

Determination of Airborne Particulate Nickel by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Although nickel is widely distributed over the face of the earth, the igneous rocks, in which it occurs, are not readily susceptible to weathering. The minerals are usually sulfides, oxides and silicates. Nickel is used primarily in the metallurgical industry, particularly in ferro alloys. The amounts of nickel emitted to the air from iron and steel plants are rather low in view of the large quantities of nickel handled.

Nickel in airborne particulates may be measured by conventional polarography, but sample preparation must be meticulous, otherwise the nickel wave may be masked. Methods using anodic stripping voltammetry show promise but more practical experience must be obtained. The sensitivity of methods using emission or X-ray spectrography is low and the accuracy is affected by matrix error. Nickel may be measured on cellulose filter samples to a limit of identification of 0.08 microgram using the Weisz ring oven (12.1).

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 of 232.0nm and the nickel is calculated by referring the measured absorbance to the appropriate calibration curve. The nickel 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 nickel found in either ambient or industrial atmospheres. Based upon the flame mode, washed glass filters and a nominal air volume of 2,000 cubic metres, one may determine down to 0.0050 micrograms of nickel per cubic metre of air. For the same conditions, but using cellulose filters, nickel may be measured down to $0.0025\mu\text{g}/\text{m}^3$. The greater sensitivity of the flameless mode allows concentrations of $0.00025\mu\text{g}/\text{m}^3$ to be determined.

3. PRINCIPLE

A prepared test sample, containing the inorganic constituents in aqueous acidic solution, is reduced in the flame or graphite furnace to the atomic state. The amount of the element of interest is measured by making use of its property of absorbing light of its characteristic frequency when in the atomic state.

4. 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.

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 in size 203 by 254mm is exhaustively washed prior to use.

5.4 *Cellulose filters*

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

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 solution of nickel

Dissolve 1g of nickel metal in about 3ml concentrated HNO_3 and make up to 1 litre. One ml of this stock solution contains 1,000 micrograms of Nickel, Ni.

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, 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 in free depth.

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*

7.2 *Preparation of the laboratory sample*

Cellulose filters (5.4) may be used without further treatment. Glass fibre filters (5.3) are purified 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 cubic metres per minute, for an appropriate period, such as 24 hours. The resistance to flow offered by the cellulose filters is much greater than 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.

7.3 *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 dissolution of the filter matrix by the dropwise addition of 1ml 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 2ml of nitric acid (5.7) and continue to heat gently until a few drops of nitric acid are left. Add about 10ml of water, bring nearly to the boil and filter through a Whatman 41 filter into a glass beaker (6.6). Transfer to a 25ml volumetric flask (6.3). Rinse down the teflon beaker with another 10ml quantity of water, warm and filter into the same beaker. Transfer to the 25ml 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 procedure 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 the flame, between the introduction of each test portion, to prevent cross contamination.

8.2.2 Test portions, furnace

Measure and insert into 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 nickel by dilution of standard solution (5.8) to cover the range of 1.0 to 5.0 micrograms of nickel per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for nickel. Set the wavelength of the microchromator at 232.0nm. Using an air-acetylene flame, aspirate an unmeasured portion of each dilute standard nickel solution for 10 seconds (8.2.1). 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 nickel in micrograms per ml. Such a representative calibration curve is given in Figure 1 (Page 54).

8.3.2 Calibration curves, furnace

By means of an automatic pipette with polyethylene tip, place identical microlitre volumes of the dilute standard nickel 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 to

12 nanograms nickel in steps of 2 nanograms (0.1 to 0.6 micrograms per ml for a 20 microlitre volume). Prepare a calibration curve of response, in arbitrary units, against concentration of nickel in micrograms per ml. Such a representative calibration curve is given in Figure 2 (Page 54).

8.4 *Determination*

8.4.1 Determination, flame

Set the wavelength of the monochromator at 232.0nm. 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 response for each unknown. Aspirate distilled water into the flame between each unknown test portion to prevent cross contamination. Measure the nickel in all the unknown test samples which can be accommodated to the wavelength of 232.0nm 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 nickel present in the test sample by referring to the appropriate calibration curve, such as, for example, Figure 2 (Page 54).

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 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 7.3. Measure nickel and express blanks in micrograms of nickel 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 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 large amounts in the filter such as Na, Ba, Si, Ca, Zn, K and Al. A zero blank has been found for glass fibre filters using the furnace mode.

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 replicate determinations on standard samples are: $3.00 \pm 0.01 \mu\text{g/ml}$ for the flame mode, $0.40 \pm 0.0072 \mu\text{g/ml}$ for the flameless mode, on 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 $0.02 \mu\text{g}$ per ml in the case of nickel for the flame mode, and $0.002 \mu\text{g}$ per ml for the flameless mode.

9.3.2 Concentration in air

This is based on a sample volume of 2,000 cubic metres and two aliquot discs 36mm in diameter. For washed glass filters and the flame mode, this minimum measurable concentration is 0.0050 micrograms of nickel per cubic metre; for cellulose filters the corresponding value is $0.0025 \mu\text{g/m}^3$. The added sensitivity of the graphite furnace lowers this value to 0.0005 micrograms of nickel per cubic metre.

9.4 Calculations

The nickel content of the test portion is expressed in micrograms per ml, X_1 . The blank X_2 , in the same units, is subtracted from X_1 to get the corrected concentration of nickel in the test sample. Multiplication by the dilution factor, usually 25, gives the total quantity of nickel 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
Nickel concentration, in g/m = T

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

10. NOTES ON PROCEDURE

10.1 *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 nickel is almost between 1 and 3 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°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.

10.4 It is customary to assume that the decrease in air flow rate during sampling is linear and for usual purpose 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 of stainless steel is used. No nickel contamination has been found to result from its use so far. As cellulose is more difficult to cut than glass fibre the die should be exceedingly sharp.

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 and cadmium measured on high volume filters (12.3, 12.4, 12.5). 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	=	232.0nm
Spectral band width	=	0.2nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Air
Fuel	=	Acetylene
Flame	=	Oxidizing, lean, blue
Sensitivity	=	0.15 μ g/ml for 1% absorption

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

10.9 *Graphite furnace*

Use of the graphite furnace results in increased sensitivity, as shown by a comparison of Figures 1 and 2. Great care must be taken with the alignment of the furnace so that no response is obtained with a distilled water blank.

Furnace operating conditions:

Wavelength	=	232.0nm
Sample size	=	20 microlitres
Purging gas	=	Argon or nitrogen
Thermal decomposition	=	drying (20sec, 100°C) charring (20sec, 1,100°C) atomizing (20sec, 2,400°C)

The use of a deuterium lamp background compensator is recommended.

11. SCHEMATIC REPRESENTATION OF PROCEDURE

11.1 Draw laboratory air sample.

11.2 Cut areal 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 West, P. W. Symposium on Air Quality, American Chemical Society, Los Angeles, April 1, 1971.
- 12.2 Lee, R. E., Patterson, R. K. and Wagman. *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. *J. Int. 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.

