Separation of Fe(II), Ni(II), Ca(II), and Mg(II) ions by Schiff bases complexation and reversed-phase high performance liquid chromatography

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A R T I C L E I N F O	A B S T R A C T
	The separation of Fe(II), Ni(II), Ca(II), and Mg(II) chelates of Schiff base ligand, N,N'- Bis(salicylidene)1,3-propylenediamine is reported on a column of silica. Metal chelates are well resolved with good peak shape and efficiencies when the mobile phase is linear gradients of Methanol in an aqueous sodium acetate (50mmol/L, pH 5.40), using diode-array detector at 240nm. The ligand N,N'-Bis(salicylidene)1,3-propylenediamine N,N'-Bis(salicylidene)1,3- propylenediamine, N,N'-Bis(salicylidene)-2,2-dimethyl-1,3-propylenediamine, and N,N' Bis(2-Hydroxyacetophenone)-2,2-dimethyl-1,3-propylenediamine have been separated in order to choose the ligand used for metal separation.

Introduction

Before determination of trace concentration of metals in different types of samples a good separation of analyte(s) is required. The common way for this purpose is liquid extraction or Ion-exchange extraction but HPLC have the advantage of doing both direct separation and determination. It has extended the possibilities for chromatographic methods in inorganic analysis. [Bader,2010]

The determination of metal ions after HPLC separation of their complexes is a useful technique. The metal complexes can be separated by HPLC and determined. According to the complex formation requirements not all chelating reagents are suitable for this purpose [Vernon,1990].

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 well designed Schiff base ligands are considered ''privileged ligands'' [Gozzi, 2004; Nworie, et al., 2016].

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 [Ali et al., 2020; Refat et al. 2021].

There are many application for Schiff bases in analytical chemistry, chemical separation and catalysis [Bader, 2010; Dalia et al., 2018]. They have been used in HPLC separation of metal ions as metal chelates after forming metal complexes in order to enhance separation performance of the column [Bader, 2010; Bader et al., 2012].

The focus of this paper is to explore the possibility of separation of iron (II) and nickel (II) in presence of magnesium (II) and calcium (II) ions.

In the first part of this study, four Schiff bases have been separated in order to understand the behavior of them under the conditions of operation.

In the second part N,N'-Bis(salicylidene)1,3-propylenediamine has been used to separate Fe(II), Ni(II), Ca(II), and Mg(II) via complex formation between metal ions and the ligand.
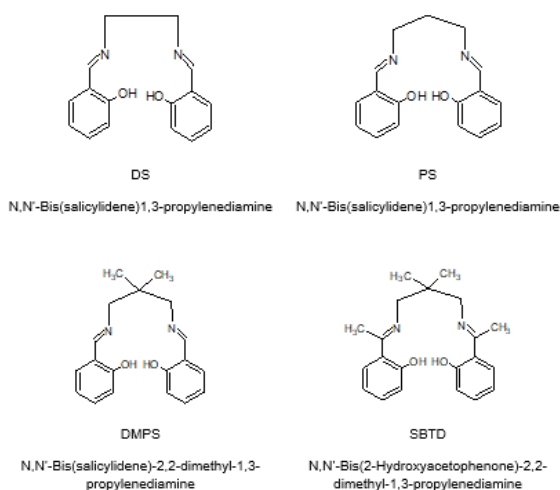
Figure 1: Structure of Schiff bases used in the study

Experimental:

All reagents were of analytical grade, and water was purified using a Milli-Q water system.

Preparation of the ligand:

The same amount of salicylaldehyde was added in ethanol to 8.4ml (0,1mol) of the diamino alkane corresponding to the bridging moiety in the targeted Schiff base. The product precipitated immediately. In case of SBTD salicylaldehyde was replaced with 2-Hydroxyacetophenone.

The product re-crystallized from ethanol, was filtered and dried to give the desired schiff's base as yellow crystals.

Metal ion standard solutions of were prepared from the nitrate or chloride salts in 10 mM nitric or hydrochloric acid. Pre-column complex formation of a metal ion with N,N'-Bis(salicylidene)1,3-propylenediamine, (PS), was performed by addition of excess of Schiff base stock solution to the metal ion standard solutions.

All experiments were performed on a LiChroGraph HPLC system consisting of HPLC pump L6200A and a spectrophotometric Merck Hitachi L-4250 Detector (Merck, Darmstadt, Germany).

HPLC Conditions:

Instrumentation: quaternary low pressure gradient high-performance liquid chromatograph LaChrom, data acquisition software HSM v 3.1

Column: Chromolith Performance RP18e, 100x4.6 mm, monolithic

Mobile phase: linear gradients of Methanol in an aqueous sodium acetate (50mmol/L, pH 5.40), Flow rate: 4.00 mL/min, Column oven temperature: 40ºC,

Detection: diode-array detector range from 200 nm to 700 nm

Results and discussion:

The obtained chromatograms are illustrated in figures 2, 3, 4 and ,5.

The figures 2, 3, and 4 show the separation of Schiff bases without metal ions. There was a very good separation in suitable time. PS has been chosen to perform complexation with metal ions because of its structure and the ability to form complexes with the studied metals.
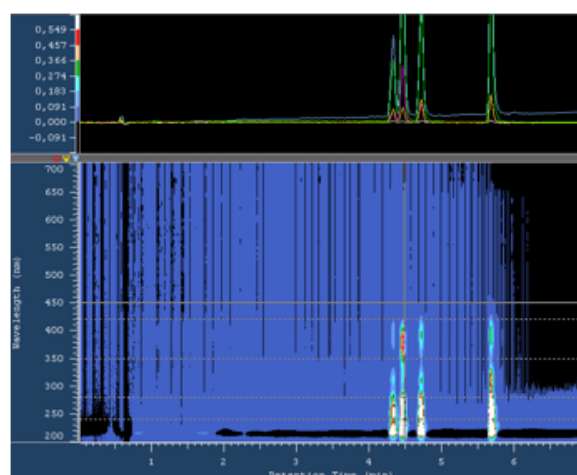

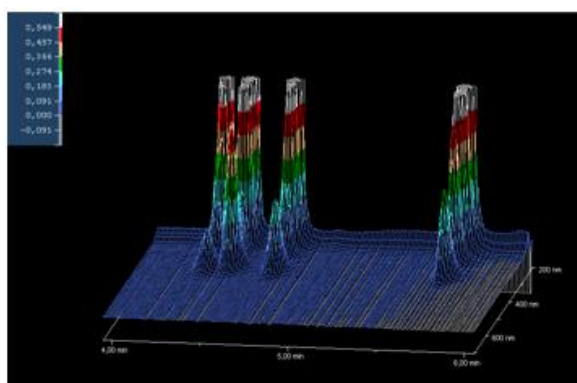Figure 2: Separation of Schiff bases – Top view

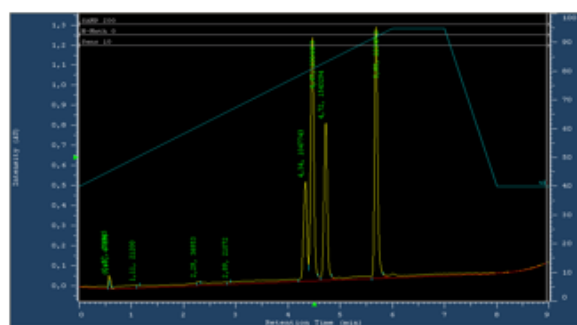Figure 3: Separation of Schiff bases at different wavelengths – 3D

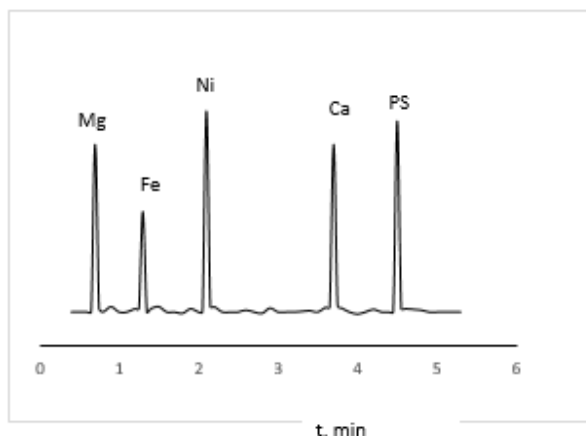
Figure 4: Separation of Schiff bases

Figure 5 : Chromatogram of Mg^{2+}, Ca^{2+}, Ni^{2+}, and Fe^{2+} comp
conditions: Column: Chromolith Performance RP18e, 100x4.6 mm, monolithic, Mobile phase:
linear gradients of Methanol in an aqueous sodium acetate (50mmol/L, pH 5.40), Flow rate: 4.00
mL/min, Column oven temperature: 40°C, Detection: diode-array detector at 240nm.

The retention times of the separated free ligands and ion chelates are listed in table 1.

Table 1: Retention times of Schif bases and chelates

Schiff Base	$t_{R\,240\,nm}$, min	Metal ion with PS	$t_{R\,240\,nm}$, min
ES	4.34	Fe(II)	1.3
PS	4.47	Ni(II)	2.1
DMPS	4.72	Mg(II)	0.7
SBTD	5.68	Ca(II)	3.75

The complex formation which depends mainly on pH, temperature, metal ion size, and the structure of the ligand, therefore the enhancing these factors to increase the stability of the complex leading the selectivity of separation. Under the optimized HPLC separation conditions Fe^{2+}, Ni^{2+}, Mg^{2+}, and Ca^{2+} ions in aqueous solutions could be determined simultaneously

The initial positive charge on the metal ion is neutralized during chelation by hyroxy groups to form a neutral complex. This could explain the retention of the metal complexes.

The metal complexes should be stable at chromatographic operation conditions, and PS as a multidentate reagent meet this requirement, it can form 6-membered chelation rings through imine nitrogen and the hydroxy groups on the benzene ring with the metal ions therefor only one type of complexes is expected. Formation of one type of complexes is preferable but formation of many types is possible depending on the type of matrix [Bader, 2010; Main, 1990].

The complex formation step is before the chromatographic separation as a batch method to form the complexes in sample solution, so the selectivity in

this step is not required in other word the selectivity toward metal ion is required to avoid reaction with interferences. The selectivity of complexation can be achieved by controlling the pH of the sample. The selectivity is necessary only in the chromatographic separation step. The selectivity in chromatographic separation is due to the kinetic behavior of the chelates during elution.
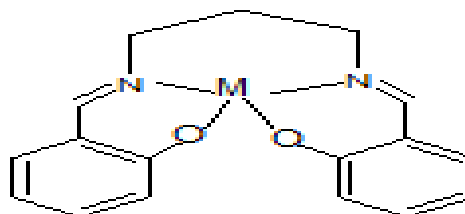

Figure 6: Suggested structure of the metal complex

Different metal complexes have different optimum absorption wavelength, so the detection wavelength 240 nm has been chosen as detection wavelength, since most metal chelates will absorb in the UV-Vis spectral region and to make the method suitable for fixed UV wavelength detector HPLC systems.

CONCLUSION

The proposed method provided simultaneous separation and determination of PS complexes of Fe^{2+}, Ni^{2+}, Mg^{2+}, and Ca^{2+} ions in aqueous solutions. The main advantages of this method are the small solvent quantity, speed, low cost, and good precision. The optimum results, in terms of separation and selectivity of HPLC have been obtained, Separation time is relatively short.

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