce fluorescence are often highly selective and very sensitive. In most cases a chelate is formed with the metal. There is often a dependence of fluorescence on the pH

similar to that of acid-base fluorescence indicators. The analytical importance of such indicators lies in the fact that they make possible acid-base titrations in colored solutions when the use of conventional indicators would be precluded. Holzbecher reported that Schiff's bases obtained from salicylaldehyde and aniline fluoresce in the alkaline medium and therefore, can be used for titration of acids with bases.<sup>22</sup> He also proposed O-[N-(O-hydroxyphenyl)formimidoyl]phenol, for quantitative determination of aluminium.<sup>23</sup>

Sabry studied the fluorescence properties of Schiff bases derived from 2-acetylbutyrolactone and spectrofluorimetric determination of primary amine-containing compounds. 2-Acetylbutyrolactone (ABL) has been characterized for use as a fluorogenic reagent for the spectrofluorimetric determination of primary amines. The reagent forms strongly fluorescent Schiff bases upon the reaction with primary amines in acid-catalyzed aqueous solutions or in dimethylformamide (DMF).<sup>24</sup>

Determination of trace cadmium with GBHA has been developed by Dong Gai. The cadmium ion can form a stable chelate with GBHA, having a ratio of 1:3 in the 12.0-13.0 pH range with maximum excitation and emission wavelengths are 227.4 nm and 320.0 nm for the cadmium chelate, respectively, and fluorescence intensity from 20 to 150 min. Linear function of concentration in the range 1.0-10.0 ng mL<sup>-1</sup> of cadmium and the detection limit is 0.65 ng mL<sup>-1</sup> of cadmium.<sup>25</sup>

### C. Schiff's bases as potentiometric sensors

Since the 1930s, potentiometric membrane sensors have found great practical applicability in different fields. The response mechanism of these sensors is based on the measurement of a potential under a zero current regime or a under a low electrical current flow. Potentiometric membrane sensors, which have been designed based on molecular recognition, contain a molecule that selectively recognizes another target species through various molecular interactions. As it is widely known, potentiometric electrodes possess as advantages the direct, simple, rapid, inexpensive and selective detection of ionic activities.<sup>26-28</sup>

Ganjali et al. have prepared potentiometric sensors for Dy(III) based on a Bis-pyrrolidene Schiff's bases, the electrode has been also used in the potentiometric determination of Fluoride ions in mouthwash by the titration against Dy(III).<sup>27</sup> They also prepared a novel Bromide ion sensor based on Iron(III)-salen, this sensor has high Bromide selectivity over a wide variety of organic and inorganic anions, specially iodide, chloride and hydroxide ions.<sup>28</sup>

A large number of different Schiff base ligands have been used as cation carriers in potentiometric sensors as they have shown excellent selectivity, sensitivity, and stability for specific metal ions.<sup>29-45</sup>

### D. Schiff's bases as solvent extraction reagents

Solvent extraction separation is based on the differences in the solubility of elements and their compounds in two immiscible liquid phases. Usually, the initial phase is an aqueous solution and the second phase is an organic solvent immiscible with water. Extraction is usually fast and simple process; it demands only very simple equipments. Stripping (re-extraction, back-extraction or scrubbing) involves bringing the element from the organic extract back to the aqueous phase.

A solvent extraction using salophen was studied by Kim et al. and applied for trace determination of Ni(II), Co(II) and Cu(II) in water samples. The salophen is another type of salen derivative. Unlike the ethylenediamine of salen, salophen included a phenyldiamine as a backbone.<sup>46</sup> In another study the salophen has been used in solvent extraction for trace determination of Fe(II) and Fe(III) in water samples.<sup>47</sup> Gyo In et al. used salen (Net<sub>2</sub>)<sub>2</sub> as a chelating agent for determination of Cu(II), Mn(II) and Zn(II) in water samples by FAAS.<sup>7</sup>

Macrocyclic Schiff bases containing either thiophene or phenol subunits were synthesized and the effect of ligand atoms on the liquid-liquid extraction of bivalent transition metal ions was studied. The phenol groups in the macrocycle led to a large increase in the extraction of transition metal ions. The least stable manganese(II) complex was extracted quantitatively into nitrobenzene as an ion pair with tetraphenylborate ion at pH 9. Copper(II) was selectively extracted from weakly acidic media, permitting its separation from manganese(II), cobalt(II), nickel(II) and zinc(II). The extractability of metal

complexes with a cyclic tetraaza Schiff base has been compared with that of the corresponding acyclic Schiff base.<sup>48</sup>

Mutual separation of zinc(II), copper(II) and manganese(II) can be achieved by a proper selection of pH using Acyclic and macrocyclic Schiff bases containing bisphenol A subunits compared with a macrocyclic Schiff base, the corresponding acyclic counterpart was found to have a reasonable reactivity toward metal ions and better solubility in organic solvents.<sup>49</sup>

In another application, a quantitative extraction of iron(III) and gallium(III) was achieved with macrocyclic Schiff base containing bisphenol A subunits. The phenol groups in the Schiff base moiety led to a large increase in the percent extraction of trivalent metal ions. The substitution of methoxy groups for phenolic OH ligands resulted in a marked decrease in the extractability of metal ions, and no iron(III) was extracted. The corresponding acyclic Schiff base was found to have a reasonable reactivity toward metal ions and a better solubility in organic solvents. The iron(III) and gallium(III) complexes with macrocyclic and acyclic Schiff bases were quantitatively extracted into nitrobenzene without the presence of bulky counter anions. A single extraction gave a good separation of iron(III) from iron(II) in the mole ratios 4:1 to 1:3. The red iron(III) complexes can be used for the extraction-spectrophotometric determination of iron(III). The apparent molar absorptivity at 518 nm is  $5.43 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ .<sup>50</sup>

### E. Schiff's bases as solid phase extraction sorbents

The solid phase typically consists of small, porous particles of silica with a bonded organic phase or of an organic polymer, such as crosslinked polystyrene. The extraction can take place in a batch mode in which the solid extractant is intimately mixed with liquid sample solution. In chemical analysis it is more common to pack the solid extractant into a small tube and pass the liquid sample through the tube.<sup>51-54</sup>

The nature and properties of the sorbent are of prime importance for effective retention of metallic species. Careful choice of the sorbent is thus crucial to the development of SPE methodology.

Two approaches are used for loading the surface with specific organic compounds, chemical immobilization and physical adsorption. In the first case, a chemical bond is formed between the solid support surface groups and those of the organic compound (*functionalized sorbent*). In the second approach, the organic compound is directly adsorbed on the functional groups of the solid support surface (*impregnated or loaded sorbent*), either by passing the reagent solution through a column packed with the adsorbent, or by soaking the adsorbent in the reagent solution.

Ganjali et al.<sup>52</sup> separated and pre-concentrated ultra-trace amounts of Cu(II) by solid phase extraction on octadecyl-bonded silica membrane disk modified with ( Bis- (2-hydroxyacetophenone) -2,2-dimethyl-1,3-propanediimine) SBTD followed by elution and ICP-AES detection in environmental and biological samples, the concentration factor was 500.

Shemirani et al.<sup>53</sup> proposed a method for the preconcentration of Cd(II), Cu(II), Zn(II), and Ni(II) using a minicolumn filled with silica gel modified with (N,N'-bis(salicylene) phenylene-1,3-diamine Schiff' base. The proposed method was applied to the analysis of the metal ions in natural water samples and to a standard reference aluminium alloy material.

Thallium ions have been separated and concentrated selectively and quantitatively during passage of aqueous real samples through an octadecyl bonded silica membrane disk modified by 4-(4-Chlorophenylazo)-2-[(4-hydroxy-phenylamino)- methyl]-phenol. The retained Thallium ions are then stripped from the disk quantitatively with a minimal amount of thiosulfate solution as eluent and measured by FAAS with an enrichment factors of about 130 and higher and limit of detection of 11.2 ng/L.<sup>54</sup>

The use of niobium(V) oxide, chemically adsorbed on silica gel surface (Nb<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub>), as an adsorbent in a pre-concentration system of copper (II) and cadmium (II) by flow system with FAAS was proposed by Budziak et al.<sup>55</sup> The enrichment factor when using a sample volume of 10.2ml and 2 min of pre-concentration was 17.5 and 20.3 for copper (II) and cadmium (II), respectively. Good accuracy was obtained by the analysis of water reference materials and environmental samples.

Mashhadizadeh et al. have developed a selective method for extraction of Cu(II) by sorption on octadecyl silica membrane disk modified with bis-(3-methoxy salicylaldehyde)- 1,6-diaminohexane and determination with atomic absorption spectrometry. The retained copper eluted with a minimum volume

of EDTA with a pre-concentration factor of 100. The maximum capacity of the disk was found to be 150  $\mu\text{g}$  of copper ion on the disk.<sup>56</sup>

In another work they have used octadecyl silica membrane disk modified by a recently synthesized Schiff base (Bis-(4-nitro phenyl azo) salicylidine-1,3-diamino propane) for flame atomic absorption spectrometric determination of  $\mu\text{g}$  amounts of Fe (III) ions in aqueous samples. The time taken for the separation and analysis of iron in 500 ml sample is 30 min at the most.<sup>57</sup>

Iron (III) has been determined by Shamspur et al. by flame atomic absorption spectroscopy (FAAS) after preconcentration on modified analcime zeolite with 5-((4-nitrophenylazo)- N- (2',4'-dimethoxyphenyl))salicylaldimine. The recoveries were > 99%, and the developed method was applied to the determination of trace Fe(III) ions in drinking water and river water samples.<sup>58</sup>

Dadfarina et al. have determined silver, zinc and copper employing FI-FAAS and a microcolumn of immobilized salen, 2,2'-[3-aza-1,5-pentanedyle bis (nitrilomethylidyne)]- bis-phenol, on surfactant-coated alumina. The practical concentration factors of 125, 210 and 166 for Ag, Zn and Cu, respectively and the detection limits of 0.3, 0.8 and 0.47  $\mu\text{g/L}$  for Cu, Ag and Zn, respectively. The data obtained by their method agreed well with the results of independent analysis of GFAAS.<sup>59</sup>

Jadid et al.<sup>60</sup> applied the modified activated carbon with 5 - (( 4 - heptyloxyphenyl ) azo ) -N - ( 4 - butyloxyphenyl)-salicylaldimine (HPBS) as a new sorbent for preconcentration of Cu(II) ions. The detection limit was 2.26 $\mu\text{g/L}$ . The procedure has been applied for the determination of copper in water samples.

Ahmadi et al.<sup>61</sup>, have used octadecyl silica membrane disks modified by N,N'-disalicylidene-1,2-phenyldiamine (salphen) for extraction and determination of Zn by FAAS. The limit of detection was 14ng/L. Their method has been applied to the determination of zinc in natural water samples, the results has been checked by spiking experiments and comparing the results with data obtained by GFAAS.

Bader has used four different structures of slanes for coating silica gel, C18 silica gel, and aminopropyl silica gel in order to extract Zn, Cd, and Cu from aqueous solutions before AAS measurements. A pre-concentration factor of 100 was obtained, considering the relation between final small volume and initial large volume of sample. The limit of detections of SPE-FAAS have been calculated. The improved LODs are 0.007, 0.362, and 0.102 ng/ml for Zn, Cd, and Cu respectively. The improved LODs are much lower than the LODs of FAAS and approaching the LODs of GFAAS.<sup>62</sup>

The microcolumn of salen I (N,N\_-bis (salicylidene) ethylenediamine) immobilized on surfactant-coated alumina has been used by Dadfarnia et. al., for on-line preconcentration of copper and lead with a flow injection-flame atomic absorption spectrometry (FI-AAS). A good relative standard deviation of 4.5 and 3.8% at 30 $\mu\text{g l}^{-1}$  ( $n = 7$ ), high enrichment factors of 100 and 75, and detection limits of 0.3, 2.6 $\mu\text{g l}^{-1}$  (3S) for Cu(II) and Pb(II) were obtained, respectively. The method developed provides an alternative procedure to techniques such as GFAAS, ICP-AES for determination of copper and lead at  $\mu\text{g l}^{-1}$  level.<sup>63</sup>

The elution step in solid phase extraction is mostly done in acidic medium, which cause decomposition of Schiff's base, in this case reloading of the ligand on the column is needed in case of physically modified sorbents. The chemically modified sorbents shows stability toward acidic elution solutions, making them more convenient for multi use, and therefore for flow injection analysis system.

## F. High-Performance Liquid Chromatography

In the last few years the rapid development of high-performance (pressure) liquid chromatography (HPLC) has also extended the possibilities for chromatographic methods in inorganic analysis. In particular liquid chromatographic methods in columns are of great importance for those inorganic compounds which are not suitable for the usual gas chromatographic methods because of low volatility or low thermal stability.<sup>64</sup>

Chromatographic methods are very suitable for the separation and determination of extractable metal chelates.

Different types of ligands or groups of compounds are suitable for HPLC such Schiff base chelates, hydrazones, dithizonates, and metal dithiocarbamates. For these groups of substances principally



reversed-phase and adsorption systems are suitable; separations by reversed-phase systems are very well reproducible.<sup>65-68</sup>

The separation of neutral copper and nickel chelates of two representative Schiff base ligands, N,N'-ethylenebis(acetylacetonimine) and N,N'-ethylenebis(salicylalimine) is reported on a column of 10 micrometer diameter silica. Both pairs of chelates are well resolved with good peak shape and efficiencies when the mobile phase is 4 : 1 methylene chloride-acetonitrile.<sup>69</sup>

An HPLC method for the determination of scandium(III) was developed, with diacetyl-N,N-bis(4-hydroxybenzoylhydrazone) (DBHB) as a pre-column chelating agent. Tetradentate DBHB formed a 1 : 1 chelate with Sc(III) ion. The Sc(III)-DBHB chelate was separated on a C18-silica gel column with a mobile phase of acetonitrile-water (30+70m/m) containing tetramethylammonium bromide and hexamethylenetetramine buffer.<sup>70</sup>

Kanbayashi. et al. have developed a method for highly selective determination of trace amounts of Co<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> and V<sup>5+</sup> ions by reversed phase high-performance liquid chromatography (HPLC) and spectrophotometric detection has been accomplished without the addition of a chromogenic reagent to the eluent. Six tetradentate Schiff-base ligands, all N,N'-o-phenylenebis(salicylalimine) (PBS) derivatives, were synthesized and made to react with the metal ions.<sup>71</sup>

## CONCLUSION

As has been illustrated in many occasions, both in the literature and in this review, Schiff's bases have clear advantages in term of easy to prepare, complex formation, and versatility.

Nowadays the promised uses of Schiff's bases in analytical chemistry field are sensors or solid phase extraction sorbents. The development of Schiff's bases based sensors and solid phase extraction sorbents is still in progress. Many papers emphasizing instrumental aspects and/or applications are published every year.

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