Capillary Gas Chromatographic Determination of Vanadium in Rock Samples Using Bis (Acetylpivalylmethane) Ethylenediimine as Complexing Agent

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Summary: A capillary gas chromatographic method has been developed for the determination of vanadium from rock samples. It is based on complexation of analyte by bis (acetylpivalylmethane) ethylenediimine (H_2APM_2en) followed by solvent extraction, elution and separation through capillary gas chromatographic column BP5 (50 m x 0.22 mm i.d.) with layer thickness 0.25 μm. The complexing reagent and copper (II), nickel (II), palladium (II) and platinum (II) as metal chelates of H_2APM_2en completely separated from oxovanadium (IV). However, high concentration of iron (II) supressed oxovanadium (IV) response. Quantitation was carried out using standard addition after acid dissolution of rock samples. The amount of vanadium was found within 101.5 - 687.5 μg /g with relative standard deviation (RSD) 2.05 - 4.27 %.

Introduction

Vanadium is reported to be micronutrient at trace levels (ppb), but is toxic at higher concentration (ppm) [1] Vanadium has been extensively determined in geological materials [2-7], crude petroleum [8-12] rain and natural water [13], airborne particles [14], catalysts [15], and steel [16]. The analytical methods are based on spectrophotometry [9,16,17], spectroflurimetry [18], atomic absorption [3, 19, 20] inductively coupled plasma atomic emission [6, 21-23], X-ray fluorescence [24,25] electroanalytical [26, 27] neutron activation analysis [28, 29] , liquid [14, 15, 30-34] and gas chromatographic techniques [11, 12, 35 -37]. GC of vanadium is based on volatile metal chelates [11, 36, 37] or naturally occuring metalloporphyrins]12, 35], using packed or capillary column connected with FID or micro-wave induced plasma atomic emission detection (MIP-AED). GC methods have been applied for the determination of vanadium in crude petroleum [11, 12, 35, 37].

The reagent H_2APM_2en has been applied for GC determination of copper and nickel in metal alloy [38] and vanadium in crude petroleum oils [11]. HPLC determination of copper and nickel and copper, nickel, iron and vanadium form crude petroleum [33]. In the present work the reagent H_2APM_2en has been applied for the determination of vanadium from rock samples.

Results and Discussion

The reagent H_2APM_2en reacts with copper(II), nickel(II), palladium(II), platinum(II) and oxovanadium(IV) to form coloured complexes, which are extractable in chloroform. After evaporation of solvent and redissolving the residues in methanol, the complexes were injected on the capillary GC column (BP5), all the complexes eluted as sharp symmetrical peaks. Complete separation was obtained between copper, nickel, oxovanadium, palladium and platinum (Fig 2). The use of the reagent for the quantitative determination of vanadium was examined using solvent extraction procedure and average peak height (n=3) was measured. Based on the concentration of vanadium in final solution, linear calibration curve was obtained with 10 -100 μg/ml with coefficient of correlation 0.9989. The detection limit measured as three times the back ground noise was 0.5 μg/ml corresponding to 0.33 ng of vanadium reaching to the detector. The rock samples contained a significant amount of iron. Therefore, the effect of iron on the CGC determination of vanadium was examined. The reagent H_2APM_2en reacts with iron (II) to form coloured complex, which is extractable in organic phase [33]. Dilli and Patsalides [11] while studying the effects of diverse ion on the GC determination of vanadium did not observe the effect of iron. In the present work a large excess of iron (1-2 mg) per aliquot was added and its effect on the

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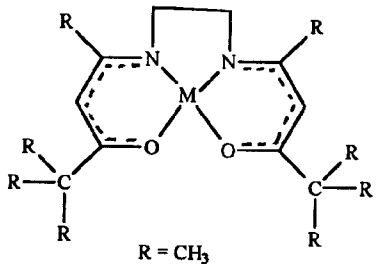
capillary GC determination of vanadium was examined. It was observed that it decreased the peak height of vanadium. Addition of excess of the reagent did not improve the response. However, in the presence of constant amount of iron when different amounts of vanadium were added, a linear increase in the peak height for vanadium was observed with coefficient of correlation 0.9981. Rock samples were therefore, analysed using standard addition technique. Four equal portions of a sample solution, prepared after acid dissolution were added different amounts of vanadium. The quantitation was carried out using graphical method. Eight samples were analysed and the vanadium found was within 101.5 - 687.5 μg/g with relative standard deviation (RSD) within 2 to 4.3 % (Fig. 3). The vanadium contents in samples observed are lower than reported Atomic Energy Mineral Centre, Lahore (Table 1) with relative deviation within 3 - 14 %. Capillary GC results obtained are quite reproducible with RSD for all the samples analysed within 2.0 to 4.3 % using standard addition technique, but are lower than the reported value. This may be because of low dissolution efficiency in nitric - hydrochloric acid mixture as has been reported for the dissolution of U_2O_8 from mineral ore samples [40].

Table 1: Analysis of rock samples for vanadium content.

S. No	Sample No.	CGC analysis μg/g(RSD)	Reported amount by A.E.M.C. Lahore μg/g	Relative deviation (%)
1.	40577	687.5 (3.35)	735	6.46
2.	40936	350.0 (4.24)	395	11.39
3.	40229	137.5 (2.85)	160	14.06
4.	40946	131.2 (2.05)	150	12.50
5.	40948	101.5 (3.64)	110	7.72
6.	40278	158.5 (4.27)	164	3.35
7.	40221	207.5 (2.56)	224	7.36
8.	40225	162.0 (2.48)	173	6.35

Experimental

The reagent H_2APM_2en and its copper (II), nickel (II), palladium (II) complexes were prepared as reported [38] . H_2APM_2en was prepared by heating acetylpivalylmethane and ethylenediamine in 2:1 molar ratio in ethanol. Copper (II) and nickel (II) complexes were prepared by heating together equimolar solution (1mM) nickel (II) acetate or copper (II) acetate and H_2APM_2en in methanol. Palladium (II) complex was prepared by refluxing together palladium-benzonitrite complex and H_2APM_2en in benzene. Oxovanadium (IV) was prepared by ligand exchange method by heating together solid bis (acetylacetone) oxovanadium (IV) and H_2APM_2 en [39] (Fig 1).



M = Cu(II), Ni(II), VO(II), Pd(II), Pt(II)

Fig. 1: Structural diagram of Metal chelates.

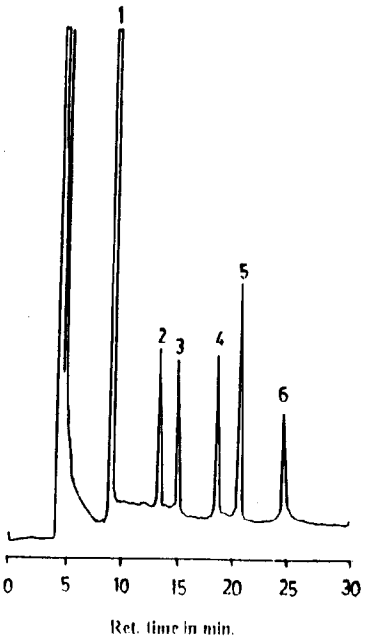


Fig. 2: Capillary GC separation of (1) H_2APM_2en and its (2) copper(II), (3) nickel (II), (4) oxovanadium (IV), (5) palladium (II) and (6) platinum (II) complexes. **Conditions:-** Column BP5 (50 m x 0.22 mm id) with layer thickness 0.25 μm. Temperatures column 260°C with programmed heating rate 10°C/min upto 280°C and stay at maximum temperature for 23 min. Injection port and detector temperatures were 280°C and 290°C respectively. Split ratio 1:15. Detection FID.

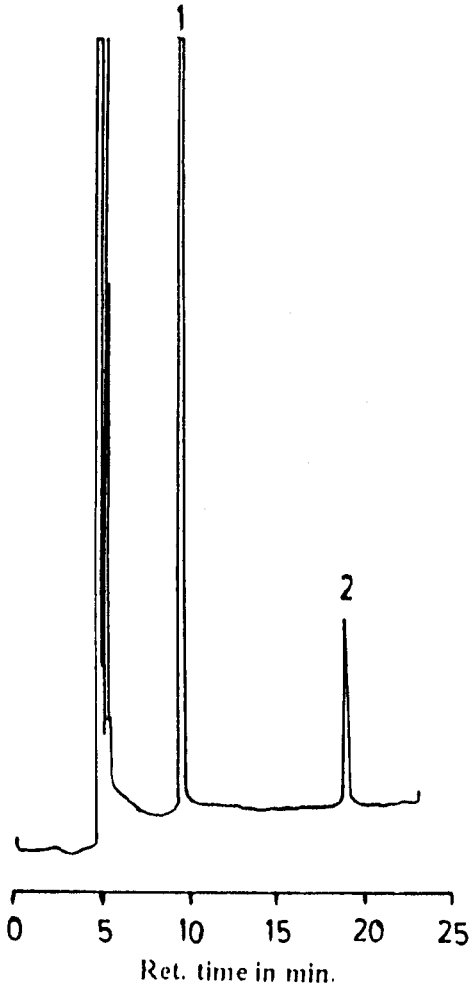


Fig. 3: Analysis of vanadium in rock samples, spiked with 50 μg vanadium. conditions same as Fig.2

Solvent extraction method

An aliquot (1 - 5 ml) containing vanadium (0 -100 μg) or copper (II), nickel(II), palladium (II), platinium (II) and oxovandium (IV) (0-100 μg each) was transferred to stopperd test tube (Quickfit) and sulphur dioxide gas was passed for 30 - 40 s. to reduce vanadium (VI) to vanadium (IV). Sodium acetate -acetic acid buffer pH 6 (2 ml, 1M) was added and tube was heated gently on oil bath to near dryness. The residue was dissolved in ethanol (3 ml) and was added H_2PM_2 en (0.1 M in ethanol w / v 5 ml) and was again heated on water bath for fifteen minutes. During heating volume of the solution reduced to 1 - 2 ml and water (10 ml) and chloroform (3 ml) were added. The contents were shaken on mechanical shaker for ten minutes and the organic layer was separated and evaporatd on water bath. The residue was redissolved in ethanol (0.5-1.0 ml) and was injected (1μl) on a capillary GC column BP-5 (50 m x 0.22 mm i.d) with layer thickness 0.25 μm at column temperature 260°C with programmed heating rate 10° C / min up to 280° C and maximum temperature was fixed for 23 min, with split ratio 1:15, injection port and flame ionization detector temperatures were 280°C and 290°C, respectively, with nitrogen flow rate 4.5 ml / min.

Analysis of Rock Samples

To the rock sample (1 g) was added aqua regia (Hydrochloric acid (37%) and nitric acid (65%) 3:1 v/v) (50 ml) and was heated to near dryness. Hydrochloric acid (37%) (10 ml) was added and again heated gently to near dryness. The residue was dissolved in water, filtered and the volume adjusted to 10 - 25 ml. Four solutions (1-2 ml) from each of the sample were taken and were added 25 to 100 μg vanadium and were processed for solvent extraction. The quantitation was carried out using graphical method.

Gas chromatography was carried out on a Perkin Elmer model 8700 gas chromatograph with split injector and FID detector. The carrier gas was oxygen free nitrogen and hydrogen was through the Shimadzu hydrogen generator. Capillary column (50 m x 0.22 mm i.d.) with layer thickness 0.25 μm was obtained from SGE Australia. Rock samples were obtained from Atomic Energy Mineral Centre, Lahore, Pakistan.

Conclusion

An analytical procedure has been described for the determination of vanadium from rock samples using capillary gas chromatography and H_2 APM_2en as derivatizing reagent. Iron affected the CGC response of vanadium, but satisfactory results were obtained using standard addition techinque with coefficent of variation within 2 - 4.3 %.

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