

MDHS

*Methods for the Determination of
Hazardous Substances*
Health and Safety Laboratory



30/2

Cobalt and cobalt compounds in air

Laboratory method using flame atomic
absorption spectrometry

April 1996

INTRODUCTION

Note 1: *This method updates and replaces MDHS 30.¹ The principal changes which have been made are (i) to modify the dissolution technique to make it more consistent with other methods described in the MDHS series, and (ii) to recommend the use of filters that are soluble using the dissolution technique described.*

Occurrence, properties and uses

1 Occurrence, properties and uses of cobalt and cobalt compounds are fully covered in HSE Guidance Note EH 68.²

Effects on health

2 The health effects of cobalt and cobalt compounds are summarised in HSE Guidance Note EH 68² and are fully covered in HSE Toxicity Review TR 29.³

Health and safety precautions

3 HSE leaflet MS(A)17⁴ summarises the risks involved in working with cobalt 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 68.²

Exposure limits

4 Schedule 1 of the Control of Substances Hazardous to Health (COSHH) Regulations⁵ specifies a maximum exposure limit (MEL) of 0.1 mg m⁻³, 8-hour time-weighted average reference period, for cobalt and cobalt compounds (as Co). This limit is reproduced in Guidance Note EH 40⁶ and the criteria on which it was based are documented in the 1994 supplement of HSE Guidance Note EH 64.⁷

Analytical methods

5 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.

6 This method has been validated⁸ 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 482.⁹ If an alternative method is used it is necessary to demonstrate that it also meets these performance requirements.

Requirements of the COSHH Regulations

7 The Control of Substances Hazardous to Health (COSHH) Regulations⁵ 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 Practices 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.¹⁰

SCOPE

Applicability

8 This MDHS describes a method for determination of the concentration of cobalt and cobalt compounds in workplace air using flame atomic absorption spectrometry. It is applicable to the determination of water-soluble cobalt

salts and the majority of cobalt-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 42¹¹ 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

9 The sample dissolution procedure has been tested⁸ on a range of cobalt-containing materials in industrial use or occurring in workplace air and was found to be effective for cobalt metal, cobalt acetate, cobalt (II) oxide, cobalt tetroxide, and samples of cobalt oxide sinter, welding fumes and dusts from 'hard metal' grinding operations.

Detection limits

10 The qualitative and quantitative detection limits for cobalt, defined as three times and ten times the standard deviation of a blank determination, have been determined⁸ to be 0.012 µg ml⁻¹ and 0.040 µg ml⁻¹. For an air sample volume of 30 litres and a sample solution volume of 10 ml this corresponds to cobalt in air concentrations of 4 µg m⁻³ and 13 µg m⁻³.

Overall uncertainty

11 Laboratory experiments⁸ indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 200 spiked filters in the range 0.6 µg to 192 µg of cobalt was determined to be 101.1 ± 1.7%.

12 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), has been determined to be less than 13% for samples in the range 0.6 µg to 2.4 µg and less than 2% for samples in the range 3 µg to 192 µg.

13 The overall uncertainty of the method, as defined by CEN,⁹ has been estimated⁸ to be less than 31% for samples in the range 0.6 µg to 2.4 µg and less than 14% for samples in the range 3 µg to 192 µg. 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 CEN⁹ 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 240.7 nm, where an excess of some transition and heavy metals have been reported¹² to depress the cobalt signal.

PRINCIPLE

15 A measured volume of air is drawn through a filter mounted in an inhalable dust sampler. The filter and collected sample are then treated with 5 ml of 1 + 1 nitric acid and heated on a hotplate until about 1 ml of concentrated nitric acid solution remains. If cobalt oxide is present, 1 ml of concentrated hydrochloric is added and the beaker is returned to the hotplate for a further 15 minutes. The resultant solution is diluted to 10 ml with water and analysed for cobalt by aspirating into the oxidising air-acetylene flame of an atomic absorption spectrometer. Absorbance measurements are made at 240.7 nm.

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 3978¹³ grade 2 water (electrical conductivity less than 0.1 mS m⁻¹ and resistivity greater than 0.01 MΩ.m at 25°C).

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

18 The cobalt 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

19 Carefully add 500 ml of concentrated nitric acid (paragraph 18) to 450 ml of water (paragraph 17) in a 2 litre beaker. Mix, allow to cool and quantitatively transfer to a 1000 ml volumetric flask. Dilute to the mark with water and mix thoroughly.

Nitric acid, diluted 1 + 9

20 Carefully add 100 ml of concentrated nitric acid

(paragraph 18) to 500 ml of water (paragraph 17) in a 1 litre beaker. Mix, allow to cool and quantitatively transfer to a 1000 ml volumetric flask. Dilute to the mark with water and mix thoroughly.

Hydrochloric acid (HCl), concentrated, ρ about 1.18 g ml^{-1} , 35% (m/m) to 38% (m/m)

21 The cobalt concentration of the acid shall be less than $0.005 \text{ } \mu\text{g ml}^{-1}$.

WARNING - Concentrated hydrochloric acid is corrosive and the 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 hydrochloric acid, and sample dissolution with hydrochloric acid should be carried out in a fume cupboard.

Stock standard cobalt solution, $1000 \text{ } \mu\text{g ml}^{-1}$ of cobalt

22 Use a commercially available standard solution at a concentration of $1000 \text{ } \mu\text{g ml}^{-1}$ of cobalt. Observe the manufacturer's expiry date or recommended shelf life.

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

23 Accurately weigh 1.000 g of cobalt metal, 99.9% Co (m/m), into a 100 ml beaker, add 20 ml of 1 + 1 nitric acid (paragraph 19), cover with a watch glass and heat on a hotplate (paragraph 32) in a fume cupboard until the metal 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 3: Cobalt standard solution prepared according to the instructions in paragraph 23 may be stored in a plastic bottle (paragraph 31) for a period of one year without deterioration.

WARNING - Cobalt and cobalt compounds have been assigned various risk phrases in the Approved Supply List¹⁴ for the *Chemicals (Hazard Information and Packaging for Supply) Regulations 1994*¹⁵ (the 'CHIP 2' Regulations). Care should be taken when working with cobalt metal and solutions containing cobalt.

Laboratory detergent solution

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

SAMPLING EQUIPMENT

Samplers for collection of the inhalable fraction of the airborne particles

25 Samplers, with protective covers, for collection of the inhalable fraction of the airborne particles, as defined in European Standard EN 481.¹⁶ Inhalable dust samplers suitable for personal sampling are described in MDHS 14.¹⁷

Note 4: 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. 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 5: 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

26 Filters, of a diameter suitable for use in the samplers (paragraph 25), with a retentivity of not less than 99.5% for particles with a $0.3 \text{ } \mu\text{m}$ diffusion diameter. The use of filters that are soluble using the sample preparation procedure described is recommended, and mixed cellulose ester filters of $0.8 \text{ } \mu\text{m}$ mean pore diameter are considered to be most suitable.

The cobalt content shall be less than $0.01 \text{ } \mu\text{g}$ per filter.

Note 6: 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 (paragraph 57).

Sampling pumps

27 Sampling pumps, complying with the provisions of draft European Standard prEN 1232,¹⁸ with an adjustable flow rate, incorporating a flowmeter or a flow fault indicator, capable of maintaining the selected flow rate (see paragraph 36) to within $\pm 5\%$ of the nominal value throughout the sampling period (see paragraph 37), 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

28 Flowmeter, portable, capable of measuring the appropriate flow rate (see paragraph 36) to within $\pm 1\%$, and calibrated against a primary standard.

Note 7: Flowmeters incorporated in sampling pumps are not suitable for accurate measurement of the flow rate. However, they can be useful for monitoring the

performance of samplers (see paragraph 41), provided they have adequate sensitivity.

Ancillary equipment

29 Flexible plastic tubing, of a diameter suitable for ensuring a leakproof fit, to connect the sampler to the pump; a belt to which the 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, to transport filters to the laboratory, if transport in the samplers is impracticable.

LABORATORY APPARATUS

Glassware, made of borosilicate glass

30 A selection of laboratory glassware: including beakers; watch glasses; measuring cylinders; and one-mark volumetric flasks, class A, complying with the requirements of BS 1792.¹⁹

Note 8: It is recommended that a set of glassware is reserved for the analysis of cobalt by this method (see paragraph 52).

Polypropylene bottle

31 A polypropylene bottle, with leakproof screw cap, for storage of stock standard solution (paragraph 23) cleaned before use by soaking in 1 + 9 nitric acid (paragraph 20) 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.

Hotplate

32 A thermostatically controlled hotplate, capable of maintaining the required surface temperatures.

Disposable gloves

33 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

34 A set of adjustable micropipettes, complying with the requirements of BS 7653-1 to BS 7653-4,²⁰⁻²³ for the preparation of solutions for calibration of the atomic absorption spectrometer (paragraph 58) and dilution of sample solutions (paragraph 64). 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.

Atomic absorption spectrometer

35 An atomic absorption spectrometer, fitted with an air-acetylene burner, supplied with compressed air and acetylene, and equipped with a cobalt hollow cathode lamp.

SAMPLING

Sampling procedure

36 Use the samplers (paragraph 25) at the design flow rate, so that they exhibit the required collection characteristics. Refer to the manufacturer's instructions.

37 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 42.¹¹)

Preparation of sampling equipment

Perform the following in an area where cobalt contamination is known to be low, and wear disposable gloves (paragraph 33) to prevent the possibility of contamination.

38 Clean the samplers (paragraph 25) before use. Disassemble the samplers, soak in laboratory detergent solution (paragraph 24), rinse thoroughly with water (paragraph 17), wipe with absorptive tissue and allow to dry thoroughly before reassembly. Alternatively, use a laboratory washing machine.

39 Load the filters (paragraph 26) into clean, dry samplers (see paragraph 38) using clean, flat-tipped tweezers (paragraph 29). Connect each loaded sampler to a sampling pump (paragraph 27) using plastic tubing (paragraph 29), ensuring that no leaks can occur. Switch on the pump, attach the calibrated flowmeter (paragraph 28) to the sampler so that it measures the flow through the sampler inlet orifice, and set the appropriate flow rate (see paragraph 36) with an accuracy of ±5%. Switch off the pump and seal the sampler with its protective cover to prevent contamination with cobalt during transport to the sampling position.

Note 9: It might be necessary to allow the pump to operate for an appropriate period to enable it to warm up and the flow rate to stabilise (refer to the manufacturer's recommendations). If this is the case, discard the used filter after the warm-up period and load a new one into the sampler for collection of the sample. Then attach the calibrated flowmeter again and readjust the flow rate to the appropriate value (see paragraph 36) with an accuracy of ±5%.

Collection of samples

40 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 29) 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.

41 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 28) 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 10: 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.

42 At the end of the sampling period (see paragraph 37), measure the flow rate with an accuracy of $\pm 5\%$ using the calibrated flowmeter (paragraph 28), 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.

43 Carefully record the sample identity and all relevant sampling data (see Appendix A). 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.

44 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 cobalt contamination is known to be low.

45 For samplers which collect the inhalable fraction of airborne particles on the filter (see note 4), remove the filter from each sampler using clean flat-tipped tweezers (paragraph 29), place in a labelled filter transport cassette (paragraph 29) and close with a lid.

46 For samplers which have an internal filter cassette (see note 4), remove the filter cassette from each sampler, fasten with the transport clip supplied by the manufacturer, and label appropriately.

47 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 4), and for samplers of the disposable cassette type, transport the samples to the laboratory in the samplers in which they were collected.

48 Transport the filter transport cassettes (see paragraph 45), sampler filter cassettes (see paragraph 46) or samplers (see paragraph 47) 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 33) during analysis to reduce the possibility of contamination and to protect the hands from corrosive and oxidising reagents.

Cleaning of glassware

49 Before use, clean all glassware (paragraph 30) to remove any residual grease or chemicals. Firstly soak overnight in laboratory detergent solution (paragraph 24) and then rinse thoroughly with water (paragraph 17). Alternatively, use a laboratory washing machine.

50 After initial cleaning (paragraph 49), clean all beakers used in the sample dissolution procedure (paragraphs 55 and 56) with hot nitric acid. Fill to one third capacity with concentrated nitric acid (paragraph 18), cover with a watch glass, heat to approximately 150°C on the hotplate (paragraph 32) in a fume cupboard for 1 hour, allow to cool, and then rinse thoroughly with water (paragraph 17).

51 After initial cleaning (paragraph 49), clean all glassware other than beakers used in the sample dissolution procedure by soaking in 1 + 9 nitric acid (paragraph 20) for at least 24 hours and then rinsing thoroughly with water (paragraph 17).

52 Glassware which has been previously subjected to the cleaning procedure described in paragraphs 49 to 51, and which has been reserved for determination of cobalt by this method, can be adequately cleaned by rinsing thoroughly with 1 + 9 nitric acid (paragraph 20) and then with water (paragraph 17).

Preparation of sample and blank solutions

53 Open the filter transport cassettes (see paragraph 45), sampler filter cassettes (see paragraph 46) or samplers (see paragraph 47) and transfer each filter into an individual, labelled 50 ml beaker using clean flat-tipped tweezers (paragraph 29). Follow the same procedure for the blank filters (paragraph 44).

54 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 4), wash any particulate material adhering to the internal surfaces into the beaker using a minimum volume of water (paragraph 17).

55 Add 5 ml of 1 + 1 nitric acid (paragraph 19) to each beaker, partially cover with a watch glass, and heat to approximately 150°C on a hotplate (paragraph 32) 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. If cobalt oxides are not

present, proceed from paragraph 57 without the addition of hydrochloric acid.

56 If cobalt oxides could be present, add 1 ml of concentrated hydrochloric acid (paragraph 21) to each beaker, cover with a watch glass, and heat to approximately 150°C on a hotplate (paragraph 32) in a fume cupboard for a further 15 minutes. Remove each beaker from the hotplate and allow to cool.

57 Carefully rinse the watch glass and the sides of each beaker with water (paragraph 17), and quantitatively transfer each solution to an individual, labelled 10 ml volumetric flask. If necessary, remove any undissolved particulate matter by filtering through a cellulose (paper) filter which has been pre-washed with 1 + 9 nitric acid (paragraph 20) and then with water (paragraph 17). Finally, dilute to the mark with water, stopper and mix thoroughly.

Analysis by flame atomic absorption spectrometry

Note 11: *Laboratory experiments⁸ have shown that flame atomic absorption measurements of cobalt are not affected significantly by variation in the nitric acid concentration within the range 1% to 25% (v/v). However, it is good laboratory practice to match sample and calibration solution matrices as far as is reasonably practicable.*

Preparation of calibration solutions

58 Prepare at least six calibration solutions to cover the range 0 $\mu\text{g ml}^{-1}$ to 2.5 $\mu\text{g ml}^{-1}$ of cobalt. Add 50 ml of water (paragraph 17) to separate, labelled 100 ml volumetric flasks. Carefully add 10 ml of concentrated nitric acid (paragraph 18) to each flask. If concentrated hydrochloric acid was used in the dissolution procedure (see paragraph 56), also add 10 ml of concentrated hydrochloric acid (paragraph 21). Accurately pipette the appropriate volume of stock standard cobalt solution (paragraph 22 or 23) into each flask and swirl to mix. Allow to cool, dilute to the mark with water (paragraph 17), stopper and mix thoroughly. Prepare these solutions fresh weekly.

Atomic absorption measurements

59 Set up the atomic absorption spectrometer (paragraph 35) to determine cobalt at a wavelength of 240.7 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 0.05 $\mu\text{g ml}^{-1}$ of cobalt.

60 Adjust the spectrometer zero while aspirating the 0 $\mu\text{g ml}^{-1}$ calibration solution (paragraph 58). Repeat this procedure regularly throughout the analysis and readjust the zero if the baseline drifts.

61 Aspirate the calibration solutions (paragraph 58) 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 cobalt 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 cobalt concentration.

62 Aspirate the sample and blank solutions (paragraph 57) 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 cobalt in the sample and blank solutions and obtain a direct read-out of the results in $\mu\text{g ml}^{-1}$ of cobalt. For instruments without this capability, determine the concentration of cobalt in $\mu\text{g ml}^{-1}$ from the calibration graph (paragraph 61).

63 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 and recalibrate the spectrometer as described in paragraph 61; and in either case reanalyse the solutions which were analysed during the period in which the sensitivity change occurred.

64 If high concentrations of cobalt 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 nitric acid concentration is 1 + 9. The final hydrochloric acid concentration should also be 1 + 9 if this acid was used in the sample dissolution procedure (see paragraph 56). Record the dilution factor.

65 Calculate the mean cobalt concentration of the blank solutions.

QUALITY CONTROL MEASURES

66 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 71.²⁴

67 If cobalt 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 cobalt 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 $\pm 2\text{SD}$ and $\pm 3\text{SD}$ 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 71.²⁴ Take care to ensure that the quality control filters are stored under conditions which ensure maximum stability.

68 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 71.²⁴ However, at present the WASP scheme does not encompass cobalt.

CALCULATIONS

Volume of air sample

69 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 cobalt in air

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

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

where $\rho(\text{Co})_0$ is the mean concentration, in $\mu\text{g ml}^{-1}$, of cobalt in the blank solutions (see paragraph 65);

$\rho(\text{Co})_1$ is the concentration, in $\mu\text{g ml}^{-1}$, of cobalt in the sample solution (see paragraph 62);

V is the volume, in litres, of the air sample (see paragraph 69);

V_0 is the volume, in ml, of the blank solutions, ie 10 ml (see paragraph 57);

V_1 is the volume, in ml, of the sample solution, ie 10 ml (see paragraph 57);

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

DF_1 is the dilution factor for the sample solutions (see paragraph 64).

TEST REPORT

71 Appendix A gives recommendations for information to be included in the test report.

APPENDIX A 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 cobalt found in the air sample, in milligrams per cubic metre;

(k) the name of the analyst;

(l) the date of the analysis.

REFERENCES

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21 British Standards Institution *Piston and/or plunger operated volumetric apparatus (POVA) Part 2: Methods of operation* BS 7653-2 BSI 1993

22 British Standards Institution *Piston and/or plunger operated volumetric apparatus (POVA) Part 3: Methods of test* BS 7653-3 BSI 1993

23 British Standards Institution *Piston and/or plunger operated volumetric apparatus (POVA) Part 4: Specification for conditions of test, safety and supply* BS 7653-4 BSI 1993

24 Health and Safety Executive, Methods for the Determination of Hazardous Substances *Analytical quality in workplace air monitoring* MDHS 71 HSE Books 1991 ISBN 0 11 885976 5

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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