Vanadium, colorimetry, catalytic oxidation, automated-segmented flow

Parameter and Code:
Vanadium, dissolved, I-2880-90 (µg/L as V): 01085

1. Application

This method is used to analyze samples of most water containing from 1.0 to 40 µg/L vanadium, provided that the interferences identified below are not exceeded. Concentrations of vanadium greater than 40 µg/L must be reduced by dilution. This modified method was implemented in the National Water Quality Laboratory in August 1990.

2. Summary of method

Small concentrations of vanadium catalyze the acid-persulfate oxidation of gallic acid. This reaction proceeds rapidly in the presence of vanadium but only slowly in its absence. The amount of colored oxidation product formed by this reaction is directly proportional to the concentration of vanadium when temperature, reaction time, and concentration of reactants are carefully controlled (Jarabin and Szarvas, 1961; Fishman and Skougstad, 1964; Weigo, 1983).

3. Interferences

3.1 Chloride, bromide, and iodide interfere when their concentrations exceed 200 mg/L (chloride), 250 µg/L (bromide), and 250 µg/L (iodide). Iron (II), iron (III), and copper (II) interfere when their concentrations exceed 300 µg/L [iron (II)], 500 µg/L [iron (III)], and 50 µg/L [copper (II)]. The concentrations of other ions are rarely large enough to interfere.

3.2 Results are erratic for samples preserved with nitric acid.

4. Apparatus

4.1 *Continuous flow autoanalyzer,* consisting of sampler, peristaltic pump, analytical cartridge, heating coil, colorimeter, voltage stabilizer, recorder and hardware/software package with personal computer for data acquisition and processing.

4.2 With this equipment, the following operating conditions are satisfactory for the range from 1 to 40 µg/L vanadium:

Flow cell ....50 mm
Wavelength ....410 nm
Rate of analysis 30/h (1:1)
Heating-coil temperature….. 60°C

5. Reagents

5.1 *Water:* All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

5.2 *Ammonium persulfate phosphoric acid reagent:* Dissolve 10.0 g $(NH_4)_2S_2O_8$ in 100 mL water. Heat solution at just below boiling for 5 minutes. Split the persulfate reagent into two equal volumes and transfer to 250-mL volumetric flasks. Immediately add 50 mL of concentrated H_3PO_4 (sp gr 1.69) to each flask. Let stand for 24 h. Just before use add 98 mL water and 2 ml, of sodium lauryl sulfate solution. These two reagent portions will allow for two consecutive days of analyses.

5.3 *Sodium hydroxide solution,* 5.0*N*: Dissolve with stirring and cooling 200 g NaOH in water. Allow to cool and dilute to 1 L.

5.4 *Sodium lauryl sulfate (SLS) solution,* 15 percent w/w: Dissolve 30 g of SLS in 170 mL of water. Place flask in an ultrasonic bath to aid in dissolving SLS. **CAUTION**: Sodium lauryl sulfate is a nasal irritant; work in a well-ventilated hood.

5.5 *Gallic acid solution,* 20 g/L: Weigh 4.0 g gallic acid monohydrate and transfer to a 200-mL volumetric flask. Add 2 mL of 5*N* NaOH and bring up to about 180 mL with water. To dissolve, set volumetric flask in an ultrasonic vibrator for 30 minutes. Bring to volume and mix. Prepare fresh daily.

5.6 *Mercuric nitrate solution,* 332 mg/L: Dissolve 350 mg $Hg(NO_3)_2 \bullet H_2O$ in about 900 mL water and dilute to 1 L.

5.7 *Vanadium standard solution I*, 1.00 mL = 100 µg V: Dissolve 0.2309 g ammonium metavanadate (NH_4VO_3) in water and dilute to 1,000 mL.

5.8 *Vanadium standard solution II*, 1.00 mL = 1.0 µg V: Dilute 10.0 mL vanadium standard solution I to 1,000 mL with water.

5.9 *Vanadium standard solution III,* 1.00 mL = 0.1 µg V: Dilute 100.0 mL vanadium standard solution II to 1,000 mL with water.

5.10 *Vanadium working solutions:* Prepare 1-L volumes each of a series of vanadium working solutions by appropriate quantitative dilution of vanadium standard solutions II and III, as follows:

Vanadium standard solution (mL)	Vanadium concentration (µg/L)
10 of III	1
50 of III	5
100 of III	10
20 of II	20
30 of II	30
40 of II	40

6. Procedure

6.1 Set up manifold (fig. 1).

6.2 Allow colorimeter, recorder, and heating coil to warm up for at least 30 minutes or until the temperature of the heating coil reaches 60°C.

6.3 Adjust the baseline to near zero scale divisions on the recorder with all reagents on line.

6.4 Before beginning analysis, aspirate three cups of the most concentrated working solution. Set reaction plateaus (peaks) to 95 percent on the recorder by adjusting STD CAL on the colorimeter.

6.5 Pour a tray of working solutions, blanks, water reference materials, and samples according to preselected protocol. Begin analysis.

7. Calculations

All vanadium concentrations are calculated automatically by the mathematical algorithms of the analytical software package. These tasks include calibrations and curve regressions followed by corrections for baseline drift.

Vanadium, catalytic oxidation manifold

8. Report

Report concentrations of vanadium, dissolved (01085), as follows: less than 10 µg/L, nearest 1 µg/L; 10 µg/L and greater, two significant figures.

9. Precision and matrix recovery

9.1 Single operator precision for dissolved vanadium for seven samples, expressed as standard deviation and percentage relative standard deviation, is as follows:

Number of Replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
5	2.8	0.11	4
6	6.4	0.19	3
7	6.8	0.41	6
5	9.5	0.19	2
7	25.1	0.25	1
7	27.4	0.82	3

9.2 Recovery of vanadium on seven samples spiked with vanadium is as follows:

Sample No.	Measured (µg/L)	Added (µg/L)	Found (µg/L)	Recovery (percent)
1	6.41	4.37	10.81	101
	6.38	4.84	10.63	88
	6.57	4.84	10.75	86
	6.42	4.75	10.78	92
2	6.50	4.37	10.79	98
	6.65	4.84	10.83	86
	0.29	4.44	10.47	94
	6.24	4.34	10.59	100
3	26.83	9.83	37.07	104
	26.76	9.64	37.22	109
	26.98	9.89	36.22	93
	26.98	9.58	37.48	113
4	2.89	1.95	4.69	92
	2.89	1.94	4.77	97
5	25.25	9.83	35.61	105
	25.31	9.64	35.75	108
	25.12	9.68	34.73	99
	25.14	9.50	35.22	106
6	9.54	4.37	13.90	100
	9.54	4.84	13.98	92
7	9.47	4.37	13.88	101
	9.60	4.84	13.81	87

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 45-47.

Fishman, M.J., and Skougstad, M.W., 1964, Catalytic determination of vanadium in water: Analytical Chemistry, v. 36, p. 1643-1646.

Jarabin, Z., and Szarvas, P., 1961, Detection of small amounts of vanadium by catalytic reaction with the addition of gallic acid: Acta University Debrecen, v. 7, p. 131; Chemical Abstracts, 1962, v. 57, 9192c.

Weigo, Q., 1983, Determination of trace vanadium in water by a modified catalytic-photometric method: Analytical Chemistry, v. 55(13), p. 2043-2047.