

MDHS

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory



42/2

Nickel and inorganic compounds of nickel in air (except nickel carbonyl)

Laboratory method using flame atomic absorption spectrometry or electrothermal atomic absorption spectrometry

March 1996

INTRODUCTION

Note 1: This method updates and replaces MDHS 42.¹ The principal changes which have been made are (i) to describe additional dissolution techniques that are effective for nickel-containing dusts that are difficult to take into solution, (ii) to recommend the use of filters that are soluble using the dissolution techniques described, and (iii) to describe the use of electrothermal atomic absorption spectrometry for the analysis of sample solutions with a low nickel concentration.

Occurrence, properties and uses

1 Occurrence, properties and uses of nickel and its inorganic compounds are fully covered in HSE Guidance Note EH 60.²

Effects on health

2 The health effects of nickel and its inorganic compounds are summarised in HSE Guidance Note EH 60² and are fully covered in HSE Toxicity Review TR 19.³

Health and safety precautions

3 HSE leaflet MS(A)14⁴ summarises the risks involved in working with nickel and what can be done to control them. Prevention and control of exposure, emergency procedures and health surveillance are described more fully in HSE Guidance Note EH 60.²

Exposure limits

4 Inorganic nickel compounds can be conveniently classified into two distinct groups according to their solubility in water, and use was made of this when setting occupational exposure limits for nickel and its inorganic compounds. The following table classifies some of the

more commercially important nickel compounds on the basis of their solubility:

Water-soluble nickel compounds

	Solubility in water (18-20°C), ⁵ in grams litre ⁻¹
nickel chloride NiCl ₂	642
nickel nitrate Ni(NO ₃) ₂	485
nickel sulphate NiSO ₄	275
nickel sulphamate Ni(SO ₃ NH ₂) ₂	No data available
nickel cyanide complex	No data available

Water-insoluble nickel compounds

nickel carbonate NiCO ₃	0.093 ⁶
nickel hydroxide Ni(OH) ₂	0.013
nickel monoxide NiO	0.001
nickel sulphide NiS	0.004
nickel subsulphide Ni ₃ S ₂	No data available

5 Schedule 1 of the Control of Substances Hazardous to Health (COSHH) Regulations⁷ specifies three maximum exposure limits (MELs) for nickel and its inorganic compounds. These long-term exposure limits, 8-hour time-weighted average reference period, are also published in Table 2 of HSE Guidance Note EH 40,⁸ and are reproduced below. The criteria on which the limits were based are documented in the 1993 edition of HSE Guidance Note EH 64.⁹

Nickel	0.5 mg m ⁻³
Nickel, inorganic compounds (as Ni)	
Soluble compounds	0.1 mg m ⁻³
Insoluble compounds	0.5 mg m ⁻³

A soluble nickel compound is defined (for this purpose) as any single nickel compound or complex which has a solubility greater than 10% by weight in water at 20°C.

Analytical methods

6 This is not a 'reference' method in the strict analytical sense of the word. There are frequently several alternative methods available for the determination of a particular analyte. With the exception of a few cases, where an exposure limit is linked to a specific method (eg rubber fume or asbestos), the use of methods not included in the MDHS series is acceptable provided that they have been shown to have the accuracy and reliability appropriate to the application.

7 This method has been validated¹⁰ to demonstrate that it complies with the *General requirements for the performance of procedures for the measurement of chemical agents in workplace atmospheres* described by the Comité Européen de Normalization (CEN) in European Standard EN 482¹¹ (see paragraphs A1.7, A2.6, A3.6, A4.6 and A5.6). If an alternative method is used, it is necessary to demonstrate that it also meets these performance requirements.

Requirements of the COSHH Regulations

8 *The Control of Substances Hazardous to Health (COSHH) Regulations*⁷ require that employers make an assessment of the health risk created by work involving substances hazardous to health, and to prevent or control exposure to such substances. The COSHH Regulations also include a requirement that persons who may be exposed to substances hazardous to health receive suitable and sufficient information, instruction and training. Employers must ensure that their responsibilities under the COSHH Regulations are fulfilled before allowing employees to undertake any procedure described in this method. Guidance is given in the Approved Codes of Practice for the Control of Substances Hazardous to Health, the *General COSHH ACOP*, and the Control of Carcinogenic Substances, the *Carcinogens ACOP*, which are included in a single publication with the COSHH Regulations.¹²

SCOPE

Applicability

9 This MDHS describes procedures for determination of the concentration of nickel and inorganic compounds of nickel in workplace air using either flame atomic absorption spectrometry or electrothermal atomic absorption spectrometry. It is applicable to the determination of water-soluble nickel compounds, insoluble nickel compounds and the majority of nickel-containing materials in industrial use or occurring in workplace air. The method is suitable for sampling times in the range 15 minutes to 8 hours.

Note 2: *HSE Guidance Note EH 42¹³ advises employers about how they should conduct investigations into the nature, extent and control of exposure to substances hazardous to health which are present in workplace air. The objective of air monitoring is usually to determine worker exposure, and therefore the procedures described*

in this method are for personal sampling in the breathing zone. The method may be used for background or fixed location sampling, but it should be recognised that, due to aerodynamic effects, samplers designed for personal sampling do not necessarily exhibit the same collection characteristics when used for other purposes.

METHOD PERFORMANCE

Effectiveness of sample dissolution procedures

10 A number of sample dissolution procedures have been described in this method (see paragraphs 61 to 64). Their effectiveness has been tested¹⁰ on a range of nickel-containing materials in industrial use or occurring in workplace air, and this is reported in the relevant appendix.

Detection limits

11 The qualitative and quantitative detection limits for nickel, defined as three times and ten times the standard deviation of a blank determination, have been determined¹⁰ separately for each of the sample dissolution procedures described in this method (see Appendices A1 to A5). The mean qualitative and quantitative detection limits were 0.016 µg ml⁻¹ and 0.054 µg ml⁻¹ respectively for flame atomic absorption spectrometry; and 0.9 ng ml⁻¹ and 3.0 ng ml⁻¹ for electrothermal atomic absorption spectrometry. For an air sample volume of 30 litres and a sample solution volume of 10 ml this corresponds to nickel in air concentrations of 6 µg m⁻³ and 18 µg m⁻³ for flame atomic absorption spectrometry; and 0.3 µg m⁻³ and 1.0 µg m⁻³ for electrothermal atomic absorption spectrometry.

Overall uncertainty

12 The bias of the analytical method and the component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), have been determined¹⁰ separately for each of the sample dissolution procedures described in this method (see Appendices A1 to A5).

13 The overall uncertainty of the method, as defined by CEN,¹¹ was estimated¹⁰ separately for each of the sample dissolution procedures described in this method (see Appendices A1 to A5). In all instances it was within the specification prescribed by CEN¹¹ for measurements for comparison with limit values, ie <50% for measurements in the range 0.1 to 0.5 times the limit value and <30% for measurements in the range 0.5 to 2.0 times the limit value.

Interferences

14 The analysis is based on atomic absorption spectrometry using an air-acetylene flame at a wavelength of 232.0 nm, where only minimal interferences have been found. Some transition metals have been reported¹⁴ to interfere with the determination of nickel. The two worst cases of iron and chromium were both investigated¹⁰ and found to be insignificant. No interferences specific to the determination of nickel are documented for electrothermal atomic absorption spectrometry.

PRINCIPLE

15 A measured volume of air is drawn through a filter mounted in an inhalable dust sampler. The sample is then taken into solution according to one of the five methods described in Appendices A1 to A5. The resultant solution is analysed for nickel by aspirating into the oxidising air-acetylene flame of an atomic absorption spectrometer. Absorbance measurements are made at 232.0 nm with background correction. For accurate determination when the concentration of nickel in the solution is low, the analysis may be repeated using electrothermal atomic absorption spectrometry. Aliquots of the sample solution are injected onto a solid, pyrolytic graphite platform mounted in a pyrolytically-coated graphite tube, and after drying and ashing stages the sample is atomised electrothermally. Absorbance measurements are made at 232.0 nm with background correction.

REAGENTS

16 During the analysis, use only reagents of recognised analytical grade. Use only distilled or de-ionised water, or water of equal purity (paragraph 17). Do not pipette by mouth.

Water

17 Water complying with the requirements of BS 3978¹⁵ grade 2 water (electrical conductivity less than 0.1 mS m⁻¹ and resistivity greater than 0.01 MΩ.m at 25°C).

Ammonium citrate leach solution, 1.7% (m/v) (NH₄)₂HC₆H₅O₇ and 0.5% (m/v) C₆H₈O₇.H₂O

18 Weigh 17 g of di-ammonium hydrogen citrate, (NH₄)₂HC₆H₅O₇, and 5 g of citric acid monohydrate, C₆H₈O₇.H₂O, into a 500 ml beaker. Add 250 ml water (paragraph 17) and swirl to dissolve. Quantitatively transfer the solution into a 1000 ml volumetric flask, dilute to the mark with water, stopper and mix thoroughly. Check, and if necessary, adjust the pH of the solution to 4.4 with ammonia or citric acid.

Note 3: This leach solution is required only for the procedure described in Appendix A1.

Nitric acid (HNO₃), concentrated, ρ about 1.42 g ml⁻¹, 69% (m/m) to 71% (m/m)

19 The nickel concentration of the acid shall be less than 0.005 µg ml⁻¹.

WARNING - Concentrated nitric acid is corrosive and oxidising, and nitric acid fumes are irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Personal protection (eg gloves, face shield or safety spectacles etc) should be used when working with concentrated or diluted nitric acid, and sample dissolution with nitric acid should be carried out in a fume cupboard.

Nitric acid, diluted 1 + 1

20 Carefully add 500 ml of concentrated nitric acid (paragraph 19) to 450 ml of water (paragraph 17) in a 2 litre beaker. Swirl to mix, allow to cool and quantitatively transfer to a 1 litre volumetric flask. Dilute to the mark with water, stopper and mix thoroughly.

Note 4: 1 + 1 nitric acid is required only for the procedure described in Appendix A2 and for preparation of the stock standard nickel solution in paragraph 26.

Nitric acid, diluted 1 + 3

21 Carefully add 250 ml of concentrated nitric acid (paragraph 19) to 600 ml of water (paragraph 17) in a 2 litre beaker. Swirl to mix, allow to cool and quantitatively transfer to a 1 litre volumetric flask. Dilute to the mark with water, stopper and mix thoroughly.

Note 5: 1 + 3 nitric acid is required only for the procedure described in Appendix A5.

Nitric acid, diluted 1 + 9

22 Add approximately 800 ml of water (paragraph 17) to a 1 litre volumetric flask. Carefully add 100 ml of concentrated nitric acid (paragraph 19) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

Perchloric acid (HClO₄), ρ about 1.67 g ml⁻¹, approximately 70% (m/m)

23 The nickel concentration of the acid shall be less than 0.002 µg ml⁻¹.

Note 6: Perchloric acid is required only for the procedure described in Appendix A3.

WARNING - Perchloric acid is corrosive and oxidising, and its fumes are irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Personal protection (eg gloves, face shield or safety spectacles etc) should be used when working with concentrated or diluted perchloric acid, and sample dissolution with perchloric acid should be carried out in a fume cupboard with a scrubber unit specially designed for use with perchloric acid.

Potassium hydrogen sulphate (KHSO₄)

24 The nickel content of the salt shall be less than 0.01 µg g⁻¹.

Note 7: Potassium hydrogen sulphate is required only for the procedure described in Appendix A5.

Stock standard nickel solution, 1000 µg ml⁻¹ of nickel

25 Use a commercially available standard solution at a concentration of 1000 µg ml⁻¹ of nickel. Observe the manufacturer's expiry date or recommended shelf life.

Alternatively prepare a stock nickel standard solution by the following procedure:

26 Accurately weigh 1.000 g of nickel metal, 99.9% Ni (m/m), into a 100 ml beaker, add 20 ml of 1 + 1 nitric acid (paragraph 20), cover with a watch glass and heat on a hotplate (paragraph 40) in a fume cupboard until the solid is completely dissolved. Remove the beaker from the hotplate, allow to cool, quantitatively transfer the solution into a 1 litre volumetric flask, dilute to the mark with water (paragraph 17), stopper and mix thoroughly.

Note 8: Nickel standard solution prepared according to the instructions in paragraph 26 may be stored in a polypropylene bottle (paragraph 35) for a period of one year without deterioration.

WARNING - Nickel and nickel compounds have been assigned various risk phrases in the Approved Supply List¹⁶ for the Chemicals (Hazard Information and Packaging for Supply) Regulations 1994¹⁷ (the 'CHIP 2' Regulations). Care should be taken when working with nickel metal and solutions containing nickel.

Working standard nickel solution, 1.00 µg ml⁻¹ of nickel

27 Accurately pipette 100 µl of stock nickel standard solution (paragraph 25 or 26) into a 100 ml volumetric flask. Add 1 ml of concentrated nitric acid (paragraph 19), dilute to the mark with water (paragraph 17), stopper and mix thoroughly. Prepare this solution fresh daily.

Laboratory detergent solution

28 A laboratory grade detergent suitable for cleaning of samplers and labware, diluted with water (paragraph 17) according to the manufacturer's instructions.

SAMPLING EQUIPMENT

Samplers for collection of the inhalable fraction of the airborne particles

29 Samplers, with protective covers, for collection of the inhalable fraction of the airborne particles, as defined in European Standard EN 481.¹⁸ Inhalable dust samplers suitable for personal sampling are described in MDHS 14.¹⁹

Note 9: In general, the collection characteristics of inhalable samplers can be such that particulate material collected on the filter is the inhalable fraction of the airborne particles, and any deposited on the internal surfaces of the sampler is not of interest. However, some samplers are designed such that airborne particles which pass through the entry orifice(s) constitute the inhalable fraction, in which case any particulate material deposited on the internal surfaces of the sampler is part of the sample. Certain samplers of this type incorporate an internal filter cassette which may be removed from the sampler to enable this material to be easily recovered. Refer to the manufacturer's instructions to ascertain what constitutes the inhalable fraction of the sample.

Note 10: Samplers manufactured in non-conducting material have electrostatic properties which may influence representative sampling. Electrostatic influences should be reduced, where possible, by using samplers manufactured from conducting material.

Filters

30 Filters, of a diameter suitable for use in the samplers (paragraph 29), with a retentivity of not less than 99.5% for particles with a 0.3 µm diffusion diameter. The use of filters that are soluble using the sample preparation procedures described in Appendices A2 to A5 is recommended, and mixed cellulose ester membrane filters of 0.8 µm mean pore diameter are considered to be most suitable.

The nickel content shall be less than 0.001 µg per filter.

Note 11: Glass fibre or other filters which do not dissolve using the sample preparation procedure described may be used, but extra care needs to be taken to ensure quantitative transfer of sample solutions to volumetric flasks (see Appendices A1 to A5).

Sampling pumps

31 Sampling pumps, complying with the provisions of draft European Standard prEN 1232,²⁰ with an adjustable flow rate, incorporating a flowmeter or a flow fault indicator, capable of maintaining the appropriate flow rate (see paragraph 48) to within ±5% of the nominal value throughout the sampling period (see paragraph 49), and capable of being worn by persons without impeding normal work activity. The pumps shall give a pulsation-free flow (if necessary, a pulsation damper shall be incorporated between the sampler and the pump, as near to the pump as possible). Flow-stabilised pumps may be required to maintain the flow rate within the specified limits.

Flowmeter

32 Flowmeter, portable, capable of measuring the appropriate flow rate (see paragraph 48) to within ±5%, and calibrated against a primary standard.

Note 12: The flowmeter incorporated in the pump may be used provided that it has adequate sensitivity, that it has been calibrated against a primary standard with a loaded filter in line, and that it is read in a vertical orientation if it is of the supported float type. However, it is important to ensure that there are no leaks in the sampling train between the sampler and the flowmeter, since in this event a flowmeter in the pump or elsewhere in line will give an erroneous flow rate.

Note 13: A soap bubble flowmeter may be used as a primary standard, provided its accuracy is traceable to national standards (see Appendix B).

Ancillary equipment

33 Flexible plastic tubing, of a diameter suitable for making a leakproof connection from the sampler to the

sampling pump; belts or harnesses to which the sampling pump can conveniently be fixed, unless the pump is sufficiently small to fit in the worker's pocket; flat-tipped tweezers for loading and unloading the filters into samplers; and filter transport cassettes or similar, if required (see paragraph 57), to transport samples to the laboratory.

LABORATORY APPARATUS

Glassware, made of borosilicate glass

34 A selection of laboratory glassware, including: beakers; watch glasses; measuring cylinders; test tubes; and one-mark volumetric flasks, class A, complying with the requirements of BS 1792.²¹

Note 14: It is recommended that a set of glassware is reserved for the analysis of nickel by this method (see paragraph 68).

Polypropylene bottle

35 A polypropylene bottle, with leakproof screw cap, for storage of stock standard solution (paragraph 26), cleaned before use by soaking in 1 + 9 nitric acid (paragraph 22) for at least 24 hours and then rinsing thoroughly with water (paragraph 17). A bottle made of an alternative plastic may be used provided that it is suitable for the intended use.

Disposable gloves

36 Disposable gloves, impermeable, to avoid the possibility of contamination from the hands and to protect them from contact with toxic and corrosive substances. PVC gloves are suitable.

Piston operated volumetric apparatus

37 A set of adjustable micropipettes, complying with the requirements of BS 7653-1 to BS 7653-4,²²⁻²⁵ for the preparation of working standard nickel solution (paragraph 27) and calibration solutions (paragraphs A1.14, A1.15, A2.12, A2.13, A3.12, A4.14 and A5.16), and dilution of sample solutions (paragraphs 76, 86 and A5.15). A suitable set might include micropipettes covering the ranges 10 µl to 100 µl, 100 µl to 1000 µl and 1000 µl to 5000 µl. Dispensers for dispensing acid.

Filter paper

38 A hardened, ashless, cellulose (paper) filter of medium filtering speed and retentivity.

Suction filtration apparatus

39 Suction filtration apparatus, for filtration of the citrate leach solution used in the sample dissolution procedure for water-soluble nickel (see Appendix A1). Suitable apparatus comprises of a water-operated or electrically driven vacuum pump, connected to a conical flask fitted with a filter funnel/support assembly (see Figure 1).

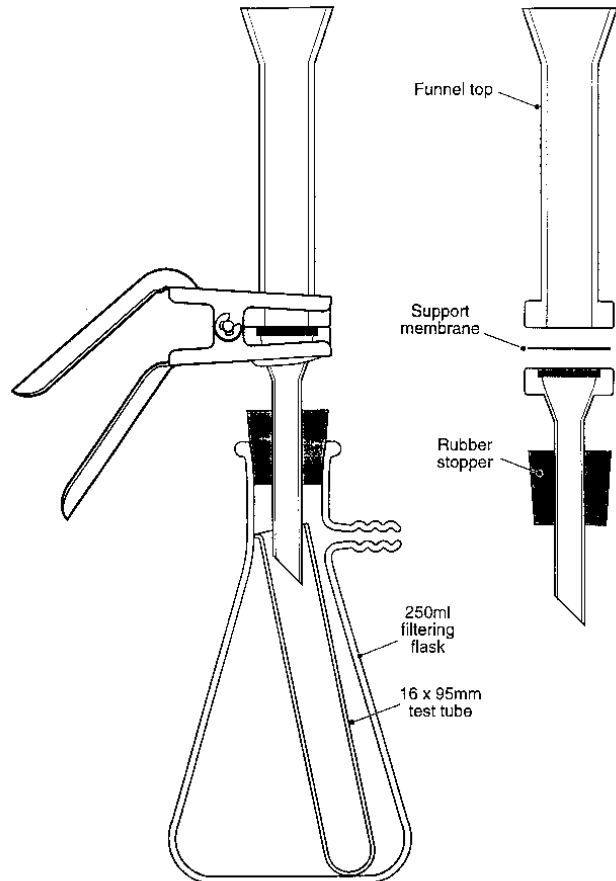


Figure 1 Suction filtration apparatus

Cellulose ester membrane filters, of a diameter suitable for use with the apparatus, are also required.

Note 15: Alternative suction filtration apparatus is available which permits simultaneous vacuum filtration of multiple samples.

Note 16: The filtration apparatus is only required for the procedure described in Appendix A1.

Hotplate

40 A thermostatically controlled hotplate, capable of maintaining the required surface temperature.

Microwave digestion system

41 A commercial, closed vessel microwave digestion system, designed for laboratory use, with power output regulation, equipped with a turntable of sample vessels able to withstand pressures in excess of 100 psi, and fitted with a pressure control system.

Note 17: The microwave digestion system and vessels are only required for the procedure described in Appendix A4.

Porcelain crucibles

42 Fused porcelain crucibles, low form, 25 ml capacity, with matching lids.

Meker burner

43 Natural gas burner, Meker pattern, Amal major.

Muffle furnace

44 Electric muffle furnace capable of maintaining a temperature of 650°C.

Note 18: *Porcelain crucibles, Meker burner and muffle furnace are only required for the procedure described in Appendix A5.*

Atomic absorption spectrometer

45 An atomic absorption spectrometer, fitted with an air-acetylene burner, supplied with compressed air and acetylene, and equipped with a nickel hollow cathode lamp. If electrothermal atomic absorption spectrometry is to be carried out, the atomic absorption spectrometer shall be capable of carrying out simultaneous background correction at 232.0 nm, either by using a continuum source such as a deuterium lamp to measure non-specific attenuation, or by using Zeeman or Smith-Hieftje background correction systems.

Electrothermal atomiser

46 An electrothermal atomiser, fitted with a solid, pyrolytic graphite platform mounted in a pyrolytically-coated graphite tube, supplied with argon as a purge gas, and equipped with an autosampler capable of injecting microlitre volumes onto the platform.

Note 19: *Some manufacturers of atomic absorption spectrometers use an alternative design of electrothermal atomiser to achieve a constant temperature environment during atomisation, and some use aerosol deposition as a means of sample introduction. The use of such accessories is acceptable, but the method performance may be different from that described in paragraphs 11 to 13, A1.4 to A1.7 and A2.3 to A2.6.*

Disposable autosampler cups

47 Disposable polystyrene autosampler cups for use in the autosampler used with the electrothermal atomiser. Soak in 1 + 9 nitric acid (paragraph 22) before use.

Note 20: *Disposable polystyrene autosampler cups are also useful for containing solutions to be pipetted in microlitre quantities.*

SAMPLING

Sampling procedure

48 Use the samplers (paragraph 29) at the design flow rate, so that they exhibit the required collection characteristics.

49 Select a suitable sampling time, such that the filter does not become overloaded with aerosol. (An 8-hour

time weighted average concentration may be derived from the results for two or more consecutive samples, as described in Guidance Note EH 42.¹³)

Preparation of sampling equipment

Perform the following in an area where nickel contamination is known to be low.

50 Clean the samplers (paragraph 29) before use. Disassemble the samplers, soak in laboratory detergent solution (paragraph 28), rinse thoroughly with water (paragraph 17), wipe with absorptive tissue and allow to dry thoroughly before reassembly. Alternatively, use a laboratory washing machine.

51 Load the filters (paragraph 30) into clean, dry samplers (see paragraph 50) using clean, flat-tipped tweezers (paragraph 33). Connect each loaded sampler to a sampling pump (paragraph 31) using plastic tubing (paragraph 33), ensuring that no leaks can occur. Switch on the pump, attach the calibrated flowmeter (paragraph 32) to the sampler so that it measures the flow through the sampler inlet orifice, and set the appropriate flow rate (see paragraph 48) with an accuracy of $\pm 5\%$. Remove the flowmeter and allow the pump to operate for an appropriate period to enable it to warm up and the flow rate to stabilise (follow the manufacturer's recommendations). Then discard the used filter and load a new one into the sampler for collection of the sample. Finally, attach the calibrated flowmeter again, readjust the flow rate to the appropriate value with an accuracy of $\pm 5\%$, switch off the pump and seal the sampler with its protective cover to prevent contamination with nickel during transport to the sampling position.

Collection of samples

52 Fix the sampler to the lapel of the worker, in the breathing zone and as close to the mouth and nose as practicable. Then, either place the sampling pump in a convenient pocket or attach it to the worker in a manner that causes minimum inconvenience, eg to a belt (paragraph 33) around the waist. When ready to begin sampling, remove the protective cover from the sampler and switch on the pump. Record the time at the start of the sampling period, and if the pump is equipped with an elapsed time indicator, set this to zero.

53 Since it is possible for a filter to become clogged, monitor the performance of the sampler frequently, a minimum of once per hour. Measure the flow rate with an accuracy of $\pm 5\%$ using the calibrated flowmeter (paragraph 32) and record the measured value. Terminate sampling and consider the sample to be invalid if the flow rate is not maintained to within $\pm 5\%$ of the nominal value throughout the sampling period.

Note 21: *Regular observation of the flow fault indicator is an acceptable means of ensuring that the flow rate of flow-stabilised sampling pumps is maintained satisfactorily, provided that the flow fault indicator indicates malfunction when the flow rate is outside $\pm 5\%$ of the nominal value.*

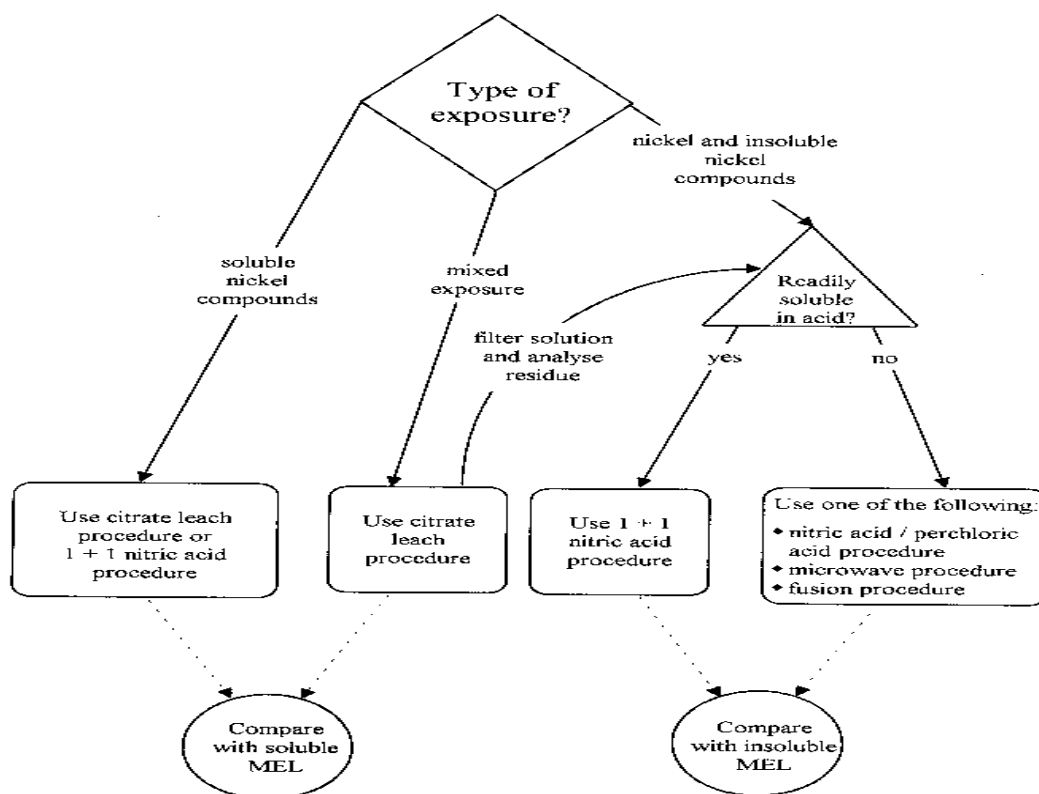


Figure 2 Schematic diagram for the selection of suitable sample dissolution procedure(s) according to the nature of the nickel-containing material present in the test atmosphere

54 At the end of the sampling period (see paragraph 49), measure the flow rate with an accuracy of $\pm 5\%$ using the calibrated flowmeter (paragraph 32), switch off the sampling pump, and record the flow rate and the time. Also observe the reading on the elapsed time indicator, if fitted, and consider the sample to be invalid if the reading on the elapsed time indicator and the timed interval between switching on and switching off the sampling pump do not agree to within $\pm 5\%$, since this may suggest that the sampling pump has not been operating throughout the sampling period. Reseal the sampler with its protective cover and disconnect it from the sampling pump.

55 Carefully record the sample identity and all relevant sampling data (see Appendix D). Calculate the mean flow rate by averaging the flow rate measurements taken throughout the sampling period and calculate the volume of air sampled, in litres, by multiplying the flow rate in litres per minute by the sampling time, in minutes.

56 With each batch of ten samples, submit for analysis two unused filters from the same lot of filters used for sample collection. Subject these blank filters to exactly the same handling procedure as the samples, but draw no air through them.

Transportation

Perform the following in an area where nickel contamination is known to be low.

57 For samplers which collect the inhalable fraction of airborne particles on the filter (see note 9), remove the filter from each sampler using clean flat-tipped tweezers

(paragraph 33), place in a labelled filter transport cassette (paragraph 33) and close with a lid.

58 For samplers which have an internal filter cassette (see note 9), remove the filter cassette from each sampler, fasten with the transport clip supplied by the manufacturer, and label appropriately.

59 For samplers designed such that airborne particles which pass through the entry orifice(s) constitute the inhalable fraction but which do not have an internal filter cassette (see note 9), and for samplers of the disposable cassette type, transport the samples to the laboratory in the samplers in which they were collected.

60 Transport the filter transport cassettes (see paragraph 57), sampler filter cassettes (see paragraph 58) or samplers (see paragraph 59) to the laboratory in a container which has been designed to prevent damage to samples in transit and which has been labelled to assure proper handling.

ANALYSIS

Wear disposable gloves (paragraph 36) during analysis to reduce the possibility of contamination and to protect the hands from corrosive and oxidising reagents.

Selection of sample dissolution procedure

61 Select a suitable sample dissolution procedure(s) according to the nature of the nickel-containing material present in the test atmosphere (see Figure 2).

Water-soluble nickel compounds

62 If it is known that no insoluble nickel compounds are in use in the workplace (see paragraph 4), and that none are produced in the processes carried out, use either the citrate leach procedure described in Appendix A1 or the 1 + 1 nitric acid dissolution procedure described in Appendix A2, and compare results with the MEL for soluble nickel compounds.

Note 22: *The procedure described in Appendix A2 is not specific for soluble nickel compounds. However, it may be used as an alternative to the procedure described in Appendix A1, in the circumstances described above, if this is more convenient.*

Nickel metal and water-insoluble nickel compounds

63 If it is known that no soluble nickel compounds are in use in the workplace (see paragraph 4), and that none are produced in the processes carried out, select one of the procedures described in Appendices A2 to A5, and compare results with the MEL for insoluble nickel compounds. Take into consideration the nature of the nickel-containing material present in the test atmosphere and the availability of laboratory apparatus. In many instances the nature of the matrix will be such that nickel is readily soluble in acid, in which case use the 1 + 1 nitric acid dissolution procedure described in Appendix A2. However, if nickel is in a more difficult matrix, eg refractory dusts or stainless steel welding fume, use one of the more vigorous dissolution procedures.

Mixed exposure to water-soluble and water-insoluble nickel compounds

64 If water-soluble and water-insoluble nickel compounds could be present in the test atmosphere, use the citrate leach procedure described in Appendix A1 to determine water-soluble nickel, and compare results with the MEL for soluble nickel compounds. Then select one of the procedures described in Appendices A2 to A5 (see paragraph 63), analyse the residue for water-insoluble nickel compounds, and compare results with the MEL for insoluble nickel compounds.

Cleaning of glassware

65 Before use, clean all glassware (paragraph 34) to remove any residual grease or chemicals. Firstly soak overnight in laboratory detergent solution (paragraph 28) and then rinse thoroughly with water (paragraph 17). Alternatively, use a laboratory washing machine.

66 After initial cleaning (see paragraph 65), clean all beakers used in the sample dissolution procedures (see paragraphs A2.8 to A2.11 and A3.8 to A3.11) with hot nitric acid. Fill to one third capacity with concentrated nitric acid (paragraph 19), cover with a watch glass, heat to approximately 150°C on the hotplate (paragraph 40) in a fume cupboard for 1 hour, allow to cool, and then rinse thoroughly with water (paragraph 17).

67 After initial cleaning (see paragraph 65), clean all glassware other than beakers used in the sample dissolution procedure by soaking in 1 + 9 nitric acid (paragraph 22) for at least 24 hours and then rinsing thoroughly with water (paragraph 17).

68 Glassware which has been previously subjected to the cleaning procedure described in paragraphs 65 to 67, and which has been reserved for determination of nickel by this method, can be adequately cleaned by rinsing thoroughly with 1 + 9 nitric acid (paragraph 22) and then with water (paragraph 17).

Preparation of sample and blank solutions

69 Refer to the relevant appendix and prepare the sample and blank solutions using the selected sample dissolution procedure (see paragraphs 61 to 64).

ANALYSIS BY FLAME ATOMIC ABSORPTION SPECTROMETRY

Preparation of calibration solutions

70 Prepare matrix-matched calibration solutions. Refer to the appendix relevant to the selected sample dissolution procedure (see paragraphs 61 to 64).

Atomic absorption measurements

71 Set up the atomic absorption spectrometer (paragraph 45) to determine nickel at a wavelength of 232.0 nm using an oxidising air-acetylene flame. Follow the manufacturer's recommendations for specific operating parameters, and use background correction. The sensitivity, defined as the concentration required to produce a signal of 1% absorbance or 0.0044 absorbance units, is about 0.07 µg ml⁻¹ of nickel.

72 Adjust the spectrometer zero while aspirating the blank calibration solution (paragraph 70). Repeat this procedure regularly throughout the analysis and readjust the zero if the baseline drifts.

73 Aspirate the calibration solutions (paragraph 70) into the flame in order of increasing concentration and make absorption measurements for each solution. For instruments controlled by a microprocessor or personal computer, generate a calibration for nickel by carrying out a linear regression. For instruments without this capability, prepare a calibration graph by plotting the absorbance of the calibration solutions versus the nickel concentration.

74 Aspirate the sample and blank solutions (paragraph 69) into the flame and make absorption measurements for each solution. For instruments controlled by a microprocessor or personal computer, use the calibration function to determine the concentration of nickel in the sample and blank solutions and obtain a direct read-out of the results in µg ml⁻¹ of nickel. For instruments without this capability, determine the concentration of nickel in µg ml⁻¹ from the calibration graph (paragraph 73).

75 Aspirate a mid-range calibration solution into the flame after each five to ten sample solutions and make an absorption measurement. If this indicates that the sensitivity has changed by more than $\pm 5\%$, take one of the following appropriate corrective measures: either use the available software facilities of the microprocessor or personal computer to correct for the sensitivity change (reslope facility); or suspend analysis, recalibrate the spectrometer as described in paragraph 73; and in either case reanalyse the solutions which were analysed during the period in which the sensitivity change occurred.

76 If high concentrations of nickel are found, dilute the sample solutions to bring the concentration within the calibration range, and repeat the analysis. Make all dilutions so that the final matrix is consistent with the dissolution procedure used. Record the dilution factor.

77 Calculate the mean nickel concentration of the blank solutions.

78 If the concentration of nickel in the sample solutions is less than $0.5 \mu\text{g ml}^{-1}$ consider repeating the analysis using electrothermal atomic absorption spectrometry (see paragraphs 79 to 87) since this technique gives more precise measurements at low concentrations.

Note 23: *Electrothermal atomic absorption spectrometry is required only for the procedures described in Appendices A1 and A2*

ANALYSIS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

Note 24: *Nickel is present at a low level in the environment and it is essential that strict standards of cleanliness are observed to avoid contamination of labware. This is particularly important when carrying out electrothermal atomic absorption spectrometry since the technique exhibits a very low detection limit. Ensure that all glassware is cleaned thoroughly before use in accordance with paragraphs 65 to 68, and that autosampler cups (paragraph 47) are stored in 1 + 9 nitric acid (paragraph 22) until required.*

Note 25: *The use of electrothermal atomic absorption spectrometry is only necessary where exposure to water-soluble nickel compounds needs to be determined. Flame atomic absorption spectrometry has been shown to meet the CEN requirements for measurement of water-insoluble nickel compounds, which have a higher maximum exposure limit.*

Preparation of working calibration solutions

79 Prepare a matrix-matched working calibration solution. Refer to the appendix relevant to the selected sample dissolution procedure (see paragraphs 61 to 64).

80 Prepare a matrix-matched working calibration blank solution. Refer to the appendix relevant to the selected sample dissolution procedure (see paragraphs 61 to 64).

Atomic absorption measurements

81 Set up the atomic absorption spectrometer (paragraph 45) and electrothermal atomiser (paragraph 46) to determine nickel at a wavelength of 232.0 nm using background correction. Follow the manufacturer's recommendations for specific operating parameters.

Note 26: *The operating parameters for electrothermal atomic absorption spectrometry vary considerably between different instruments, much more so than for flame atomic absorption spectrometry. A Perkin-Elmer 5100PC atomic absorption spectrometer with Zeeman HGA-600 graphite furnace module and AS-60 autosampler was used in the validation of this method,¹⁰ and the operating parameters used are given in Appendix C. The characteristic mass for nickel, defined as the number of picograms required to give 0.0044 absorbance-seconds, was determined to be 12 pg for this analytical system. This is equivalent to a sample solution concentration of 0.60 ng ml^{-1} of nickel for a $20 \mu\text{l}$ sample solution injection volume.*

82 Program the autosampler to prepare calibration solutions in situ on a pyrolytic graphite platform mounted in the pyrolytically-coated graphite tube of the electrothermal atomiser. Prepare at least six calibration solutions to cover the range 0 ng ml^{-1} to 50 ng ml^{-1} using the working calibration solution (paragraph 79) and the working calibration blank solution (paragraph 80). See Table 2 for typical autosampler injection volumes.

Note 27: *The procedure described above may be varied to accommodate the use of electrothermal atomisers of alternative design (see note 19).*

Note 28: *Calibration solutions may be prepared in volumetric flasks as an alternative to preparation in situ using the autosampler.*

Note 29: *Sample test solutions should be diluted (see paragraph 86) before analysis by electrothermal atomic absorption spectrometry (see paragraph 78) if results obtained by flame atomic absorption spectrometry indicate that the nickel concentration is above the upper limit of the calibration range for electrothermal atomic absorption spectrometry (see paragraph 82).*

83 Set-up the analytical sequence in the microprocessor or personal computer. Specify an appropriate number of replicate analyses for each solution, and insert a calibration blank solution and a mid-range calibration solution after each five to ten sample solutions to monitor for baseline drift and sensitivity change respectively.

84 Place the working calibration solution (paragraph 79), the working calibration blank solution (paragraph 80), and the sample and blank solutions (paragraph 69) in separate acid-washed autosampler cups (see note 24) and position as appropriate in the autosampler carousel. Analyse the calibration, sample and blank solutions, using the microprocessor or personal computer software to generate a calibration and obtain a direct read-out of sample and blank results in ng ml^{-1} of nickel.

85 If significant baseline drift is observed during the course of the analysis, or if the sensitivity changes by more than $\pm 5\%$, take one of the following appropriate corrective measures: either use the available software facilities of the microprocessor or personal computer to correct for the sensitivity change (reslope facility); or suspend analysis and recalibrate the spectrometer as described in paragraph 84. In either case reanalyse the solutions which were analysed during the period in which the sensitivity change occurred.

86 If concentrations of nickel above the upper limit of the calibration range are found, dilute the sample solutions to bring them within the calibration range, and repeat the analysis. Make all dilutions so that the final matrix is consistent with the dissolution procedure used. Record the dilution factor.

87 Calculate the mean nickel concentration of the blank solutions.

QUALITY CONTROL MEASURES

88 Analytical quality requirements, guidance on the establishment of a quality assurance programme and details of internal quality control and external quality assessment schemes are fully described in MDHS 71.²⁶

89 If nickel analysis is performed frequently it is recommended that internal quality control is performed. In such instances, prepare quality control filters by spiking a large batch of filters with microlitre volumes of a solution of known nickel concentration. Analyse a random selection of at least 20 filters, each along with a different analytical batch, and calculate the mean value and standard deviation of the readings. Assuming that the distribution of these values is Gaussian, construct a Shewhart chart with warning and action limits at $\pm 2SD$ and $\pm 3SD$ respectively. Subsequently, analyse a quality control filter with each analytical batch and plot the result on the Shewhart chart. Compare the internal quality control result with the target value and take appropriate action if the warning or action limits are exceeded, as recommended in MDHS 71.²⁶ Take care to ensure that the quality control filters are stored under conditions which ensure maximum stability.

90 It is strongly recommended that all laboratories undertaking the determination of toxic elements in workplace air should participate in an external quality assessment scheme such as HSE's Workplace Analysis Scheme for Proficiency (WASP). Details of WASP are given in MDHS 71.²⁶ However, at present the WASP scheme does not encompass nickel.

CALCULATIONS

Volume of air sample

91 Calculate the mean flow rate during the sampling period by averaging the flow rate measurements taken at the start and end of the sampling period. Then calculate

the volume, in litres, of the air sample by multiplying the mean flow rate, in litres per minute, by the sampling time, in minutes.

Concentration of nickel in air

92 Calculate the concentration of nickel in air, $\rho(\text{Ni})$, in milligrams per cubic metre (mg m^{-3}), using the equation:

$$\rho(\text{Ni}) = \frac{[\rho(\text{Ni})_1 \cdot V_1 \cdot \text{DF}_1 - \rho(\text{Ni})_0 \cdot V_0 \cdot \text{DF}_0]}{V}$$

where $\rho(\text{Ni})_0$ is the mean concentration, in $\mu\text{g ml}^{-1}$, of nickel in the blank solutions (see paragraphs 77 and 87);

$\rho(\text{Ni})_1$ is the concentration, in $\mu\text{g ml}^{-1}$, of nickel in the sample solution (see paragraphs 74 and 84);

V is the volume, in litres, of the air sample (see paragraph 91);

V_0 is the volume, in ml, of the blank solutions, ie 10 ml or 50 ml (see paragraph 69);

V_1 is the volume, in ml, of the sample solution, ie 10 ml or 50 ml (see paragraph 69);

DF_0 is the dilution factor for the blank solutions, ie 1;

DF_1 is the dilution factor for the sample solutions (see paragraphs 76 and 86).

Note 30: For low concentrations of nickel in air determined by electrothermal atomic absorption spectrometry, calculate results in micrograms per cubic metre by using solution concentrations in ng ml^{-1} in the above equation.

TEST REPORT

93 Appendix D gives recommendations for information to be included in the test report.

APPENDIX A1 Citrate leach procedure for dissolution of water-soluble nickel compounds

SCOPE

A1.1 This appendix describes a dissolution procedure for water-soluble nickel compounds using an ammonium citrate leach solution.

METHOD PERFORMANCE

Effectiveness of sample dissolution procedure

A1.2 A citrate leach procedure for the determination of water-soluble nickel compounds was tested by NiPERA²⁷ in an interlaboratory test programme, and was found¹⁰ to be fully effective.

Note 31: *The citrate leach procedure was considered to be preferable to a simple water leach because (i) buffering the pH ensures reproducibility by minimising the effects on nickel solubility caused by foreign hydrolysable salts; (ii) the complexing ability of the citrate ion towards higher valency elements, eg Fe(III), prevents unwanted precipitation of hydrolytic products; and (iii) nickel forms relatively weak complexes with citrate, so solubility in citrate solution is the same as that in water.*

A1.3 The procedure described in this method has been modified somewhat to avoid what were considered to be unnecessary steps. The revised procedure was compared with that described by NiPERA using one of the dusts from the interlaboratory test programme, and was found¹⁰ to be equally effective.

Note 32: *The changes that were made to the procedure described by NiPERA were to omit the use of methanol to remove any hydrophobic organic material and to make the dust wettable. Methanol destroys the mixed cellulose ester membrane filters recommended in this procedure. The ammonium citrate leach solution was oxidised by NiPERA using perchloric acid; this step was omitted as it was found that the ammonium citrate did not interfere with the determination of nickel by either flame or electrothermal atomic absorption spectrometry.*

Detection limits

A1.4 The qualitative and quantitative detection limits as determined¹⁰ for this procedure were 0.012 µg ml⁻¹ and 0.040 µg ml⁻¹ respectively for flame atomic absorption spectrometry; and 0.96 ng ml⁻¹ and 3.2 ng ml⁻¹ for electrothermal atomic absorption spectrometry. For an air sample volume of 30 litres and a sample solution volume of 10 ml this corresponds to nickel in air concentrations of 4 µg m⁻³ and 13 µg m⁻³ respectively for flame atomic absorption spectrometry; and 0.3 µg m⁻³ and 1.1 µg m⁻³ respectively for electrothermal atomic absorption spectrometry.

Overall uncertainty

A1.5 Laboratory experiments¹⁰ indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 100 spiked filters in the range 0.6 µg to 192 µg of nickel was determined to be 99.4 ± 3.5% using flame atomic absorption spectrometry; and the mean analytical recovery for 60 spiked filters in the range 0.05 µg to 3 µg of nickel was determined to be 100.9 ± 3.8% using electrothermal atomic absorption spectrometry.

A1.6 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), was determined¹⁰ to be less than 6% for samples in the range 0.6 µg to 2.4 µg and less than 3% for samples in the range 3 µg to 192 µg using flame atomic absorption spectrometry; and less than 7% for samples at a level of 0.05 µg and less than 4% for samples in the range 0.1 µg to 3 µg using electrothermal atomic absorption spectrometry.

A1.7 The overall uncertainty of the method, as defined by CEN,¹¹ was estimated¹⁰ to be less than 26% for samples in the range 0.6 µg to 2.4 µg and less than 13% for samples in the range 3 µg to 192 µg using flame atomic absorption spectrometry; and less than 23% for samples at a level of 0.05 µg and less than 17% for samples in the range 0.1 µg to 3 µg using electrothermal atomic absorption spectrometry. This assumes that the coefficient of variation of the method that arises from inter-specimen sampler variability, CV(inter), is negligible and that the coefficient of variation of the method that arises from pump flow rate variability, CV(flow), is limited to 5%. The overall uncertainty is therefore within the specifications prescribed by CEN¹¹ for measurements for comparison with limit values, ie <50% for measurements in the range 0.1 to 0.5 times the limit value and <30% for measurements in the range 0.5 to 2.0 times the limit value.

PRINCIPLE

A1.8 The soluble nickel compounds are leached from the sample filter by immersing the filter in a solution of ammonium citrate. The resultant leach solution is filtered through a membrane filter and diluted to 10 ml for subsequent analysis by either flame or electrothermal atomic absorption spectrometry.

PREPARATION OF SAMPLE AND BLANK SOLUTIONS

A1.9 Open the filter transport cassettes (see paragraph 57), sampler filter cassettes (see paragraph 58) or samplers (see paragraph 59) and transfer each filter into an individual, labelled 50 ml beaker using clean flat-tipped tweezers (paragraph 33). Follow the same procedure for the blank filters (paragraph 56).

A1.10 If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the filter cassette or sampler form part of the sample (see note 9),

wash any particulate material adhering to the internal surfaces into the beaker using the ammonium citrate solution used to leach the sample filters (see paragraph A1.11).

A1.11 Add 5 ml ammonium citrate solution (paragraph 18) to each beaker, cover with a watch glass, and allow to leach for 60 minutes. Ensure that the sample filters are fully immersed throughout the leach period.

A1.12 Filter each leach solution through a cellulose ester membrane filter using suction filtration apparatus (paragraph 39), collecting the filtrate in an individual, labelled test tube (see Figure 1). Rinse the sample filter and beaker with three 1 ml aliquots of ammonium citrate solution, allowing the solution to completely drain from the filter funnel between washings. Quantitatively transfer the filtrate to a 10 ml volumetric flask, rinsing out the test tube with a further 1 ml of ammonium citrate solution. Finally, dilute to the mark with ammonium citrate solution, stopper and mix thoroughly.

A1.13 If applicable (see paragraph 64), retain the sample filter and the secondary filter (the membrane filter used for filtration of the leach solution) for subsequent analysis for water-insoluble nickel compounds.

PREPARATION OF CALIBRATION SOLUTIONS

Flame atomic absorption spectrometry

A1.14 Prepare at least six calibration solutions to cover the range $0 \mu\text{g ml}^{-1}$ to $5 \mu\text{g ml}^{-1}$ of nickel. Accurately pipette the appropriate volumes of stock standard nickel solution (paragraph 25 or 26) into separate, labelled 100 ml volumetric flasks, dilute to the mark with ammonium citrate solution (paragraph 18), stopper and mix thoroughly. Prepare these solutions fresh weekly.

Electrothermal atomic absorption spectrometry

A1.15 Prepare a working calibration solution at a concentration of 50 ng ml^{-1} of nickel. Accurately pipette 0.5 ml of working standard nickel solution (paragraph 27) into a 100 ml volumetric flask. Dilute to the mark with ammonium citrate solution (paragraph 18), stopper and mix thoroughly. Prepare this solution fresh daily.

A1.16 Use the ammonium citrate solution as a working calibration blank solution.

ANALYSIS

Flame atomic absorption spectrometry

A1.17 Proceed with the analysis as described in paragraphs 71 to 78.

Electrothermal atomic absorption spectrometry

A1.18 Proceed with the analysis as described in paragraphs 81 to 87.

APPENDIX A2 1 + 1 Nitric acid sample dissolution procedure for nickel and water-insoluble nickel compounds

SCOPE

A2.1 This appendix describes a dissolution procedure for nickel and water-insoluble nickel compounds using 1 + 1 nitric acid on a hotplate.

METHOD PERFORMANCE

Effectiveness of sample dissolution procedure

A2.2 This sample dissolution procedure has been tested¹⁰ on a range of nickel-containing materials in industrial use or occurring in workplace air and has been found to be effective for nickel metal, nickel oxide (black), nickel oxide (green), nickel hydroxide, nickel phosphide and nickel sulphide.

Detection limits

A2.3 The qualitative and quantitative detection limits as determined¹⁰ for this procedure were $0.024 \mu\text{g ml}^{-1}$ and $0.080 \mu\text{g ml}^{-1}$ respectively for flame atomic absorption spectrometry; and 0.87 ng ml^{-1} and 2.9 ng ml^{-1} for electrothermal atomic absorption spectrometry. For an air sample volume of 30 litres and a sample solution volume of 10 ml this corresponds to nickel in air concentrations of $8 \mu\text{g m}^{-3}$ and $27 \mu\text{g m}^{-3}$ respectively for flame atomic absorption spectrometry; and $0.3 \mu\text{g m}^{-3}$ and $1.0 \mu\text{g m}^{-3}$ respectively for electrothermal atomic absorption spectrometry.

Overall uncertainty

A2.4 Laboratory experiments¹⁰ indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 170 spiked filters in the range 0.6 μg to 960 μg of nickel was determined to be $102.4 \pm 3.0\%$ using flame atomic absorption spectrometry; and the mean analytical recovery for 60 spiked filters in the range 0.05 μg to 3.0 μg of nickel was determined to be $102.1 \pm 1.1\%$ using electrothermal atomic absorption spectrometry.

A2.5 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), was determined¹⁰ to be less than 14% for samples at a level of 0.60 μg and less than 6% for samples in the range 2.4 μg to 960 μg using flame atomic absorption spectrometry; and less than 8% for samples in the range 0.05 μg to 3 μg using electrothermal atomic absorption spectrometry.

A2.6 The overall uncertainty of the method, as defined by CEN,¹¹ was estimated¹⁰ to be less than 30% for samples in the range 0.6 μg to 2.4 μg and less than 19% for samples in the range 3 μg to 960 μg using flame atomic absorption spectrometry; and less than 23% for samples at a level of 0.05 μg and less than 19% for

samples in the range 0.10 µg to 3 µg using electrothermal atomic absorption spectrometry. This assumes that the coefficient of variation of the method that arises from inter-specimen sampler variability, CV (inter), is negligible and that the coefficient of variation of the method that arises from pump flow rate variability, CV (flow), is limited to 5%. The overall uncertainty is therefore within the specifications prescribed by CEN¹¹ for measurements for comparison with limit values, ie <50% for measurements in the range 0.1 to 0.5 times the limit value and <30% for measurements in the range 0.5 to 2.0 times the limit value.

PRINCIPLE

A2.7 The filter and collected sample are treated with 5 ml of 1 + 1 nitric acid and heated on a hotplate until about 1 ml of concentrated nitric acid solution remains. This is diluted to 10 ml for subsequent analysis for nickel by either flame or electrothermal atomic absorption spectrometry.

PREPARATION OF SAMPLE AND BLANK SOLUTIONS

A2.8 Open the filter transport cassettes (see paragraph 57), sampler filter cassettes (see paragraph 58) or samplers (see paragraph 59) and transfer each filter into an individual, labelled 50 ml beaker using clean flat-tipped tweezers (paragraph 33). Follow the same procedure for the blank filters (paragraph 56).

A2.9 If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the filter cassette or sampler form part of the sample (see note 9), wash any particulate material adhering to the internal surfaces into the beaker using a minimum volume of water (paragraph 17).

A2.10 Add 5 ml of 1 + 1 nitric acid (paragraph 20) to each beaker, partially cover with a watch glass, and heat to approximately 150°C on a hotplate (paragraph 40) in a fume cupboard until the filter has dissolved and the solution has been reduced to approximately 1 ml. Remove each beaker from the hotplate and allow to cool.

A2.11 Carefully rinse the watch glass and the sides of each beaker with water (paragraph 17) and quantitatively transfer the solution to an individual, labelled 10 ml volumetric flask. If necessary, remove any undissolved particulate material by filtering through a cellulose (paper) filter (paragraph 38) which has been pre-washed with 1 + 9 nitric acid (paragraph 22) and then with water. Finally dilute to the mark with water, stopper and mix thoroughly.

PREPARATION OF CALIBRATION SOLUTIONS

Flame atomic absorption spectrometry

A2.12 Prepare at least six calibration solutions to cover the range 0 µg ml⁻¹ to 5 µg ml⁻¹ of nickel. Add 50 ml of

water (paragraph 17) and 10 ml of concentrated nitric acid (paragraph 19) to separate, labelled 100 ml volumetric flasks. Accurately pipette the appropriate volume of stock standard nickel solution (paragraph 25 or 26) into each flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly. Prepare these solutions fresh weekly.

Electrothermal atomic absorption spectrometry

A2.13 Prepare a working calibration solution at a concentration of 50 ng ml⁻¹ of nickel. Add 50 ml of water (paragraph 17) and 10 ml of concentrated nitric acid (paragraph 19) to a labelled 100 ml volumetric flask. Accurately pipette 0.5 ml of working standard nickel solution (paragraph 27) into the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly. Prepare this solution fresh daily.

A2.14 Prepare a working calibration blank solution following the above procedure but omitting the 0.5 ml of working standard nickel solution (paragraph 27).

ANALYSIS

Flame atomic absorption spectrometry

A2.15 Proceed with the analysis as described in paragraphs 71 to 78.

Electrothermal atomic absorption spectrometry

A2.16 Proceed with the analysis as described in paragraphs 81 to 87.

APPENDIX A3 Nitric acid/perchloric acid sample dissolution procedure for nickel and water-insoluble nickel compounds

SCOPE

A3.1 This appendix describes a dissolution procedure for nickel and water-insoluble nickel compounds using nitric acid and perchloric acid on a hotplate. It is particularly useful in instances when nickel compounds present in the sample are not readily soluble in acid, and the 1 + 1 nitric acid procedure described in Appendix A2 could be ineffective.

METHOD PERFORMANCE

Effectiveness of sample dissolution procedure

A3.2 This sample dissolution procedure has been tested¹⁰ on a range of nickel-containing materials in industrial use or occurring in workplace air and has been found to be effective for welding fumes and dusts from nickel smelting operations.

Detection limits

A3.3 The qualitative and quantitative detection limits as determined for this procedure were $0.008 \mu\text{g ml}^{-1}$ and $0.026 \mu\text{g ml}^{-1}$ respectively for flame atomic absorption spectrometry. For an air sample volume of 30 litres and a sample solution volume of 10 ml this corresponds to nickel in air concentrations of $3 \mu\text{g m}^{-3}$ and $9 \mu\text{g m}^{-3}$ respectively.

Overall uncertainty

A3.4 Laboratory experiments¹⁰ indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 100 spiked filters in the range $3 \mu\text{g}$ to $960 \mu\text{g}$ of nickel was determined to be $101.5 \pm 2.7\%$ using flame atomic absorption spectrometry.

A3.5 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), was determined¹⁰ to be less than 3% for samples in the range $3 \mu\text{g}$ to $960 \mu\text{g}$ using flame atomic absorption spectrometry.

A3.6 The overall uncertainty of the method, as defined by CEN,¹¹ was estimated¹⁰ to be less than 17% for samples in the range $3 \mu\text{g}$ to $960 \mu\text{g}$ using flame atomic absorption spectrometry. This assumes that the coefficient of variation of the method that arises from inter-specimen sampler variability, CV (inter), is negligible and that the coefficient of variation of the method that arises from pump flow rate variability, CV (flow), is limited to 5%. The overall uncertainty is therefore within the specifications prescribed by CEN¹¹ for measurements for comparison with limit values, ie <50% for measurements in the range 0.1 to 0.5 times the limit value and <30% for measurements in the range 0.5 to 2.0 times the limit value.

PRINCIPLE

A3.7 The filter and collected sample are treated with 5 ml of nitric acid and 1 ml of perchloric acid and heated on a hotplate until about 1 ml of acid solution remains. This is diluted to 10 ml for subsequent analysis for nickel by flame atomic absorption spectrometry.

PREPARATION OF SAMPLE AND BLANK SOLUTIONS

A3.8 Open the filter transport cassettes (see paragraph 57), sampler filter cassettes (see paragraph 58) or samplers (see paragraph 59) and transfer each filter into an individual, labelled 50 ml beaker using clean flat-tipped tweezers (paragraph 33). Follow the same procedure for the blank filters (paragraph 56).

A3.9 If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the filter cassette or sampler form part of the sample (see note 9), wash any particulate material adhering to the internal surfaces into the beaker using a minimum volume of water (paragraph 17).

A3.10 Add 5 ml of concentrated nitric acid (paragraph 19),

cover the beaker and digest on a hotplate until the filter dissolves. Slide back the watch glasses so that the beakers are only partially covered, add 1 ml of perchloric acid (paragraph 23), and continue to heat until dense, white fumes of perchloric acid are evolved and until approximately 1 ml of acid remains. Remove each beaker from the hotplate and allow to cool.

A3.11 Carefully rinse the watch glass and the sides of each beaker with water (paragraph 17) and quantitatively transfer the solution to an individual, labelled 10 ml volumetric flask. If necessary, remove any undissolved particulate material by filtering through a cellulose (paper) filter (paragraph 38) which has been pre-washed with 1 + 9 nitric acid (paragraph 22) and then with water. Finally dilute to the mark with water, stopper and mix thoroughly.

PREPARATION OF CALIBRATION SOLUTIONS

Flame atomic absorption spectrometry

A3.12 Prepare at least six calibration solutions to cover the range $0 \mu\text{g ml}^{-1}$ to $5 \mu\text{g ml}^{-1}$ of nickel. Add 50 ml of water (paragraph 17) and 10 ml of perchloric acid (paragraph 23) to separate, labelled 100 ml volumetric flasks. Accurately pipette the appropriate volume of stock standard nickel solution (paragraph 25 or 26) into each flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly. Prepare these solutions fresh weekly.

ANALYSIS

Flame atomic absorption spectrometry

A3.13 Proceed with the analysis as described in paragraphs 71 to 78.

APPENDIX A4 Microwave-assisted sample dissolution procedure for nickel and water-insoluble nickel compounds

SCOPE

A4.1 This appendix describes a microwave-assisted dissolution procedure for nickel and water-insoluble nickel compounds using nitric acid. It is particularly useful in instances when nickel compounds present in the sample are not readily soluble in acid, and the 1 + 1 nitric acid procedure described in Appendix A2 could be ineffective.

Note 33: *The procedure described is for use with lined sample vessels designed for carrying out microwave digestions at pressures up to 200 psi. These vessels consist of a chemically resistant inner liner and cover (usually made of Teflon), which contains and isolates the sample solution from a higher strength outer pressure vessel structure. Other types of sample vessel designed to operate at equivalent or higher pressures may be used.*

METHOD PERFORMANCE

Effectiveness of sample dissolution procedure

A4.2 This sample dissolution procedure has been tested¹⁰ on a range of nickel-containing materials in industrial use or occurring in workplace air and has been found to be effective for welding fumes and dusts from nickel smelting operations.

Detection limits

A4.3 The qualitative and quantitative detection limits as determined¹⁰ for this procedure were 0.024 µg ml⁻¹ and 0.080 µg ml⁻¹ respectively for flame atomic absorption spectrometry. For an air sample volume of 30 litres and a sample solution volume of 50 ml this corresponds to nickel in air concentrations of 0.04 mg m⁻³ and 0.13 mg m⁻³ respectively.

Overall uncertainty

A4.4 Laboratory experiments¹⁰ indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 100 spiked filters in the range 3 µg to 960 µg of nickel was determined to be 101.8 ± 1.7% using flame atomic absorption spectrometry.

A4.5 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), was determined¹⁰ to be less than 17% for samples in the range 3 µg to 12 µg and less than 3% for samples in the range 15 µg to 960 µg using flame atomic absorption spectrometry.

A4.6 The overall uncertainty of the method, as defined by CEN,¹¹ was estimated¹⁰ to be less than 40% for samples at a level of 3 µg and less than 18% for samples in the range 12 µg to 960 µg using flame atomic absorption spectrometry. This assumes that the coefficient of variation of the method that arises from inter-specimen sampler variability, CV (inter), is negligible and that the coefficient of variation of the method that arises from pump flow rate variability, CV (flow), is limited to 5%. The overall uncertainty is therefore within the specifications prescribed by CEN¹¹ for measurements for comparison with limit values, ie <50% for measurements in the range 0.1 to 0.5 times the limit value and <30% for measurements in the range 0.5 to 2.0 times the limit value.

PRINCIPLE

A4.7 The filter and collected sample are digested with 5 ml of concentrated nitric acid in a closed vessel using a microwave digestion system. The resultant solution is diluted to 50 ml for subsequent analysis for nickel by flame atomic absorption spectrometry.

CLEANING OF TEFLON LINERS

A4.8 Clean the teflon liners of the sample vessels with concentrated nitric acid before use. Follow the procedure

described in paragraphs A4.11 and A4.12 and then rinse the liners thoroughly with water (paragraph 17).

PREPARATION OF SAMPLE AND BLANK SOLUTIONS

A4.9 Open the filter transport cassettes (see paragraph 57), sampler filter cassettes (see paragraph 58) or samplers (see paragraph 59) and transfer each filter into the teflon liner of a labelled sample vessel using clean flat-tipped tweezers (paragraph 33). Follow the same procedure for the blank filters (paragraph 56).

A4.10 If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the filter cassette or sampler form part of the sample (see note 9), wash any particulate material adhering to the internal surfaces into the teflon liner using a minimum volume of water (paragraph 17).

A4.11 Add 5 ml of concentrated nitric acid (paragraph 19) to each liner and cover with its lid. Then seal the sample vessels with their screw caps and place them, evenly distributed, in the turntable of the microwave digestion system (paragraph 41).

A4.12 Program the microwave digestion system to operate for 30 minutes at full power, using the pressure control system to prevent the pressure in the control vessel exceeding 100 psi. When the program has run, allow the vessels to cool and the pressure to return to <10 psi.

A4.13 Remove the turntable from the microwave digestion system and place in a fume cupboard. Carefully open each sample vessel, rinse the lid and sides of the liner with water (paragraph 17), and quantitatively transfer the solution to an individual, labelled 50 ml volumetric flask. If necessary, remove any undissolved particulate matter by filtering through a cellulose (paper) filter (paragraph 38) which has been pre-washed with 1 + 9 nitric acid (paragraph 22) and then with water. Finally dilute to the mark with water, stopper and mix thoroughly.

Note 34: *The procedure described is for a microwave digestion system with a nominal output power of 700 W with pressure control. If the system also has temperature control, this can also be utilised to control the sample dissolution conditions, but the method performance could be different from that given above.*

PREPARATION OF CALIBRATION SOLUTIONS

Flame atomic absorption spectrometry

A4.14 Prepare at least six calibration solutions to cover the range 0 µg ml⁻¹ to 5 µg ml⁻¹ of nickel. Add 50 ml of water (paragraph 17) and 10 ml of concentrated nitric acid (paragraph 19) to separate, labelled 100 ml volumetric flasks. Accurately pipette the appropriate volume of stock standard nickel solution (paragraph 25 or 26) into each flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly. Prepare these solutions fresh weekly.

ANALYSIS

Flame atomic absorption spectrometry

A4.15 Proceed with the analysis as described in paragraphs 71 to 78.

APPENDIX A5 Potassium hydrogen sulphate fusion procedure for nickel and water-insoluble nickel compounds

SCOPE

A5.1 This appendix describes a fusion procedure for nickel and water-insoluble nickel compounds using potassium hydrogen sulphate. It is particularly useful in instances when nickel compounds present in the sample are not readily soluble in acid, and the dissolution procedure described in Appendices A2, A3 and A4 could be ineffective.

Note 35: *The fusion procedure is only suitable for dissolution of samples collected for sampling times in the range 2 to 8 hours. For shorter sampling times, the overall uncertainty does not meet the specification prescribed by CEN¹¹ for measurements in the range 0.1 to 0.5 times the limit value, ie <50%.*

METHOD PERFORMANCE

Effectiveness of sample dissolution procedure

A5.2 This sample dissolution procedure has been tested¹⁰ on a range of nickel-containing materials in industrial use or occurring in workplace air and has been found to be effective for welding fumes and dusts from nickel smelting operations.

Detection limits

A5.3 The qualitative and quantitative detection limits as determined¹⁰ for this procedure were 0.021 µg ml⁻¹ and 0.071 µg ml⁻¹ respectively for flame atomic absorption spectrometry. For an air sample volume of 30 litres and a sample dilution volume of 250 ml this corresponds to nickel in air concentrations of 0.17 mg m⁻³ and 0.6 mg m⁻³ respectively.

Overall uncertainty

A5.4 Laboratory experiments¹⁰ indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 54 spiked filters in the range 12 µg to 960 µg of nickel was determined to be 100.6 ± 2.2% using flame atomic absorption spectrometry.

A5.5 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), was determined¹⁰ to be less than 6% for samples in the

range 12 µg to 960 µg using flame atomic absorption spectrometry.

A5.6 The overall uncertainty of the method, as defined by CEN,¹¹ was estimated¹⁰ to be less than 17% for samples in the range 12 µg to 960 µg using flame atomic absorption spectrometry. This assumes that the coefficient of variation of the method that arises from inter-specimen sampler variability, CV (inter), is negligible and that the coefficient of variation of the method that arises from pump flow rate variability, CV (flow), is limited to 5%. The overall uncertainty is therefore within the specifications prescribed by CEN¹¹ for measurements for comparison with limit values, ie <50% for measurements in the range 0.1 to 0.5 times the limit value and <30% for measurements in the range 0.5 to 2.0 times the limit value.

PRINCIPLE

A5.7 The filter and collected sample are placed in a fused porcelain crucible and wet-ashed with 0.5 ml concentrated nitric acid. 2.5 g of molten potassium hydrogen sulphate is then poured over the sample which is then covered with the crucible lid and placed in a muffle furnace at 650°C for 1 hour. The fused bead is dissolved in 10 ml of 1 + 3 nitric acid, made to 25 ml with water, and further diluted by a factor of ten for subsequent analysis for nickel by flame atomic absorption spectrometry.

PREPARATION OF SAMPLE AND BLANK SOLUTIONS

A5.8 Open the filter transport cassettes (see paragraph 57), sampler filter cassettes (see paragraph 58) or samplers (see paragraph 59) and transfer each filter into an individual, labelled 30 ml fused porcelain crucible (paragraph 42) using clean flat-tipped tweezers (paragraph 33). Follow the same procedure for the blank filters (paragraph 56).

A5.9 If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the filter cassette or sampler form part of the sample (see note 9), wash any particulate material adhering to the internal surfaces into the crucible using a minimum volume of water (paragraph 17).

A5.10 Add 0.5 ml of concentrated nitric acid (paragraph 19) to each crucible and wet-ash the filter by gently heating over a Meker burner (paragraph 43) and slowly boiling off the nitric acid (care should be taken to avoid loss of sample during heating as the acid will spit if heated strongly).

A5.11 Weigh 2.5 g portions of potassium hydrogen sulphate (paragraph 24) into separate porcelain crucibles (paragraph 42) and heat over a Meker burner (paragraph 43) until molten. Then pour a portion of molten flux over each ashed sample (paragraph A5.10) and cover with a crucible lid.

A5.12 Place the covered crucibles in a muffle furnace (paragraph 44) at a temperature of 650°C. Remove the

crucibles after 1 hour and place on a heat-proof surface and allow to cool.

A5.13 Remove the crucible lids and gently tap each fused bead into an individual, labelled 50 ml beaker. Rinse each crucible with two 5 ml aliquots of 1 + 3 nitric acid (paragraph 21) and add the washings to the beaker. Cover the beakers with watch glasses and heat on a hotplate to dissolve the fused beads.

A5.14 Carefully rinse the watch glass and the sides of each beaker with water (paragraph 17) and quantitatively transfer each solution to an individual, labelled 25 ml volumetric flask. If necessary, remove any undissolved particulate material by filtering through a cellulose (paper) filter (paragraph 38) which has been pre-washed with 1 + 9 nitric acid (paragraph 22) and then with water. Finally dilute to the mark with water, stopper and mix thoroughly.

A5.15 Further dilute the sample solutions for analysis. Accurately pipette 1 ml of each sample solution (paragraph A5.14) into an individual, labelled 10 ml volumetric flask, dilute to the mark with water (paragraph 17), stopper and mix thoroughly.

PREPARATION OF CALIBRATION SOLUTIONS

Flame atomic absorption spectrometry

A5.16 Prepare at least six calibration solutions to cover the range $0 \mu\text{g ml}^{-1}$ to $5 \mu\text{g ml}^{-1}$ of nickel. Add 50 ml of water (paragraph 17) and 10 ml of 1 + 9 nitric acid (paragraph 22) to separate, labelled 100 ml volumetric flasks. Weigh out an appropriate number of 1 g portions of potassium hydrogen sulphate (paragraph 24), transfer a portion to each flask and swirl to dissolve. Accurately pipette the appropriate volume of stock standard nickel solution (paragraph 25 or 26) into each flask, dilute to the mark with water (paragraph 17), stopper and mix thoroughly. Prepare these solutions fresh weekly.

ANALYSIS

Flame atomic absorption spectrometry

A5.17 Proceed with the analysis as described in paragraphs 71 to 78.

APPENDIX B Primary standard for calibration of portable flowmeter

The primary standard should preferably be a flowmeter whose accuracy is traceable to national standards, used with careful attention to the conditions of the calibration certificate. A bubble flowmeter may be used. This is an arrangement whereby the pump under test draws a soap film up a calibrated tube. The passage of the film is accurately timed between two marks whose separation defines a known volume. A one litre burette can form a suitable tube. The volume between the marks can be checked by filling the burette with water (paragraph 17), allowing temperatures to stabilise, drawing off a known volume and weighing the water, making allowance for the dependence of volume on temperature. A suitable bubble solution can be made by mixing one part of concentrated washing-up liquid, two parts glycerol and four parts water. The burette must be thoroughly wetted with the solution and several attempts at drawing the film up the tube may be necessary before the tube is wet enough for this to be achieved consistently. (Traceability of the calibration will require checking of the clocks and use of certificated weights.)

APPENDIX C Typical operating parameters for determination of nickel by electrothermal atomic absorption spectrometry

Mode:	Peak area
Integration time:	10 seconds
Background correction:	Zeeman
Injection volumes:	20 μl of calibration, sample or blank solution

Table 1 Typical temperature profile for determination of nickel using electrothermal atomic absorption spectrometry

Step	Ramp time (sec)	Hold time (sec)	Furnace temp ($^{\circ}\text{C}$)	Argon flow (ml min^{-1})	Read
1 Dry	1	50	120	300	
2 Ash	1	30	1400	300	
3 Cool down	1	15	20	300	
4 Atomise	0	10	2600	0	*
5 Clean	1	5	2700	300	

Table 2 Typical autosampler injection volumes for the in-situ preparation of calibration, sample and blank solutions

	Volume of working calibration solution (μl)	Volume of working calibration blank solution (μl)	Volume of sample or blank solution (μl)
0 ng ml^{-1} calibration solution	-	20	-
10 ng ml^{-1} calibration solution	4	16	-
20 ng ml^{-1} calibration solution	8	12	-
30 ng ml^{-1} calibration solution	12	8	-
40 ng ml^{-1} calibration solution	16	4	-
50 ng ml^{-1} calibration solution	20	-	-
Sample or blank solution	-	-	20
Sample solution dilution	-	(20 - x)	x

APPENDIX D Recommendations for the test report

It is recommended that the test report should include the following information:

- a) a complete identification of the air sample, including the date of sampling, the place of sampling, and the identity of the individual whose breathing zone was sampled;
- b) a reference to this MDHS and a description of any deviation from the procedures described;
- c) the type and diameter of filter used;
- d) the type of sampler used;
- e) the type of sampling pump used;
- f) the type of flowmeter used, the primary standard against which it was calibrated, and the range of flow rates for which the flowmeter was calibrated;
- g) the time at the start and at the end of the sampling period, and the sampling time in minutes;
- h) the volume of air sampled, in litres;
- i) the name of the person who collected the sample;
- j) the time-weighted average mass concentration of nickel found in the air sample, in milligrams per cubic metre;
- k) the name of the analyst;
- l) the date of the analysis.

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British Standards are available from:

British Standards Institution
389 Chiswick High Road
London W4 4AL
Tel: 0181 996 7000
Fax: 0181 996 7001

ADVICE

Advice on this method and the equipment used can be obtained from the Health and Safety Executive, Health and Safety Laboratory, Broad Lane, Sheffield, S3 7HQ (telephone 0114 289 2000).

The Health and Safety Executive wishes, wherever possible, to improve the methods described in this series. Any comments that might lead to improvements would therefore be welcome and should be sent to the above address.

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