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Note

Determination of vanadate(V) by conductometric anion chromatography

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Vanadium is a trace element essential for living systems, where it is found as oxovanadium(IV) or vanadate(V). Depending on the valence state of the element, different biological activity can be observed, *e.g.*, vanadate(V) behaves as a strong inhibitor of Na,K$^+$-ATPase, whereas oxovanadium(IV) is less inhibitive towards the enzyme[1,2]. In addition, vanadate(V) is reduced to vanadium(IV) on interaction with certain biological matrices[3]. Also, the action of therapeutic drugs against manic-depressive illness involves the reduction of vanadate to vanadium(IV)[4].

As we are interested in the study of the distribution of vanadium in plants and the redox interaction of vanadate with plant components[5,6], we needed an analytical method for the selective determination of vanadate(V) and oxovanadium(IV). The methods commonly applied to biological systems allow the determination of total vanadium[7,8].

This paper presents the results of an attempt to develop a method for the quantitation of vanadate(V) in biological matrices by means of ion chromatography (IC) without the use of a pre-concentration column. It is almost a decade since IC using conductivity detection was seen as a potential tool for the rapid separation and quantitation of inorganic and organic anions[9]. The requirement for conductivity detection restricts the applicability of IC so that the list of anions that can be successfully determined by common techniques is limited to anions of sufficiently strong acids. Yet, the list of anions that can be determined has been extended to include also anions of weak acids by employing basic or low-conductivity eluents[10]. However, with the exception of a study on the retention of some inorganic anions in a reversed-phase chromatographic system[11], no application of IC to vanadate(V) analysis has so far been reported.

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EXPERIMENTAL

Sample solutions

Standard solutions were prepared by dissolving analytical-reagent grade chemicals in deionized, doubly distilled water.

Eluent

Aqueous solutions of boric acid, ranging from $2.5 \cdot 10^{-4}$ to $1.5 \cdot 10^{-2}$ *M* over the pH range 5–7, were tested.

Apparatus

The chromatographic system consisted of a Wescan 260 ion analyser equipped with a Wescan 269-001 anion-exchange column and a Wescan 213 A conductivity detector. The flow-rate was 1.7 ml min^{-1}. The sample size was 1 ml.

RESULTS AND DISCUSSION

As mentioned above, the requirement for conductivity detection restricts the applicability of IC to anions that dissociate sufficiently under the elution conditions. With the eluents commonly used for anion determinations (phthalate, benzoate, etc.), poor sensitivity was observed in the vanadate(V) analysis owing to the comparatively high background conductance.

Better results were obtained by using aqueous solutions of H_3BO_3 as eluents. H_3BO_3 is a very weak acid and therefore has a very low conductivity. The eluent concentration and pH were adjusted to obtain suitable retention times and sensitivity. At an eluent concentration of $9.6 \cdot 10^{-3}$ *M* and over the pH range 6.5–6.9 chromatograms such as reported in Fig. 1 were observed. The single peak can probably

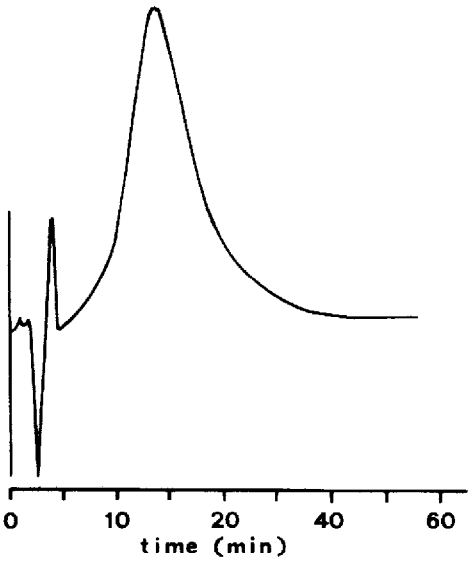

Fig. 1. Chromatogram of 25 ppm of vanadate. Eluent: aqueous solution of H_3BO_3, 9.6 m*M*, pH 6.8.

be ascribed to $H_2VO_4^-$, which is the main component in dilute aqueous solutions of vanadate over the pH range 4–9, whereas a mixture of polyvanadates is expected in more concentrated solutions[12].

Calibration graphs were obtained by plotting the height of the peak against the VO_3^- concentration in the range 0–15 ppm. The linearity of the plots (Fig. 2) was good, as judged from the correlation coefficients calculated according to the method of least squares. The detection limit, evaluated as the concentration that gives a response comparable to the noise of the detector, was less than 1 mg/l.

In order to check the effectiveness and the specificity of the method, potential interferences related to coelution problems were established by the analysis of a series of anion standards. Anions such as chloride, perchlorate, acetate, nitrate, nitrite and sulphate, eluted under the above conditions (see, *e.g.*, Fig. 3), exhibited retention times close each to other and significantly shorter than that of vanadate. However, the pH of the mobile phase had a considerable effect on the selectivity of the separation. Comparison of the results obtained at different pH values (Fig. 4) showed that the more basic the medium was, the more effective was the separation of vanadate from the other anions. However, it must be noted that a pH above 7 can result in damage to the chromatographic column and that the usefulness of an increase in basicity may be limited at eluent concentrations higher than $1 \cdot 10^{-3}$ *M* because of the increase in the background conductivity. Hence the pH range 6.6–6.8 and a mo-

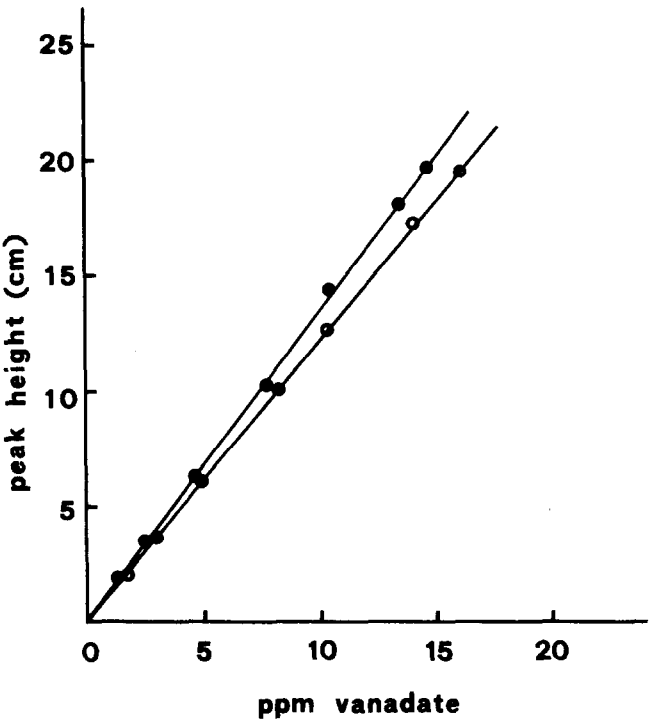

Fig. 2. Calibration graphs for vanadate(V). Eluent: H_3BO_3, 9.6 m*M*, (●) pH 6.8 (r = 0.997, s.d. = 0.34) and (○) pH 6.6 (r = 0.999, s.d. = 0.10).

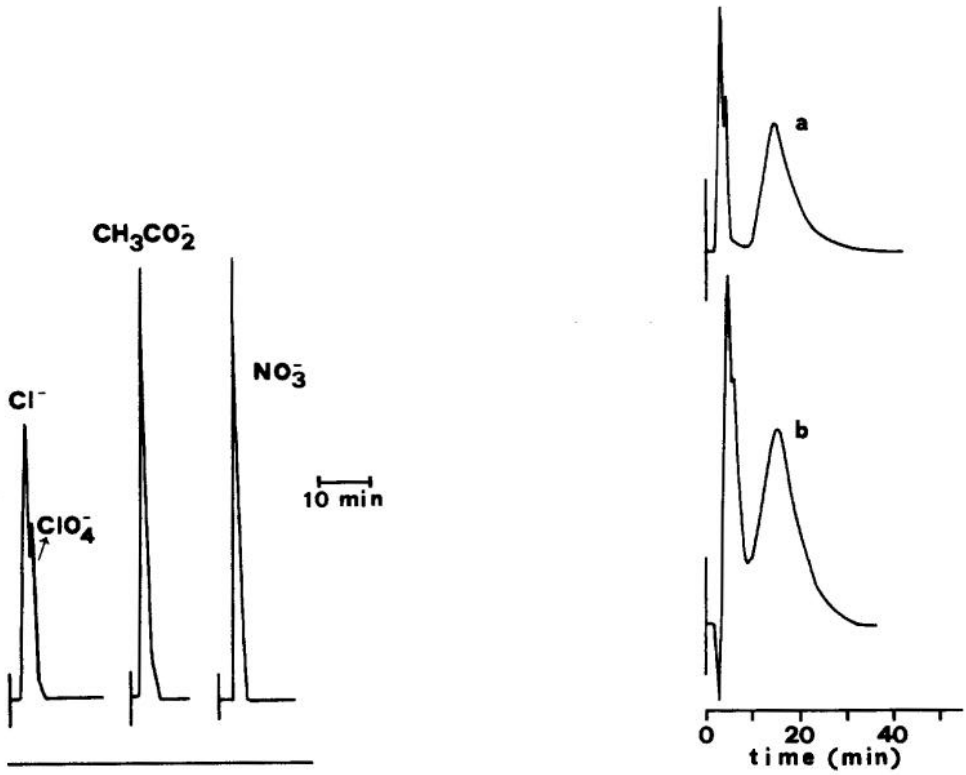

Fig. 3. Separation of 1.6 ppm of Cl^-, 2.4 ppm of ClO_4^-, 7.0 ppm of CH_3COO^- and 4.5 ppm of NO_3^-. Conditions as in Fig. 1.

Fig. 4. Separation of (a) 1.6 ppm of Cl^-, 2.4 ppm of ClO_4^- and 20.8 ppm of VO_3^- with 9.6 m*M* H_3BO_3, pH 6.8; (b) 0.80 ppm of Cl^-, 2.4 ppm of ClO_4^- and 26.0 ppm of VO_3^- with 9.6 m*M* H_3BO_3, pH 6.6.

bile phase concentration of $9.6 \cdot 10^{-3}$ *M* appeared to be a good compromise between selectivity and sensitivity.

On the other hand, with decreasing pH, whereas the sensitivity remaining good enough, the peaks of the non-metallic anions tested were shifted to later retention times and thus gave rise to serious interferences in the vanadate analysis.

The above method has been also used to determine the amount of vanadate reduced by polygalacturonic acid according to the reaction described previously[5,6]. A single peak was again obtained for residual vanadate, the amount of which, evaluated by use of the calibration graph, agreed well with that reported in Table II in ref. 6. Based on three replicate analyses, it was found that 1.0 g of polygalacturonic acid (2.04 mol of reducing end-units) reacted with $7.8 \cdot 10^{-4}$ mol of vanadate ($7.84 \cdot 10^{-4}$–$7.88 \cdot 10^{-4}$ mol measured by spectrometric analysis of vanadium; calculated value, $8.16 \cdot 10^{-4}$ mol).

Further, the method can be applied to the determination of oxovanadium(IV) provided that this species is oxidized to vanadate(V).

We are now attempting to extend the applications of the method to the analysis of vanadate(V) and oxovanadium(IV) in more complex biological systems.

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