Automated Colorimetric Method for the Determination of Vanadium in Fresh Water

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Abstract

The manual gallic acid/persulphate method for the determination of vanadium (Fishman and Skougstad, 1964) was automated using Technicon AutoAnalyzer equipment. Vanadium in fresh water samples in the concentration range 1 to 100 $\mu g\ dm^{-3}$ V was determined at a rate of 30 samples per hour. The analysis of an interlaboratory quality control sample gave a vanadium concentration of 405 $\mu g\ dm^{-3}$ V by the automated method. The reference value for the sample was 400 $\mu g\ dm^{-3}$ V. Interference and recovery tests were carried out. The mean recovery of vanadium from spiked samples was 104%.

Introduction

The determination of vanadium in environmental water samples is important, as it plays a role in plant growth. Vanadium is known to stimulate the growth of green algae (Arnon and Wessel, 1953; Montiel, 1975), and has been found in porphyrin pigments of biological origin (Muniyappan, 1955). The element is also strongly suspected as being essential in human nutrition, and bears a relationship to cholesterol metabolism (Hopkins and Mohr, 1971).

Despite its role in plant growth, vanadium has been somewhat neglected in environmental studies, because of the lack of a suitable analytical method for its determination which is both sensitive and rapid. Flame atomic absorption spectrometry, which is commonly used for the determination of metallic elements, is insufficiently sensitive for the determination of vanadium in natural waters (Varian Techtron, 1972). The catalytic colorimetric method of Fishman and Skougstad (1964) and of Standard Methods (1975) is sensitive, but tedious to carry out, as it is a manual method requiring a reaction time of 1 h. An automated colorimetric method for vanadium in silicates has been described using Na_2WO_4, H_3PO_4 and HNO_3 in the range 0 to 40 mg dm^{-3} V (Technicon, 1974), but is not sufficiently sensitive for water samples. To obtain a method which is both sensitive and convenient, it was decided to automate the manual standard method (Standard Methods, 1975). This paper describes an automated gallic acid/persulphate catalytic method suitable for direct determination of vanadium in fresh water samples.

Reagents

Analytical grade chemicals and deionised water were used to prepare reagents. Care must be taken to preclean all glassware with dilute nitric acid (0,5 mol dm^{-3}) prior to use. The reagents used were similar to those of the standard manual method (Standard Methods, 1975):

1. **Mercuric nitrate reagent** — dissolve 0,35 g $Hg(NO_3)_2 \cdot H_2O$ in 1 dm^3 water acidified with 10 cm^3 conc. HNO_3.

2. **Persulphate reagent** — dissolve 5,0 g $(NH_4)_2S_2O_8$ in 50 cm^3 water, heat to just below boiling point, remove from heat and carefully add 50 cm^3 conc. H_3PO_4. The reagent must be allowed to stand overnight before use, and should be discarded if more than 72 h old.

3. **Gallic acid reagent** — dissolve 2,0 g $H_6C_7O_5$ in 100 cm^3 warm water, heat until just below boiling point and filter hot through a Whatman no. 42 filter paper. Allow to stand overnight. The gallic acid might crystallise out, in which case the reagent must be heated slightly just before use to redissolve the gallic acid. Discard the reagent if it turns amber.

4. **Sample diluent** — dilute 10 cm^3 conc. HNO_3 to 1 dm^3 with water.

5. **Wash water to sampler** — same as sample diluent, except that a few drops Brij-35 wetting agent must be added.

6. **Calibration standards** — stock standards of 1 000, 100 and 1,00 mg dm^{-3} V are prepared from a Merck titrisol ampoule containing 1,00 g vanadium as $VOSO_4$, by dilution with water acidified with HNO_3 (10 cm^3 conc. HNO_3 to 1 dm^3 water). Working standards in the range 1,0 to 100 $\mu g\ dm^{-3}$ V are prepared daily, immediately before use.

Apparatus

A Technicon AutoAnalyzer consisting of sampler II, peristaltic pump II, colorimeter II and recorder was used, with the manifold outlined in Fig. 1.

Technicon fittings

(A) TA1 fitting as debubble.

(B) Double T fitting no. T116-0489-01.

(C) A10 fitting no. T116-B034-01A.

(D) 20 turn mixing coil with injection nipple no. T157-B089-01.

(E) A10 fitting with 10 turn coil no. T157-0226.

(F) Polyethylene tubing no. 562-2006-01; 1,3 mm i.d., 320 mm length.

(G) Heating bath II with a G-coil thermostated at 37°C.

(H) Polyethylene tubing 1,3 mm i.d., 140 mm length, plus 21 turn delay coil no. T116-0152-03 insulated with paper tightly packed in and around delay coil.

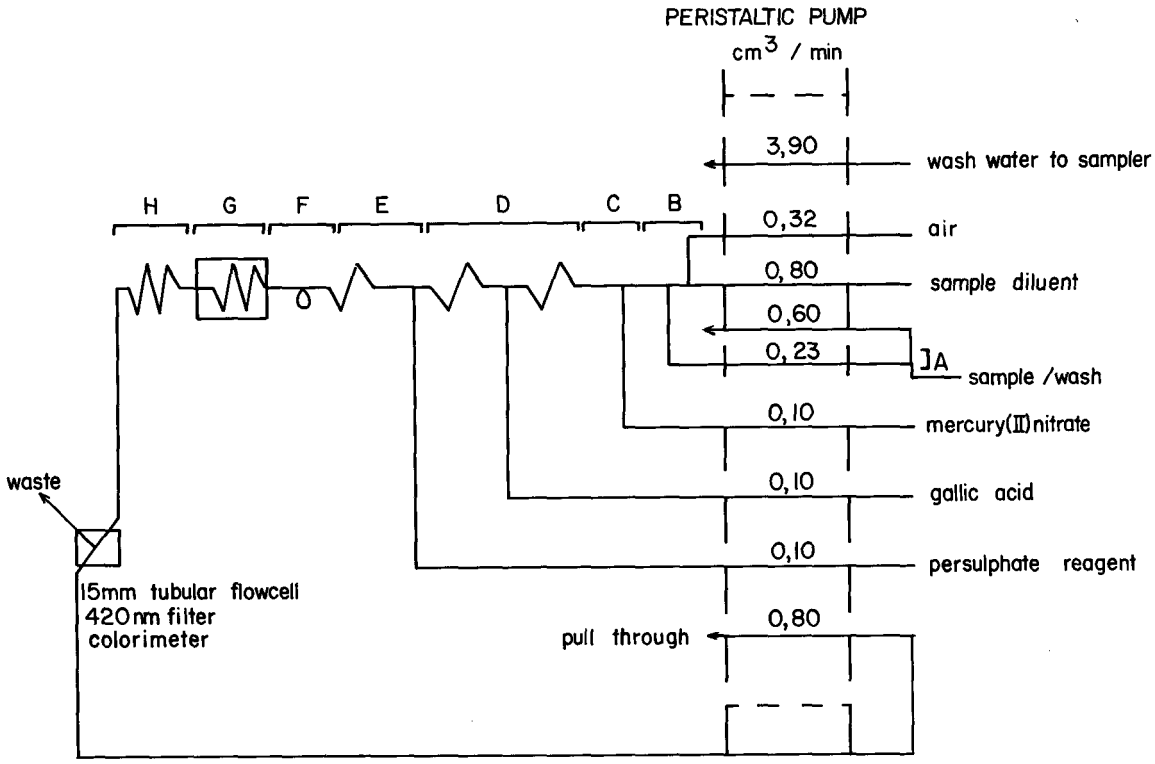

Figure 1
Vanadium Manifold

Method

Before pumping reagents through the manifold, the lines should be cleaned by pumping an acidified wetting agent (Brij or Contrad) followed by deionised water through all reagent lines and sample line. When the baseline has stabilized on pumping reagents, the highest standard (usually 100 $\mu g\ dm^{-3}$ V) is sampled to set the colorimeter sensitivity at full scale deflection on the recorder. The calibration standards and unknown samples can then be analyzed.

Samples were analyzed at a rate of 30 h^{-1}, with a sample to wash ratio of 1 : 1. The aspirated sample (0,23 $cm^3\ min^{-1}$) was automatically diluted on the manifold with sample diluent (0,80 $cm^3\ min^{-1}$), effecting a dilution ratio of 4,5 times. The diluted sample stream was segmented with air (0,32 $cm^3\ min^{-1}$), and then the mercuric nitrate (0,10 $cm^3\ min^{-1}$), gallic acid (0,10 $cm^3\ min^{-1}$) and persulphate (0,10 $cm^3\ min^{-1}$) reagents added in succession, with 10 turn mixing coils (60 s delay) between additions (Fig. 1).

The mixture was then passed through a 37°C heating bath for 244 s, followed by a delay coil providing a delay of 463 s. The delay coil was well insulated by packing tissue paper in and around the coil to maintain the temperature of the flowstream after it left the heating bath. The absorbance was measured in the colorimeter at 420 nm. A standard calibration setting of around 10 (giving a full scale absorbance of 0,060) was used to obtain full scale deflection on the recorder for a 100 $\mu g\ dm^{-3}$ V standard. By working at a smaller standard calibration setting, samples in the range 100 to 1 000 $\mu g\ dm^{-3}$ V could also be analyzed. The reaction time between addition of the last reagent (persulphate) and measurement of the absorbance was 816 s.

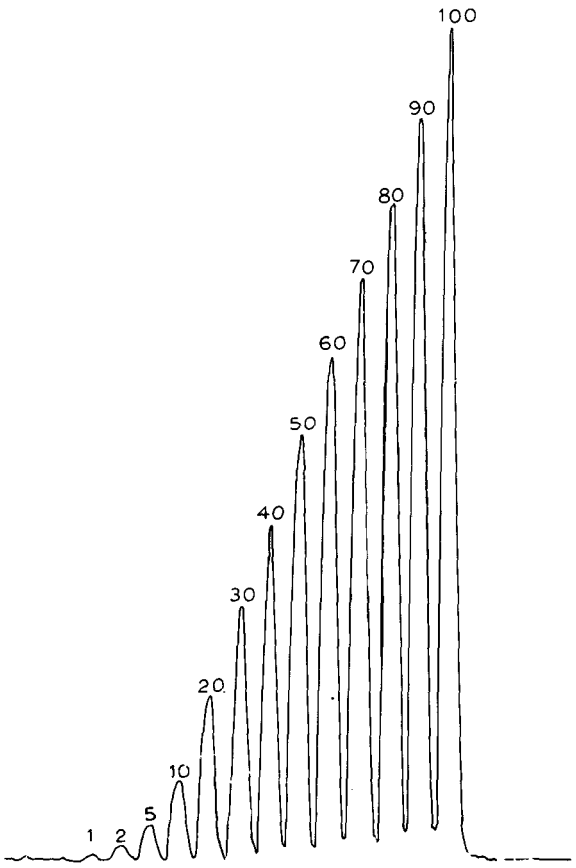

Figure 2
Calibration with vanadium standards (1 to 100 $\mu g.dm^{-3}$ V).

TABLE 1
AUTOMATED VANADIUM METHOD — SCREENING FOR INTERFERENCES

Salt* used	Concentration of salt (μmol.dm^{-3})	Apparent vanadium reading (μg.dm^{-3} V)
NH_4Cl	5 600	<1
$Fe(NH_4)_2(SO_4)_2$	36	5
$Fe(NH_4)(SO_4)_2$	36	2
$K_2Cr_2O_7$	1,9	1
$(NH_4)_6Mo_7O_{24}$	0,15	2
$CuCl_2$	7,9	3
$CoCl_2$	85	<1
$NiCl_2$	510	<1
$AlCl_3$	370	2
$NaNO_3$	1 300	<1
$MgSO_4$	2 500	<1
NaF	10 500	<1
KI	0,79	<1
$SbCl_3$	8,2	<1
H_3AsO_4	13	<1
$Ca(NO_3)_2$	2 500	<1
$AgNO_3$	93	<1
Si ('titrisol')	1 400 (as Si)	<1

*Interference possible from either anion or cation part of each salt.

TABLE 2
RECOVERY OF VANADIUM ADDED TO WATER SAMPLES

Vanadium concentrations in μg dm^{-3}	Sample number				
	1	2	3	4	5
Raw sample	18	26	1	2	5
After adding 25 μg dm^{-3} V	43	51	26	27	30
Found on analysis	44	50	27	29	32
V Recovered	26	24	26	27	27
% Recovered	104%	96%	104%	108%	108%
Average recovery	104 ± 5%				

Results

A calibration graph is shown in Fig. 2. The calibration was linear from 0 to 100 μg dm^{-3} V. Reproducibility was within 1% at 100 μg dm^{-3} V. Typical values for triplicate analysis of a water sample were 51,0; 50,7 and 51,1 μg dm^{-3} V. Analysis of an interlaboratory quality control sample containing 80 μg dm^{-3} Be, 300 μg dm^{-3} Li, 300 μg dm^{-3} Sr and 400 μg dm^{-3} V gave a vanadium concentration of 405 μg dm^{-3} with the automated method (Smith, 1979), showing the accuracy of the method to be good. Interferences were tested for by making up serial dilutions of pure salts supposedly containing no vanadium as indicated in Table 1, and running them on the vanadium AutoAnalyzer channel as if for a normal analysis of unknown samples. Any peak observed was read as an interference, and read off against the calibration curve. Concentration limits given by Fishman and Skougstad (1964) were used as a guide in choosing concentration ranges to be tested. The results of the tests for interferences are shown in Table 1. Of the salts tested, most showed negligible interference on vanadium up to the concentrations shown in Table 1. Slight interference was observed for salts containing Cr, Mo, Cu, Al and Fe at the concentrations given in Table 1. Depending on the freshness and purity of the reagents, chloride salts sometimes caused slight interference at chloride concentrations above 200 mg dm^{-3} Cl.

Recovery of vanadium added to water samples is shown in Table 2. The average recovery was 104%.

Discussion

In this automated vanadium method, the order of addition of the gallic acid and persulphate reagents is the reverse of that used by Fishman and Skougstad (1964). In the latter method gallic acid is added last, while in the automated method described in this paper, the persulphate reagent is added last. It was found that Cr (VI) interference was 15 times greater when persulphate was added before gallic acid.

The manifold dilution of the sample (4,5 times) was incorporated in the method to reduce interference by potential interferents in fresh water samples, such as chloride or iron (Fishman and Skougstad, 1964).

Conclusion

With the automated catalytic method for the determination of vanadium described in this paper, batch analysis of a large number of fresh water samples for vanadium is easily carried out. Flow system automation of the manual catalytic colorimetric standard method (Standard Methods, 1975) was successfully achieved, and did away with the tedium that close watch on reaction time necessitated in the manual method. The automated method has good reproducibility and accuracy, and provides a technique which makes vanadium determination in fresh water samples readily carried out by those laboratories having automated equipment.

Acknowledgement

Gratitude is expressed to Mr R. Smith for supplying the interlaboratory quality control sample. Thanks are also extended to Mr J.N. van Jaarsveld for searching through Technicon litera-

ture for automated vanadium methods, and to Mr H.R. van Vliet for proof-reading the manuscript. This paper is published by permission of the Department of Water Affairs.

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