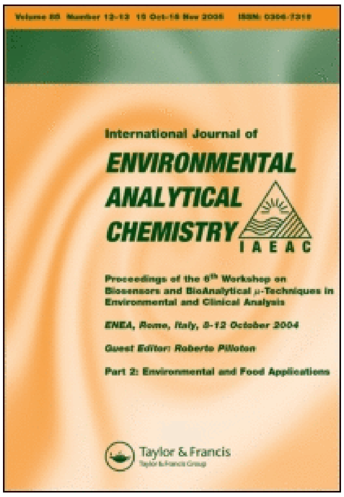

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The Accurate Measurement of Vanadium in Airborne Particulates

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The accurate and rapid measurement of vanadium in airborne particulates is described, with particular reference to so-called high-volume air samples collected on glass fibre filters. The method involves the acid digestion of a part of the filter followed by analysis using atomic absorption spectroscopy (AA). The use of both conventional flame AA and AA with a graphite furnace atomizer was investigated.

It was found that vanadium determinations are subject to large interferences from other elements when using the flame mode. The elements Al, Si, Zn, K, and Na, which are present in fairly large concentrations in the sample, all gave an enhancement of the vanadium signal. The combined interference of the sample matrix was examined as a function of analyzing wavelength, burner height and vanadium concentration.

The use of the heated graphite atomizer removed all interferences from the system and lowered minimum detectable concentrations by two orders of magnitude. The glass fibre filter blank for vanadium was found to be below the detection limit. Minimum detectable vanadium concentrations, using the graphite furnace, are 0.00025 mcg/m^3 for an air sample of 2000 m^3.

INTRODUCTION

Vanadium is moderately toxic to humans and animals, although trace amounts may be essential for life processes.[1] Vanadium is emitted into the atmosphere from industries using the metal, its compounds or alloys. Other sources are power plants and utilities consuming residual and crude oils and coals containing vanadium. Present maximum amounts permitted in the air in the U.S.A. are 100 and 500 mcg/m^3 for vanadium oxide fumes and dust, respectively. Such concentrations are possible in industrial situations but unlikely in urban environments where average concentrations in the range 0.01 to 0.40 mcg/m^3 are typical.[2] Although present levels may not constitute a health hazard, the measurement of vanadium in air can still be useful for pollution studies. This includes work on pollution dispersal and the tracing of pollution sources.

A number of analytical techniques have been used for measuring vanadium in airborne particulates. These include atomic absorption[3,4] and emission spectroscopy,[2] spectrophotometric methods[5] and neutron activation.[6] The analysis of most metals by atomic absorption (AA) is relatively simple and accurate, but this is not necessarily the case for vanadium where significant interferences may exist. These include the effects of elements such as aluminum,[7] the alkali metals,[7,8] and iron[7,8] which may also be present in the sample.

The present work was undertaken to investigate the validity of using AA for measuring vanadium in air samples. The many interferences found in using conventional flame AA were absent when using the flameless AA technique. The latter is considerably more sensitive and is suitable for the levels of vanadium typically found in air.

METHOD DEVELOPMENT

Sample preparation

The manner of sample preparation and the subsequent analytical problem depend to a large extent on the air sampler and the type of filter used. High-volume samplers with glass fibre filters are used routinely by several sampling networks and hence the subsequent method and analysis are based primarily on this sampling mode.

The preparation of the glass fibre filters prior to use, the actual air sampling, and the digestion of the filters have all been described in detail in previous publications.[9,10] The digestion method preferred by us includes dissolution of the filter with hydrofluoric acid, treatment with nitric acid, and subsequent filtering and making up to volume with distilled water. Washing of the filters prior to use was found unnecessary for the case of vanadium. In the digestion step, complete recovery could only be achieved if the digest was not taken to dryness after the hydrofluoric acid dissolution step (see "Flameless AA Analysis", below). The amount of filter treated is usually two 36-mm diameter circles (about 1/20 of an 8 × 10 in. filter) and the final volume of the sample is made up to 25 ml. For a 2000-m^3 air sample and a preparation as described above, the concentration of vanadium in mcg/m^3 is found by dividing the sample concentration in mcg/ml by four.

Flame AA analysis

The prepared sample contains not only metals from the collected air particulates, but also metals originating from the glass fibre filter. An unexposed filter, or filter blank, digested as described above contains the following elements, with the approximate concentrations, in mcg/ml: Na (400), Al (180), Si (400), Ba (300), Zn (200), Ca (200), K (150). The analytical problem is therefore to measure vanadium in the presence of rather large amounts of other metals.

The AA instrument used for the flame mode was a Perkin Elmer 403. A nitrous oxide-acetylene flame was employed with instrument conditions as recommended by the manufacturer. An analyzing wavelength of 318 nm was used.

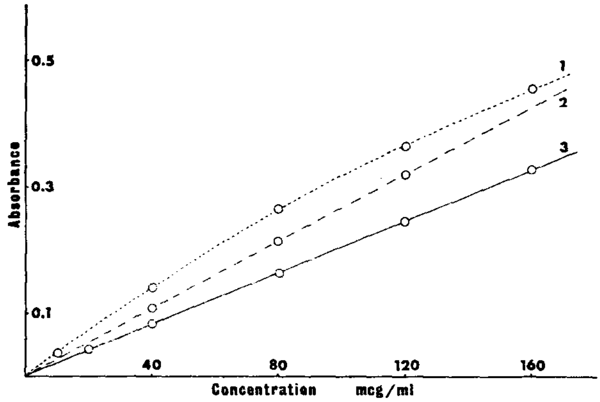

FIGURE 1 Comparison of calibration curves by flame AA for standards prepared in filter blank (1), solution of 180 mcg/ml Al (2), and water (3).

Figure 1 shows calibration curves obtained for standards in water and two other solutions. The standards in water, line 3, give a straight line for concentrations to about 160 mcg/ml. Standards made up in a solution of 180 mcg/ml Al show an enhancement of 30%, line 2, but again a straight line results. Line 1, standards in filter blank, shows even more enhancement and results in a curve. Note that line 1 passes through the origin, i.e. no vanadium is present in the blank.

It is interesting to note how serious errors can enter the analysis if the incorrect calibration curve is used. For a sample giving an absorbance of 0.265 (80 mcg V/ml), use of curves 2 or 3 of Figure 1 results in vanadium concentrations of 100 and 130 mcg/ml, respectively. Even if the method of additions is employed, using the last two points on line 1, an incorrect concentration of 110 mcg/ml is obtained. This is caused by the curvature of line 1.

Initially it was thought that aluminum was chiefly responsible for the enhancement effect. The effect of varying aluminum concentrations is shown in Figure 2. This result is similar to that obtained by Sachdev *et al.*,[7] but in our case the plateau does not appear to be reached at 200 mcg Al/ml.

The characteristics of the interferences were also examined as a function of analyzing wavelength and burner height. Figure 3 shows calibration curves for standards in water and filter blank (W and B) for three analyzing wavelengths. It can be seen that the three sets of curves have the same shape and differ only by constant factors. Hence the enhancement is probably not caused by a true spectral interference, i.e., where the lines of an interfering element overlap the vanadium line. Figure 4 shows the absorbance of 160 mcg/ml vanadium solutions in water (W) and filter blank (B) as a function of height above the burner. The height was measured from the centre of the light beam at the middle of the burner to the burner surface. A result qualitatively similar to that found by Sachdev *et al.*,[7] was obtained, with the additional information that the enhancement, line B/W, also changes and has its maximum at a point different from the absorbance curves. This would indicate that the interferences act in a dynamic process, changing with the chemical and/or physical conditions in the flame. The use of a deuterium lamp background compensator did not alter the interferences.

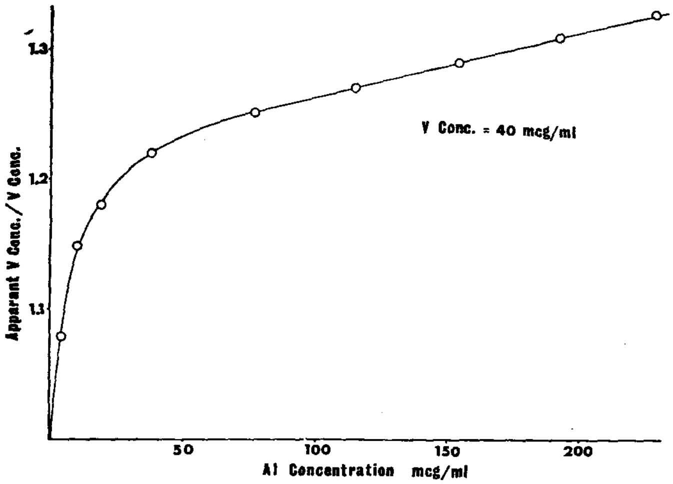

FIGURE 2 Aluminum enhancement for flame AA. The vanadium concentration was constant at 40 mcg/ml.

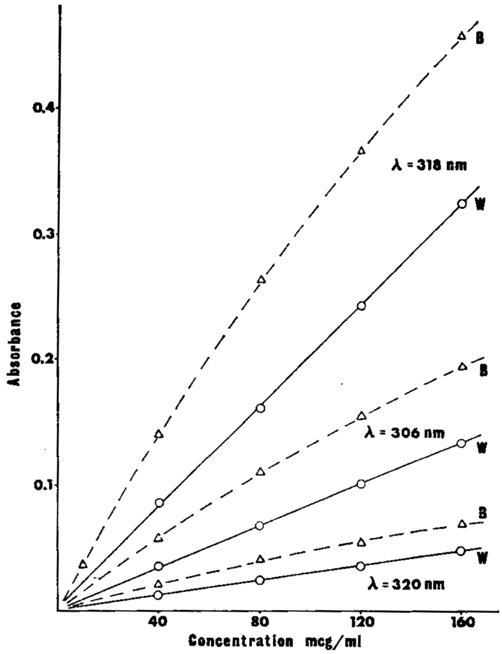

FIGURE 3 Calibration curves for three analyzing wave-lengths (λ = 318, 306, 320 nm) for flame AA. B and W represent standards in filter blank and water, respectively.

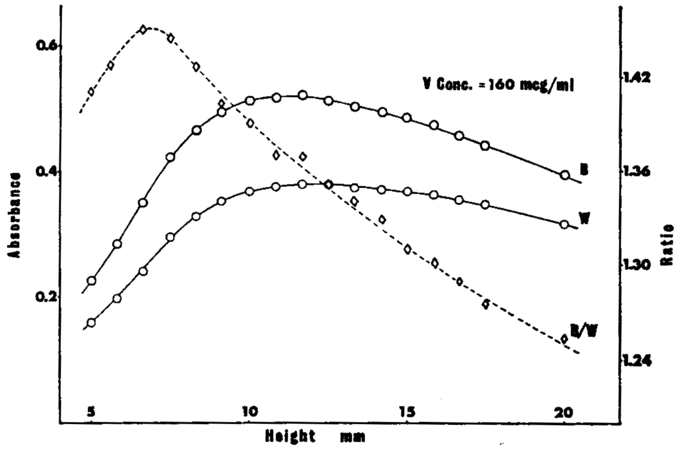

FIGURE 4 Absorbance as a function of height above the burner for a standard solution of 160 mcg/ml vanadium in filter blank (B) and water (W). The ratio of curves B and W, B/W, is also shown, using the right-hand ordinate.

Table I shows the enhancement of the signal by elements present in the filter blank. Except for Ca and Ba, the interferences are considerable, with Al making the largest contribution. As may be expected, the interference effects are not additive and a saturation effect occurs. This can be seen by comparing the enhancement of Al, Al + Si, and Al + Si + K.

TABLE I
Interferences for flame AA

Interfering element(s) present at 200 mcg/ml	Relative absorbance of 20 mcg V/ml with and without interfering ions
Na	1.11 ±0.03
Al	1.30
Si	1.22
Ba	1.05
Zn	1.14
Ca	1.03
K	1.10
Al, Si	1.40
Al, Si, K	1.40

The above results indicate that the measurement of vanadium in a glass fibre digest can be problematic. Large interferences occur so that standards must be used which match the sample exactly in composition. Alternatively, standards and samples can be prepared with a large excess of certain elements, i.e. Al, Na, Si, so that the interferences remain constant. In either case, flame conditions must be carefully controlled and held constant so that the interferences do not change. The minimum detectability with the flame mode was found to be 0.2 mcg/ml. For many air samples this is not sufficiently sensitive and for this and other reasons the flameless AA mode was investigated.

Flameless AA analysis

The graphite furnace atomizer can now be used routinely for atomic absorption to achieve sensitivities two orders of magnitude better than the flame.[10,11] The instrument used by us was the Perkin Elmer 403 with HGA-70 atomizer. Furnace conditions were 20 sec drying at 100°C, 20 sec charring at 1100°C, and 8 sec atomizing at 2600°C. A deuterium lamp background compensator was used.

Figure 5 shows the calibration curve obtained using standards in water (circles) and filter blank (triangles). Over the linear response range up to 0.5 mcg/ml *no* interferences were detectable. The addition of large amounts of aluminum to vanadium standards also had no effect. To further check for the absence of possible interferences, a dilution test was carried out. Table II gives the results and shows that no interferences are present.

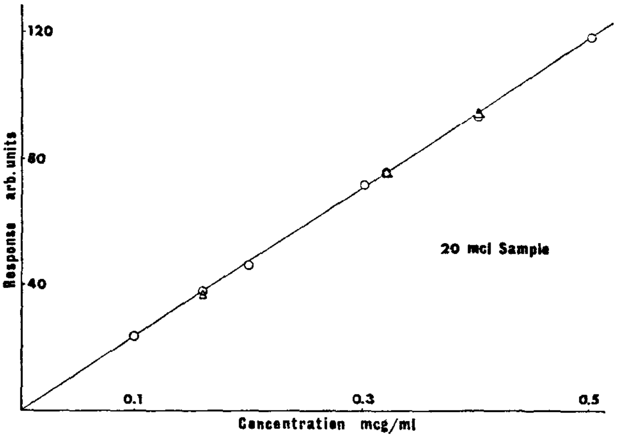

FIGURE 5 Calibration curve for graphite furnace AA; circles represent standards in water, triangles standards in filter blank.

TABLE II
Dilution test

Sample (ml)	Water (ml)	Total vol. (ml)	V (mcg/ml)	Total V (mcg)
4	0	4	0.400	1.60
4	1	5	0.321	1.61
4	2	6	0.267	1.60
4	4	8	0.204	1.63
4	6	10	0.154	1.54
				1.60 ± 0.03

Twenty filter blanks were prepared, 10 from water-washed filters and 10 from unwashed filters. Vanadium was found not be present, or at least below the detection limit in each case. The detection limit was 0.001 mcg/ml for a maximum sample injection of 100 mcl. This represents 0.1 ng vanadium or a concentration in air of 0.00025 mcg/m^3 for samples prepared as in "Sample Preparation". The reproducibility of analyses was checked by doing ten

TABLE III

Furnace AA responses to different vanadium oxidation states

Vanadium source	Medium	Colour (1000 mcg/ml)	Probable ox. state	Response to 0.40 mcg/ml (arb. units)
V_2O_5	dil. HCl	yellow	+5	38±1
V_2O_5	NH_4OH(29%)	clear	+5	38
V(metal)	dil. HNO_3	blue	+4	38
$VOSO_4$	dil. HNO_3	blue	+4	37
$(C_5H_7O_2)_3V$	dil. HNO_3	green	+3	36

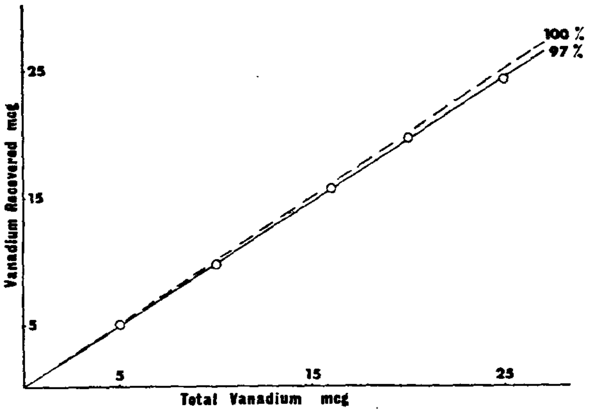

FIGURE 6 Recovery of vanadium added to filters. Circles represent experimental points, the dashed line 100% recovery.

replicate determinations on a standard 0.5 mcg/ml solution. The coefficient of variation was 2.3%.

A check was made on the response of the instrument to different oxidation states of vanadium. Table III shows the solutions which were prepared and the probable oxidation state of the vanadium. Within the error of the procedure, all gave the same response. The fact that the V^{+3} solution is somewhat lower may reflect impurities present in the parent compound.

A check was also carried out on the digestion procedure. Exact amounts of vanadium were added to filters using standard solutions. The filters were dried, then digested as in "Sample Preparation" and the vanadium was measured. Figure 6 shows that on the average 97% recovery was possible. As noted previously, this recovery was only possible if the hydrofluoric acid was not evaporated to dryness after the filter dissolution. Some additional experiments indicated that the loss (about 15%) on heating to dryness may be caused by formation of insoluble vanadium-silicon compounds.

DISCUSSION

A recent comparison of methods[4] has shown that vanadium determinations from glass fibre filters are prone to errors. Direct flame AA determinations were found to give results a factor of 1.7 times higher than those using the method of additions. The discrepancy was ascribed to matrix effects and our results (see Figure 1) would agree with this conclusion.

The fact that no interference effects were found with the carbon rod atomizer was quite surprising. It is apparent that temperature alone is not the only property of the atomizer (flame or furnace) to lead to the interferences. Enhancements have been found in studies of cationic interferences of Group I and II elements, and many of these can be satisfactorily explained by ionization effects.[12] The explanation is that more easily ionized elements depress the ionization of the element of interest and hence cause the enhancement. The first ionization potential of vanadium is 6.7 V, whereas aluminum and the alkali metals have lower ionization potentials. Hence the ionization explanation may be correct for these cases. However, silicon and iron have higher ionization potentials than vanadium and enhancement still occurs.

Filter collection efficiencies must also be considered if the vanadium amounts are to be related to air volumes. Pilz *et al.*,[5] have shown that all forms of vanadium are collected on glass fibre filters at flow rates up to 120 l/hr through a 9 cm diameter disc. This would indicate the suitability of glass fibre filters for high-volume samplers. The flow rate through a high-volume sampler is considerably greater than that used by Pilz *et al.*,[5] however, and hence this aspect deserves further attention.

The validity of taking area aliquots must also be considered. Lead[9] has been found to be uniformly distributed over the filter surface for a large number of filters. This was also found for cadmium,[10] where one exception has been noted, however. A limited number of investigations has shown that vanadium is also uniformly distributed. This is perhaps not unexpected since the mass median diameter of vanadium particulates has been found to be in the region of 0.1 microns,[13] which is similar to the values found for lead.[14]

These small particle diameters, compared to those of most other metals, probably stem from the fact that vanadium and lead originate from combustion processes.

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