Capillary gas chromatographic determination of vanadium in crude petroleum oil using fluorinated ketoamines as derivatizing reagents

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Abstract

The separation of oxovanadium(IV) complexes of four tetradentate ligands, bis(trifluoroacetylacetone)ethylenediimine ($H_2F_3AA_2$en), bis(trifluoroacetylacetone)propylenediimine ($H_2F_3AA_2$S), bis(trifluoroacetylacetone)-*dl*-stilbenediimine (*dl*-$H_2F_3AA_2$S) and bis(trifluoroacetylacetone)-*meso*-stilbenediimine (*meso*-$H_2F_3AA_2$S) from their copper(II), nickel(II) and palladium(II) complexes was obtained on a BP-1 column (12 m×0.22 mm I.D.) with a film thickness of 0.25 μm. Each of the complexes gave a single peak, except oxovanadium complexes of $H_2F_3AA_2$Pn and *meso*-$H_2F_3AA_2$S, which gave two peaks, due to the separation of their diastereoisomers. Solvent extraction procedures have been developed for the determination of vanadium. The reagent *dl*-$H_2F_3AA_2$S was used to determine vanadium in crude petroleum oils from lower Indus basin oil fields.

Keywords: Petroleum; Vanadium; Ketoamines

1. Introduction

Vanadium is a micronutrient that is present at ppb levels and it is reported to be toxic at the ppm level [1]. Its determination in crude petroleum oils is significant from an environmental perspective. Vanadium is organically bound in crude petroleum oils and can also poison and foul catalysts in refinery operations [2].

A number of analytical methods have been used for the determination of vanadium from crude petroleum oils and include atomic absorption spectrometry [3], inductivity coupled plasma atomic emission [4], radioisotope X-ray fluorescence spectrometry [5], flow injection analysis [6], neutron

activation analysis [7], gas [8] and liquid chromatography [9,10]. Dilli and Patsalides [8] have used bis(acetylpivalylmethane)ethylenediimine (H_2APM_2-en) for the gas chromatographic (GC) determination of vanadium in crude petroleum oils at levels of 0.1 μg/g. Zeng and Uden [11] have demonstrated that size exclusion chromatography is an effective and reproducible sample pretreatment procedure for removal of heavy oil matrices, prior to GC coupled with microwave-induced plasma atomic emission detection. They have reported the use of high temperature capillary GC for the detection of vanadyl, nickel and iron porphyrins in crude petroleum oils at ppm levels [12]. Recently, the reagents bis(salicylaldehyde)tetramethylethylenediimine [9] and H_2APM_2en were used for the high-performance liquid chromatographic (HPLC) determination of

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vanadium and vanadium, iron, nickel and copper from crude oils from lower Indus Basin oil fields at levels of 70–230 ng/g metal ion [10]. Capillary GC has enormous capability for the separation of complex mixtures, however, the use of capillary GC for metal analyses requires adequate thermal stability and that the metal derivatives are volatile under GC operating conditions. Oxovanadium(IV) chelates of the fluorinated ligands $H_2F_3AA_2en$, $H_2F_3AA_2Pn$, dl-$H_2F_3AA_2S$ and $meso$-$H_2F_3AA_2S$ have sufficient thermal stability and volatility [13,14] and, in this work, were examined for the determination of vanadium using capillary GC (Fig. 1).

The reagents $H_2F_3AA_2en$ and $H_2F_3AA_2Pn$ were studied extensively as complexing reagents for copper(II), nickel(II), iron(II), cobalt(II), palladium(II) and oxovanadium(IV) [15–17]. The gas chromato-

graphic analysis of copper(II), nickel(II), palladium(II), platinum(II) and oxovanadium(IV) complexes of $H_2F_3AA_2en$, $H_2F_3AA_2Pn$, dl-$H_2F_3AA_2S$ and $meso$-$H_2F_3AA_2S$ has been reported using on packed columns using flame ionization detection (FID) or electron capture detection (ECD) [13,14,18,19]. Uden and Zeng [20] reported the use of capillary GC with atomic emission detection and HPLC to characterise the isomerism of the oxovanadium complex of $H_2F_3AA_2Pn$ [20]. HPLC elution and separation of copper(II), nickel(II), palladium(II) and oxovanadium(IV) complexes of dl-$H_2F_3AA_2S$ and $meso$-$H_2F_3AA_2S$ have also been reported [21].

2. Experimental

2.1. Preparation of reagent and metal chelates

The reagents $H_2F_3AA_2en$, $H_2F_3AA_2Pn$, dl-$H_2F_3AA_2S$ and $meso$-$H_2F_3AA_2S$ were prepared as reported [15,19] by heating together trifluoroacetylacetone (0.01 M) and ethylenediamine, propylenediamine, dl-stilbenediamine or $meso$-stilbenediamine (0.005 M) in ethanol. Copper(II) and nickel(II) chelates were prepared by refluxing together methanolic solutions of copper(II) acetate or nickel(II) acetate with the appropriate reagent. The oxovanadium complexes were prepared using a ligand exchange method by heating together bis(acetylacetone)oxovanadium(IV) and the appropriate reagent at a temperature of 160–200°C [17]. Palladium(II) complexes were prepared by refluxing together palladium(II) benzonitrile complex and the appropriate reagent in benzene [14].

2.2. Solvent extraction of vanadium

The solution (1–10 ml) was passed through sulphur dioxide for 10–15 s to reduce vanadium(VI) to vanadium(IV). A 2-ml volume of a 1 M ammonium acetate buffer was added to the solution and the mixture was heated to dryness in an oil bath. The residue was dissolved in ethanol (5 ml) and 2 ml of the reagent solution (1%, w/v) were added. The contents were heated in a water bath for 15 min and the volume of the solution was reduced by approxi-
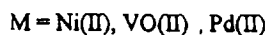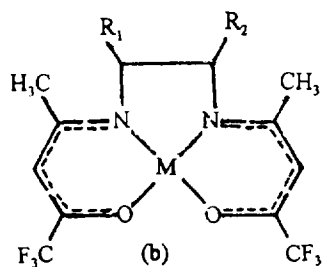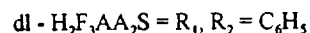
$H_2F_3AA_2en = R_1, R_2 = H$

$H_2F_3AA_2Pn = R_1 = CH_3, R_2 = H$

$meso$ - $H_2F_3AA_2S = R_1, R_2 = C_6H_5$

dl - $H_2F_3AA_2S = R_1, R_2 = C_6H_5$
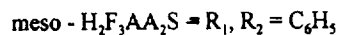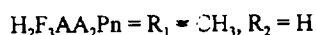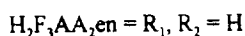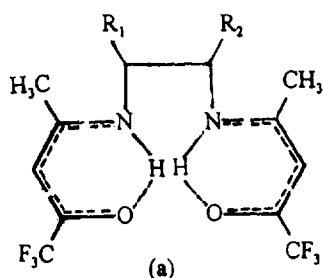
$M = Ni(II), VO(II), Pd(II)$

Fig. 1. Structural representation of (a) reagent and (b) metal chelates.

mately 50%. Water (5 ml) and chloroform (5 ml) were added to the residue. The mixture was shaken for 5 min and the organic layer was separated and transferred to a sample vial. The solvent was evaporated and the residue was dissolved in ethanol (0.2 ml). A 1-μl volume of the solution was injected onto the BP-1 column (12 m×0.22 mm I.D.; film thickness, 0.25 μm), at a column temperature of 220°C and with a programmed heating rate of 4°C/min up to 260°C, and then held at 260°C for 2 min. The injector and detector temperatures were fixed at 275 and 280°C, respectively. The split ratio was 1:10, the nitrogen flow-rate was 3.5 ml/min and detection was by FID.

2.3. Determination of vanadium in crude petroleum oils

A 50-ml volume of sulphuric acid (95–98%) was added to the crude oil sample (50 g) and the mixture was heated on a hot plate until white fumes of sulphur trioxide evolved. A 100-ml volume of nitric acid (65%) and 25 ml of perchloric acid (70%) were added slowly to the partially cooled mixture. The mixture was heated gently and brown fumes of nitrogen oxides evolved. More nitric acid was added until the solution became clear. The solution was concentrated to about 1–3 ml and the volume was adjusted to 25 ml with water. A 10-ml volume of the solution was removed and the pH was adjusted to 6.5 with ammonia solution (1%) and the solvent extraction procedure was followed. Blanks were prepared simultaneously.

2.4. Standard addition technique

To 3 ml volumes of a solution prepared from crude petroleum oil from the Thora oil field (3 ml) were added vanadium (8, 16 and 24 μg, respectively) and the extraction procedure was followed. The amount of vanadium in the oil samples was evaluated using a graphical method.

2.5. Determination of vanadium by atomic absorption

A 10-ml solution prepared from crude petroleum oil from the Thora oil field was concentrated and the

volume was adjusted to 5 ml. A 200-μg amount of vanadium (in a volume of 1 ml) was added to the solution and the volume was adjusted to 10 ml with aluminum nitrate (2 mg/ml). Vanadium was determined by nitrous oxide–acetylene flame atomization under the conditions recommended by the manufacturer.

Oil samples from Leghari, Tando Alam and the Thora oil field, located in the lower Indus Basin in Badin and the Hyderabad Districts, were collected when oil was actually being pumped out.
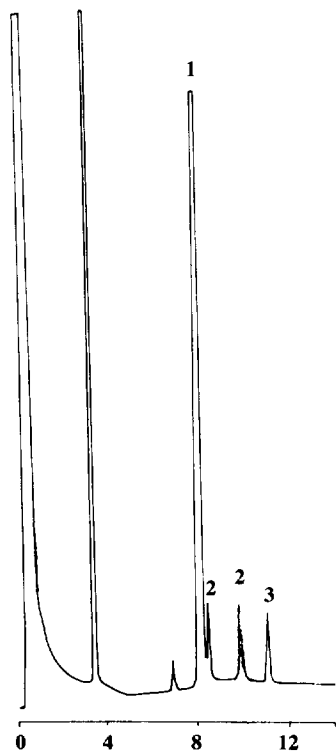
A Perkin-Elmer 8700 gas chromatograph with a split injection system, a FID detection system and an EPSON LX-800 printer were used. Pure hydrogen gas, obtained from a hydrogen generator OPGS-1.5000S (Shimadzu) was used for FID detection and pure nitrogen gas, obtained from Pakistan Oxygen Company (Karachi, Pakistan) was used as the carrier gas. A BP1 column (12 m×0.22 mm I.D.) with a film thickness of 0.25 μm (SGE Australia) was used. A Varian Spectra AA20 atomic absorption spectrometer with a nitrous oxide–acetylene flame atomizer was used. Trifluoroacetylacetone (Fluka), ethylenediamine and propylenediamine (E. Merck) were used. dl-Stilbenediamine and meso-stilbenediamine were prepared as reported [22,23]. All the solvents and chemicals were of Merck G.R. grade.

3. Results and discussion

When copper(II), nickel(II), palladium(II) or oxovanadium(IV) complexes (1 mg/ml) of $H_2F_3AA_2en$, $H_2F_3AA_2Pn$, dl-$H_2F_3AA_2S$ or $meso$-$H_2F_3AA_2S$ were injected onto the BP1 column (after appropriate dilution), each of the complexes eluted as a sharp and single peak, except for dioxovanadium complexes of $H_2F_3AA_2Pn$ and $meso$-$H_2F_3AA_2S$, which gave two peaks. Uden and Zeng [20] also observed two peaks from the F_3AA_2PnVO complex using capillary GC and HPLC. They attributed the two peaks to the separation of diastereoisomers. The isomers are observed due to different arrangements of the methyl group with respect to the V=O group. The vanadium chelates dl-F_3AA_2SVO and $meso$-F_3AA_2SVO contain two phenyl groups at the bridge position, but in the case of dl-F_3AA_2SVO, they are present at diaxial positions [24] and indicate a pair of enantiomers that

failed to separate chromatographically. However, meso-F_3AA_2SVO has these phenyl groups arranged in an axial–equatorial configuration. Thus, the two peaks seen using capillary GC (Fig. 2) could be due to the separation of diastereoisomers due to the different arrangements of V=O with respect to phenyl groups. The oxovanadium complexes of $H_2F_3AA_2en$ and dl-$H_2F_3AA_2S$ gave single peaks, which are ideal for the quantitative determination of vanadium.
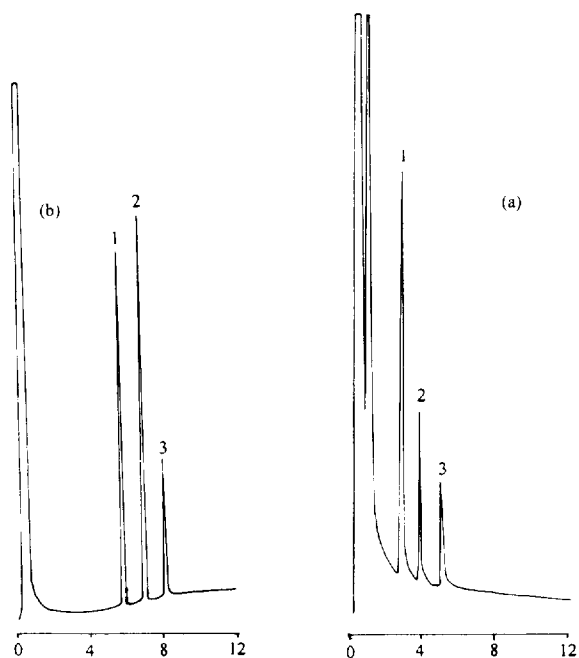
The separation of copper(II), nickel(II), palladium(II) and oxovanadium(IV) complexes of $H_2F_3AA_2en$, $H_2F_3AA_2Pn$, dl-$H_2F_3AA_2S$ and meso-$H_2F_3AA_2S$ was examined using a BP-1 column. It was observed that nickel(II), oxovanadium(IV) and palladium(II) or copper(II), oxovanadium(IV) and palladium(II) complexes completely separated. The excess derivatizing reagent eluted first and therefore

it not affect the separation (Fig. 3a–b). However, the copper(II) and nickel(II) coeluted and did not separate, as has been reported by Uden and Zeng [20] for the copper(II) and nickel(II) chelates of $H_2F_3AA_2Pn$ from a DB-5 column (6 m×0.25 mm I.D.). The reagents $H_2F_3AA_2en$ and dl-$H_2F_3AA_2S$ were examined for the solvent extraction and for determination of vanadium using FID detection system. Linear calibration curves were obtained by plotting average peak height ($n=3$) vs. amount of vanadium, with 0–250 and 0–200 μg/ml vanadium for $H_2F_3AA_2en$ and dl-$H_2F_3AA_2S$, respectively. The coefficients of correlation (r), calculated from $n=5$ standards, were 0.9974 and 0.9998 for F_3AA_2enVO and dl-F_3AA_2SVO, respectively. The coefficients of variation (C.Vs.) of replicate analyses ($n=3$) for 100 μg/ml solutions were found to be 3.24 and 2.53% using $H_2F_3AA_2en$ and dl-$H_2F_3AA_2S$ complexing reagents, respectively. The detection limits measured as three times the background noise were 5.0 and 3.0 μg/ml, corresponding to 0.50 and 0.30 ng/injection,

Retention time in minutes

Fig. 2. Capillary GC separation of the diastereoisomers of meso-F_3AA_2SVO (1) Ni(II), (2) isomers of VO(II) and (3) Pd(II). Conditions were as described in Section 2.

Retention time in minutes

Fig. 3. Capillary GC separation of (1) Ni(II), (2) VO(II) and (3) Pd(II) complexes of (a) $H_2F_3AA_2en$ and (b) dl-$H_2F_3AA_2S$. Conditions were as described in Section 2.

for $H_2F_3AA_2$en and dl-$H_2F_3AA_2$S, respectively. The reagent dl-$H_2F_3AA_2$S was better for the FID of vanadium because of substitution of two phenyl groups at the bridge position, as has been reported for copper and nickel complexes using a packed column [14,19].

The reagent dl-$H_2F_3AA_2$S was used for the determination of vanadium in crude petroleum oils after oil decomposition, followed by complexation and solvent extraction of vanadium.

The metal chelates are highly stable and loss in weight occurs at temperatures above 180°C. The use of the solvent extraction procedure developed, which involves the evaporation of the solvent using a water bath, to preconcentrate the sample by at least 50%, did not effect the quantitative determination. Quantitation was carried out using capillary GC (conditions are given in Section 2) and the amount of vanadium was determined from the calibration curve for vanadium. The amounts of vanadium obtained in Leghari, Tando Alam and Thora crude petroleum oil were 0.44, 0.49 and 0.52 μg/g, with C.Vs. (n=3) of 2.9,

5.8 and 3.3%, respectively. The oil sample from Thora was also analysed using the standard addition technique and the amount found was 0.53 μg/g with a C.V. (n=3) of 3.04% (Fig. 4). The oil sample from the Thora oil field was also analysed using nitrous oxide–acetylene flame atomic absorption, after spiking the sample with 20 μg/ml vanadium. The amount of vanadium found was 0.64 μg/g with a C.V. of 1.4% (n=3).

4. Conclusion

The copper(II), nickel(II), palladium(II) and oxo-vanadium(IV) chelates of four tetradentate B-ketoamine ligands derived from trifluoro-acetylacetone were examined using capillary GC on a methyl silaxone (BP-1) column, in concert with FID. A method has been proposed for the determination of vanadium in petroleum oils using complexation, solvent extraction and capillary GC. A detection limit at the sub ng/injection level was obtained for vanadium.

(a)

(b)

1

1

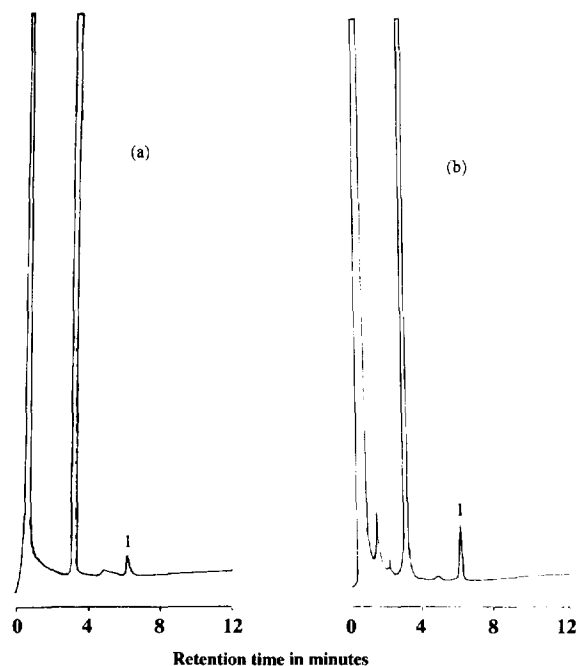0   4   8   12   0   4   8   12

Retention time in minutes

Fig. 4. Capillary GC analysis of (1) vanadium in crude petroleum oil from the Thora oil field, chromatogram of (a) the oil sample and (b) a sample spiked with 24 μg of vanadium. Conditions were as described in Section 2.

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