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# High-performance liquid chromatographic determination of vanadium in crude petroleum oils using bis(salicylaldehyde)tetramethylethylenediimine

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## Abstract

A method was developed for the complexation and solvent extraction of the oxovanadium(IV) complex of bis(salicylaldehyde)tetramethylethylenediimine ( $H_2SA_2Ten$ ) in chloroform. The complex was eluted from a normal-phase high-performance liquid chromatographic (HPLC) column using chloroform or chloroform–1,2-dichloroethane–acetonitrile (78:17:5) as eluent. The detection limit for vanadium was 2.5 ng per injection. The method was applied to the determination of vanadium in crude petroleum oils in the range 0.47–0.54  $\mu g/g$  oil. Copper and nickel could also be extracted simultaneously, and there was complete separation between copper, nickel and vanadium using HPLC conditions. A coin containing copper, nickel and vanadium was analysed.

## 1. Introduction

A number of methods have been reported for the determination of vanadium in crude oils, including atomic absorption [1], inductively coupled plasma atomic emission [2] and radioisotope X-ray fluorescence spectrometry [3], flow-injection analysis [4], neutron activation analysis [5] and gas chromatography (GC) [6]. High-performance liquid chromatographic (HPLC) methods are interesting because of the ease of separation and the capability for the simultaneous determination of a number of metal ions, using a suitable complexing agent.

A number of complexing reagents have been used for the HPLC separation of vanadium from cobalt, iron, chromium, nickel, copper, pal-

ladium, aluminium and zinc [7–13]. Some of the complexing reagents used are 8-hydroxyquinoline [14,15], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol [13], 2-(3,5-dibromo-2-pyridylazo)-5-diethylaminophenol [10,16], 2,2'-dihydroxyazobenzene [11,17], 2-(8-quinolyazo)-5-N,N-diethylaminophenol [12] and 4-(2-pyridylazo)resorcinol [18,19]. Normal-phase [14], reversed-phase [12–15] and ion-pair reversed-phase [9–11,16] modes have been used. Vanadium has been determined in rain and sea water and airborne particles [12,13,15].

The reagent bis(salicylaldehyde)tetramethylethylenediimine [2,3-dimethyl-2,3-N,N'-butanebis(salicylaldimine)] ( $H_2SA_2Ten$ ) has been used for the determination of copper and nickel using GC and normal-phase HPLC [14]. The copper and nickel were extracted as metal chelates in toluene from aqueous solution. How-

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ever, using the specified conditions vanadium was not extracted from the aqueous phase. Dilli and Patsalides [6] used bis (acetyl-pivalyl-methane) ethylenediimine for the GC determination of vanadium in crude oils by derivatization in methanol, followed by solvent extraction in carbon disulphide. A slightly modified method of Dilli and Patsalides [6] was used in this work for the HPLC determination of vanadium using  $H_2SA_2Ten$  as complexing agent. HPLC methods reported for the determination of vanadium involved derivatization and elution of vanadium as vanadium(V) [9–18]. Recently, vanadium(IV) and vanadium(V) have been separated using 4-(2-pyridylazo)resorcinol as chelating agent by reversed-phase HPLC [19], but the present work was based on the separation and determination of vanadium(IV) from copper(II) and nickel(II) using solvent extraction and normal-phase HPLC.

## 2. Experimental

$H_2SA_2Ten$  reagent was prepared by heating together salicylaldehyde and 2,3-dimethyl-2,3-aminobutane in a 2:1 molar ratio. Its copper(II), nickel(II) and oxovanadium(IV) chelates were prepared by refluxing together an equimolar solution of copper(II) acetate, nickel(II) acetate or vanadium(IV) sulphate in methanol and the reagent for 15–30 min as reported previously [20,21]. Elemental analyses, carried out by Elemental Micro Analysis (Devon, UK) agreed with the expected values [20].

A Hitachi Model 655A liquid chromatograph connected with a variable-wavelength UV monitor, a Rheodyne Model 7125 injector and a Hitachi D2500 chromatointegrator was used.

A silica gel 100 (5  $\mu m$ ) column (200  $\times$  4.6 mm I.D.) (Hewlett-Packard) and a column (250  $\times$  4 mm I.D.) packed with LiChrosorb Si 100 (5  $\mu m$ ) were used.

Acetic acid (glacial), sulphuric acid (95–98%), nitric acid (65%), ammonia solution (35%) and perchloric acid (69%) (Merck) were used.

### 2.1. Solvent extraction of vanadium

Sulphur dioxide was passed through solutions containing different amounts of vanadium (0–250  $\mu g$ ) for 30 s, then glacial acetic acid (0.5 ml) and 35% ammonia solution (0.5 ml) were added. The contents were heated gently on an oil-bath and most of the solvent was evaporated. The residue was dissolved in ethanol (5 ml) and 2 ml of  $H_2SA_2Ten$  reagent solution (1.0% w/v in ethanol) were added. The contents were warmed at 60–70°C for 15 min and transferred into a separating funnel containing water (20 ml). Chloroform (5 ml) was added and the contents were mixed well. The layers were allowed to separate and the organic layer was collected. An aliquot (5  $\mu l$ ) of the extract was injected on to the column (200  $\times$  4.6 mm I.D.) and the complex was eluted with chloroform at a flow-rate of 0.9 ml/min followed by UV detection at 300 nm.

### 2.2. Simultaneous extraction of copper, nickel and vanadium

Through an aliquot of solution (1–5 ml) containing copper, nickel and vanadium (0–150  $\mu g$ ) was bubbled sulphur dioxide for 30 s, then glacial acetic acid (0.5 ml) and 35% ammonia solution (0.5 ml) were added. Most of the solvent was evaporated on an oil-bath and the same extraction procedure as in Section 2.1 was followed. The extract (5  $\mu l$ ) was injected on to the column (250  $\times$  4 mm I.D.) packed with LiChrosorb Si 100 and the complexes were eluted with 1,2-dichloroethane–chloroform–acetonitrile (78:17:5, v/v/v) at a flow-rate of 0.9 ml/min, followed by UV detection at 270 nm.

### 2.3. Determination of vanadium in crude oils

To crude oil samples (5–30 g) obtained from the Khaskhely, Lashari and Thora oil fields located in the south Indus Basin near Hyderabad, Sindh, Pakistan, were added 95–98% sulphuric acid (10 ml), 65% nitric acid (20 ml), and perchloric acid (4 ml). The contents were heated gently, then more nitric acid was added

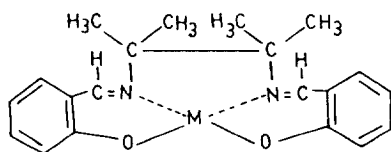
until the solution became clear. The solution was concentrated to 1–2 ml and the volume was adjusted to 10 ml with water. A 5–10 ml volume of the solution was taken and the same procedure as in Section 2.1 was followed.

#### 2.4. Determination of copper and nickel in a coin

To a coin (25 pasia) (2.321 g) was added hydrochloric acid (25 ml) and the mixture was heated gently. More hydrochloric acid (25 ml) was added until the solution became clear. The solution was concentrated to 1–2 ml and the volume was adjusted to 100 ml with water. A 0.1 ml volume of the solution was taken and the procedure as in Section 2.2 was followed.

### 3. Results and discussion

The reagent  $\text{H}_2\text{SA}_2\text{Ten}$  reacts selectively with vanadium(IV) to form a complex,  $\text{SA}_2\text{TenVO}$  (Fig. 1). Therefore, sulphur dioxide was bubbled through the solution to reduce vanadium(VI) to vanadium(IV). The reagent failed to extract vanadium(IV) from aqueous solution. Therefore, prederivatization was carried out in ethanol. Oxovanadium(VI) acetate is more soluble in ethanol, so acetic acid was added to the solution, before heating the solution to dryness, in order to convert oxovanadium(IV) sulphate into oxovanadium(IV) acetate. Using these conditions with a heating time of 15 min, followed by extraction in chloroform, the transfer of vanadium from the aqueous to the organic phase was quantitative. This was checked by extracting



M = Cu, Ni, VO

Fig. 1. Formula of metal chelates.

250–2000  $\mu\text{g}$  of vanadium(IV) in chloroform (5 ml) and measuring the absorbance of the solution at 598 nm spectrophotometrically. A linear calibration graph was obtained that obeyed Beer's law. This extraction procedure was used for the determination of vanadium at trace levels using HPLC with UV detection.

The vanadium chelate was easily eluted from the silica gel 100 column ( $200 \times 4.6$  mm I.D.) with chloroform, giving a symmetrical peak with a retention time of 3.60 min. The excess of the reagent eluted with a retention time of 3.00 min and did not interfere with the determination of vanadium (Fig. 2). The response of the detection at 300 nm was checked by injecting 5  $\mu\text{l}$  of extracts of different concentrations and measuring the average peak height ( $n = 3$ ). A linear calibration graph was obtained in the range 0–250  $\mu\text{g}$  of vanadium. The detection limit measured as three times the background noise was 2.5  $\mu\text{g}$  of vanadium in 5 ml, corresponding to 2.5 ng of vanadium per injection.

Test solutions containing different amounts of vanadium were also analysed and relative error

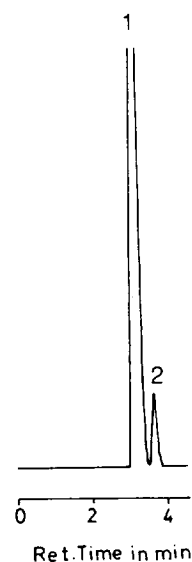


Fig. 2. HPLC separation of (1) reagent and (2) oxovanadium complex. Column, silica gel 100 ( $200 \times 4.6$  mm I.D.); eluent, chloroform; flow-rate, 0.9 ml/min; detection, UV at 300 nm.

was found to be 0–4.1%. The vanadium concentrations in the crude petroleum oils obtained from Khaskhely, Lashari and Thora oil fields were found to be in the ranges 0.54, 0.50 and 0.47  $\mu\text{g/g}$ , respectively, with relative standard deviations of 4–10%.

When the extraction procedure was checked for the simultaneous extraction and subsequent HPLC determination of copper, nickel and vanadium, it was interesting that the use of sulphur dioxide to reduce vanadium(VI) to vanadium(IV) did not prevent the derivatization of copper and nickel. The optimum separation between copper, nickel and vanadium on the column (250  $\times$  4 mm I.D.) packed with LiChrosorb Si 100 was obtained when the complexes were eluted isocratically using chloroform–1,2-dichloroethane–acetonitrile (78:17:5, v/v/v) at a flow-rate of 0.9 ml/min with UV detection at

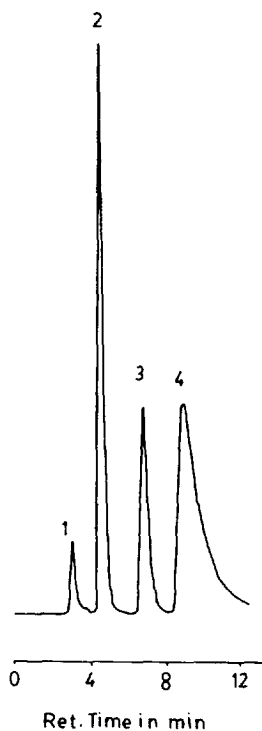


Fig. 3. HPLC separation of (1) reagent and (2) vanadium, (3) nickel and (4) copper chelates. Column, LiChrosorb Si 100 (250  $\times$  4 mm I.D.); eluent, 1,2-dichloroethane–chloroform–acetonitrile (78:17:5); flow-rate, 0.9 ml/min; detection, UV at 270 nm.

270 nm (Fig. 3). Linear calibration graphs for the simultaneous determination of copper, nickel and vanadium were obtained in the range 0–150  $\mu\text{g}$ , with correlation coefficients ( $r$ ) of 0.999, 0.988 and 0.986 for vanadium, nickel and copper, respectively.

The reagent  $\text{H}_2\text{SA}_2\text{Ten}$  also reacts with cobalt(II) and iron(II) to form coloured complexes. Their effect on the determination of copper, nickel and vanadium was checked at a level of 1000  $\mu\text{g}$  of cobalt and iron. The cobalt(II) and iron(II) chelates were not eluted from the column and did not interfere in the determination of copper, nickel and vanadium.

Finally, a coin was analysed for its contents of copper, nickel and vanadium. The copper and nickel concentrations were found to be  $40.9 \pm 0.9\%$  and  $8.6 \pm 0.5\%$  ( $n = 3$ , 95% confidence level), respectively. The coin sample solution was also spiked with vanadium (50  $\mu\text{g}$ ) to check the simultaneous extraction and determination of vanadium and the relative error was 5%.

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