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Determination of Airborne Particulate Vanadium by Atomic Absorption Spectrophotometry

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DETERMINATION OF AIRBORNE PARTICULATE VANADIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

by

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NOTE:

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ABSTRACT

The accurate measurement of vanadium present in airborne particulate matter is described. Samples of airborne particulates are taken by high volume or low volume techniques, by drawing a measured volume of air through dry filter media. The filter materials that are used may include washed glass fibre, analytical grade cellulose, or organic membrane filters.

The filter, or an areal aliquot thereof, with collected particulates, is wet ashed and the acid digest is made up to a standard volume with water. If microgram sensitivity is sufficient, the vanadium in the prepared sample is very rapidly assayed by atomic absorption spectroscopy, operating in the flame mode. If nanogram sensitivity is required and reduced analytical output can be accepted, then atomic absorption analysis may be done with the graphite furnace.

RÉSUMÉ

La détermination précise du vanadium présent dans les particules aéroportées est décrite. Des échantillons de particules aéroportées sont prélevés au moyen de techniques à grand et à faible débit, en aspirant un volume déterminé d'air à travers un milieu filtrant sec. Le matériel des filtres que l'on utilise comprend la fibre de verre lavée, la cellulose ou d'autres matériaux organiques de qualité analytique.

Le filtre, ou une aliquote de ce dernier contenant les particules recueillies, est minéralisé et la solution acide obtenue est complétée à un volume pré-déterminé d'eau. Si une sensibilité au microgramme prés est suffisante, la teneur en vanadium dans l'échantillon préparé est très rapidement évaluée par spectroscopie d'absorption atomique à la flamme. Si une sensibilité au nanogramme près est requise et qu'un nombre réduit des déterminations est acceptable, alors l'analyse par absorption atomique peut être effectuée avec le four en graphite.

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1. TITLE

DETERMINATION OF AIRBORNE PARTICULATE VANADIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

2. INTRODUCTION

Vanadium is moderately toxic to humans and animals. Chronic exposure to environmental air concentrations has been statistically associated with the incidence of cardiovascular disease and certain types of cancer. Vanadium is emitted into the atmosphere from industries producing the metal, its chemical compounds, and alloys. Other emitting sources are power plants and utilities consuming residual and crude oils and coals containing vanadium. The industrial uses of vanadium and the consumption of vanadium-containing fuels are increasing markedly.

Previously, emission spectrography and ring oven methods have been used to measure vanadium in high volume air samples. In this report vanadium is determined by atomic absorption spectroscopy using either the conventional flame mode or the flameless graphite furnace technique to effect reduction of the sample to the atomic state.

3. FIELD OF APPLICATION

The method is applicable to the measurement of the levels of suspended particulate vanadium found in either ambient or industrial atmospheres. With the conventional flame mode, washed glass filters, and a nominal air sample volume of 2000 m^3, vanadium is measurable to 0.025 $\mu g/m^3$, and interferences arise if the background contains certain other elements. For the same test sample, the use of the graphite furnace eliminates possible errors arising from matrix effects and greatly increases the sensitivity to 0.0004 $\mu g/m^3$.

4. PRINCIPLE

In the method to be described, airborne particulates are collected by drawing air through a filter. The filter or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation is simple and rapid. The aqueous acidic solution is reduced in the flame or graphite tube to the atomic state. The amount of vanadium present in the sample is measured by the amount of light it absorbs at 318.4 nm, a characteristic wavelength of vanadium, and referring this absorbance to the appropriate calibration curve. Vanadium levels are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable are found in section 10, Expression of Results.

5. REACTIONS

The most important reactions relate to the complete dissolution of the particulate sample in acidic media to form a homogeneous test sample. As microgram quantities of material may be involved, losses due to incomplete solution, volatility, or adsorption must be avoided.

6. REAGENTS

6.1 Air, Compressed. In pressure cylinders or online.

6.2 Acetylene, Compressed. In pressure cylinders.

6.3 Nitrous Oxide, Compressed. In pressure cylinders.

6.4 Glass Filters. Commercially available material exhaustively washed prior to use, 203 x 254 mm in size.

6.5 Cellulose Filters. Ashless, acid-washed, analytical grade, 203 x 254 mm in size.

6.6 Water. Distilled at least twice from glass or quartz.

6.7 Hydrofluoric Acid. 49%, reagent grade, in polyethylene containers.

6.8 Nitric Acid. 71%, reagent grade.

6.9 Standard Solution of Vanadium. Dissolve 1.7856 g of vanadium pentoxide (V_2O_5) in 10 ml concentrated hydrochloric acid and dilute to 1 litre with water. One millilitre of this stock solution contains 1000 µg vanadium, as the element.

7. APPARATUS

7.1 Spectrophotometer, Atomic Absorption. With meter, recorder or digital readout, and monochromator with wavelength dial reading to 0.1 nm.

7.2 Pipettes, Glass. Millilitre capacities, 'to deliver'.

7.3 Volumetric Flasks. Borosilicate with ground-glass stopper, 25 ml capacity.

7.4 Bottles, Polyethylene. Screw cap, 'leak-free' for storage of test samples, 30 ml capacity.

7.5 Beakers, Teflon. Griffin form, 100 ml capacity.

7.6 Beakers, Borosilicate. Graduated, Griffin form, with Teflon-coated rim, 150 ml capacity.

7.7 Hot Plate. Electric, with temperature control, thermostat, and ceramic heating surface.

7.8 Büchner Funnel. Polypropylene, custom made, with sintered false bottom and vacuum connection, 216 x 267 x 85 mm in free depth.

7.9 Graphite Furnace. A suitable instrument is available commercially to the Massmann design.

7.10 Strip Chart Recorder. To display and record the response from the furnace.

7.11 Pipettes, Automatic. Eppendorf design, with capacities 10 - 100 µl.

8. SAMPLING AND SAMPLES

8.1 Preparation of Laboratory Sample. Cellulose filters (6.5) may be used without treatment. Purify glass fibre filters (6.4) by placing a group of 100 such filters in the special Büchner funnel and extracting repetitively with distilled water. Mount the filter in a conventional high volume or other sampler head. Draw air through the filter at a flow rate between 1.13 and 1.60 m^3/min for an appropriate period, such as 24 h. The resistance to flow offered by the cellulose filters is much greater than that for glass and an appreciably smaller total volume of air will be taken with cellulose. Calculate and record the total volume of air sampled, in cubic metres, as the product of mean flow rate and time.

8.2 Preparation of Test Sample. Cut areal aliquots from the exposed surface of a filter using a circular metal punch. The cutting edge of the punch is carefully wiped with lens tissue between each use to prevent carry over of contamination from one sample to another. Place one or more such discs in a Teflon beaker. Initiate the digestion of a glass fibre filter matrix with the dropwise addition of 1 ml of hydrofluoric acid (6.7). Gently warm the contents of the beaker at low heat until the hydrofluoric acid is almost completely evaporated. Heating to dryness at this point may result in a loss of vanadium of about 15% (13.1). Then, add 1 - 2 ml of nitric acid (6.8) and continue to heat gently until only a few drops of nitric acid remain. Add about 10 ml of water, bring nearly to the boil, and filter through a Whatman 41 filter into a glass beaker (7.6). Transfer to a 25 ml volumetric flask (7.3). Rinse down the Teflon beaker with another 10 ml of water, warm, and filter into the same beaker. Transfer to the 25 ml volumetric flask and make up test sample to mark. Mix the contents of the volumetric flask thoroughly, and transfer to a polyethylene storage bottle (7.4). The test sample is now ready for analysis. Cellulose filters can be digested or extracted using nitric acid.

9. PROCEDURE

9.1 Safety Precautions. Follow normal precautions for the handling of compressed gases. Observe manufacturer's instructions on lighting and extinguishing the flame. *TEST GAS SUPPLY SYSTEM FOR LEAKS BEFORE USE AND EACH TIME A CYLINDER OF FUEL IS REPLACED.*

9.2 Test Portions.

9.2.1 Flame. Introduce the test portion into the flame by *CONTINUOUS* aspiration, through polyethylene tubing, of an *UNMEASURED* portion of the test sample. Aspirate distilled water into the flame between the introduction of each test portion to prevent cross contamination.

9.2.2 Furnace. Measure and insert in the furnace test portions of 10 - 100 µl of the test sample using an automatic pipette (7.11).

9.3 Calibration Curves.

9.3.1 Flame. Using 'to deliver' pipettes, prepare known concentrations of vanadium by dilution of standard solution (6.9) with filter blank solution (9.5.2) to cover the range 20 - 200 µg vanadium/ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for vanadium. Set the wavelength of the monochromator at 318.4 nm. Using a nitrous oxide - acetylene flame, aspirate an unmeasured portion of each dilute standard vanadium solution for 10 s (9.2.1). At the same time, aspirate into the flame a blank of distilled water. From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of vanadium in micrograms per millilitre. A representative calibration curve is given in Figure 1. Also included in Figure 1 are lines representing standards made up in water and an aqueous 180 µg/ml solution of aluminum. It can be seen that the matrix effect is considerable and is dependent on the concentrations of a number of interfering elements (13.1).

9.3.2 Furnace. Using an automatic pipette with polyethylene tip, place identical microlitre volumes of the dilute standard vanadium solutions and a distilled water blank in the furnace. Measure and record the response of each test portion following the predetermined measuring cycle. Cover the range 2 - 10 ng vanadium in steps of 2 ng (0.1 - 0.5 µg/ml for a 20 µl volume). Prepare a calibration curve of response, in arbitrary units, against concentration of vanadium in micrograms per millilitre. A representative calibration curve is given in Figure 2.

9.4 Determination.

9.4.1 Flame. Set the wavelength of the monochromator at 318.4 nm. Observing conditions of 9.2.1 and 9.3.1, aspirate an unmeasured test portion of each unknown test sample into the flame. Record the response for each unknown. Aspirate distilled water into the flame between each unknown test portion to prevent cross contamination. Measure the vanadium in all the unknown test samples that can be accommodated to the wavelength of 318.4 nm and the corresponding calibration curve.

9.4.2 Furnace. Measure into the furnace, by automatic pipette, a similar test portion of each unknown test sample. Follow the drying and heating programs previously established. Record the response for each test portion in arbitrary units. Derive the amount of vanadium present in the test sample by referring to the appropriate calibration curve, such as, for example, Figure 2.

9.5 Blank Tests.

9.5.1 Reagents. In parallel with preparation of calibration curves, prepare a reagent blank of the acids and distilled water used in the preparation of calibration curves and test samples. Change or purify reagents, as necessary, if blanks are unsatisfactory.

9.5.2 Reagents Plus Filters. In parallel with the preparation of calibration curves and test samples, prepare areal test portions from unexposed filter media as described in paragraph 8.2. Measure vanadium and express blanks in micrograms of vanadium per millilitre.

10. EXPRESSION OF RESULTS

10.1 Blanks. The glass filter blank value for any element may vary considerably with the batch. This has been very noticeable with manganese and beryllium. For this reason, filter blanks should be determined regularly. It should also be noted that part of the filter blank value is due to matrix interferences from elements present in larger amounts in the filter such as Na, Ba, Si, Ca, Zn, K, and Al.

10.2 Instrumental Precision. This is defined as the standard deviation of a number of replicate determinations and is expressed in micrograms per millilitre. Typical precisions for 10 replicate determinations on standard samples are: 100.0 ± 0.5 µg/ml for the flame mode and 0.50 ± 0.012 µg/ml for the flameless mode, on a 20 µl sample.

10.3 Minimum Measurable.

10.3.1 Concentration in Test Sample. This is taken as twice the blank deviation or instrument precision, whichever is larger. This value is 0.1 µg/ml for vanadium in the flame mode and 0.0014 µg/ml in the flameless mode.

10.3.2 Concentration in Air. This is based on a sample volume of 2000 m^3 and two aliquot discs 36 mm in diameter. The minimum measurable concentration is 0.0250 µg vanadium/m^3 for the flame mode, regardless of whether glass or cellulose filters are used. The increased sensitivity of the graphite furnace reduces the minimum concentration measurable to 0.0004 µg/m^3.

10.4 Calculations. The vanadium content of the test portion is expressed in micrograms per millilitre, X_1. The blank, X_2, in the same units, is subtracted from X_1 to get the corrected concentration of vanadium in the test sample. Multiplication by the dilution factor, usually 25, gives the total quantity of vanadium in the test sample in micrograms. For high volume filters of nominal size 203 x 254 mm:

total exposed filter surface = 4.159×10^4 mm^2
areal test portion, 2 x 36 mm discs = 2036 mm^2
surface multiplication factor = 20.43
dilution factor = 25
volume of air sample, m^3 = V
response, unknown test portion = X_1
response, total blank = X_2
vanadium concentration, µg/m^3 = T

$$T = \frac{(X_1 - X_2) \times 20.43 \times 25}{V}$$

For the flame mode, where standards are made up in a filter blank, $X_2 = 0$. It has been found experimentally that $X_2 = 0$ for the flameless mode.

11. NOTES ON PROCEDURE

11.1 Collection Efficiencies. Little is known about actual collection efficiencies, and in methods for the analysis of particulate metals these efficiencies are usually ignored. The size of particulate vanadium is between 1 and 3 µm, according to Lee et al. (13.2).

11.2 Temperature and Pressure. The effect of temperature and pressure during the sampling period has been largely disregarded in the past. Since these factors must have some effect on the measured air volume, it is recommended that these corrections be introduced routinely. Agreement is increasing that if standard conditions of temperature and pressure are to be used to correct the final volume, these should be 25 °C and 760 mm Hg.

11.3 Sampling Periods. Although the method described is nominally based upon high volume samples taken for a 24 h sampling period, there is no valid reason why samples may not be taken for shorter time periods, at slower flow rates, or both. If high volume samples are taken on cellulose, it is particularly appropriate to take air sample volumes of 1000 m^3 or less. The lower particulate loading, so obtained, minimizes particulate falloff.

11.4 Air Flow Rates. It is customary to assume that the decrease in air flow rate during sampling is linear, and for purposes of calculation the mean value of initial and final flow rates is taken. This assumption is not correct, although the error introduced by this oversimplification is not ordinarily serious.

11.5 Preparation of Test Portions. For the preparation of areal test portions, the use of a sharp circular metal die is preferred over the use of scissors or rectilinear templates of large perimeter. Areal test portions prepared by these latter are less likely to be identical in size. A circular die of limited diameter machined from solid metal is very rigid, and areal aliquots can be reproduced accurately. In the method described, a punch of stainless steel is used. No vanadium contamination has been found to result from its use.

11.6 Distribution on Filters. In the repetitive and consecutive areal test portions cut from an exposed high volume filter, the assumption is implicit that the element of interest is uniformly distributed across the exposed surface of the filter. This assumption is established as fact, at least in the case of lead and cadmium measured on high volume filters (13.3, 13.4, 13.5). This uniform distribution cannot be assumed in certain 'membrane' type filters because of inherently high pressure drop and faulty geometry of commercially available filter holders. With such filters, areal aliquotting cannot be used (13.6).

11.7 Calibration Curves. When possible, several calibration curves relating to different sensitivities are helpful. This minimizes the possibility that the concentration of the metal in the unknown test sample will not match one or another of the curves. See the method for lead in this series where two calibration curves are given for the flame and one for the furnace (13.7).

11.8 Operating Conditions.

11.8.1 Flame. The optimum operating conditions are as given:

wavelength = 318.4 nm
spectral band width = 0.7 nm
source = hollow cathode
source current = as recommended
oxidant = nitrous oxide
fuel = acetylene
flame = reducing, red
sensitivity = 2.2 µg/ml for 1% absorption.

Change the acetylene container before cylinder pressure drops below 50 psig.

11.8.2 Graphite Furnace. A representative curve for vanadium measured by the graphite furnace is given in Figure 2, which shows greatly increased sensitivity over the flame. Furnace operating conditions:

wavelength = 318.4 nm
sample size = 20 µl
purging gas = argon or nitrogen

thermal decomposition, drying: 20 s, 100 °C
thermal decomposition, charring: 25 s, 1100 °C
thermal decomposition, atomizing: 8 s, 2500 °C

The use of a deuterium lamp background compensator is recommended.

12. SCHEMATIC REPRESENTATION OF PROCEDURE

12.1 Draw laboratory air sample.

12.2 Cut areal test portion from exposed surface.

12.3 Digest the test portion.

12.4 Adjust digest to volume to give test sample.

12.5 Aspirate test portion into flame.

12.6 Alternatively, add test portion to furnace, as measured by microlitre pipette.

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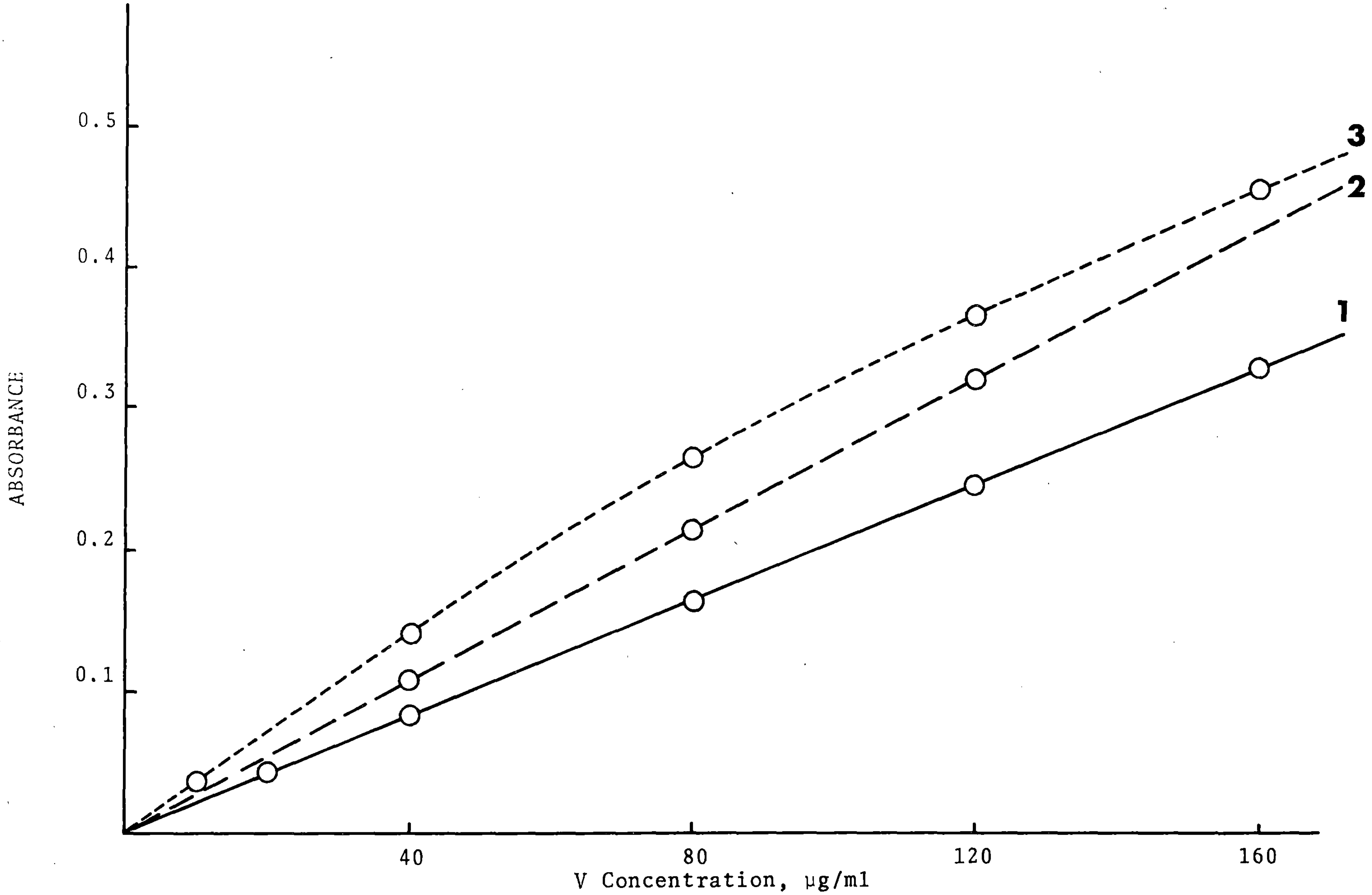

Figure 1. Absorbance vs concentration of vanadium for the flame mode Line 1, aqueous standards. Line 2, standards in Al solution Line 3, standards in filter blank

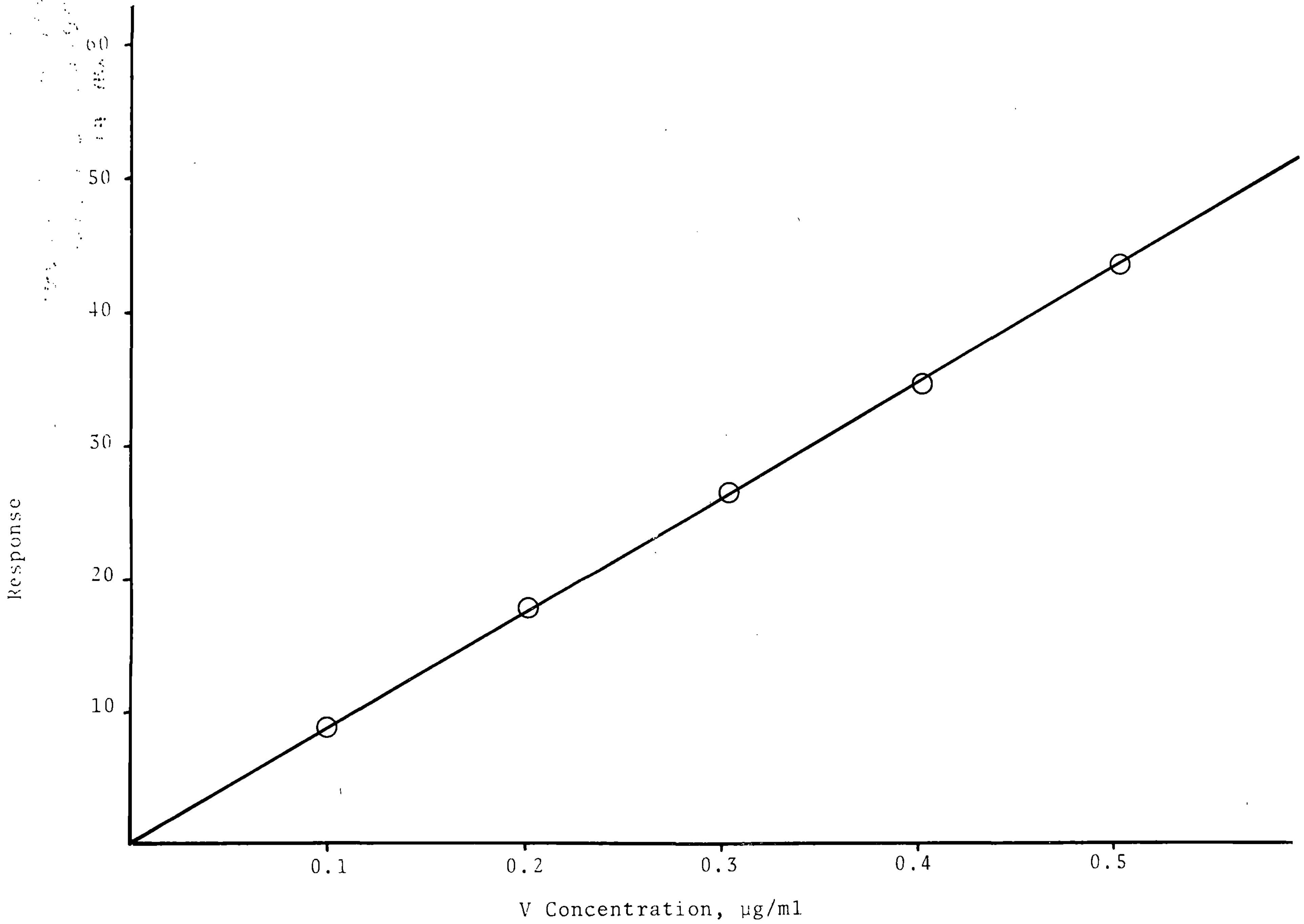

Figure 2. Response vs concentration of vanadium for the furnace mode. 20μl samples