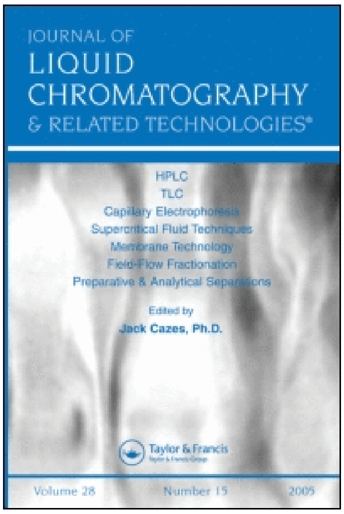

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High Performance Liquid Chromatographic Determination of Copper(II), Nickel(II), Palladium (II), and Platinum(II) Using Solvent Extraction and *bis*(Isovalerylacetone)ethylenediimine as Complexing Reagent

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC DETERMINATION OF COPPER(II), NICKEL(II), PALLADIUM(II), AND PLATINUM(II) USING SOLVENT EXTRACTION AND BIS(ISOVALERYLACETONE)ETHYLENE-DIIMINE AS COMPLEXING REAGENT

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ABSTRACT

The separation of copper(II), nickel(II), palladium(II), palatinum(II) and oxovanadium(IV) complexes of bis(isovalerylacetone)ethylenediimine (H_2IVA_2en)was obtained on reversed phase HPLC column Nova Pak C-18 (150x3.9mm) or Microsorb C-18 (150x4.6mm), when the complexes were isocratically eluted with binary mixture of methanol and water. The detection was obtained using UV detection at 254nm. The detection limits were obtained at sub ng of metal ions. The reagent was used for the extraction of copper, nickel, palladium and platimum from aqueous solution in cyclohexane. Linear calibrations for simultaneous extraction of copper and nickel in an aliquot (4ml) were within 2-20ug, palladium 25-125ug and palatinum 50-300ug The relative percentage error for the analyses of test solution were within 1-10%.

INTRODUCTION:

The extraction of traces of metallic elements into organic solvents as metal chelate compounds, followed by their determination using atomic absorption spectrometry has become the method of the choice in many laboratories. These methods have important advantages of lower limits of detection and excellent selectivity, but suffers from the defect, that each element has to be determined separately. However multielements could be determined simultaneously using atomic emission detectors [1], but involves expensive equipment with high running cost. It was therefore, we investigated the possible use of high performance liquid chromatography (HPLC) for simultaneous multielemental analysis after necessary solvent extraction with bis(isovalerylacetone)ethylenediimine [N,N'-ethylenebis(5-methyl-4-oxoheptane-2-imine)] (H_2IVA_2en) as complexing reagent. The reversed phase HPLC mode was used, because the metal chalets are easily eluted and better separated. The chromatograms proved reproducible with retention times and peak heights remaining constant.

The reagent H_2IVA_2en is reported earlier for the extraction of copper, nickel and palladium from aqueous solutions and their quantitative determinations on gas chromatograph using flame ionization detection (FID) system [2]. In the present work the reagent has been used for the solvent extraction of copper, nickel, palladium and platinum, and their determination, using HPLC connected with UV detector.

EXPERIMENTAL

The reagent bis(isovalerylacetone)ethylenediimine (H_2IVA_2en) and its copper, nickel, palladium and oxovanadium complexes were prepared as reported (2,3). The platinum(II) complex was prepared following general procedure of Belcher et al [4], where platinum(II) chloride-acetonitrile adduct (0.001M) dissolved in benzene was refluxed with equimolar amount of reagent (0.001 M) in benzene for 48 hrs. Benzene was distilled off and the product was vacuum dried. The residue was extracted with n-hexane. The product obtained was recrystallized from n-hexane.

Hitachi 655A liquid chromatograph connected with variable UV monitor Rheodyne 7125 injector and recorder 561 was used. Column Nova Pak C-18 (150x3.09 mm) (Waters) and Microsorb C-18 (150 x 4.6 mm) (Hewlett Packard) were used.

The stock solution of copper(II), nickel(II), palladium(II) and platinum(II) containing 1 mg cm^3 were prepared from $CuCl_2.2H_2O$, $NiCl_2.6H_2O$, $PdCl_2$ and $PtCl_2$ (Merck).

Analytical Procedure for HPLC Determination of Copper(II) nickel (II) and platinum (II).

Solution (1-4 cm^3) containing 0-20 µg copper and nickel and 0-300 µg platinum(II) was transferred to well stoppered test tube (10 cm^3), (Quickfit), and was added sodium bicarbonate buffer (2 cm^3) (pH 8), followed by ethanol (1 cm^3) and reagent solution (2 cm^3) (1% W/V in ethanol) for copper and nickel and (3 cm^3) (1.5 % W/V in ethanol) for platinum. The contents were heated on water bath at 80 °C for 13-20 min. The mixture was allowed to cool and cyclohexane (2 cm^3) was added and contents were mixed thoroughly on mechanical shaker for 15 min. The solvent of the extract (1 cm^3) was evaporated and redissolved in methanol (1 cm^3). The solution (5 µl) was injected on Microsorb C-18 column (150 x 4.6 mm) and complexes were eluted with 15% water in methanol, with a flow rate of 1 cm^3/min. The detection was achieved using UV detector fixed at 254 nm.

ANALYTICAL PROCEDURE FOR PALLADIUM(II)

Solution (1-2 cm^3) containing palladium(II) (0-125 µg) was transferred to well stoppered test tube, followed by potassium bromide (1 g), sodium bicarbonate buffer (pH 8) (2 cm^3) and reagent solution (3 cm^3) (1% W/V in ethanol). The contents were then treated as for copper and nickel.

RESULTS AND DISCUSSION

Some interesting results were observed when metal complexes of H_2IVA_2en were investigated for their separations on Nova Pak C-18 column. The copper, nickel, palladium and oxovanadium complexes were easily separated, when complexes were eluted with a binary mixture of methanol: water (82:18). The retention volumes for oxovanadium, palladium, nickel and copper complexes were 4.66, 6.44, 7.05 and 8.44 cm^3 using flow rate of 0.7 cm^3/min. However the reagent indicated the retention volume of 3.57 cm^3 and overlapped with the vanadium complex elution (Fig. 1).

When a mixture of oxovanadium, nickel, palladium, platinum and copper complexes was injected on the column Microsorb C-18 (150 x 4.6 mm) and the complexes were eluted isocratically with a binary mixture of 15% water in methanol and flow rate was adjusted to 1 cm^3/min. adequate resolution between all the five metal complexes was obtained as sharp and symmetrical peaks. The retention volumes of the reagent and its oxovanadium, platinum, palladium, nickel and copper complexes were 3.83, 4.43, 7.75, 9.81, 10.31 and 12.46 cm^3 respectively. There was complete separation between all the metal complexes, except some overlapping was observed with palladium and nickel chelates, with resolution factor (R_s) calculated to be 1.1 (Fig. 2).

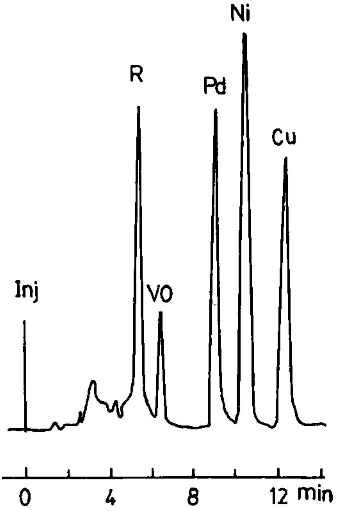


Fig.1 HPLC separation of the reagent, oxovanadium, palladium, nickel and copper complexes of H_2IVA_2en on Nova Pak C-18 column (150 x 3.9 mm). Eluent. Methanol: Water (82:18). Flow rate of 0.7 cm^3/min.

Linear calibration ranges for all the complexes were checked. Pure metal chelate solution having concentration 1 mg/cm^3 with appropriate dilutions were prepared in methanol. A fixed volume of each standard solution was injected at the optimized conditions of separation. Average peak height of at least two injections was measured and plotted versus concentration. Linear calibrations were obtained with 40-400 ng of metal chelates, corresponding to 5.5-103 ng of metal ion. Approximate detection limits measured

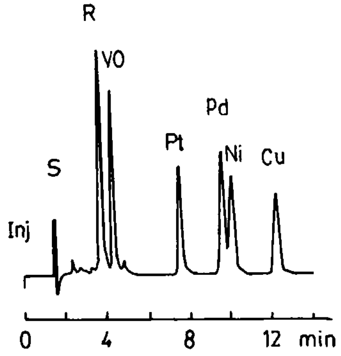
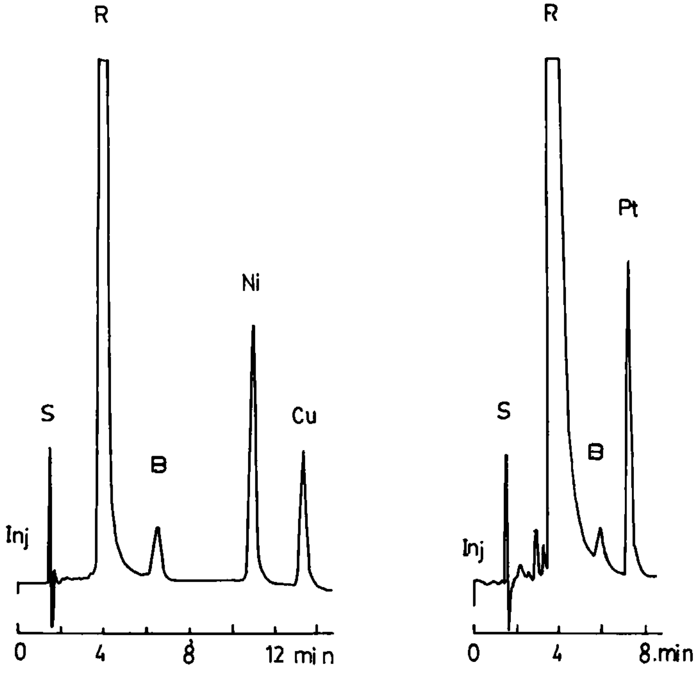


Fig.2 HPLC separation of Reagent, oxovanadium, platinum, palladium, nickel and copper chelates of H_2IVA_2en on Microsorb C-18 (150 x 4.6 mm). Elution: Water: Methanol (15:85). Flow rate 1 cm^3/min. Detection UV 254 nm. Detector settings 0.16 AUFS.

at least thrice the background noise were observed within 0.5-4 ng of complex, corresponding to 103-690 pg of metal ion.

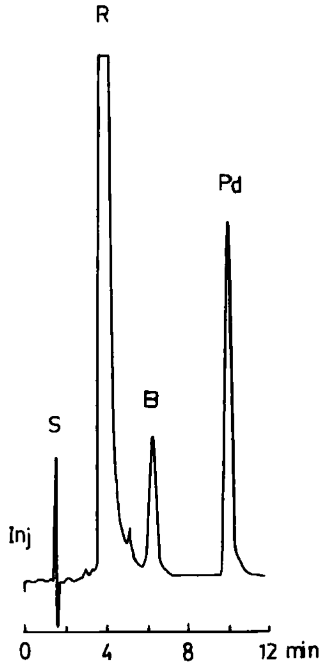
The extraction procedures were used for precolumn derivatization and quantitative transfer of copper, nickel, palladium and platinum from aqueous to organic phase, followed by HPLC determination (Fig. 3 abc). It was observed that excess of the reagent did not interfere. The effect of pH on the extraction of platinum as platinum(II) chelate in cyclohexane was investigated, and it was observed that extraction of platinum was maximum at pH 8.



(a) (b)

Fig.3 HPLC elution and separation (a) extract of copper and nickel (b) platinum (c) palladium. Conditions same as Fig.2 R=Reagent, B=Buffer solution.

The reagent H_2IVA_2en was assessed for the simultaneous determination of copper and nickel in a mixture, but palladium and platinum were determined separately. Different amounts of copper and nickel or platinum or palladium were transferred to different test tubes and the complexes were extracted and eluted



(c)

Fig. 3 (continued)

on HPLC column. The linear calibration curves for simultaneous determination of copper and nickel were found with 2-20 µg in 4 cm^3 of water. The platinum linear calibration was with 50-300 µg in 1.2 cm^3 of water. Similarly for the palladium it was 25-125 µg in 1.5 cm^3.

In order to test the validity of the calibration curves test solution of copper, nickel, platinum and palladium were analysed. The amount of metal ions present in the test samples were evaluated from the calibration curves. The results of analysis indicated relative % error within % error with ± 1-6, + 3-10 ±, 2-4 and ± 3-6 for nickel copper, palladium and platinum respectively.

REFERENCES

1. Boumans,P.W.J.M., "Inductively coupled plasma Emission Spectroscopy. Part II. Applications and Fundamentals", Wiley, New York, 1987, pp 27-150.
2. Khuhawar,M.Y., Vasandani, A.G.M. and Soomro, A.I. J. Chem. Soc. Pak. 12, 119 (1990).
3. Lindoy, L.F. Moody, W.E. and Tayer, D.Inorg. Chem. 16, 1465 (1977).
4. Belcher,R., Blessel,K., Cardwell, T., Prainca, M., Stephen, W.I. and Uden, P.C. J. Inorg. Nucl. Chem. 35, 1127 (1973).