

MDHS

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



46/2

Platinum metal and soluble platinum compounds in air

Laboratory method using electrothermal
atomic absorption spectrometry or
inductively coupled plasma-mass
spectrometry

December 1996

INTRODUCTION

Note 1: This method updates and replaces MDHS 46.¹ The principal changes which have been made are (i) to recommend the use of filters that are soluble using the dissolution technique described for platinum metal, and (ii) to describe the use of inductively coupled plasma-mass spectrometry for the analysis of sample solutions with a low platinum concentration.

Occurrence, properties and uses

1 Occurrence, properties and uses of platinum metal and soluble platinum compounds are fully covered in HSE Guidance Note EH 65/24.²

Effects on health

2 The health effects of platinum metal and soluble platinum compounds are reviewed in HSE Guidance Note EH 65/24.²

Health and safety precautions

3 A high standard of control is required when handling soluble platinum compounds as they are potent skin and respiratory sensitisers. Appropriate protective clothing and approved eye protection should be worn to prevent contact with these compounds. Exposure by inhalation to dust, spray or mist should be controlled by local exhaust ventilation. Respiratory protective equipment might also be needed when local exhaust ventilation is inadequate.

Exposure limits

4 The Health and Safety Commission has approved an occupational exposure standard, 8-hour time-weighted average reference period, for platinum metal:

Platinum metal 5 mg m⁻³

This limit is published in Table 2 of HSE Guidance Note EH 40.³

5 A maximum exposure limit, 8-hour time-weighted average reference period, is proposed for halogeno-platinum compounds:

Halogeno-platinum compounds (as Pt) 0.002 mg m⁻³

This limit will be published in Schedule 1 of the COSHH (Amendment) Regulations 1996⁴ and in Table 1 of HSE Guidance Note EH 40,³ and will come into effect in January 1997.

Note 2: Halogeno-platinum compounds are co-ordination compounds in which platinum is directly co-ordinated to one or more halide (ie fluoride, chloride, bromide or iodide) ions. For substances which contain platinum and halide ions, but in which the halogen is not directly linked by a bond to the platinum, the occupational exposure standard for soluble platinum compounds is applicable (see paragraph 6).

6 An occupational exposure standard, 8-hour time-weighted average reference period, is proposed for other soluble platinum compounds:

Platinum compounds, soluble, except
halogeno-platinum compounds (as Pt) 0.002 mg m⁻³

This limit will be published in Table 2 of HSE Guidance Note EH 40,³ and it will also come into effect in January 1997.

Analytical methods

7 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.

8 This method has been validated⁵ 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 482.⁶ If an alternative method is used it should also meet these performance requirements.

Requirements of the COSHH Regulations

9 The Control of Substances Hazardous to Health (COSHH) Regulations⁷ 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.⁸

SCOPE

Applicability

10 This MDHS describes methods for determination of the concentration of platinum metal and soluble platinum compounds in workplace air using electrothermal atomic absorption spectrometry or inductively coupled plasma-mass spectrometry. The majority of insoluble platinum compounds in industrial use or occurring in workplace air are also determined by the method for platinum metal.

11 The method described does not distinguish between halogeno-platinates and other soluble platinum compounds. Therefore when there is mixed exposure to halogeno-platinates and other soluble platinum compounds, the convention is that all platinum measured is assumed to derive from halogeno-platinates, and control to the requirements of the maximum exposure limit for halogeno-platinates is necessary.

12 The method for soluble platinum compounds has also been shown⁵ to be suitable for use with sampling times in the range 30 minutes to 8 hours for analysis by inductively coupled plasma-mass spectrometry; and for sampling times in the range 4 hours to 8 hours for analysis by electrothermal atomic absorption spectrometry. The method for platinum metal is suitable for use with sampling times in the range 30 minutes to 8 hours using either analytical technique.

Note 3: *HSE Guidance Note EH 42⁹ 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

0.07 M hydrochloric acid leach procedure for soluble platinum compounds

13 The effectiveness of the 0.07 M hydrochloric acid leach procedure for soluble platinum compounds was not tested (see note 4).

Note 4: *The 0.07 M hydrochloric acid leach procedure used in the previous version of MDHS 46¹ has been retained for continuity. It has its origins in an earlier method for soluble lead, which uses 0.07 M hydrochloric acid to simulate stomach acid. This approach was devised because inhaled particles that deposit in the upper respiratory tract are transferred to the digestive tract by ciliary action. Any substance that is soluble in stomach acid is therefore likely to be absorbed. Although this is a reasonable way to look at things for a systemically toxic substance, it is not really appropriate if the principal cause for concern is respiratory sensitisation, as is the case for halogeno-platinates. However, in the microgram amounts collected in air samples, soluble platinum compounds should be no more or no less soluble in 0.07 M hydrochloric acid than in water, so it was concluded that it was unnecessary to modify or test the sample dissolution method in revising MDHS 46.*

Aqua regia method for platinum metal

14 The effectiveness of the 50% (v/v) aqua regia dissolution procedure described in MDHS 46 was tested⁵ on a commercially available platinum metal powder of particle size 0.27 µm to 0.47 µm and was found to be fully effective.

Detection limits

15 The qualitative and quantitative detection limits for platinum, defined as three times and ten times the standard deviation of a blank determination, have been determined⁵ to be 3.6 ng ml⁻¹ and 12 ng ml⁻¹ for electrothermal atomic absorption spectrometry; and 0.003 ng ml⁻¹ and 0.010 ng ml⁻¹ for inductively coupled plasma-mass spectrometry. For an air sample volume of 30 litres and a sample solution volume of 10 ml this corresponds to platinum in air concentrations of 0.001 mg m⁻³ and 0.004 mg m⁻³ for electrothermal atomic absorption spectrometry; and 0.001 µg m⁻³ and 0.003 µg m⁻³ for inductively coupled plasma-mass spectrometry.

Overall uncertainty

16 Laboratory experiments⁵ indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 80 spiked filters in the range 0.096 µg to 3.84 µg of platinum was determined to be 102.3% using electrothermal atomic absorption spectrometry; and the mean analytical recovery for 110 spiked filters in the range 0.012 µg to 3.84 µg of platinum was determined to be 100.3% using inductively coupled plasma-mass spectrometry.

17 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), has been determined⁵ to be less than 17% for samples in the range 0.096 µg to 0.96 µg and less than 7% for samples in the range 0.48 µg to 3.84 µg using electrothermal atomic absorption spectrometry; and less than 4% for samples in the range 0.012 µg to 3.84 µg using inductively coupled plasma-mass spectrometry.

18 The overall uncertainty of the method, as defined by CEN,⁶ has been estimated⁵ assuming that the flow rate is controlled to within ±5% of the nominal value, that the coefficient of variation that arises from inter-specimen sampler variability, CV (inter), is negligible and that the sampler bias is less than ±10%. It was found to be less than 46% for samples in the range 0.096 µg to 0.96 µg and less than 29% for samples in the range 0.48 µg to 3.84 µg using electrothermal atomic absorption spectrometry; and less than 24% for samples in the range 0.012 µg to 3.84 µg using inductively coupled plasma-mass spectrometry. The overall uncertainty of the inductively coupled plasma-mass spectrometry method is therefore within the specifications prescribed by CEN⁶ 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. The electrothermal atomic absorption spectrometry method only meets the CEN specifications when the sampling time is between 4 hours and 8 hours.

Interferences

19 Electrothermal atomic absorption spectrometry is performed at a wavelength of 265.9 nm with a solid pyrolytic graphite platform mounted in a pyrolytically-coated graphite tube. No interferences specific to the determination of platinum are documented for electrothermal atomic absorption spectrometry.

20 For analysis by inductively coupled plasma-mass spectrometry, the recommended and most abundant isotope of platinum is mass 195. There are no isotopes of other metals occurring at this mass, and the only documented potential interferent is ¹⁷⁹hafnium oxide.

PRINCIPLE

21 A measured volume of air is drawn through a filter mounted in an inhalable dust sampler.

22 If soluble platinum compounds are to be determined, the filter and collected sample are treated with 5 ml of

0.07 M hydrochloric acid and agitated by mechanical shaking or using an ultrasonic bath. The leach solution is then filtered under suction through a mixed cellulose ester filter of 0.8 µm mean pore diameter and diluted to 10 ml. The resultant solution is analysed by either electrothermal atomic absorption spectrometry or inductively coupled plasma-mass spectrometry. If platinum metal is also to be determined, the secondary filter used for filtration of the leach solution is kept for further treatment.

23 If platinum metal is to be determined, the sample filter and the secondary filter used for filtration of the leach solution (if applicable) are placed in a 50 ml beaker and treated with 10 ml of 50% (v/v) aqua regia. The beaker is heated on a hotplate to dissolve the filters, and the resultant solution is then evaporated to dryness. The residue is redissolved in 2 ml of concentrated hydrochloric acid and evaporated to dryness twice more. Finally, the residue is redissolved in 0.07 M hydrochloric acid and analysed for platinum by either electrothermal atomic absorption spectrometry or inductively coupled plasma-mass spectrometry.

REAGENTS

24 During the analysis, use only reagents of recognised analytical grade. Use only distilled or de-ionised water, or water of equal purity (paragraph 25). Do not pipette by mouth.

Water

25 Water complying with the requirements of BS 3978¹⁰ grade 2 water (electrical conductivity less than 0.1 mS m⁻¹ and resistivity greater than 0.01 MΩ.m at 25°C).

Hydrochloric acid (HCl), concentrated, ρ about 1.18 g ml⁻¹, 35% (m/m) to 38% (m/m)

26 The platinum concentration of the acid shall be less than 1.0 ng 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.

Hydrochloric acid (HCl), 0.07 M

27 Carefully add 5.8 ml of concentrated hydrochloric acid (paragraph 26) to 500 ml of water (paragraph 25) in a 1000 ml volumetric flask. Dilute to the mark with water and mix thoroughly.

Hydrochloric acid (HCl), diluted 1 + 1

28 Carefully add 500 ml of concentrated hydrochloric acid (paragraph 26) to 450 ml of water (paragraph 25) 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 (HNO₃), concentrated, ρ about 1.42 g ml⁻¹, 69% (m/m) to 71% (m/m)

29 The platinum concentration of the acid shall be less than 1.0 ng 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 + 9

30 Add approximately 800 ml of water (paragraph 25) to a 1 litre volumetric flask. Carefully add 100 ml of concentrated nitric acid (paragraph 29) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

Aqua regia, 50% (v/v)

31 Add approximately 400 ml of water (paragraph 25) to a 1 litre volumetric flask. Carefully add 125 ml of concentrated nitric acid (paragraph 29) to the flask and swirl to mix. Carefully add 375 ml of concentrated hydrochloric acid (paragraph 26) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

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

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

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

33 Accurately weigh 0.1000 g of platinum metal, 99.9% Pt (m/m), into a 50 ml beaker. Add a minimum volume of 50% (v/v) aqua regia (paragraph 31), heat on a hotplate (paragraph 45) in a fume cupboard and evaporate just to dryness. Add 5 ml of concentrated hydrochloric acid (paragraph 26) and again evaporate to dryness. Dissolve the residue in 20 ml 1 + 1 hydrochloric acid (paragraph 28), remove the beaker from the hotplate, allow to cool, and quantitatively transfer the solution into a 100 ml volumetric flask. Finally, dilute to the mark with water (paragraph 25), stopper and mix thoroughly.

Note 5: Platinum standard solution prepared according to the instructions in paragraph 33 may be stored in a plastic bottle (paragraph 42) for a period of one year without deterioration.

WARNING - Soluble platinum compounds are potent in producing skin and respiratory sensitisation. Great care should be taken when working with platinum compounds and solutions containing platinum.

Working standard platinum solution, 100 µg ml⁻¹ of platinum

34 Accurately pipette 10 ml of stock platinum standard solution (paragraph 32 or 33) into a 100 ml volumetric flask. Carefully add 10 ml of concentrated hydrochloric acid (paragraph 26), dilute to the mark with water (paragraph 25), stopper and mix thoroughly. Prepare this solution fresh weekly.

Laboratory detergent solution

35 A laboratory grade detergent suitable for cleaning of samplers and laboratory glassware, diluted with water (paragraph 25) according to the manufacturer's instructions.

SAMPLING EQUIPMENT

Samplers for collection of the inhalable fraction of the airborne particles

36 Samplers, with protective covers, for collection of the inhalable fraction of the airborne particles, as defined in European Standard EN 481.¹¹ Inhalable dust samplers suitable for personal sampling are described in MDHS 14/2.¹²

Note 6: 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 7: 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

37 Filters, of a diameter suitable for use in the samplers (paragraph 36), 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 procedure described is recommended, and mixed cellulose ester filters of 0.8 µm mean pore diameter are considered to be most suitable.

Note 8: 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 76).

Sampling pumps

38 Sampling pumps, complying with the provisions of draft European Standard prEN1232,¹³ with an adjustable flow rate, incorporating a flowmeter or a flow fault indicator, capable of maintaining the selected flow rate (see paragraph 54) to within $\pm 5\%$ of the nominal value throughout the sampling period (see paragraph 55), 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

39 Flowmeter, portable, capable of measuring the appropriate flow rate (see paragraph 54) to within $\pm 1\%$, and calibrated against a primary standard.

Note 9: *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 59), provided they have adequate sensitivity.*

Ancillary equipment

40 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

41 A selection of laboratory glassware, including: beakers; watch glasses; measuring cylinders; and one-mark volumetric flasks, class A, complying with the requirements of BS 1792.¹⁴

Note 10: *It is recommended that a set of glassware is reserved for the analysis of platinum by this method (see paragraph 70).*

Polypropylene bottle

42 A polypropylene bottle, with leakproof screw cap, for storage of stock standard solution (paragraph 33), cleaned before use by soaking in 1 + 9 nitric acid (paragraph 30) for at least 24 hours and then rinsing thoroughly with water (paragraph 25). A bottle made of an alternative plastic may be used provided that it is suitable for the intended use.

Figure 1 Suction filtration apparatus

Disposable beakers, polypropylene

43 Disposable plastic beakers, as an alternative to 50 ml glass beakers, for use in the 0.07 M hydrochloric acid leach procedure for soluble platinum compounds.

Suction filtration apparatus

44 Suction filtration apparatus, for filtration of the 0.07 M hydrochloric acid leach solution used in the sample dissolution procedure for soluble platinum compounds (paragraphs 71 to 74). 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 Fig 1). Mixed cellulose ester membrane filters, of a diameter suitable for use with the apparatus, are also required.

Note 11: *Alternative suction filtration apparatus is available which permits simultaneous vacuum filtration of multiple samples.*

Hotplate

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

Disposable gloves

46 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.

Filter paper

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

Piston operated volumetric apparatus

48 A set of adjustable micropipettes, complying with the requirements of BS 7653-1 to BS 7653-4,¹⁵⁻¹⁸ for the preparation of solutions for calibration of the atomic absorption spectrometer (paragraph 77), calibration of the inductively coupled plasma-mass spectrometer (paragraph 86) and dilution of samples (paragraphs 84 and 91). 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

49 An atomic absorption spectrometer equipped with a platinum hollow cathode lamp.

Electrothermal atomiser

50 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 12: *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 could be different from that described in paragraphs 15 to 18.*

Inductively coupled plasma-mass spectrometer

51 An inductively coupled plasma-mass spectrometer, normally equipped with a quadrupole mass spectrometer, and an autosampler.

Disposable autosampler cups

52 Disposable polystyrene autosampler cups for use with the electrothermal atomiser autosampler. Soak in 1 + 9 nitric acid (paragraph 30) before use.

Note 13: *Disposable polystyrene autosampler cups are also useful for containing solutions to be pipetted in microlitre quantities.*

Disposable autosampler tubes

53 Disposable polystyrene autosampler tubes for use with the inductively coupled plasma-mass spectrometer autosampler.

SAMPLING

Sampling procedure

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

55 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 42.⁹)

Preparation of sampling equipment

56 Clean the samplers (paragraph 36) before use. Disassemble the samplers, soak in laboratory detergent solution (paragraph 35), rinse thoroughly with water (paragraph 25), wipe with absorptive tissue and allow to dry thoroughly before reassembly. Alternatively, use a laboratory washing machine.

Perform the following in an area where platinum contamination is known to be low, and wear disposable gloves (paragraph 46) to prevent the possibility of contamination.

57 Load the filters (paragraph 37) into clean, dry samplers (see paragraph 56) using clean, flat-tipped tweezers (paragraph 40). Connect each loaded sampler to a sampling pump (paragraph 38) using plastic tubing (paragraph 40), ensuring that no leaks can occur. Switch on the pump, attach the calibrated flowmeter (paragraph 39) to the sampler so that it measures the flow through the sampler inlet orifice, and set the appropriate flow rate (see paragraph 54) with an accuracy of $\pm 5\%$. Switch off the pump and seal the sampler with its protective cover to prevent contamination with platinum during transport to the sampling position.

Note 14: *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 54) with an accuracy of $\pm 5\%$.*

Collection of samples

58 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 40) 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.

59 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 39) 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 15: 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.

60 At the end of the sampling period (see paragraph 55), measure the flow rate with an accuracy of $\pm 5\%$ using the calibrated flowmeter (paragraph 39), 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.

61 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.

62 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 platinum contamination is known to be low.

63 For samplers which collect the inhalable fraction of airborne particles on the filter (see note 6), remove the filter from each sampler using clean flat-tipped tweezers (paragraph 40), place in a labelled filter transport cassette (paragraph 40) and close with a lid.

64 For samplers which have an internal filter cassette (see note 6), remove the filter cassette from each sampler, fasten with the transport clip supplied by the manufacturer, and label appropriately.

65 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 6), and for samplers of the disposable cassette type, transport the samples to the laboratory in

the samplers in which they were collected.

66 Transport the filter transport cassettes (see paragraph 63), sampler filter cassettes (see paragraph 64) or samplers (see paragraph 65) 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 46) during analysis to protect the hands from corrosive and oxidising reagents.

Cleaning of glassware

67 Before use, clean all glassware (paragraph 41) to remove any residual grease or chemicals. Firstly soak overnight in laboratory detergent solution (paragraph 35) and then rinse thoroughly with water (paragraph 25). Alternatively, use a laboratory washing machine.

68 After initial cleaning (paragraph 67), clean all beakers used in the sample dissolution procedure (paragraphs 71 to 76) with hot nitric acid. Fill to one third capacity with concentrated nitric acid (paragraph 29), cover with a watch glass, heat to approximately 150°C on the hotplate (paragraph 45) in a fume cupboard for 1 hour, allow to cool, and then rinse thoroughly with water (paragraph 25).

69 After initial cleaning (paragraph 67), clean all glassware other than beakers used in the sample dissolution procedure by soaking in 1 + 9 nitric acid (paragraph 30) for at least 24 hours and then rinsing thoroughly with water (paragraph 25).

70 Glassware which has been previously subjected to the cleaning procedure described in paragraphs 67 to 69, and which has been reserved for determination of platinum by this method, can be adequately cleaned by rinsing thoroughly with 1 + 9 nitric acid (paragraph 30) and then with water (paragraph 25).

Preparation of sample and blank solutions

71 Open the filter transport cassettes (see paragraph 63), sampler filter cassettes (see paragraph 64) or samplers (see paragraph 65) and transfer each filter into an individual, labelled 50 ml beaker (paragraph 41) or a disposable plastic beaker (paragraph 43) using clean flat-tipped tweezers (paragraph 40). Follow the same procedure for the blank filters (paragraph 62).

72 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 6), wash any particulate material adhering to the internal surfaces into the beaker using an aliquot of the 5 ml of 0.07 M hydrochloric acid used to leach the sample filters (see paragraph 73).

73 Add 5 ml of 0.07 M hydrochloric acid (paragraph 27) to each beaker, cover with a watch glass, place on the

orbital mixer or other mechanical shaking device and agitate for 30 minutes to dissolve the soluble platinum species. Alternatively, use an ultrasonic bath. Ensure that the sample filters are fully immersed throughout the leach period.

74 Filter each leach solution through a mixed cellulose ester membrane filter using suction filtration apparatus (paragraph 44), collecting the filtrate in an individual, labelled test tube (see Fig 1). Transfer the sample filter to the filtration apparatus, rinse the sample filter and beaker with three 1 ml aliquots of 0.07 M hydrochloric acid, 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 0.07 M hydrochloric acid. Finally, dilute to the mark with 0.07 M hydrochloric acid, stopper and mix thoroughly.

75 If applicable (see paragraph 23), retain the sample filter and the secondary filter (the membrane filter used for filtration of the leach solution) for subsequent analysis for platinum metals.

76 Using flat-tipped tweezers transfer the sample filter and the secondary filter used for filtration of the leach solution (if applicable) into a 50 ml low form beaker, add 10 ml of 50% (v/v) aqua regia (paragraph 31) and cover with a watch glass. Place on a hotplate (paragraph 45), heat to dissolve the filters and then evaporate just to dryness. Redissolve in 2 ml of concentrated hydrochloric acid (paragraph 26) and repeat the evaporation twice. Allow to cool, add 5 ml 0.07 M hydrochloric acid (paragraph 27), and heat to dissolve the residue. Carefully rinse the watch glass and the sides of each beaker with 0.07 M hydrochloric acid (paragraph 27) 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 47) which has been pre-washed with 0.07 M hydrochloric acid. Finally dilute to the mark with 0.07 M hydrochloric acid, stopper and mix thoroughly.

Analysis by electrothermal atomic absorption spectrometry

Note 16: *It is essential that strict standards of cleanliness are observed to avoid contamination of labware 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 67 to 70, and that autosampler cups (paragraph 52) are stored in 1 + 9 nitric acid (paragraph 30) until required.*

Preparation of working calibration solutions

77 Prepare a working calibration solution at a concentration of 500 ng ml⁻¹ of platinum. Accurately pipette 500 µl of working standard platinum solution (paragraph 34) into a 100 ml volumetric flask and dilute to the mark with 0.07 M hydrochloric acid (paragraph 27), stopper and mix thoroughly. Prepare this solution fresh weekly.

78 Prepare a working calibration blank solution following the procedure in paragraph 77, but omitting the 500 µl of working standard platinum solution.

Atomic absorption measurements

79 Set up the atomic absorption spectrometer (paragraph 49) and electrothermal atomiser (paragraph 50) to determine platinum at a wavelength of 265.9 nm using background correction. Follow the manufacturer's recommendations for specific operating parameters.

Note 17: *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,⁵ and the operating parameters used are given in Appendix B. The characteristic mass for platinum, defined as the number of picograms required to give 0.0044 absorbance-seconds, was determined to be 100 pg for this analytical system. This is equivalent to a sample solution concentration of 5 ng ml⁻¹ of platinum for a 20 µl sample solution injection volume.*

80 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 500 ng ml⁻¹ using the working calibration solution (paragraph 77) and the working calibration blank solution (paragraph 78). See Table 2 for typical autosampler injection volumes.

Note 18: *The procedure described above may be varied to accommodate the use of electrothermal atomisers of alternative design (see note 12).*

Note 19: *Calibration and test solutions may be prepared in volumetric flasks as an alternative to preparation in situ using the autosampler.*

81 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.

82 Place the working calibration solution (paragraph 77), the working calibration blank solution (paragraph 78), and the sample and blank solutions (paragraphs 74 and 76) in separate acid-washed autosampler cups (paragraph 52) 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 platinum.

83 If significant baseline drift is observed during the course of the analysis, or if the sensitivity changes by more than ±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 82. In either case reanalyse the solutions which were analysed during the period in which the sensitivity change occurred.

84 If concentrations of platinum 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 hydrochloric acid concentration is 0.07 M. Record the dilution factor.

85 Calculate the mean platinum concentration of the blank solutions.

Analysis by inductively coupled plasma-mass spectrometry

Note 20: *It is essential that strict standards of cleanliness are observed to avoid contamination of labware when carrying out inductively coupled plasma-mass spectrometry, since the technique exhibits extremely low detection limits. Ensure that all glassware is cleaned thoroughly before use in accordance with paragraphs 67 to 70.*

Preparation of calibration solutions

86 Prepare at least six calibration solutions to cover the range 0 ng ml⁻¹ to 500 ng ml⁻¹ of platinum. Accurately pipette the appropriate volumes of working standard platinum solution (paragraph 34) into separate, labelled 100 ml volumetric flasks. Dilute to the mark with 0.07 M hydrochloric acid (paragraph 27), stopper and mix thoroughly. Prepare these solutions fresh daily.

87 Set up the inductively coupled plasma-mass spectrometer (paragraph 51) to determine platinum at a mass of 195 (other masses may also be used). Follow the manufacturer's recommendations for specific operating parameters.

Note 21: *The operating parameters for inductively coupled plasma-mass spectrometry vary considerably between different instruments. A Perkin-Elmer Elan 5000 inductively coupled plasma-mass spectrometer was used in the validation of this method,⁵ and the operating parameters used are given in Appendix C.*

88 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 instrumental drift and sensitivity change respectively.

89 Place the calibration solutions (paragraph 86) and the sample and blank solutions (paragraphs 74 and 76) in separate acid-washed autosampler tubes (paragraph 53) and position as appropriate in the autosampler tray. Analyse the calibration, sample and blank solutions, and use the instrument's computer software to generate a

calibration and obtain a direct read-out of sample and blank results in ng ml⁻¹ of platinum.

90 If significant instrumental drift is observed during the course of the analysis, take one of the following appropriate corrective measures: either use available computer software facilities to correct for the sensitivity change (reslope facility); or suspend analysis and recalibrate the spectrometer as described in paragraph 89. In either case reanalyse the solutions which were analysed during the period in which the sensitivity change occurred. An internal standard element may also be added to all solutions to correct for drift in sensitivity.

91 If concentrations of platinum 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 hydrochloric acid concentration is 0.07 M. Record the dilution factor.

92 Calculate the mean platinum concentration of the blank solutions.

QUALITY CONTROL MEASURES

93 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 71.¹⁹

94 If platinum 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 platinum 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 71.¹⁹

95 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 71.¹⁹ However, at present the WASP scheme does not encompass platinum.

CALCULATIONS

Volume of air sample

96 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 platinum in air

97 Calculate the concentration of platinum in air, $\rho(\text{Pt})$, in micrograms per cubic metre ($\mu\text{g m}^{-3}$), using the equation:

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

where

$\rho(\text{Pt})_0$ is the mean concentration, in ng ml^{-1} , of platinum in the blank solutions (see paragraphs 85 and 92);

$\rho(\text{Pt})_1$ is the concentration, in ng ml^{-1} , of platinum in the sample solution (see paragraphs 82 and 89);

V is the volume, in litres, of the air sample (see paragraph 96);

V_0 is the volume, in ml, of the blank solutions, ie 10 ml (see paragraphs 74 and 76);

V_1 is the volume, in ml, of the sample solution, ie 10 ml (see paragraphs 74 and 76);

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

DF_1 is the dilution factor for the sample solutions (see paragraphs 84 and 91).

TEST REPORT

98 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, including information about which sample dissolution method and which analytical technique were used, 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 platinum found in the air sample, in micrograms per cubic metre;
- (k) the name of the analyst;
- (l) the date of the analysis.

APPENDIX B TYPICAL OPERATING PARAMETERS FOR DETERMINATION OF PLATINUM 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 platinum 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	50	10	125	300	
2 Ash	25	5	1300	300	
3 Cool down	1	15	20	300	
4 Atomise	0	10	2700	0	*
5 Clean	1	5	2750	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	-
100 ng ml ⁻¹ calibration solution	4	16	-
200 ng ml ⁻¹ calibration solution	8	12	-
300 ng ml ⁻¹ calibration solution	12	8	-
400 ng ml ⁻¹ calibration solution	16	4	-
500 ng ml ⁻¹ calibration solution	20	-	-
Sample or blank solution	-	-	20
Sample solution dilution	-	(20 - x)	x

APPENDIX C TYPICAL OPERATING PARAMETERS FOR DETERMINATION OF PLATINUM BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

RF generator power	1000 watts
Plasma gas flow rate	15 l min ⁻¹
Auxiliary gas flow rate	1 l min ⁻¹
Nebuliser gas flow rate	0.95 l min ⁻¹
Dwell time	40 ms
Sweeps/reading	50
Replicate time	2000 ms
Scanning mode	Peak hop
Number of replicates	5
Points/spectral peak	1
Resolution	Normal
Atomic mass measured	195
Internal standard	Not used

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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 (tel: 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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