

High Performance Liquid Chromatographic Determination of Nickel in a Nickel Aluminum Alloy Using Spectrofluorimetric Detection

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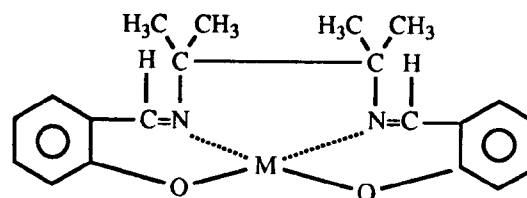
Summary: Copper(II), nickel(II), palladium(II) and oxovanadium(IV) chelates of bis(salicylaldehyde) tetramethylethylenediimine (H_2SA_2Ten) were separated on normal phase high performance liquid chromatographic (HPLC) column, Si 100, 5μ . The chelates were eluted with a ternary mixtures of 1,2-dichloroethane: chloroform: acetonitrile (70:28:2, v/v/v). The detection was achieved using a spectrofluorimetric detector. The linear calibration range for each of the complex at optimized spectrofluorimetric detection were determined. A solvent extraction procedure in chloroform was examined for the determination of nickel and method was applied for the estimation of nickel in a nickel aluminum alloy.

Introduction

Tetradentate Schiff bases derived from salicylaldehyde have been used as complexing reagents for copper(II), nickel(II), palladium(II) platinum(II), cobalt(II), iron(II) and oxovanadium(IV) [1-5] and for the high performance liquid chromatographic separation and determination of copper, nickel, palladium and oxovanadium [6-10]. The work mostly involved spectrophotometric detection. Averill and Broman [11] have reported the preparation of bis(salicylaldehyde) tetramethylethylenediimine [2,3-Dimethyl-2,3-*N,N'*-butane bis(salicylaldimine)] (H_2SA_2Ten) and electro-analytical properties of its cobalt complex. The reagent H_2SA_2Ten (Fig. 1) has been reported as reagent for copper and nickel using solvent extraction in toluene, followed by gas chromatography (GC) and normal phase HPLC determination. HPLC was connected to a UV monitor [9]. Recently spectrofluorimetric properties of copper(II), nickel(II), palladium(II), cobalt(II) and oxovanadium(IV) complexes of H_2SA_2Ten have been investigated [12]. In the present work H_2SA_2Ten have been examined for the separation of copper(II), nickel(II), palladium(II) and oxovanadium(IV) on normal phase HPLC using a spectrofluorimetric detector.

Results and Discussion

The reagent H_2SA_2Ten react with copper(II), nickel(II), palladium(II) and oxovanadium(V) complexes to form coloured complexes. The reagent and its metal chelate indicate



Metal complex of H_2SA_2Ten where
 M is Cu, Ni, VO, Pd

Fig.1: Structure of metal chelates of H_2SA_2Ten , where $M=Cu(II)$ $Ni(II)$, $VO(II)$, $Pd(II)$.

fluorescence. The optimal wavelengths of excitation and emission for the reagent and its metal chelates are summarized in Table 1 [12]. The reagent and its metal chelates easily eluted with a binary mixtures of 1,2-dichloroethane and chloroform. An optimal separation between reagent and its copper(II), nickel(II), palladium(II) and oxovanadium(IV) chelates was obtained, when eluted with ternary mixture of 1,2-dichloroethane:chloroform:acetonitrile (Fig. 2). The response of the detector for each of the complex at the optimized wavelengths was measured by injecting different amounts of complex and measuring the average peak height ($n=3$). Linear calibration were obtained with 0.2-1.6 μg of each of the complex. The coefficient of correlation (γ) for copper, nickel, palladium and oxovanadium complexes were 0.998, 0.997, 0.999 and 0.994 respectively.

Table-1: Optimal excitation and emission wavelengths for fluorescence measurement of reagent and their metal chelates.

Compound	Excitation Wavelength nm	Emission wavelength nm
H ₂ SA ₂ Ten	360	440
SA ₂ TenPd	330	370
SA ₂ TenCo	340	400
SA ₂ TenVo	365	430
SA ₂ TenCu	370	440
SA ₂ TenNi	340	420

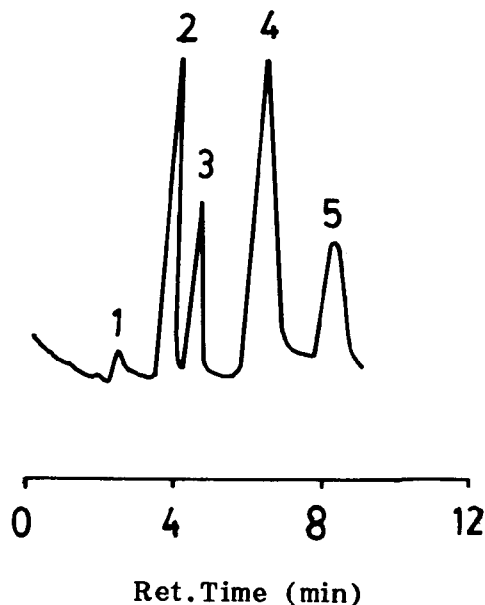


Fig. 2: HPLC separation of (1) reagent (2) oxovanadium(IV), (3) palladium(II), (4) nickel(II) and (5) copper(II) chelates of H₂SA₂Ten on column (250 x 4 mm i.d) packed with Lichrosorb Si 100, 5 μ . Eluent: 1,2-Dichloroethane: chloroform:acetonitrile (70:28:2, v/v/v). Flow rate 0.9 mL/min. Detection: Spectrofluorimetric wavelengths, excitation 280 nm, emission 370 nm.

All the metal ions could equally be determined using solvent extraction procedure and H₂SA₂Ten as complexing reagent. But in the present work nickel was determined in nickel aluminum alloy using precolumn derivatization and extraction in chloroform. The derivatization of nickel in aqueous ethanolic solution at pH 8, followed by extraction in chloroform, resulted in transfer of nickel from aqueous to organic phase

quantitatively. The excess of the reagent added for the derivatization did not interfere to the HPLC elution and detection of nickel chelates (Fig. 3). Linear calibration curve was obtained with 0-250 μ g/2ml of extract by plotting average peak height (n=3) versus concentration (Fig. 4) with coefficient

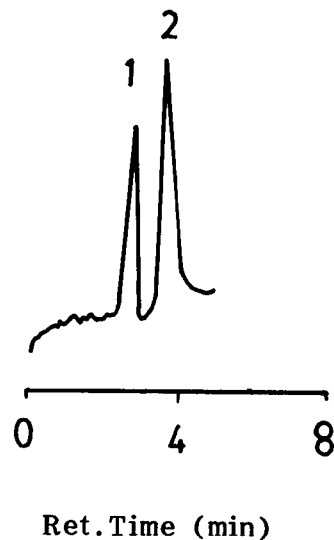


Fig. 3: HPLC determination of nickel. (1) Reagent (2) nickel(II) chelate of H₂SA₂Ten. Column (250 x 4 mm id) packed with Lichrosorb Si, 100 5 μ . Eluent: 1,2-dichloroethane:acetonitrile (80:19:1, v/v/v). Flow rate 0.9 mL/min. Detection spectrofluorimetric. Wavelengths: excitation 340 nm, emission 420 nm.

of correlation 0.990. The detection limit measured as three times the background noise was 1.5 μ g/mL of chloroform when 5 μ L was injected. It corresponded to 7.5 ng per injection. Finally a nickel-aluminum alloy was analysed for the contents of nickel and it was found to contain 52.0% with a coefficient of variation of 4.6% as compared to the reported value of 50% (Merck). The analysed value agreed reasonably with the expected value.

Experimental

The reagent H₂SA₂Ten and its copper(II), nickel(II) palladium(II) and oxovanadium(IV) complexes were prepared as reported earlier [9,11].

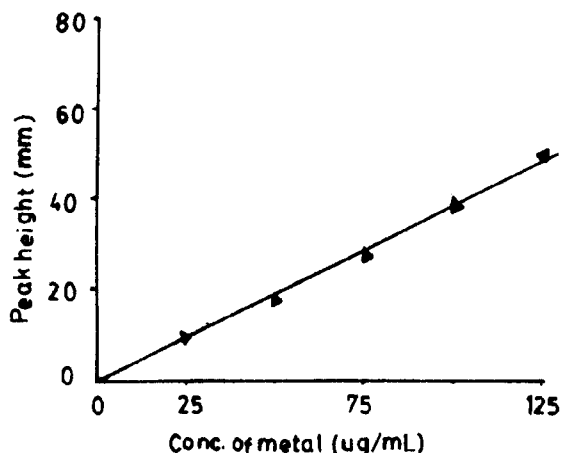


Fig. 4: Calibration curve of the extraction of nickel as nickel chelate compound of H_2SA_2Ten . Conditions same as Fig. 3.

Hitachi 655A liquid chromatograph connected with Hitachi F1200 spectrofluorimetric detector, Rheodyne 7125 injector and Hitachi D2500 chromato-integrator was used. Column (250 x 4 mm i.d) packed with Licrosorb Si100, 5μ was used.

Pure copper(II), nickel(II), palladium(II) and oxovanadium(IV) complexes of H_2SA_2Ten containing 1mg/mL after appropriate dilution were injected on HPLC column. The complexes were eluted isocratically with a ternary mixture of 1,2-dichloroethane:chloroform:acetonitrile (70:28:2, v/v/v), using flow rate of 0.9 mL/min. For simultaneous detection of copper(II), nickel(II), palladium(II) and oxovanadium(IV). Excitation and emission wavelengths were fixed at 280 nm and 370 nm respectively.

Solvent extraction of nickel

To a well stoppered test tube was transferred solutions (0.1-5.0 mL) containing (0-250 μ g) of nickel, sodium bicarbonate buffer (2 mL) (pH 8) and reagent solution (1% in ethanol) (1 mL). The contents were heated on water bath for 10 min. and were allowed to cool. Chloroform (2 mL) was added and layers were mixed well. The layers were allowed to separate and an aliquot from the chloroform layer (1-5 μ l) was injected on the HPLC column and fluorescence response was measured using excitation and emission wavelengths fixed at 340 nm and 420 nm respectively.

Analysis of Raney Nickel

Raney nickel [(Nickel-aluminum alloy) (Merck)] (0.25 g) was added to hydrochloric acid (8 ml, 37%) and nitric acid (3 mL, 65%). The contents were heated on hot plate and when most of Raney nickel dissolved, contents were heated to near dryness. The residue was dissolved in water and volume was adjusted to 100 mL. Solution (0.1 ml) was taken and was added ammonium fluoride (0.3 mL, 1M) to mask aluminum. The remaining extraction procedure was followed as above.

Conclusion

A method has been developed based on normal HPLC separation of copper(II), nickel(II), palladium(II) and oxovanadium(IV) as complexes of H_2SA_2Ten using spectrofluorimetric detection. Solvent extraction procedure in chloroform has been examined for nickel and the method has been applied for the analysis of nickel in nickel aluminum alloy. There is a reasonable correlation between expected and analysed value.

References

1. A. Pasini and M. Gullotti, *J. Coord. Chem.*, **3**, 319 (1974).
2. A. Pasini, M. Gullotti and R. Ugo, *J. Chem. Soc. Dalton Trans*, 346 (1977).
3. E. Casarotti, M. Gullotti, A. Pasini, *J. Chem. Soc. Dalton Trans*, 757 (1977).
4. E. Casarotti, M. Gullotti, A. Pasini and R. Ugo, *J. Chem. Soc. Dalton Trans*, 2147 (1981).
5. H. Kanatomi, I. Murase and A.E. Martell, *J. Inorg. Nucl. Chem.*, **38**, 1465 (1976).
6. P.C. Uden, I.E. Biglay and F. H. Walters, *Anal. Chim. Acta*, **79**, 175 (1975).
7. M.Y. Khuhawar and A.G. Bhatti, *Ind. J. Chem.*, **26A**, 180 (1987).
8. P.C. Uden, D.M. Parees and F.H. Walters, *Anal. Lett.* **8**, 795 (1975).
9. M.Y. Khuhawar and G.Q. Khaskheli, *J. Chem. Soc. Pak.*, **13**, 10 (1991).
10. M.Y. Khuhawar and A.G. Bhatti, *J. Chem. Soc. Pak.*, **12**, 324 (1990).
11. D.A. Averill and R.E. Broman, *Inorg. Chem.*, **17**, 3389 (1978).
12. M.Y. Khuhawar, Shah Nawaz Lanjwani and G.Q. Khaskheli, *J. Chem. Soc. Pak.* (Press).