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Determination of vanadium as 4-(2-pyridylazo)resorcinol–hydrogen peroxide ternary complexes by ion-interaction reversed-phase liquid chromatography

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Abstract

The separation and determination of the vanadium(V) ternary complex formed with 4-(2-pyridylazo)resorcinol (PAR) and hydrogen peroxide using ion-interaction reversed-phase high-performance liquid chromatography on a C_{18} column has been investigated. The optimal mobile phase was a methanol–water solution (32:68, v/v) containing 3 m*M* tetrabutylammonium bromide, 5 m*M* acetic acid and 5 m*M* citrate buffer at pH 7, with absorbance detection at 540 nm. The stoichiometry of the ternary complex of vanadium at pH 6 in 10 m*M* acetate buffer using the mole ratio and Job's method by HPLC indicated that the mole ratio of V(V):PAR:H_2O_2 was 1:1:1. The optimal conditions for precolumn formation of the ternary complex were 10 m*M* acetate, 7 m*M* H_2O_2, 0.3 m*M* PAR, and pH 6.

The method gave relative standard deviations of retention time, peak area and peak height for the ternary complex of 0.187, 0.45 and 0.57%, respectively. The detection limit (at a signal-to-noise ratio of 3) for V(V) was 0.09 ng/ml in the digested sample using a 100-μl injection loop (or 0.09 μg/g in the solid fertiliser sample). The method was applied to the analysis of fertilisers (phosphate rocks and nitrogen, phosphorus and potassium fertiliser). The results for vanadium obtained by the HPLC method agreed well with those from magnetic sector inductively coupled plasma MS analysis.

Keywords: Complexation; Fertilisers; Vanadium; Metal cations; Pyridylazoresorcinol; Hydrogen peroxide

1. Introduction

Vanadium(V) has known oxidation states of +2, +3, +4 and +5, with the most stable oxidation state of +4. Mixed oxidation states of vanadium are also known and typically occur as a mixture of +4 and +5 [1]. Vanadium is widely dispersed in the Earth's crust and is present at a concentration of approximately 0.02% (w/w). Studies have indicated that vanadium exhibits considerable toxicity related to heart muscle contraction and renal failure in mammals [2], with stock losses due to contaminated feeds being reported [3]. It has been reported in the literature that the presence of low levels (ng ml^{-1}) of V is required for normal cell development, but vanadium becomes toxic at the μg ml^{-1} level [4]. Additionally, it has been shown that V(V) is considerably more toxic than V(IV) [5]. Vanadium

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speciation from yeast systems has been performed using flow injection coupled with flame atomic absorption spectrometry, FT-NMR and electron spin resonance [6]. Nitrogen, phosphorus and potassium (NPK) fertilisers generated from phosphate rocks can also be contaminated with vanadium and this is known to affect the growth of plants to which such fertilisers have been applied. The determination of vanadium has therefore been of substantial interest in environmental and nutritional research areas.

Several analytical methods have been developed for the determination of vanadium at μg ml^{-1}/ng ml^{-1} levels, including atomic absorption spectrometry (AAS) [7], inductively coupled plasma atomic emission spectrometry (ICP-AES) [8], inductively coupled plasma mass spectrometry (ICP-MS) [9], reversed-phase high-performance liquid chromatography (RP-HPLC) [10–15] and spectrophotometry [16,17]. The main disadvantage of AAS, ICP-AES and ICP-MS for the determination of vanadium is interference by the sample matrix. For example, the main isotope of vanadium (^{51}V, 99.75% abundance) is known to suffer from spectral interference from $^{35}Cl^{16}O$ in chlorine-containing matrices during ICP-MS analysis using standard quadrupole units.

Several papers have described the use of chelating agents such as 4-(2-pyridylazo)resorcinol (PAR) [10–13,15,16], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (BrPADAP) [17] and 2-(5-nitro-2-pyridylazo)-5[*N*-*n*-propyl-*N*-(3-sulfopropyl)amino]-phenol (nitro-PAPS) [14] for precolumn complex formation with vanadium. Subsequent analysis of the vanadium complex was achieved by separation on a C_{18} column using RP-HPLC [10–15] or by using spectrophotometric methods [15–17]. However, a broad peak was obtained for the vanadium complex using the RP-HPLC methods of Zhang et al. [10] and Tadayo and Massourni [11], whilst the method of Oszwaldowski and Jarosz [12] showed a baseline disturbance at the retention time of the V(V)–citrate–PAR complex when applied to a steel sample. Tsai and Hsu report the speciation of V(V) and V(IV) using PAR in an acetate buffer [15]. This method was applied to the analysis of a pure vanadium catalyst, but interferences were observed for a wide range of common metal ions. In addition, there is evidence in the literature of the elution of the vanadium complex in the void volume [13]. Studies by Chen et al. [14] using precolumn formation of vanadium with nitro-PAPS showed that the complex had to be injected into the HPLC within 90 min of preparation in order to obtain reliable results. The spectrophotometric methods cited in the literature indicated low sensitivity [16,17].

The aim of the present research was to develop a HPLC method for the separation and determination of total vanadium and to apply this to the analysis of phosphate fertilisers. Suitable separation selectivity from matrix ions in this complex sample and good detection sensitivity were required for this method to be successful. This new method is based on the formation of a ternary complex using PAR and an auxiliary complexing agent.

2. Experimental

2.1. Instrumentation

The chromatographic system consisted of a Waters (Milford, MA, USA) Model 510 pump, a Rheodyne (Cotati, CA, USA) model 7125 stainless steel 6-port injector (100-μl loop), a SPD-6AU UV–Vis spectrophotometric detector (Shimadzu, Tokyo, Japan) operated at 540 nm, and a Maxima 820 Chromatography Data Station (Waters). A NovaPak C_{18} reversed-phase column (150 mm×3.9 mm I.D., particle size 14 μm, Waters) was used as the analytical column, and was fitted with a NovaPak C_{18} (10 μm particle size) guard column housed in a Waters Guard-Pak precolumn module. The flow-rate of the mobile phase was maintained at 1.0 ml min^{-1}, while the column temperature was kept at 30 °C.

A Finnigan Element (Bremen, Germany) magnetic sector ICP-MS instrument was used to analyse vanadium in the digested fertiliser samples. The medium resolution mode (normally $M/\Delta M \cong 3000$) was selected to analyse ^{51}V, since at this resolution setting, the major interference ($^{35}Cl^{16}O$) associated with this isotope was avoided.

Screw-top Savillex PTFE beakers (Savillex, MN, USA) were used for digestion of fertiliser samples. Spectrophotometric studies were carried out using a Cary 5E UV–Vis–near IR spectrophotometer (Varian, Mulgrave, Victoria, Australia).

2.2. Reagents

Standard ammonium metavanadate (NH_4VO_3, 99.99% purity) was obtained from Aldrich (Milwaukee, WI, USA) and a stock solution of 1.000 mg ml^{-1} NH_4VO_3 was prepared in 1 *M* HNO_3. A standard vanadium solution (0.100 mg ml^{-1}) was used in ICP-MS studies and was obtained from QCD Analysts (NJ, USA). Standard vanadyl sulfate ($VOSO_4$, 99.99% purity) was obtained from Aldrich.

All water used was distilled and then deionised using a Millipore (Bedford, MA, USA) Milli-Q water purification system to yield a final conductance of 18 MΩ. HPLC grade methanol was obtained from Merck (Darmstadt, Germany). PAR monosodium salt hydrate was obtained from Aldrich and solutions of the dye were freshly prepared in water before use. All other reagents used, namely citric acid (99.5% purity, Aldrich), tetrabutylammonium bromide (TBABr, Sigma, St. Louis, MO, USA), ammonium hydroxide (Ajax Chemicals, Sydney, Australia), acetic acid (BDH, Poole, UK), hydrochloric acid (BDH), nitric acid (Ajax) and hydrogen peroxide (30%, w/v, BDH, Victoria, Australia) were of analytical grade.

Mobile phases were prepared by dissolving TBABr, acetic acid and citric acid in water, adding the required amount of methanol, adjusting the pH with ammonium hydroxide and then diluting with water. The optimum mobile phase was methanol–water (32:68, v/v) containing 3 m*M* tetrabutylammonium bromide, 5 m*M* acetic acid and 5 m*M* citrate buffer at pH 7.

Six fertiliser samples were used in this work, including three phosphate rocks obtained from Jordan, South Africa and Morocco and three NPK fertilisers from Norway, Thailand, and Australia.

2.3. Procedures

2.3.1. Sample preparation

Each fertiliser was ground to pass through a 70 mesh sieve. Duplicate 0.1000 g powdered fertiliser samples were added to Savillex 7 ml screwtop PTFE beakers and a few drops of water were added to wet the powdered fertiliser. Concentrated HNO_3 (1.0 ml) and HCl (2.0 ml) were added and the lids fitted and sealed. The samples were then digested on a hotplate at 100 °C until a clear solution was obtained (about 48 h for phosphate rock and 24 h for NPK fertiliser). During the digestion, the lid was carefully opened 2–3 times to release the pressure inside the beaker. The beakers were then removed from the hotplate and allowed to cool. The lids were carefully opened and the sample solutions were evaporated to incipient dryness at 100 °C. Water (2 ml) followed by concentrated HNO_3 (2 ml) were then added to the beaker. The lids of the vials were closed and each was heated at 60 °C on a hotplate until the solutions became colourless. Each solution was transferred to a beaker, made up to 20 ml with water and then filtered through a 0.45-μm filter. The solution was then divided into two portions, with the first being used for HPLC experiments. The second portion was analysed by ICP-MS after taking 4 ml of the original solution and diluting to 20 ml with water.

2.3.2. Precolumn complex formation

The following techniques were used for precolumn formation of the ternary complex for standard solutions and for samples.

In the case of standard solutions, acetic acid (2.50 ml, 0.1 *M*) was added to a 25-ml beaker followed by about 5 ml of water. A freshly prepared PAR solution (0.75 ml, $5 \cdot 10^{-3}$ *M*) was added, followed by the required volume of a standard solution of NH_4VO_3. The solution was then adjusted to pH 6 with dilute ammonia. Hydrogen peroxide (0.20 ml, 30%, w/v) was added and the solution was then transferred to a 25-ml volumetric flask and made up to the mark with water. A 100-μl aliquot of the solution of the ternary complex was injected onto the HPLC column. The concentration of vanadium was determined by measuring peak areas.

In the case of fertiliser samples, the digested sample (2.00 ml) was added to 2.50 ml of acetic acid solution (0.1 *M*) followed by 1.50 ml of freshly prepared PAR solution ($5 \cdot 10^{-3}$ *M*). Each solution was adjusted to pH 6 with ammonia solution, 0.2 ml of hydrogen peroxide (30%, w/v) was then added, the solution transferred to a 25-ml volumetric flask and diluted with water. The sample solution was filtered through a 0.45-μm filter before being injected onto the HPLC column using a 100-μl loop. The analyte concentrations were determined using standard addition.

2.3.3. ICP-MS

Prior to ICP-MS analysis, each sample was spiked with indium (100 ng ml^{-1}) to act as an internal standard. Vanadium was quantified using freshly prepared external calibration solutions (QCD Analysts, NJ, USA). Instrument drift was monitored using standard solutions throughout the analytical sequence. Typical detection limits for vanadium have been reported previously as 5 pg g^{-1} using magnetic sector ICP-MS in the medium resolution mode [9]. Both HPLC and ICP-MS measurement were performed on the same sample digest.

3. Results and discussion

3.1. Selection of an appropriate vanadium ternary complex

In this work, two peaks due to binary complexes of vanadium with PAR were observed in both acetate and citrate media, irrespective of whether ammonium metavanadate (NH_4VO_3) or vanadyl sulfate ($VOSO_4$) were used as starting material, and were attributed to V(V)–PAR and V(IV)–PAR complexes. The peak area of the V(IV)–PAR complex was always larger than the V(V)–PAR complex (Fig. 1). To eliminate this problem, a ternary complex of vanadium with PAR and hydrogen peroxide was employed. On formation of this complex from a mixture of V(IV)–PAR and V(V)–PAR complexes, a single ternary complex of V(V)–PAR–H_2O_2 complex was observed (Fig. 1). This ternary complex could be formed in both acetate buffer and citrate buffer throughout the pH range of 5.0–6.5, although detection sensitivity of the ternary complex was higher in the acetate buffer, while the stability of the V(V)–PAR–H_2O_2 complex was at least 5 h. This time frame allowed both the RP-HPLC and ICP-MS analyses to be performed before any noticeable sample degradation had occurred.

Fig. 2 shows a comparison of spectra of the ternary V(V) complex and blank at pH 6, with the maximum absorbance of the complex occurring at 540 nm. This wavelength was therefore used as the detection wavelength for HPLC measurements.

The mole ratios of [V(V)]:[PAR]:[H_2O_2] in the complex at pH 6 in acetate buffer were investigated using both the mole ratio method and Job's method of continuous variations. Both approaches indicated good agreement and the mole ratio for [V(V)]:[PAR]:[H_2O_2] was observed to be 1:1:1.

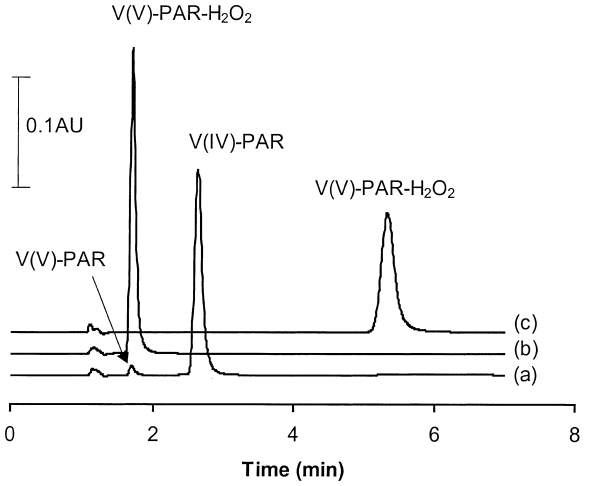

Fig. 1. Chromatograms of (a) V(V)–PAR and V(IV)–PAR, (b,c) V(V)–PAR–H_2O_2. Mobile phase for (a) and (b) was 34% (v/v) methanol in 10 m*M* acetate buffer at pH 6.5. Mobile phase for (c) was 34% (v/v) methanol containing 2 m*M* TBABr in 10 m*M* acetate buffer at pH 6.5. Separator column: NovaPak C_{18} (150× 3.9 mm I.D., 4 μm); flow-rate: 1 ml min^{-1} temperature 30 °C; detection by absorbance at 540 nm.

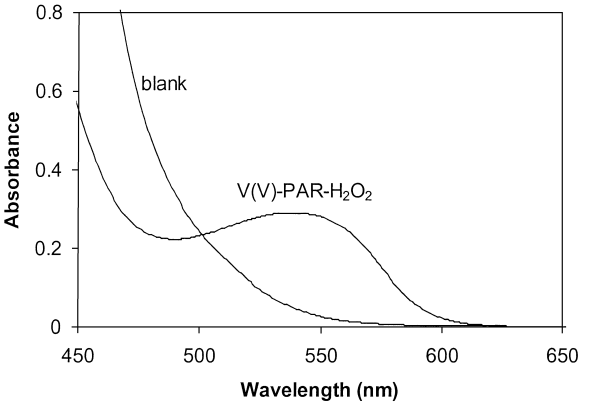

Fig. 2. Absorption spectra of V(V)–PAR–H_2O_2 (444 ng ml^{-1}) and blank at pH 6. Conditions: [PAR] = 0.15 m*M* for blank and 0.05 m*M* for V(V)–PAR–H_2O_2; [H_2O_2] = 7.056 m*M*; [acetate] = 10 m*M*.

3.2. Separation parameters

The ternary complex of V(V)–PAR–H_2O_2 showed a very similar retention time to that of V(V)–PAR (Fig. 1a and b). It is probable that the addition of the small, hydrophilic H_2O_2 molecule to the complex did not significantly alter the hydrophobicity, which means that both the binary and ternary complexes of vanadium show similar hydrophobic interaction with the C_{18} stationary phase. The retention of V(V)–PAR–H_2O_2 could be increased by adding the cationic tetrabutylammonium ion (TBA^+) to the mobile phase (Fig. 1c), indicating that the ternary complex was anionic.

Five mobile phase parameters affected the retention and peak area of V(V)–PAR–H_2O_2 complex; namely the percentage of methanol, pH, concentration of acetate, concentration of citrate, and concentration of TBABr. A mobile phase comprising 32% (v/v) methanol, 3 m*M* TBABr, 5 m*M* acetic acid and 5 m*M* citric acid at pH 7 showed a good separation of vanadium from the matrix ions [Nb(V) and Co(III)] (Fig. 3), with elution of all the matrix ions being completed within 45 min.

3.3. Optimisation of ternary complex formation

The above HPLC method was used to find the formation conditions for the ternary complex which yielded the highest sensitivity. The concentration of the acetate buffer was varied over the range 5–20 m*M*, with 10 m*M* providing the best sensitivity. The concentration of H_2O_2 was varied over the range 3.5–28.2 m*M* and both peak height and peak area of the vanadium complex increased strongly from 3.5 to 7.1 m*M* and remained relatively constant above 7.1 m*M*. The pH was varied over the range 5.0–6.5, with pH 6 offering the greatest peak height and peak area. The concentration of PAR was varied over the range 0.10–0.30 m*M* for a standard vanadium sample in 10 m*M* acetate buffer containing 7.1 m*M* H_2O_2 at pH 6. Peak height was maximised at 0.15 m*M* PAR, but 0.30 m*M* PAR was used with the fertiliser samples to allow for complexation of PAR by matrix components, in particular iron, of these samples. The optimal conditions for formation of the ternary complex were therefore 10 m*M* acetate, 7 m*M* H_2O_2, 0.3 m*M* PAR, at pH 6.

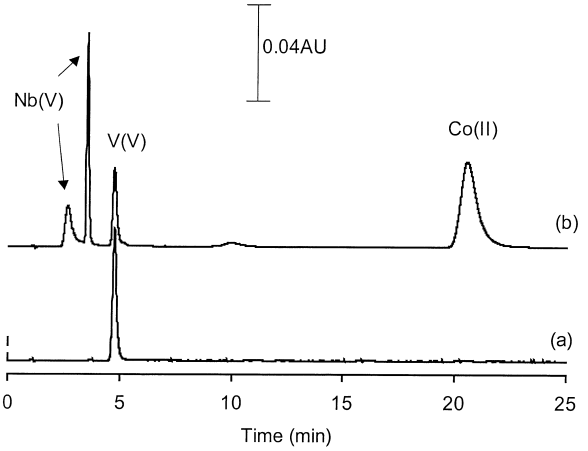

Fig. 3. Chromatograms of (a) V(V)–PAR–H_2O_2 (0.178 μg ml^{-1}), (b) mixture of Nb(V)–PAR (2 μg ml^{-1}), V(V)–PAR–H_2O_2 (0.2 μg ml^{-1}) and Co(II)–PAR (2 μg ml^{-1}). Mobile phase was methanol–water (32:68, v/v) containing 5 m*M* acetate, 3 mm TBABr and 5 m*M* citrate buffer at pH 7; other conditions were identical to those outlined in Fig. 1.

3.4. Analytical performance parameters

The effect of potentially interfering metal ions was investigated, with no interference being observed from Cd^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+}, Mn^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Nb^{5+}, Ag^+ and Ti^{4+} when present at 100 μg ml^{-1}. This conclusion was reached due to the absence of a chromatographic peak above the background noise for these metal ions, or a decrease in the signal intensity for vanadium when these cations were present.

The detection limit for V(V)–PAR–H_2O_2 (determined at a signal-to-noise ratio of 3) was 0.09 ng ml^{-1} in the injected sample solution. Since each of the fertiliser samples was diluted by a factor of 1000 the above values corresponded to detection limits in the solid fertiliser samples of 0.09 μg g^{-1}. Seven replicate injections of 177.6 ng ml^{-1} standard vanadium solution gave RSD (relative standard deviation) values for retention time, peak area and peak height of 0.187, 0.45 and 0.57%, respectively. External standard calibration curves exhibited good linearity up to at least 450 ng ml^{-1} ($r^2 = 1.000$) and the standard addition calibration curves also showed good linearity ($r^2 = 0.9954$ to $r^2 = 0.9999$).

3.5. Determination of vanadium in fertiliser samples

Phosphate rock fertiliser samples contain silica, while NPK fertilisers contain inorganic fillers, thus it was necessary for each digested sample solution to be filtered. Further, all fertiliser samples contained Fe(III) and the red Fe(III)–PAR complex was found to change to brown over a 2-h period, with precipitation of this complex occurring with some samples. For this reason, it was necessary to filter the samples after ternary complex formation, prior to injection onto the HPLC column. This precipitation and subsequent filtration does not appear to affect the levels of vanadium in the sample as a result of coprecipitation. This was concluded due to the very close agreement between the vanadium concentrations from the chromatographic and spectroscopic techniques, where the sample for ICP-MS analysis was taken prior to the addition of the PAR and H_2O_2 reagents, and hence before precipitation had occurred. Three phosphate rock fertilisers and three NPK fertilisers from different sources were chosen for analysis (see Table 1). The chromatographic separation of phosphate rock C and NPK fertilisers showed no baseline disturbances over the retention time range 6–42 min if the Fe(III)–PAR complex had decomposed. Therefore, fertiliser samples could be injected onto the HPLC column every 6 min.

Chromatograms obtained with and without the addition of vanadium are illustrated in Fig. 4 for phosphate rock fertiliser (South Africa), whilst Fig. 5 displays similar chromatograms for NPK (16-20-0) fertiliser. The V(V)–PAR–H_2O_2 peak was well resolved from other components present in each of the samples, with the added vanadium being used to confirm the peak identity. Other phosphate rock fertilisers (from Morocco and Jordan) and NPK fertilisers (15:15:15 and 16:3.5:10) showed similar chromatograms.

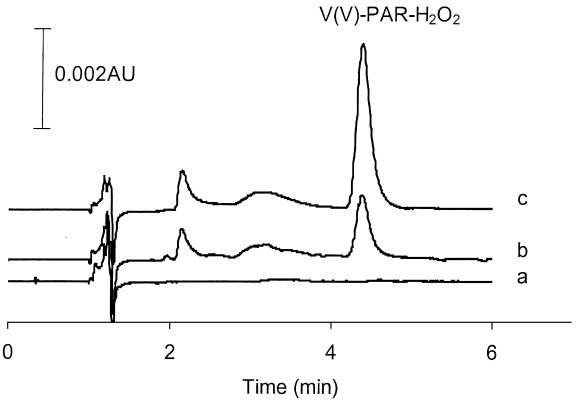

Fig. 4. Chromatograms of (a) blank, (b) phosphate rock fertiliser, (c) phosphate rock fertiliser spiked with 32 ng ml^{-1} of NH_4VO_3. The sample contained [PAR]=0.30 m*M*; [acetate]=10 m*M*; [H_2O_2]=7.1 m*M*. Chromatographic conditions were identical to those outlined in Fig. 3.

Both external standard and standard addition methods were used to quantify the vanadium content of the fertiliser samples. Results obtained using the standard addition method are compared with the ICP-MS results in Table 1. There is good agreement between the two methods and the results show that the NPK fertiliser from Thailand contained the highest levels of vanadium.

Table 1
Comparison of vanadium levels found in fertilisers by RP-HPLC and magnetic sector ICP-MS. All values are expressed as μg g^{-1} in the original sample

Samples	Source	Sample vanadium concentration	
		HPLC (R^2)	ICP-MS
Phosphate rock	South Africa	18.06 (0.9978)	18.24
	Morocco	90.71 (0.9999)	99.16
	Jordan	123.2 (0.9998)	107.2
NPK fertiliser	Norway (15:15:15)	37.13 (0.9987)	40.91
	Thailand (16:20:0)	181.2 (0.9995)	177.3
	Australia (16:3.5:10)	7.482 (0.9954)	7.173

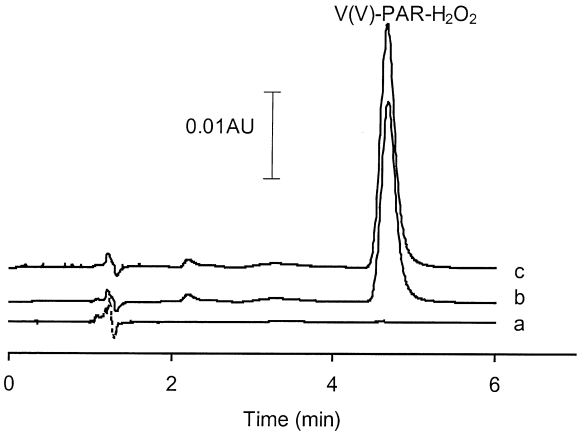

Fig. 5. Chromatograms of (a) blank, (b) NPK (16:20:0) fertiliser, (c) NPK (16:20:0) fertiliser spiked with 40 ng ml^{-1} of NH_4VO_3. The sample contained [PAR]=0.30 m*M*; [acetate]=10 m*M*; [H_2O_2]=7.1 m*M*. Chromatographic conditions were identical to those outlined in Fig. 3.

4. Conclusions

The retention and separation of vanadium in fertilisers as the anionic V(V)–PAR–H_2O_2 ternary complex was achieved on a C_{18} column using tetrabutylammonium as the ion-interaction reagent in the mobile phase. The separation selectivity of the complex is controlled mainly by the concentration of methanol and the concentration of tetrabutylammonium in the mobile phase. The sensitivity of the method was dependent on the conditions used for the precolumn complex formation, with pH, concentration of PAR, and concentration of hydrogen peroxide all exerting considerable effects. Based on a comparison with magnetic sector ICP-MS, accurate results using standard addition methods were obtained for the determination of vanadium in all fertilisers. Since appreciable contamination by vanadium was present in some fertilisers, further investigation of uptake of vanadium by plant tissue would be beneficial.

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References

[1] F.A. Cotton, G. Wilkinson, in: Advanced Inorganic Chemistry, 5th ed., Wiley, New York, 1988, p. 665.
[2] S.P. Parker, 8th ed., Encyclopaedia of Science and Technology, Vol. No. 18, McGraw-Hill, New York, 1997.
[3] A. Frank, A. Madej, V. Galagan, L.R. Petersson, Sci. Total Environ. 181 (1996) 73.
[4] F.H. Nielsen, Clin. Biochem. Nutr. Aspects Trace Elem. 6 (1982) 379.
[5] G.R. Willsky, D.A. White, B.C. McCabe, J. Biol. Chem. 259 (1984) 13273.
[6] B. Patel, G.E. Henderson, S.J. Haswell, R. Grzeskowiak, Analyst 115 (1990) 1063.
[7] A. Adachi, S. Sawada, K. Shida, E. Nakamura, T. Okano, Anal. Lett. 32 (1999) 2327.
[8] R.G. Wuilloud, J.A. Gasquez, R.A. Olsina, L.D. Martinez, Anal. Chim. Acta 420 (2000) 73.
[9] A.T. Townsend, J. Anal. At. Spectrom. 15 (2000) 307.
[10] X.-S. Zhang, X.-P. Zhu, C.-S. Lin, Talanta 33 (1986) 838.
[11] F. Tadayon, A. Massoumi, J. Chromatogr. Sci. 37 (1999) 371.
[12] S. Oszwaldowski, M. Jarosz, Mikrochim. Acta 126 (1997) 241.
[13] X.Y. Ming, Y.H. Wu, G. Schwedt, Fresenius J. Anal. Chem. 342 (1992) 556.
[14] B. Chen, Q. Zhang, H. Minami, S. Inoue, M. Uto, J. Chromatogr. Sci. 37 (1999) 306.
[15] S.-J.J. Tsai, S.-J. Hsu, Analyst 119 (1994) 403.
[16] X. He, M. Tubino, A.V. Rossi, Anal. Chim. Acta 389 (1999) 275.
[17] M. Jarosz, S. Oszwaldowski, Chem. Anal. (Warsaw) 38 (1993) 109.