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Determination of Airborne Particulate Chromium by Atomic Absorption Spectrophotometry

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DETERMINATION OF CHROMIUM IN AIRBORNE PARTICULATES BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

by

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NOTE:

These methods were originally prepared for Task Force Number 1 (Air) of the Scientific Committee on Problems of the Environment (SCOPE) of the International Council of Scientific Unions. The format follows that of the International Standards Organization.

ABSTRACT

The accurate measurement of chromium 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 chromium 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.

RESUME

La détermination précise du chrome 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 chrome dans l'échantillon préparé est très rapidement évaluée par spectroscopie d'absorption atomique à la flamme. Si une sensibilité au nanogramme près est requisé 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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2. INTRODUCTION

Chromium is used principally in the manufacture of steel and other alloys or for chrome plating. Chromite ore, $FeO.Cr_2O_3$, is the most important source of chromium. The ore, because of its high resistance to heat, is used to manufacture refractories. Chromium, finding its way into the air from the metallurgical industry, is probably in the trivalent or zero state. The toxicity of trivalent chromium has not been demonstrated (13.1). Chromium sesquioxide, an extremely insoluble compound, is probably the most abundant form of airborne trivalent chromium. Divalent chromium compounds are so easily oxidized that they cannot exist in ambient air. Hexavalent chromium in the air probably originates from the production of chromates and dichromates by the chemical industry. The highly coloured salts of chromium have been used as pigments and as mordants in the textile industry. Hexavalent chromium compounds are extremely toxic. Contact with the skin should be avoided, and inhalation as dust can severely irritate the nasal mucosa and respiratory tract. Ingestion may be fatal.

Gravimetric, titrimetric, and colorimetric methods for chromium determination have been of limited use in air quality studies. The Weisz ring oven method has been used to measure the chromium content of particulates collected on sample tapes, with a detection limit of 0.15 μg and a range of 0.3 - 1.0 μg. Atomic absorption methods have been widely used to determine chromium because of their sensitivity and speed. In this report chromium 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 chromium 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, chromium is measurable to 0.015 $\mu g/m^3$. If the sample is taken on analytical grade cellulose, the minimum quantity measurable is decreased to a point that is dependent upon the chromium content of the reagents used to dissolve the cellulose. Analytical grade cellulose contains less than 0.25 μg Cr per aliquot disc 36 mm in diameter. Since levels of chromium in urban air are low and the possibility of contamination from chromium-containing metals in the laboratory may be rather high, every care must be taken to ensure that the chromium being measured is actually due to the air sample.

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 atomized in the flame or graphite tube and scrutinized by an atomic absorption spectrophotometer. The amount of chromium present in the sample is measured by the amount of light it absorbs at 357.8 nm, a characteristic wavelength of chromium, and referring this absorbance to the appropriate calibration curve. Chromium 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 acid 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. If a portion of the airborne chromium to be measured is in the form of Cr_2O_3, some difficulty may be encountered in solubilizing all the chromium. Using the test sample preparation method outlined in paragraph 8.3, only a total of 5 - 10 μg of Cr_2O_3 will be solubilized per digestion. This represents a maximum of 0.1 $\mu g/m^3$, a figure approximately six times the 'normal' value expected for the chromium content of urban air.

6. REAGENTS

6.1 Air, Compressed. In pressure cylinders or online.

6.2 Acetylene, Compressed. In pressure cylinders.

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

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

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

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

6.7 Nitric Acid. 71%, reagent grade.

6.8 Standard Solutions of Chromium. Dissolve the amount of chromium salt equivalent to 1 g of chromium in water and dilute to 1 litre with water. One millilitre of stock solution contains 1000 μg chromium/ml. Both trivalent and hexavalent chromium gave equal responses using the atomic absorption conditions described in paragraphs 11.8 and 11.9.

7. APPARATUS

7.1 Spectrophotometer, Atomic Absorption. With 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 and thermostat. Ceramic heating surface recommended.

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

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. Full span pen deflection $\leqslant 0.5$ s.

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

8. SAMPLING AND SAMPLES

8.1 Air Sampling. If high volume sampling is used, draw air through the filter at a flow rate between 1.13 and 1.60 m^3/min. A time period of 24 h is appropriate when glass fibre filters are used. Since the resistance to flow offered by the cellulose filters is much greater than that for glass, an appreciably smaller total volume will be taken with cellulose for a similar sampling time.

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 Laboratory Sample. As soon as possible after the sampling has been completed, the filter should be carefully removed from the filter head, placed in an envelope with complete documentation, and transmitted to the laboratory in the quickest reliable way.

8.3 Preparation of Test Sample. Cut areal aliquots from the exposed surface of a filter using a circular metal punch. A suitable punch is one made of a material which will not release chromium during the punching process, a criterion that may be determined by establishing the chromium content of filter blanks having no contact with metal during preparation. 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 dissolution of the glass fibre filter matrix by the dropwise addition of 1 ml of hydrofluoric acid (6.6). Gently warm the contents of the beaker at low heat until the hydrofluoric acid is almost completely evaporated. At this point, add 1 - 2 ml of nitric acid (6.7) and continue to heat gently until 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 at 25 °C. 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 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 chromium by dilution of standard solution (6.8) with filter blank solution prepared as in section 8.3 from unexposed filter to cover the range of 1.0 - 5.0 µg chromium/ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for chromium. Set the wavelength of the monochromator at 357.8 nm. Using a nitrous oxide - acetylene flame, aspirate an unmeasured portion of each dilute standard chromium solution for 10 s (9.2.1). At the same time, aspirate into the flame a solution of filter blank. From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of chromium in micrograms per millilitre. A representative calibration curve is given in Figure 1, with the corresponding curve for chromium standards in water.

9.3.2 Furnace. Using an automatic pipette with polyethylene tip, place identical microlitre volumes of the dilute standard chromium 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 0.2 - 1.0 ng chromium in steps of 0.2 ng (0.01 - 0.05 µg/ml for a

20 µl volume). Prepare a calibration curve of response, in arbitrary units, against concentration of chromium in micrograms per millilitre. A representative calibration curve is given in Figure 2. Preparation of standards in filter blank is not necessary for furnace work as the matrix effects observed do not occur with the furnace.

9.4 Determination.

9.4.1 Flame. Set the wavelength of the monochromator at 357.8 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 chromium in all the unknown test samples that can be accommodated to the wavelength 357.8 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 chromium 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 Filter Blanks. In parallel with the preparation of calibration curves and test samples, prepare areal test portions from unexposed filter media as described in 8.3. Measure chromium and express blanks in micrograms of chromium 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, beryllium, and chromium. For this reason, filter blanks should be determined regularly. However, the filter blank values for chromium within a given batch of filters are extremely uniform. If filters from a known batch are used when possible, detection limits of the method may be lowered.

Extreme care must be taken to isolate and eliminate chromium interferences normally present in the laboratory. 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 the 10 repeat determinations on standard samples are: 2.00 ± 0.01 μg/ml for the flame mode and 0.05 ± 0.0008 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 0.06 μg/ml for chromium using the flame mode and glass fibre filters. With the flameless mode the blank deviation is the determining factor, which may vary for different filter batches. Minimum measurable may be as high as 0.04 μg/ml for glass fibre filters.

10.3.2 Concentration in Air. This is based upon a sample volume of 2000 m^3 and two aliquot discs 36 mm in diameter. The minimum measurable concentration is 0.015 μg chromium/m^3 for the flame mode and 0.010 μg chromium/m^3 for the flameless mode. These values are lower for cellulose filters as explained in section 3.

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

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

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

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 particle size of particulate chromium is between 0.6 and 4.5 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 used to correct the final volume, these conditions 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, air sample volumes of 1000 m^3 or less are particularly appropriate. The lower particulate loading, so obtained, minimizes particulate falloff. The much more favourable blank resulting from the use of cellulose and the attendant increase in sensitivity should be borne in mind when the sampling procedure is being planned.

11.4 Air Flow Rate. It is customary to assume that the decrease in air flow rate during sampling is linear, and for usual 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 chromium-free solid metal is very rigid, and areal aliquots can be reproduced accurately. In this method a punch made of brass is used. No chromium 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 (13.3, 13.4, 13.5) and cadmium (one exception was noted in 13.5) measured on high volume filters. 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 = 357.8 nm
spectral band width = 1.4 nm
source = hollow cathode
source current = as recommended
oxidant = nitrous oxide
fuel = acetylene
flame = reducing, rich red
sensitivity = 0.026 µg/ml for 1% absorption.

Change the acetylene cylinder before pressure drops to 50 psig.

11.8.2 Graphite Furnace. The calibration curve for the flame mode obeys Beer's Law up to 8.0 µg chromium/ml of test sample as illustrated by Figure 1. A representative curve for chromium measured by the graphite furnace is given in Figure 2, which shows greatly increased sensitivity over the flame. Furnace operating conditions are as given:

wavelength = 357.8 nm
sample size = 20 µl
purging gas = argon or nitrogen

thermal decomposition, drying: 15 s, 100 °C
thermal decomposition, charring: 15 s, 230 °C
thermal decomposition, atomizing: 15 s, 2400 °C

The use of a deuterium lamp background compensator is recommended.

11.9 Solubility of Chromium Salts. Most chromium salts likely to be found in ambient air will be soluble if the digestion procedure in paragraph 8.3 is followed. Complete recovery of added trivalent ($CrCl_3 \cdot 6H_2O$) and hexavalent (K_2CrO_4) chromium has been demonstrated in our laboratory. Chromium compounds that may be difficult to dissolve are chromium sesquioxide (Cr_2O_3), elemental chromium (Cr), chromium arsenide (CrAs), chromium nitride (CrN), and chromium silicide (Cr_3Si_2). The solubility of Cr_2O_3 has been discussed in section 5. CrAs, CrN, Cr_3Si_2, and elemental chromium are not likely to be found in ambient air. Elemental chromium is not found in nature, and airborne chromium in the vicinity of electroplating plants or producers of chromium alloys will likely be in the oxide form. The fluorides of chromium, CrF_2, and CrF_3 have melting points above 1000 °C and loss of chromium during digestion of the glass fibre filter with hydrofluoric acid does not occur

11.10 Glass Fibre Filters.

11.10.1 Washing Technique. Glass fibre filters must be washed before use. At present, the expedient used is to attempt to leach out impurities with boiling distilled water. A special Büchner funnel, rectangular rather than circular, was constructed of polypropylene by Bel Art Products, Pequannock, New Jersey. This was designed to hold one box of 8 x 10 in. filters.
To improve the access of the hot distilled water, spacers were placed in the pile at intervals of every 10 filters. Submerge

the pile of filters in boiling water, allow to steep for 30 min, and withdraw the water by suction. Repeat this process. Allow the washed glass filters to dry in air in a dust-free location.

11.10.2 Chromium Content. With a flameless atomic absorption spectrophotometer equipped with a background corrector, chromium was shown to be present in the acid digest of glass fibre filters having no previous contact with metal. Two 36 mm discs contained 1.64 - 3.35 μg chromium of which 0.3 μg was derived from the reagents used to dissolve the two discs. The variability of the chromium content of the glass fibre was less if filters from the same batch were used.

12. SCHEMATIC REPRESENTATION OF PROCEDURE

12.1 Draw laboratory air sample.

12.2 Cut areal test portion from exposed surface.

12.3 Digest areal 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 measured by microlitre pipette to furnace.

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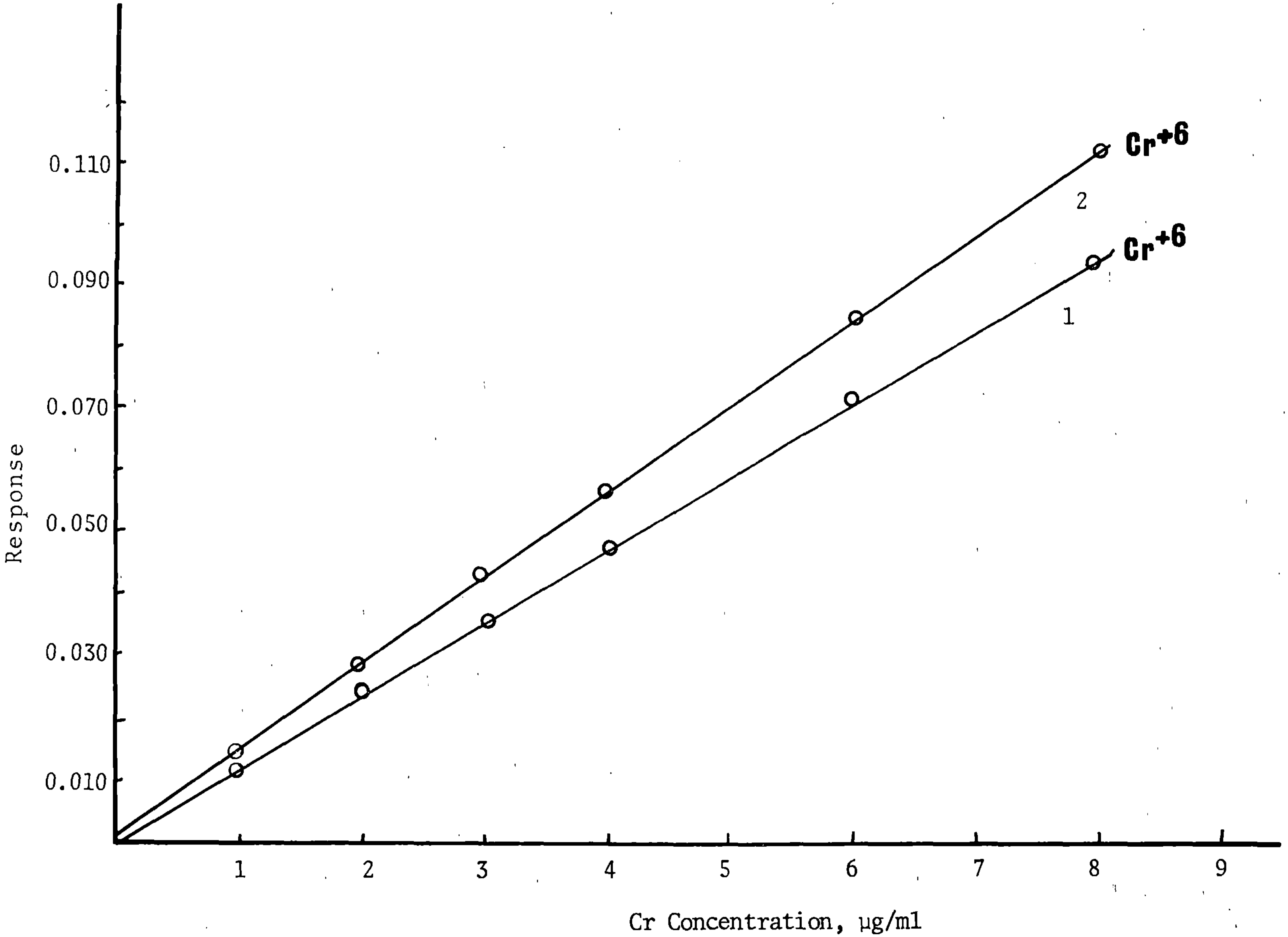

Figure 1. Absorbance vs concentration of hexavalent chromium for the flame mode. Line 1, aqueous standards. Line 2, Standards in filter blank

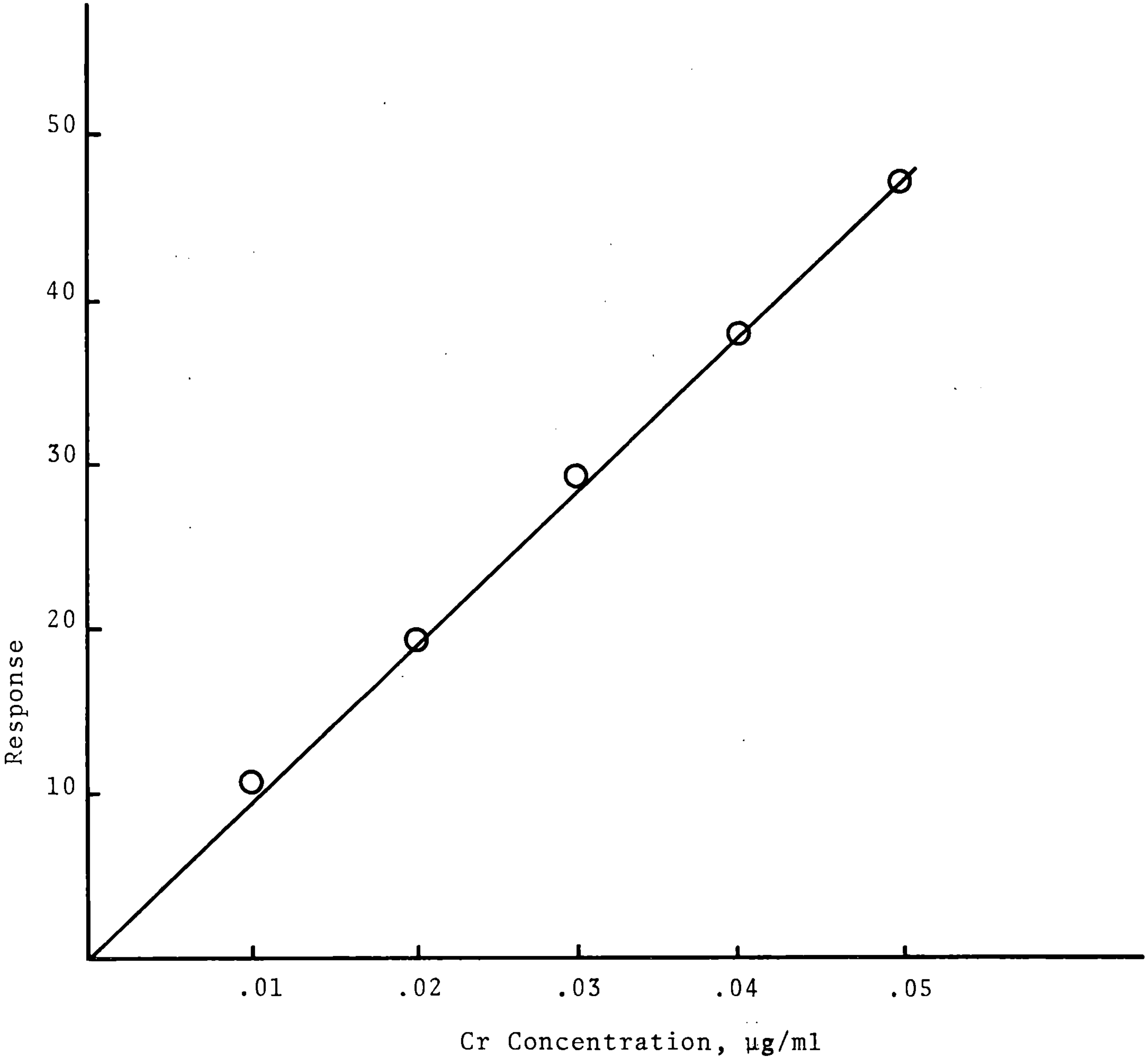

Figure 2. Response vs concentration of chromium for the furnace mode. 20 μl samples.