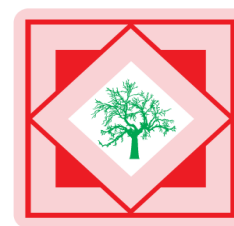




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Selective separation of trace amount of copper(II), manganese(II), cadmium(II), and nickel(II) ions with tetradentate schiff base ligand by reversed-phase high performance liquid chromatography and spectrophotometric detection.

Nabil Bader¹, Milan Hutta², Heinz-Martin Kuss³

¹Chemistry Department, Faculty of science, Benghazi university, Benghazi, Libya.

²Department of Analytical Chemistry, Faculty of Natural Sciences, Comenius University, Bratislava 842 15, Slovak Republic.

³Instrumental analytical chemistry department, Duisburg-Essen university, Essen, Germany

ABSTRACT

The separation of neutral copper, manganese, cadmium, and nickel 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 350nm.

INTRODUCTION

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.[1]

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

Complexation of metal ions in the form of stable complexes formed pre-column or pre-capillary has been used extensively to separate metal ions in HPLC [2]

Most of these complexes absorb in the UV or visible region, which facilitates direct photometric detection. Using normal phase (NP), reversed phase (RP) or ion interaction liquid chromatography.[3,4]

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.[5-11]

The separation of neutral copper and nickel chelates of two representative Schiff base ligands, *N,N'*-ethylenebis(acetylacetonimine) and *N,N'*-ethylenebis(salicylaldimine) 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.[12]

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. [13]

Kanbayashi. *et al.* have developed a method for highly selective determination of trace amounts of Co^{2+} , Cu^{2+} , Ni^{2+} and V^{5+} 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(salicylaldimine) (PBS) derivatives, were synthesized and made to react with the metal ions. [14]

MATERIALS AND METHODS

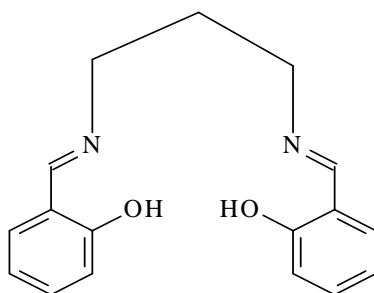
All other reagents were of analytical grade. Water was purified using a Milli-Q water system.

Preparation of the ligand:

The product re-crystallized from ethanol, was filtered and dried to give the desired schiff's base as yellow crystals. *N,N'*-Bis(salicylidene)1,3-propylenediamine=(H_2sal -1,3-pn)

The same amount of salicylaldehyde was added to 8.4ml (0,1mol) of 1,3-diaminopropane in ethanol. The product precipitated immediately.

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



N,N'-Bis(salicylidene)1,3-propylenediamine

Metal ion standard solutions 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 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

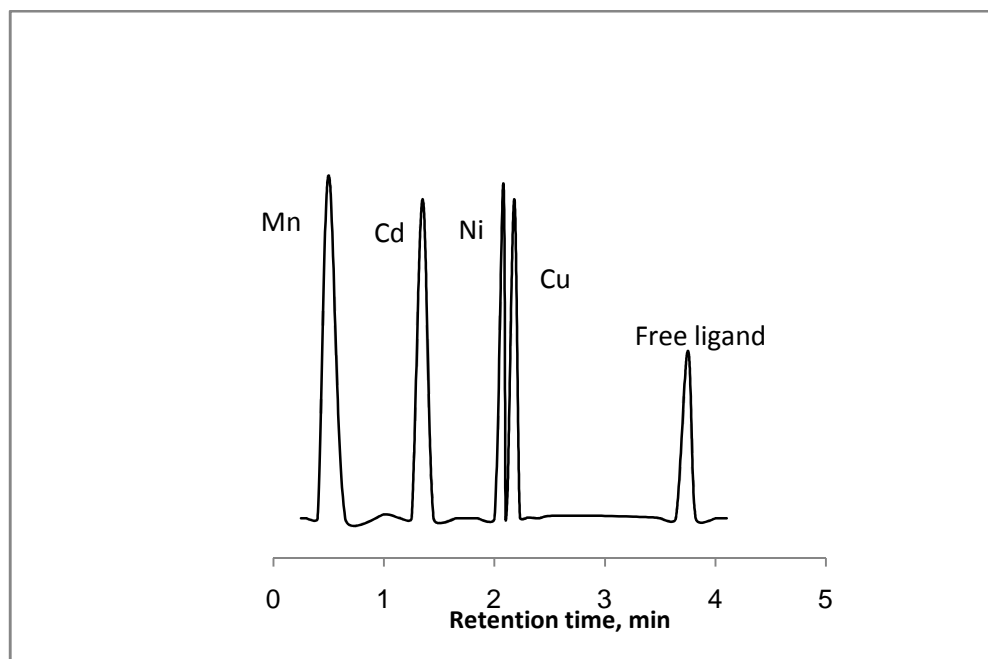
Mobile phase: linear gradients of Methanol in an aqueous sodium acetate (50mmol/L, pH 5.40), Flowrate: 3.00 mL/min, Column oven temperature: 40°C, Detection: diode-array detector range from 200 nm to 700 nm

RESULTS AND DISCUSSION

The chromatogram of the separated chelates is illustrated in figure (1).

As can be seen from Fig. 1, the chelates of Cu^{2+} , Mn^{2+} , Cd^{2+} , and Ni^{2+} ions gave separated peaks in the chromatogram.

The retention times of the separated ion chelates were as following 0.5, 1.35, 2.08, and 2.18 min. for Mn^{2+} , Cd^{2+} , Ni^{2+} , and Cu^{2+} respectively, and 3.75 min. for the free Schiff base.



Figure(1): Chromatogram of Cu^{2+} , Mn^{2+} , Cd^{2+} , and Ni^{2+} complexes and the free ligand. (HPLC 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), Flowrate: 3.00 mL/min, Column oven temperature: 40°C, Detection: diode-array detector at 350nm).

The influence of foreign ions on the separation performance has been checked. The presence of Ag^+ , Fe^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} in 1:1 ratio interfere only the peak of Cd ion complex, the separation of all these elements from the element under study except Cd can be established.

The main step in this application is the complex formation which depends mainly on pH, temperature, cation size, and the structure of the ligand. Optimization of these factors to enhance the stability of the complex leads to high selectivity of the developed analytical method. The Schiff base used is able to coordinate metals through imine nitrogen and the hydroxy groups on the benzene ring.

The pH of complexes solution has been adjusted using the proper concentration of NaOH, but in case of using acetic acid/acetate buffer no separation has been observed.

Based on these results, a method for the simultaneous determination of Mn^{2+} , Cd^{2+} , Ni^{2+} , and Cu^{2+} ions in aqueous solutions under the optimized conditions can be established.

CONCLUSION

The suggested method can be applied in separation and qualitative analysis of Copper(II), Manganese(II), Cadmium(II), and Nickel(II) ions in aqueous solution.

The selectivity towards metal ions, which is due to the kinetic behavior of the chelates during elution, provides a good concept for the design of reagents for HPLC coupled with spectrophotometry.

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