

# MDHS 99

## *Methods for the Determination of Hazardous Substances*

Health and Safety Laboratory

## Metals in air by ICP-AES

June 2006

### Scope

1. This MDHS describes a method for measuring exposure to a range of metal and metalloid elements in workplace air using inductively coupled plasma-atomic emission spectrometry (ICP-AES). The method is suitable for both long-term and short-term exposure measurements.

2. The measurement uncertainty has been estimated for the following elements: Antimony (Sb), Arsenic (As), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Indium (In), Iron (Fe), Lead (Pb), Manganese (Mn), Nickel (Ni), Selenium (Se), Tellurium (Te), Tin (Sn), Vanadium (V), Yttrium (Y), Zinc (Zn).

### Summary

3. A measured volume of air is drawn through a filter mounted in a sampler close to the breathing zone. The filter is treated with hydrochloric, nitric and hydrofluoric acids to dissolve the metals and the resultant solution analysed by ICP-AES.

### Prerequisites

4. Users of this method will need to be familiar with the content of MDHS 14.<sup>1</sup>

### Safety

5. People using this method should be familiar with normal laboratory practice and carry out a suitable risk assessment. This method does not address all the safety problems associated with its use. It is the user's responsibility to establish appropriate health and safety practices and to ensure compliance with regulatory requirements.

### Equipment

6. Samplers: Designed to collect the inhalable or respirable fraction of airborne particles. Samplers must comply with the requirements of BS EN 13205,<sup>2</sup> see MDHS 14 for further guidance.

7. Sampling medium: 0.8 µm mean pore diameter, mixed cellulose ester membrane filter, of suitable diameter for use in the selected samplers.

8. Sampling pumps: Complying with the requirements of BS EN 1232,<sup>3</sup> and compatible with the samplers used.

9. Portable flowmeter: Calibrated against a primary standard (see MDHS 14).

10. Flexible tubing: Suitable diameter to ensure a leakproof fit between the sampler and the pump.

11. Belt: To which the pump can conveniently be fixed.

12. Flat-tipped tweezers: For handling filters.

13. Filter cassettes: To transport samples to the laboratory.

14. Microwave digestion system: Designed for closed vessel sample digestion with power output regulation and temperature control within  $\pm 2$  °C.

15. Lined sample vessels: Internal volume of at least 50 ml, designed for microwave digestion at pressures up to 3000 kPa (435 psi) or greater with controlled pressure relief, and capable of withstanding an operating temperature of at least 180 °C.

16. Glassware: Selection of borosilicate laboratory glassware including beakers and class A volumetric flasks, complying with the requirements of BS EN ISO 1042.<sup>4</sup>

17. Plasticware: Selection of suitably calibrated laboratory plasticware including beakers, volumetric flasks and centrifuge tubes with suitable rack.

18. Pipettors and dispensers: Piston operated pipettors, complying and tested in accordance with BS EN ISO 8655.<sup>5</sup>

19. Pipette tips: Compatible with the pipettors.

20. Disposable gloves: Nitrile gloves have been found to be acceptable.

21. Inductively coupled plasma – atomic emission spectrometer: Axial or radial ICP-AES instrument with autosampler.

22. Autosampler tubes: Suitable for use with the autosampler.

## Reagents

23. Water: Complying with the requirements of BS EN ISO 3696<sup>6</sup> grade 2 water (electrical conductivity less than  $0.1 \text{ mS m}^{-1}$  and resistivity greater than  $0.01 \text{ M}\Omega\cdot\text{m}$  at  $25 \text{ }^\circ\text{C}$ ).

24. Nitric acid ( $\text{HNO}_3$ ): Concentrated,  $\rho$  about  $1.42 \text{ g ml}^{-1}$ , 69% (m/m) to 71% (m/m), recognised analytical grade.

25. Hydrochloric acid (HCl): Concentrated,  $\rho$  about  $1.18 \text{ g ml}^{-1}$ , 35% (m/m) to 36% (m/m), recognised analytical grade.

26. Hydrofluoric acid (HF): Concentrated,  $\rho$  about  $1.16 \text{ g ml}^{-1}$ , about 48% (m/m), recognised analytical grade.

## Solutions

27. Standard solutions: Commercially available standard solutions of the metals and metalloids of interest at suitable concentrations, typically  $1000 \text{ } \mu\text{g ml}^{-1}$  or  $10,000 \text{ } \mu\text{g ml}^{-1}$  single or multi-element. These should have a certified concentration, traceable to national standards and any solutions used must be carefully selected to ensure chemical compatibility, both with other standard solutions and the acid matrix in use.

## Sample collection

28. Connect each uniquely labelled sampler, loaded with the required sampling medium, to a sampling

pump using flexible tubing, ensuring that no leaks can occur. Remove the protective cover from each sampler, switch on the sampling pump, attach the calibrated flowmeter to the sampler so that it measures the flow through the sampler inlet orifice(s), and set the required volumetric flow rate. Switch off the sampling pump and seal the sampler with its protective cover to prevent contamination during transport to the sampling position.

29. Retain at least one unused loaded sampler from each batch of ten prepared for use as a blank; a minimum of three blanks are required in total for the analysis. Treat these as if to be used for sampling in respect of storage and transport to and from the sampling position, but draw no air through the filters.

30. Position the sampler in the worker's breathing zone, as close to the nose and mouth as is reasonably practicable, eg fasten it to the worker's lapel. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, eg to a belt around the waist, or place it in a convenient pocket.

31. Decide whether the nature of the process is likely to result in a significant difference between the actual exposure of the worker and the concentration of metals and metalloids measured by a sampler mounted on the lapel. For example, in the case of sampling a welder wearing a face shield, mount the sampler as close as possible to the worker's nose and mouth.

32. When ready to begin sampling, remove the protective cover from the sampler and switch on the sampling pump. Record the time and volumetric flow rate at the start of the sampling period, and if the sampling pump is fitted with an integral timer, check that this is reset to zero. Check periodically that the equipment is still working, and if necessary adjust the flow rate.

33. At the end of the sampling period, record the time and calculate the duration of the sampling period. Check the malfunction indicator and consider the sample to be invalid if there is evidence that the sampling pump was not operating properly throughout the sampling period. Measure the volumetric flow rate at the end of the sampling period using the calibrated flowmeter, and record the measured value. Reseal the sampler with its protective cover and disconnect it from the sampling pump.

34. Transport the filters to the laboratory for analysis either in the sampler or in labelled filter transport cassettes. Take particular care to prevent the collected sample from becoming dislodged from heavily loaded filters.

## Sample preparation

35. The method described is a microwave digestion using nitric, hydrochloric and hydrofluoric acids. Other methods may be more suitable, depending upon the equipment available and the analytes of interest. These are well documented in BS ISO 15202-2.<sup>7</sup>

36. Transfer each filter, including blanks, into the liner of a labelled sample vessel using clean flat-tipped forceps.

37. Add 3 ml of nitric acid, followed by 1 ml of hydrochloric acid and 1 ml of hydrofluoric acid. If airborne particles deposited on the internal surfaces of the filter cassette or sampler form part of the sample, use the nitric acid to carefully rinse the internal surfaces into the liner.

38. Seal the sample vessels and place them, evenly distributed, into the turntable of the microwave digestion system. Include a temperature or pressure control vessel containing the acids and a blank filter.

39. Program the microwave digestion system to reach an operating temperature of at least 180 °C in less than 10 minutes then hold the operating temperature for a further 15 minutes.

40. Once the program has finished, allow the vessels to cool, then carefully open each sample vessel in a fume cupboard.

41. Quantitatively transfer each solution to an individual, labelled 25 ml polypropylene volumetric flask or centrifuge tube, rinse the liner into the vessel and dilute to the mark with water. Seal the vessel and mix thoroughly to produce the test solution.

## Instrument conditions

### Axial or radial viewing of the plasma

42. If instruments with both axial and radial plasma are available, or if the instrument to be used is a dual-view instrument, decide which orientation is best suited to the measurement task.

### Sample introduction system

43. As the test solutions contain hydrofluoric acid it will be necessary to use a corrosion-resistant sample introduction system.

### Analytical wavelengths

44. Select one or more emission lines on which to

make measurements for each metal or metalloid of interest. The more sensitive lines will usually be most favourable, but avoid the use of wavelengths on which there is a direct spectral overlap. The wavelengths used to validate this method can be found in Table 1, Appendix A.

### Background correction

45. Ensure that background correction points are suitably positioned to correct the background shift created by the sample matrix in use.

### Plasma, auxiliary and nebuliser gas flows

46. Under normal circumstances, use the default gas flows recommended by the instrument manufacturer, as these should give compromise operating conditions that are best suited to multi-element analysis. However, if desired, the nebuliser gas flow may be optimised for specific applications.

### RF power

47. Under normal circumstances, use the default RF power recommended by the instrument manufacturer, as this will give compromise operating conditions that are best suited to multi-element analysis. However, if desired, the RF power may be optimised for specific applications.

### Viewing height (radial plasma only)

48. Under normal circumstances, use the default viewing height recommended by the instrument manufacturer, as this will give compromise operating conditions that are best suited to multi-element analysis. However, if desired, the viewing height may be optimised for specific applications.

### Sample introduction parameters

49. Use the sample uptake rate recommended by the manufacturer of the nebuliser, or optimise its performance to achieve a suitable compromise between signal intensity and sample uptake rate.

50. Use a suitable wash-out time, wash-out rate and read delay. Carry out tests to ensure that there is no significant carry-over of analyte between measurements.

## Calibration

51. Prepare working standard solutions to include all the metals and metalloids of interest at suitable concentrations, typically 0-50 mg l<sup>-1</sup> for radial viewing.

For example, to prepare standards at concentrations of 0, 1, 2, 10, 20 and 50 mg l<sup>-1</sup> add approximately 25 ml water, 16 ml concentrated nitric acid and 4 ml concentrated hydrochloric acid to each of six labelled, 100 ml volumetric flasks. Then, in turn, accurately pipette 0, 0.1, 0.2, 1, 2 and 5 ml of 1000 mg l<sup>-1</sup> stock solution. Dilute almost to the mark with water, stopper and swirl to mix. Dilute to the mark with water, stopper and mix thoroughly. Store in a polypropylene bottle for a maximum of one month.

Note: The acid matrix of the calibration solutions should match that of the test solutions. However, as the test solutions contain hydrofluoric acid, an equal concentration of nitric acid should be substituted when preparing the calibration solutions. It is safer, and enables the calibration solutions to be prepared in volumetric glassware. Ensure that any solutions used are compatible with each other and also with the acid matrix in use.

52. Carry out performance checks on a daily basis to verify that the ICP-AES instrument is operating to an acceptable standard.

53. Analyse the calibration solutions in increasing order of concentration. Use the instrument software to generate a calibration function for the analytes of interest. Repeat the calibration if the correlation coefficient for any of the metals and metalloids of interest, R<sup>2</sup>, is not > 0.999.

## Sample analysis

54. Aspirate the laboratory blank and sample test solutions into the plasma and record emission measurements for each solution. Use the stored calibration function to determine the concentration of the analytes of interest.

55. Analyse a mid-range calibration solution after the initial calibration and then after every ten test solutions. If the measured concentration of an analyte of interest has changed by more than ± 5% either use the instrument software to correct for the sensitivity change (reslope facility), or suspend analysis and recalibrate the spectrometer. In either case, reanalyse the test solutions that were analysed during the period in which the sensitivity change occurred, or if this is not possible, reprocess the data to take account of the sensitivity change.

56. Analyse quality control solutions (see paragraphs 63 and 64) and if the measured concentration of an analyte of interest is more than ± 5% from the expected value, suspend analysis and recalibrate the spectrometer.

57. Review the relative standard deviation of all results and if a result has a relative standard deviation that is significantly higher than expected, taking into consideration the measured concentration, repeat the analysis of the solution concerned.

58. If the concentration of any of the analytes of interest in a sample test solution is found to be above the upper limit of the calibration range, dilute the solution by a suitable factor, matrix-matching as necessary, and repeat the analysis. Record the dilution factor.

## Quality control

### Method uncertainty

59. Estimate the uncertainty of the method following guidance in BS EN 482.<sup>8</sup>

### Method detection and quantification limits

60. Subject ten unused filters to the entire sample preparation and analytical process described in this method.

61. Calculate the method detection limit and the quantification limit for each of the metals or metalloids of interest as three times and ten times the sample standard deviation of the mean concentration values, respectively.

62. Repeat this exercise whenever the experimental conditions are changed significantly.

### Quality control solutions

63. Subject spiked filters to the entire sample preparation and analytical process to estimate the method accuracy on the sample batch, expressed as a percentage recovery relative to the true spiked value. The filters should be spiked with a known quantity of stock standard solution or working standard solution, as appropriate. Process these quality control samples at a frequency of at least 1 per 20 samples or minimum of one per batch.

64. Standard solutions prepared from stock solutions from a different batch number or source can be used as an independent quality control sample to verify that the analysis is within control.

### External quality assessment

65. It is strongly recommended that all laboratories undertaking the measurement of toxic metals and metalloids in workplace air should participate in an

external quality assessment scheme such as HSE's Workplace Analysis Scheme for Proficiency (WASP).

## Calculations

66. 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.

67. Calculate the mean concentration of each of the analytes of interest in the blank test solutions.

68. Calculate the mass concentration of each analyte in the air sample using the equation:

$$\rho_M = \frac{[(\rho_{M,1} \times V_1 \times F) - (\rho_{M,0} \times V_0)]}{V}$$

where

$\rho_M$  is the calculated mass concentration of analyte in the air sample, in  $\text{mg m}^{-3}$ ;

$\rho_{M,0}$  is the mean concentration of analyte in the blank solutions, in  $\text{mg l}^{-1}$ ;

$\rho_{M,1}$  is the concentration of analyte in the sample solution, in  $\text{mg l}^{-1}$ ;

$V$  is the volume, in l, of the air sample;

$V_0$  is the volume, in ml, of the blank solutions;

$V_1$  is the volume, in ml, of the sample solution;  
and

$F$  is the dilution factor used in paragraph 58 above ( $F = 1$  in the absence of dilution).

## Appendix A: Additional information

### Overall uncertainty

A1. The overall uncertainty of the method for sampling and analysis, for comparison with limit values, has been demonstrated<sup>9</sup> to comply with the requirements of BS EN 482.<sup>8</sup> This states that the overall uncertainty must be < 30% between 0.5 and 2 times the limit values, and < 50% between 0.1 and 0.5 times the limit values of the analytes determined.

### Detection limits

A2. Achievable method detection limits and quantification limits for each of the analytes, as well as the wavelengths used in the validation of this method, are shown in Table 1.

**Table 1** Detection limits<sup>9</sup>

Analyte	Wavelength (nm)	Plasma viewing	Method detection limit (µg/l)	Quantification limit (µg/l)
Antimony	206.836	axial	13	43
Arsenic	193.696	axial	19	62
Beryllium	313.042	radial	0.3	0.9
Cadmium	228.802	axial	2.8	9.5
Chromium	267.716	radial	3.3	11
Cobalt	228.616	axial	2.3	7.7
Copper	324.752	radial	15	50
Indium	230.606	axial	10	33
Iron	259.939	radial	14	46
Lead	220.353	axial	10	33
Manganese	257.610	radial	1.0	3.1
Nickel	221.648	radial	10	34
Selenium	196.026	axial	17	55
Tellurium	214.281	axial	28	94
Tin	189.927	radial	63	210
Vanadium	309.310	radial	1.2	42
Yttrium	371.029	radial	0.6	2.1
Zinc	206.200	radial	15	51

## References

- 1 *General methods for sampling and gravimetric analysis of respirable and inhalable dust* MDHS14/3 (Third edition) HSE Books 2000 Web only: [www.hse.gov.uk/pubns/mdhs/index.htm](http://www.hse.gov.uk/pubns/mdhs/index.htm)
- 2 BS EN 13205:2002 *Workplace atmospheres. Assessment of performance of instruments for measurement of airborne particle concentrations* British Standards Institution ISBN 0 580 39193 0
- 3 BS EN 1232:1997 *Workplace atmospheres. Pumps for personal sampling of chemical agents. Requirements and test methods* British Standards Institution ISBN 0 580 28328 3
- 4 BS EN ISO 1042:2000 *Laboratory glassware. One-mark volumetric flasks* British Standards Institution ISBN 0 580 30111 7
- 5 BS EN ISO 8655:2002 *Piston-operated volumetric instruments* Parts 1-6 British Standards Institution
- 6 BS EN ISO 3696:1995 *Water for analytical laboratory use. Specification and test methods* British Standards Institution ISBN 0 580 16312 1
- 7 BS ISO 15202-2:2001 *Workplace Air. Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry. Sample preparation* British Standards Institution ISBN 0 580 45324 3
- 8 BS EN 482:2006 *Workplace atmospheres. General requirements for the performance of procedures for the measurement of chemical agents* British Standards Institution
- 9 Taylor C A, Howe A M *Final report on project R48113. ICP-AES method for metals in air: Pt 2 - Analysis* HSL/2002/05 available at: [www.hse.gov.uk/research/hsl\\_pdf/2002/hsl02-05.pdf](http://www.hse.gov.uk/research/hsl_pdf/2002/hsl02-05.pdf)

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