

# Determination of Chromium in Airborne Particulates by Atomic Absorption Spectrophotometry

## 1. INTRODUCTION

Chromium is used principally in the manufacture of steel and other alloys or for chrome plating. Chromite ore,  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ , 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 (12.1). 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 be expected in ambient air. Hexavalent chromium, in the air, probably originates from the production of chromates and dichromates by the chemical industry. The highly colored 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  $0.15\mu\text{g}$  and a range of  $0.3\text{-}1.0\mu\text{g}$ . Atomic absorption methods have been widely used to determine chromium because of their sensitivity and speed.

In the method to be described, airborne particulates are collected by drawing the air through a filter. The filter, or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation of this sample is simple and rapid. The aqueous acidic sample is scrutinized by an atomic absorption spectrophotometer at the wavelength  $357.8\text{nm}$  and the chromium content is calculated by referring the absorbance found to the appropriate calibration curve. By the use of a graphite furnace, additional sensitivity may be achieved beyond that of the usual flame mode. The chromium values found are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable will be found under the section "Expression of Results" (9).

## 2. FIELD OF APPLICATION

The method is applicable to the measurement of the levels of suspended particulate chromium found in either ambient or industrial atmospheres.

Based upon the flame mode, washed glass filters and a nominal air sample volume of 2,000 cubic metres, chromium is measurable to 0.015 micrograms per cubic metre. If the sample is taken on analytical grade cellulose, the minimum quantity measurable is decreased to a point which is dependent upon the chromium content of the reagents used to dissolve the cellulose. Analytical grade cellulose contains less than 0.25 micrograms Cr per aliquot disc 36mm in diameter. As levels of chromium in urban air are low and since 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.

### 3. PRINCIPLE

A prepared test sample containing the inorganic constituents in aqueous acidic solution is atomized in a flame or heated graphite tube. The absorption of light of characteristic wavelength by the atoms of the element of interest is used to measure the concentration of that element.

### 4. 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  $\text{Cr}_2\text{O}_3$ , some difficulty may be encountered in solubilizing all the chromium. Using the test sample preparation method outlined in 7.3, only a total of from 5-10 $\mu\text{g}$  of  $\text{Cr}_2\text{O}_3$  will be solubilized per digestion. This represents a maximum of 0.1 $\mu\text{g}$  per cubic metre, a figure approximately six times the "normal" value expected for the chromium content of urban air.

### 5. REAGENTS

#### 5.1 *Air, compressed*

In pressure cylinders or online.

#### 5.2 *Acetylene, compressed*

In pressure cylinders.

#### 5.3 *Glass filters*

Commercially available material is exhaustively washed prior to use; in size 203 by 254mm.

#### 5.4 *Cellulose filters*

Ashless, acid washed, analytical grade, in size 203 by 254.

#### 5.5 *Water*

Distilled at least twice from glass or quartz.

#### 5.6 *Hydrofluoric acid*

49%. Reagent grade, in polyethylene containers.

#### 5.7 *Nitric acid*

71%. Reagent grade.

#### 5.8 *Standard solutions of chromium*

Dissolve the amount of chromium salt equivalent to 1 gram of chromium in water and dilute to 1 litre with water. 1ml of this stock solution contains 1,000 micrograms of chromium, Cr. Both trivalent and hexavalent chromium have been found to give equal response using the atomic absorption conditions described in 10.8 and 10.9.

### 6. APPARATUS

#### 6.1 *Spectrophotometer, atomic absorption*

With meter, recorder or digital readout and monochromator with wavelength dial reading to 0.1 nanometre.

#### 6.2 *Pipettes, glass*

Millilitre capacities, "to deliver".

#### 6.3 *Volumetric flasks*

Borosilicate with ground glass stopper, 25ml capacity.

#### 6.4 *Bottles, polyethylene*

Screw cap, "leak free" for storage of test samples, 30ml capacity.

#### 6.5 *Beakers, teflon*

Griffin form, 100ml capacity.

#### 6.6 *Beakers, borosilicate*

Graduated, Griffin form, with teflon coated rim, 150ml capacity.

#### 6.7 *Hot plate*

Electric, with temperature control, thermostat, and ceramic heating surface.

#### 6.8 *Büchner funnel*

Polypropylene, custom made, with sintered false bottom and vacuum connection, 216 by 267 by 85mm.

#### 6.9 *Graphite furnace*

One suitable instrument is available commercially to the Massmann design.

#### 6.10 *Strip chart recorder*

To display and record the response from the furnace.

#### 6.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

### 7. SAMPLING AND SAMPLES

#### 7.1 *Air Sampling*

Draw air through the filter at a flow rate between 1.13 and 1.60 cubic metres per minute if high volume sampling is used. An appropriate time period is 24 hours when glass fibre filters are used. The resistance to flow offered by the cellulose filters is much greater than for glass and 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.

#### 7.2 *Preparation of the 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.



### 7.3 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 which 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 filter matrix by the dropwise addition of 1 ml of hydrofluoric acid (5.6). Gently warm the contents of the beaker, at low heat, until the hydrofluoric acid is almost completely evaporated. At this point, add 1 to 2 ml of nitric acid (5.7) and continue to heat gently until a few drops of nitric acid are left. Add about 10 ml of water, bring nearly to the boil and filter through a Whatman 41 filter into a glass beaker (6.6). Transfer to a 25 ml volumetric flask (6.3). Rinse down the teflon beaker with another 10 ml quantity 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 after adjustment to volume. Transfer contents of volumetric flask to polyethylene storage bottle (6.4). The test sample is now ready for analysis. The above method applies to the digestion of glass fibre filters. Cellulose filters can be digested or extracted using nitric acid.

## 8. PROCEDURE

### 8.1 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.

### 8.2 Test Portions

#### 8.2.1 Test portions, 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 flame, between the introduction of each test portion, to prevent cross contamination.

#### 8.2.2 Test portions, furnace

Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (6.11).

### 8.3 Calibration Curves

#### 8.3.1 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of chromium by dilution of standard solution (5.8) with filter blank solution prepared as in (7.3) from unexposed filter to cover the range of 1.0 to 5.0 micrograms of chromium per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for chromium. Set the wavelength of the monochromator at 357.8nm. Using nitrous oxide-acetylene flame, aspirate an unmeasured portion of each dilute standard chromium solution for 10 seconds (8.2.1). 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 ml. Such a representative calibration curve is given in Figure 1, with the corresponding curve for chromium standards in water (Page 111).

#### 8.3.2 Calibration curves, furnace

By means of 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 to 1.0 nanogram chromium in steps of 0.2 nanogram; 0.01 to 0.05 micrograms per ml for a 20 microlitre volume. Prepare a calibration curve of response, in arbitrary units, against concentration of chromium in micrograms per ml. Such 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.

### 8.4 Determination

#### 8.4.1 Determination, flame

Set the wavelength of the monochromator at 357.8nm. Observing conditions of 8.2.1 and 8.3.1, aspirate an unmeasured test portion of each unknown test sample into the flame. Record the responses 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 which can be accommodated to the wavelength 357.8nm and the corresponding calibration curve.

#### 8.4.2 Determination, furnace

Measure into the furnace, by automatic pipette, a similar test portion of each unknown test sample. Follow the drying and heating programmes 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 (Page 111).

## 8.5 *Blank Tests*

### 8.5.1 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.

### 8.5.2 Filter blanks

In parallel with the preparation of calibration curves and test samples, prepare areal test portions from unexposed filter media as described in 7.3. Measure chromium and express blanks in micrograms of chromium per ml.

## 9. EXPRESSION OF RESULTS

### 9.1 *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. It should be noted, however, that the filter blank values for chromium within a given batch of filters are extremely uniform. If, where possible, filters from a known batch are used, 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.

### 9.2 *Instrumental precision*

This is defined as the standard deviation of a number of replicate determinations and is expressed in micrograms per ml. Typical precisions for ten repeat determinations on standard samples are  $2.00 \pm 0.01$  micrograms per ml for the flame mode, against  $0.05 \pm 0.0008$  micrograms per ml for the flameless mode using a  $20\mu\text{l}$  sample.

### 9.3 *Minimum measurable*

#### 9.3.1 Concentration in test sample

This is taken as twice the blank deviation, or instrument precision, whichever is larger. This is 0.06 micrograms per ml in the case of chromium, using the flame mode and glass fibre filters. For the flameless mode the blank deviation is the determining factor and this may vary for different filter batches. Minimum measurable may be as high as 0.04 micrograms per ml for glass fibre filters.



### 9.3.2 Concentration in air

This is based upon a sample volume of 2,000 cubic metres and two aliquot discs 36mm in diameter. The minimum measurable concentration is 0.015 micrograms per cubic metre for the flame mode and 0.010 micrograms per cubic metre for the flameless mode. These values are lower for cellulose filters as explained in Section 2.

### 9.4 Calculations

The chromium content of the test solution is expressed in micrograms of chromium per ml,  $X_1$ . 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  $\mu\text{g}$  per ml. Multiplication by the dilution factor, usually 25, gives the total quantity of chromium in the test sample, in micrograms.

For high volume filters of nominal size, 203 by 254mm:

Total exposed filter surface	=	$4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2 x 36mm discs	=	$2,036 \text{ mm}^2$
Surface multiplication factor	=	20.43
Dilution factor	=	25
Volume of air sampled, cubic metres	=	V
Response, unknown test portion	=	$X_1$
Response, total blank	=	$X_2$
Chromium concentration, in $\mu\text{g}/\text{m}^3$	=	T

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

## 10. NOTES ON PROCEDURE

10.1 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 almost all between 0.6 and 4.5 microns according to Lee (12.2).

10.2 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. There is increasing agreement that if standard conditions of temperature and pressure are to be used to correct the final volume, these conditions should be  $25^\circ\text{C}$  and 760mm Hg.

10.3 Although the method described is nominally based upon high volume samples taken for a 24-hour 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 1,000 cubic metres or less. The



lower particulate loading, so obtained, minimizes particulate fall-off. This 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.

10.4 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 is not correct, although the error introduced by this oversimplification is not ordinarily serious.

10.5 For the preparation of areal test portions, the use of a sharp circular metal die is to be 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 very easily reproduced with accuracy. In the method described, a punch made of brass is used. No chromium contamination has been found to result from its use.

10.6 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 (12.3, 12.4, 12.5) and cadmium (one exception was noted in 12.5) measured on high volume filters. This uniform distribution cannot be assumed in certain "membrane" type filters due to inherently high pressure drop and faulty geometry of commercially available filter holders. In the case of such filters, areal aliquotting cannot be used (12.6).

10.7 It is helpful, when it is possible, to have several calibration curves, relating to different sensitivities. 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 method for lead in this series where two calibration curves are given for the flame and one for the furnace (12.7).

#### 10.8 *Operating conditions, flame*

The optimum operating conditions are as given:

Wavelength	=	357.8nm
Spectral band width	=	1.4nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Nitrous oxide
Fuel	=	Acetylene
Flame	=	Reducing, rich red
Sensitivity	=	0.026 $\mu$ g/ml for 1% absorption

Change acetylene cylinder before pressure drops to 50 psig.

### 10.9 Graphite furnace

The calibration curve for the flame mode obeys Beer's Law up to 8.0 micrograms of chromium per 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:

Wavelength	=	357.8nm
Sample size	=	20 microlitres
Purging gas	=	Argon or nitrogen
Thermal composition	=	drying (15sec, 100°C) charring (15sec, 230°C) atomizing (15sec, 2,400°C)

The use of a deuterium lamp background compensator is recommended.

10.10 Most chromium salts, likely to be found in ambient air, will be soluble if the digestion procedure in 8.3 is followed. Complete recovery of added trivalent ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ) and hexavalent ( $\text{K}_2\text{CrO}_4$ ) chromium has been demonstrated in our laboratory. Chromium compounds which may be difficult to dissolve are chromium sesquioxide ( $\text{Cr}_2\text{O}_3$ ), elemental chromium (Cr), chromium arsenide (CrAs), chromium nitride (CrN) and chromium silicide ( $\text{Cr}_3\text{Si}_2$ ). The solubility of  $\text{Cr}_2\text{O}_3$  has been discussed in Section 4. CrAs, CrN,  $\text{Cr}_3\text{Si}_2$  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,  $\text{CrF}_2$  and  $\text{CrF}_3$ , have melting points above 1,000° and loss of chromium during digestion of the glass fibre filter with hydrofluoric acid does not occur.

10.11 The following is an outline of the method for washing glass fibre filters prior to use.

At present, the expedient used is to attempt to leach out the impurities by means of 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 Gelman A filters. To improve the access of the hot distilled water, spacers are placed in the pile at intervals of every 10 filters. The pile of filters is covered with boiling water, allowed to steep for 30 minutes and the water is withdrawn by suction. This process is repeated. The washed glass filters are allowed to air dry in a dust-free location.

10.12 With the use of flameless atomic absorption, equipped with a background corrector, it was shown that chromium is present in the acid digest of glass fibre filters having no previous contact with metal. Two 36mm discs were shown to contain from 1.64 to 3.35 micrograms of chromium of which 0.3 micrograms were 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.

## 11. SCHEMATIC REPRESENTATION OF PROCEDURE

- 11.1 Draw laboratory air sample.
- 11.2 Cut area test portion from exposed surface.
- 11.3 Digest areal test portion.
- 11.4 Adjust digest to volume to give test sample.
- 11.5 Aspirate test portion into flame.
- 11.6 Or, add test portion to furnace, measured by microlitre pipette.

## 12. REFERENCES

- 12.1 Chromium, alloys, compounds. Encyclopedia of Occupational Health and Safety. International Labour Office, Geneva, Switzerland.
- 12.2 Lee, R. E., Patterson, R. K. and Wagman, J. *J. Envir. Sci. and Tech.* **2**, 288, 1968.
- 12.3 Dubois, L., Teichman, T., Airth, J. M. and Monkman, J. L. The Metal Content of Urban Air. *Journal A.P.C.A.* **16**, **2**, 77, 1966.
- 12.4 Zdrojewski, A., Quickert, N., Dubois, L. and Monkman, J. L. The Accurate Measurement of Lead in Airborne Particulates. *Int. J. Envir. Anal. Chem.* **2**, 63, 1972.
- 12.5 Zdrojewski, A., Quickert, N., and Dubois, L. The Accurate Measurement of Cadmium in Airborne Particulates. *Int. J. Envir. Anal. Chem.* September 1972.
- 12.6 Pierce, J. O. and Meyer, J. H. Sampling and Analysis Considerations in Evaluating Levels of Atmospheric Lead. *Atmos. Environment* **5**, 811, 1971.
- 12.7 Monkman, J. L. Determination of Airborne Particulate Lead by Atomic Absorption Spectroscopy, see p.1.



