

Note

Kinetic thermometric determination of vanadium in atmospheric aerosols based on its catalytic effect on the oxidation of tannic acid by bromate ion

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Abstract

The catalytic effect of vanadium(V) on the oxidation of tannic acid by bromate ion was studied in order to develop a simple method for determination of vanadium(V). By using the initial rate method and monitoring the reaction thermometrically, vanadium can be determined at the typical levels found in atmospheric aerosols (5–50 ppb) with a relative standard deviation of 6.3%. The sensitivity of the determination is enhanced by the presence of citric or tartaric acid. The proposed method is subject to interference only by iron in concentrations over 75 times that of vanadium, which is rarely the case with atmospheric aerosols. The results obtained are compared with those provided by the two most frequently used techniques for vanadium determination in atmospheric aerosols, viz. ICP-AES and graphite furnace AAS.

Keywords: Aerosol; Bromate; Kinetics; Oxidation; Tannic acid; Vanadium

1. Introduction

Several methods for the determination of vanadium by its catalytic effects on the oxidation of various compounds have been reported recently [1–6], each of which relies on bromate ion as oxidant and photometric monitoring. The differences lie in the organic compounds used, which include bromophenol blue, perphenazine, catechol, *p*-aminobenzoic acid and acridine orange.

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In previous work [7–11] our group developed various kinetic methods for determining vanadium based on its catalytic effects and thermometric monitoring. The thermometric apparatus used for this purpose was a modified version of that originally developed by Lumbarres et al. [12]. One of the greatest assets of thermometric monitoring is the absence of interference from coloured compounds and from precipitates. This methodology involves measuring the variation of temperature with time during the catalysed reaction. Provided that the reaction is first order with respect to the catalyst, (dT/dt) is proportional to the catalyst concentration.

This methodology allows the determination of trace amounts of species by using straightforward and inexpensive instrumentation, and offers detection limits similar to or even better than those of other, more expensive techniques, including inductively coupled plasma atomic emission spectroscopy (ICP-AES) and graphite furnace atomic absorption spectroscopy (GFAAS).

In this work we have developed a new method for determination of vanadium based on its catalytic action on an unpublished reaction involving oxidation of tannic acid by bromate ion. Tannic acid, also known as “Chinese gallotannin”, is a polymer of variable composition consisting primarily of gallic acid and D-(+)-glucose. Zhang et al. [13] found that the sensitivity of the catalytic determination of vanadium by its effect on the oxidation of bromophenol blue by bromate ion was enhanced by the presence of citric acid. Both citric acid and a similar complexing agent (tartaric acid) were tested for enhancement of the analytical features of the proposed method.

The purpose of this work was to optimize the pH and the concentrations of the oxidant and substrate involved in the oxidation of tannic acid by bromate ion with a view to determining vanadium(V) in atmospheric aerosols.

2. Experimental

2.1. Apparatus

The experimental set-up consisted of the following elements:

- (a) The thermometric system described elsewhere [7,8].
- (b) A Unicam 939 atomic absorption spectrophotometer equipped with a GF 90 graphite furnace and an FS 90 autosampler, also from Unicam.
- (c) A Perkin-Elmer 2000 sequential plasma emission spectrophotometer equipped with an AS90 autosampler from the same manufacturer.
- (d) An MCV high-volume trap for collection of atmospheric particulates at an air flow rate of up to $90 \text{ m}^3 \text{ h}^{-1}$.

2.2. Reagents

The reagents used included the following:

- (a) A 1000 ppm stock vanadium solution made by dissolving 2.297 g of NH_4VO_3 in 1 l of distilled water, from which working strength standards were subsequently prepared fresh daily by appropriate dilution.

(b) A nearly saturated tannic acid solution containing 21.265 g of the acid, 19.213 g of tartaric acid and 18.75 ml of 4 N H_2SO_4 , made up to 500 ml with water.

(c) A 1.40 M bromate solution prepared by dissolving 21.124 g of NaBrO_3 in distilled water.

(d) A 65% solution of HNO_3 and a 40% solution of HF, both made from Suprapur-grade Merck reagents.

2.3. Procedure

2.3.1. Sampling of atmospheric aerosols

Airborne particulates were collected on Whatman 41 cellulose filters placed in a high-volume trap at an air flow rate of $60 \text{ m}^3 \text{ h}^{-1}$.

2.3.2. Digestion of the filters

Filters were digested by calcination in a muffle furnace. One fourth of each filter was placed in a 100-ml porcelain crucible and calcined by gradually increasing the temperature. After 1 h at 100°C , the temperature was raised by 100°C each hour up to 450°C , then maintained for a further 5 h.

After the filter had been calcined, the ash was decomposed by 10 ml of cold 5% nitric acid. The slightly turbid solution obtained was poured into a polytetrafluoroethylene (PTFE) beaker, and 500 μl of concentrated HF was added to dissolve silicates. To remove excess HF and acidity, the solution was evaporated to dryness at a temperature not exceeding 270°C . Finally, the beaker contents were made up to 25 ml with distilled water to obtain a totally clear solution.

2.3.3. Determination of vanadium by the proposed kinetic thermometric method

A 10 ml portion of tannic acid/tartaric acid/ H_2SO_4 mixture, 10 ml of sample or the required volume of standard, and distilled water to 47.5 ml were placed in the thermometric cell. As soon as a horizontal baseline was recorded (i.e. $dT/dt = 0$), 2.5 ml of 1.4 M NaBrO_3 was injected and the initial slope of the resulting curve was used to calculate the initial reaction rate. All solutions were kept in a thermostatted room to assure rapid baseline stabilization for thermometric measurements.

2.3.4. Determination of vanadium by ICP-AES and GFAAS

The remaining 15 ml of solution was analysed for vanadium by using these two techniques. The optimal calcination and atomization temperatures for the graphite furnace were 1200 and 2700°C , respectively. The ICP-AES determination involved measurement of the emission line for vanadium at 292.402 nm and the following optimal experimental conditions: nebulizer flow rate 1.190 l min^{-1} of Ar; radio-frequency power 1180 W ; observation height 14 mm .

2.3.5. Controls

Simultaneously with the five samples, five unsampled cellulose filters were analysed to determine their vanadium content. No vanadium was detected in any filter blank by any of the techniques used.

3. Results and discussion

3.1. Optimization of the reaction conditions

The experimental variables potentially affecting the reaction rate were pH, substrate (tannic acid) concentration and oxidant (bromate ion) concentration. As noted in the introduction, the potential effects of citric and tartaric acid on the sensitivity were also investigated.

Fig. 1 shows the variation of the initial reaction rate with pH, obtained by using 0.01 M tannic acid, 0.02 M citric acid, 40 ppb of vanadium and 0.035 M bromate.

Curve [1] shows the initial rate of the catalysed plus the uncatalysed reaction. Curve [3] results from subtracting curve [2] from curve [1]. Unlike curve [1], curve [3] shows a maximum at pH 1.35, which was taken as the optimum pH.

Fig. 2 shows the variation of the initial reaction rate with the tannic acid and bromate ion concentrations. The graphs show the typical influence of a substrate and an oxidant on the reaction rate. The signal increased sharply at low concentrations of both reaction ingredients and subsequently saturated at higher concentrations. Those concentrations where the signal did not significantly increase any further (viz. 0.07 M bromate ion and 0.01 M tannic acid) were taken as optimal because the initial rate was at a maximum.

As noted earlier, Zhang et al. [13] found that the sensitivity in the kinetic determination of vanadium based on its catalytic effect on the oxidation of bromophenol blue by bromate ion was increased by addition of citric acid. We also found citric acid to enhance the sensitivity of the oxidation of tannic acid by bromate ion, as did the similar complexing agent tartaric acid. As can be seen in

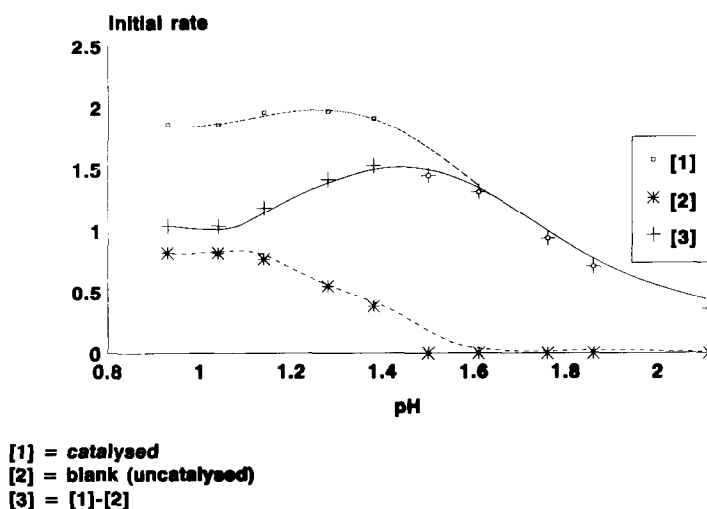


Fig. 1. Influence of pH on the catalysed (\square) and the uncatalysed (\ast) reaction.

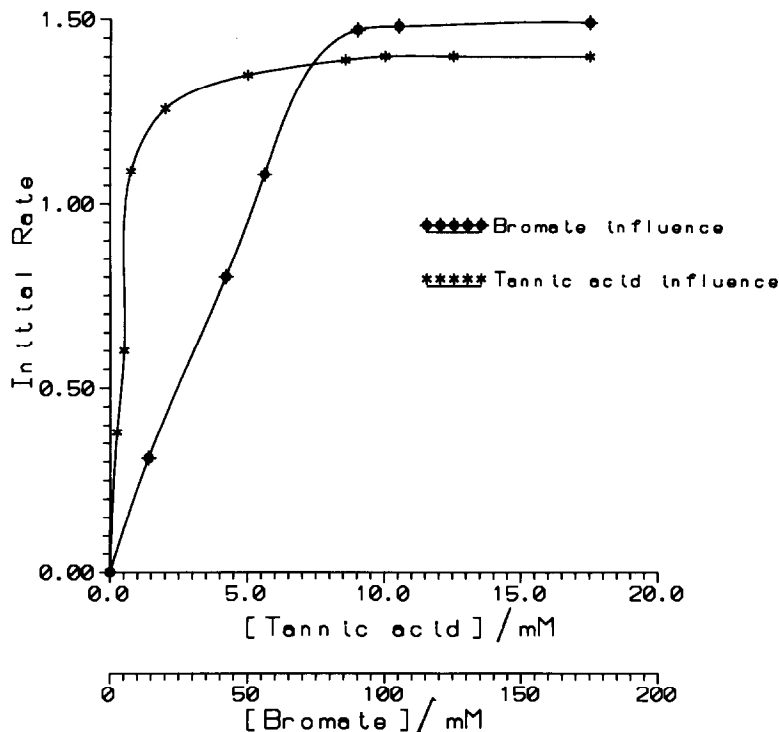


Fig. 2. Influence of tannic acid concentration on the catalysed and the uncatalysed reaction. $[\text{HCit}] = 0.02 \text{ M}$, $[\text{V(V)}] = 40 \text{ ppb}$, $[\text{BrO}_3^-] = 0.07 \text{ M}$, $\text{pH } 1.35$. Influence of bromate ion concentration on the catalysed and the uncatalysed reaction. $[\text{HTan}] = 0.01 \text{ M}$, $[\text{V(V)}] = 40 \text{ ppb}$, $\text{pH } 1.35$.

Fig. 3, comprising kinetic curves obtained at optimal values of all other parameters ($\text{pH } 1.53$, 0.07 M bromate ion and 0.01 M tannic acid), both acids increased the sensitivity of the proposed method by a factor of ≈ 2 . The optimum concentrations of tartaric and citric acid in this respect were 0.08 M and 0.04 M , respectively. Either enhancer can thus be used at will, as each has a similar effect.

3.2. Reproducibility

Ten measurements of the initial reaction rate (dT/dt) made under the optimal experimental conditions on a vanadium standard containing 40 ppb of the metal provided a relative standard deviation (RSD) = 6.2%

3.3. Interferences

Potential interference with the determination was checked on the basis of the intended types of sample: atmospheric aerosols, which, based on reported data [14] and our own experience [15,16], typically contain calcium, sodium, potassium, iron,

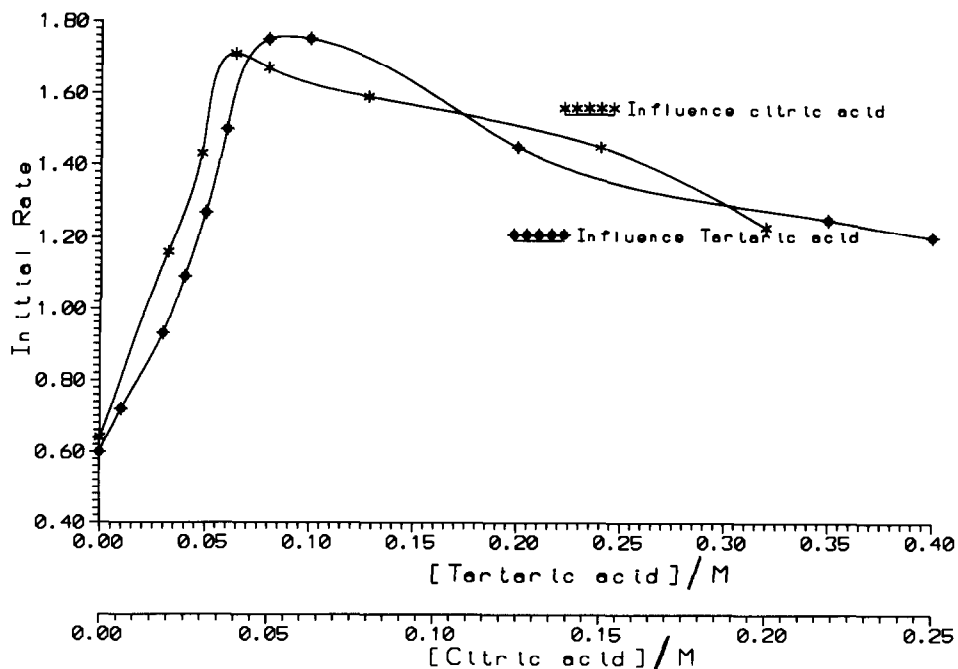


Fig. 3. Effect of the addition of citric or tartaric acid on the sensitivity of the proposed kinetic thermometric method (pH 1.35; 0.07 M bromate ion and 0.01 M tannic acid).

magnesium, aluminium and silicon as major metals. Some of these metals can be present in aerosols at concentrations ≈ 150 times higher (by weight) than that of vanadium, so this was the *interferent-to-analyte* ratio tested in the experiments both for the above-mentioned major metals and for minor metals in aerosols (cadmium, copper, lead, manganese, nickel, chromium and zinc)—in fact, if minor metals did not interfere at this ratio, they would not do so at real levels. Chloride and sulphate ion were also tested at the same ratios as the metals. Because samples were decomposed by nitric acid and hydrogen fluoride, nitrate and fluoride ion were tested at concentrations 10^4 times higher than that of the analyte.

A given foreign species was considered not to interfere with the determination if the initial reaction rate in its presence did not differ from that obtained in its absence by more than $\pm 2\sigma$ (the standard deviation for the method, calculated from the reproducibility). The vanadium concentration used in these experiments was again 40 ppb.

The proposed method was only interfered with by iron concentrations 75 times higher than that of vanadium, which is rarely the case with atmospheric aerosols.

3.4. Analysis of atmospheric aerosols. Comparison with ICP-AES and GFAAS

Five aerosol samples were used to compare the results provided by the proposed tannic acid method and the two techniques most frequently used for determining

Table 1

Comparison of the results obtained in the analysis of five aerosol samples by the proposed kinetic thermometric method, ICP-AES and GFAAS^a

Sample	Proposed method		ICP-AES		GFAAS	
	ppb	ng m ⁻³	ppb	ng m ⁻³	ppb	ng m ⁻³
1	228	16.3	240	17.1	259	19.1
2	110	10.7	183	17.8	135	12.9
3	154	11.0	189	13.5	192	14.4
4	139	11.3	125	10.1	168	11.8
5	146	11.3	112	8.7	146	11.3

^a The ICP-AES technique revealed the iron-to-vanadium ratio to be lower than 75 (between 16 and 37).

vanadium in atmospheric aerosols: ICP-AES [17] and GFAAS [18–20]. The most serious shortcoming of the GFAAS technique for the determination of vanadium lies in the high atomization temperature required, which considerably shortens the serviceable life of graphite tubes. One emission line of the hydroxyl group at 309.279 nm interferes with the most sensitive ICP-AES line for vanadium (309.311 nm). Such an interference is usually avoided by using a less sensitive but interference-free line for vanadium (viz. that at 292.402 nm).

Table 1 shows the results (in ng m⁻³ of V in air and in ppb) obtained in the analysis of the five aerosol samples by using the proposed kinetic thermometric method, ICP-AES and GFAAS. As can be seen, the results were quite consistent.

4. Conclusions

(a) The proposed kinetic thermometric method for the determination of vanadium features a wide linear application range (5–50 ppb). The calibration graphs obtained for its implementation corresponded to the straight line equation

$$\text{initial rate} = 0.034 \times [\text{vanadium}](\text{ppb}) + 0.661$$

($r^2 = 0.9928$, where r is the correlation coefficient)

(b) The proposed kinetic thermometric method, based on an undocumented oxidation reaction between tannic acid and bromate ion, allows the reliable determination of trace amounts of vanadium in such samples as atmospheric aerosols.

(c) The method provides results similar to those of other techniques which are more expensive to set up and maintain, such as ICP-AES and GFAAS.

(d) Our instrumentation involves thermometric monitoring; the most serious disadvantage of the proposed method is slow baseline stabilization and the lack of heat transfer between the thermometric cell and the calorimeter used.

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References

- [1] P. Viñas, C. Piqueras, M. Hernández-Córdoba and M. Sánchez-Pedreño, *An. Quim.*, 85 (1989) 195.
- [2] W. Li and S. Zhou, *Fenxi Huaxue*, 19 (1990) 111.
- [3] A.C. Zotou and C.G. Papadopoulos C.G., *Analyst*, 115 (1990) 323.
- [4] F. Xue, Z. Zhang and L. Chen, *Fenxi Huaxue*, 17 (1989) 622.
- [5] S.B. Jonnalagadda and P. Sawunyana P., *Fresenius' J. Anal. Chem.*, 340 (1991) 173.
- [6] M. León, M. Ternero, M. Callejón and A. Guiraum, *Anal. Chim. Acta*, 224 (1991) 89.
- [7] R. Forteza and V. Cerdà, *Anal. Chem.*, 58 (1986) 453.
- [8] R. Forteza, J.M. Estela and V. Cerdà, *Analyst*, 116 (1991) 1171.
- [9] R. Forteza, A. Canals, A. Caro, J.M. Estela and V. Cerdà, *Fresenius' J. Anal. Chem.*, 345 (1993) 432.
- [10] R. Forteza, M.T. Oms, J. Cárdenas and V. Cerdà, *Analisis*, 18 (1990) 491.
- [11] J. Mateu, R. Forteza, M. Colom-Altés and V. Cerdà, *Analyst*, 119 (1984) 1077.
- [12] J. Lumbarres, C. Mongay and V. Cerdà, *J. Therm. Anal.*, 22 (1982) 275.
- [13] Z. Zhang, F. Zue and P. Jiang, *Gaodeng Xuexiao Huaxue Xuebao*, 10 (1989) 305.
- [14] W. Frenzel, *Fresenius' J. Anal. Chem.*, 340 (1990) 525.
- [15] J. Mateu, M. Colom-Altés, R. Forteza and V. Cerdà, *EROS 2000 Fourth Workshop on the North Western Mediterranean Sea*, J.M. Martin and H. Barth (Eds.), *Water Pollution Research Report No. 30*, CEC, Brussels, 261 pp.
- [16] J. Mateu J., M. Colom-Altés, R. Forteza and V. Cerdà, *J. Environ. Sci. Health, Part A*, 29 (1994) 321.
- [17] I.G. Yudelevich, B.I. Zaksas, Ye. A. Petrova and A.S. Chevevko, *Fresenius' J. Anal. Chem.*, 340 (1991) 560.
- [18] S. Guerzoni, R. Lenaz, G. Quarantoto, G. Rampazzo, A. Correggiari and P. Bonelli, *G. Geol.*, 51/2 (1989) 117.
- [19] F. Valerio, C. Brescianini, A. Lazzarotto and D. Balducci, *Toxicol. Environ. Chem.*, 13 (1986) 113.
- [20] T.A. Pakkanen and A. Hillamo, *J. Aerosol Sci.*, 19 (1988) 1303.