

Metals and metalloids in air by X-ray fluorescence spectrometry

MDHS91/2

Methods for the
Determination of
Hazardous Substances

Health and Safety
Laboratory

Scope

- 1 This method describes the determination of concentrations of metallic and submetallic elements of atomic number equal to or greater than titanium ($Z \geq 22$) using X-ray fluorescence spectrometry (XRFS).
- 2 Quantitative analysis can be achieved using K spectral lines or using L lines for elements of atomic number greater than or equal to that of lead ($Z \geq 82$). Analysis using L spectral lines for elements of atomic number 60–82 can only be regarded as semi-quantitative unless there is a body of sampling and analysis data to the contrary, or unless the attenuation coefficient of the sample matrix for the fluorescence wavelength is known to be low ($< 200 \text{ cm}^2\text{g}^{-1}$). The use of L lines for elements of atomic number less than 60 can only provide qualitative information on the composition of the sample collected.
- 3 In certain cases, measurements made using XRF lines that are normally suitable for quantitative analysis can only be regarded as semi-quantitative, typically when it is necessary to measure an XRF line which is strongly absorbed by the sample matrix, or when the particle size of the sample is large.
- 4 The XRFS method is suitable for the determination of metals and metalloids in dust samples with a maximum mass of approximately 0.5 mg when deposited on a 25 mm diameter filter, or 1 mg on a 37 mm diameter filter.
- 5 This limit is governed by two factors: Firstly, analytical results are calculated on the assumption that there is a linear relationship between XRF line intensity and the mass of element on the filter. As loadings increase, deviations from linearity occur due to matrix absorption effects. The extent of deviation is related to the composition of the sample. Although significant deviations are not usually found for dust loadings as high as 1 mg on a 25 mm diameter filter, theoretical calculations¹ indicate that it is prudent not to exceed a maximum sample loading limit of 0.5 mg. Occasionally, samples of extreme composition are encountered which have a very high mass absorption coefficient for the XRF line measured. In such cases, the maximum sample loading on a 25 mm diameter filter should be reduced to 0.2 mg; Secondly, experience has also shown that dust can become dislodged from the filter during handling or transit of the samples at higher loadings than 1 mg on a 25 mm diameter filter.
- 6 XRFS analysis of air samples collected on suitable filters requires no sample preparation before analysis, unlike other analytical techniques such as inductively coupled plasma atomic emission spectroscopy (ICP-AES) that require dissolution of the sample. XRFS analysis can be regarded as a quantitative technique under appropriate conditions although the non-destructive nature of the technique makes it suitable for screening of air samples followed by the use of more accurate techniques such as ICP-AES if necessary.

7 This method was developed and validated using a sequential wavelength dispersive XRF spectrometer. However, simultaneous wavelength dispersive spectrometers are equally suitable, as are energy dispersive spectrometers which demonstrate adequate sensitivity and can achieve adequate resolution or deconvolution of the XRF lines of interest.

Summary

8 A measured volume of air is drawn through a filter mounted in a suitable inhalable or respirable dust sampler. The dust collected on the filter can then be analysed directly without further sample preparation by X-ray fluorescence spectrometry.

9 The use of alternative methods not included in the MDHS series is acceptable provided they can demonstrate the accuracy and reliability appropriate to the application.

Recommended sampling

10 For long-term personal exposures: Maximum sampling time: 8 hours; Sampling flow rate and duration will depend on individual sampler requirements and aerosol concentration. Filter loading should not exceed 0.5 mg on a 25 mm diameter filter.

11 For short-term exposures: Sampling time: 15 minutes; Sampling flow rate will depend on individual sampler requirements. Filter loading should not exceed 0.5 mg on a 25 mm diameter filter.

12 A longer sampling time ensures a heavier deposit and therefore greater sensitivity. Sampling times should therefore be as long as is reasonably practical and should be representative of the working periods of individuals exposed. General guidance on workplace monitoring is given in HSG173.²

13 To avoid sampler overloading where dust concentrations are high, several consecutive samplers should be employed.

14 Fixed point sampling may be used to determine background levels of dust in the workplace, although it is not appropriate to compare background samples with workplace exposure limits (WELs)³ because the distribution of dust is not uniform. In addition to this discrepancy, because of aerodynamic effects, background samplers will not exhibit the same characteristics as when mounted on the body, and will usually underestimate the inhalable dust concentration. Background samplers should be positioned at approximately head height, away from obstructions, fresh air inlets or strong winds. The sampling procedures are otherwise the same as for personal sampling.

Prerequisites

15 Users of this procedure will need to be familiar with the content of MDHS14⁴ and PD CEN/TR 15230.⁵

Safety

16 Users of this procedure should be familiar with normal laboratory practice and carry out a suitable risk assessment. It is the user's responsibility to establish appropriate health and safety practices and to ensure compliance with regulatory requirements.

17 Those who carry out and supervise the procedures described in this MDHS could be exposed to X-ray radiation and therefore should be aware of the requirements of the Ionising Radiation Regulations 1999 and code of practice.^{6,7}

Equipment

18 Either an appropriate inhalable or respirable dust sampler, as described in MDHS14,⁴ cleaned and operated according to the manufacturer's instructions.

19 Personal sampling pumps that meet the requirements of BS EN 13137.⁸

20 Filters: Retentivity of not less than 99.5% for particles with a 0.3 μm diffusion diameter. Filters of 25 mm diameter are preferable, since the whole filter can be exposed to the X-ray beam. The use of membrane filters is recommended as airborne particles are deposited as a thin layer on the surface. Mixed cellulose ester membrane filters of 0.8 μm mean pore diameter are suitable. If further characterisation of calibration filters is to be carried out by techniques such as ICP-AES then appropriate soluble filters should be selected for compatibility with the subsequent analysis. Glass fibre filters are not generally considered suitable for quantitative measurements because of the variable absorption of fluorescence X-rays emitted from a particle according to depth of penetration into the filter medium.

21 A portable flow meter calibrated against a primary standard, with a measurement uncertainty typically less than $\pm 2\%$.

22 Flexible plastic tubing of a suitable diameter for making a leak-proof connection from the sampling head to the pump; flat-tipped tweezers for loading and unloading the filters into and from samplers; and filter transport cassettes to transport samples to the laboratory.

Laboratory apparatus and reagents

23 Water: Complying with the requirements of ISO 3696 grade 2 water (electrical conductivity less than 0.1 m.S.m^{-1} and resistivity greater than 0.01 $\text{M}\Omega.\text{m}$ at 25 $^{\circ}\text{C}$).⁹

24 Pure elemental compounds (particle size preferably $< 5 \mu\text{m}$): Metals and metalloids of accurately known composition, suitable for preparation of filters for calibration of the XRF spectrometer in the form of a homogeneous fine powder. Commonly, the metal or metal oxide is used but other compounds may be preferable for some elements. Grinding in a suitable mill may be required if the particle size is not sufficiently fine.

25 Elemental standard solutions ($10\,000 \mu\text{g.ml}^{-1}$): Use commercially available standard solutions of the metals and metalloids. Multi-element standard solutions may be suitable in some cases where the XRF lines of the analytes do not coincide.

26 Graphite powder: Suitable for compression in a die to form a solid pellet for use as a drift correction monitor or quality control sample. Elemental impurities shall be less than $10 \mu\text{g}\cdot\text{g}^{-1}$. Ultra-purity electrode carbon has been found to be suitable.

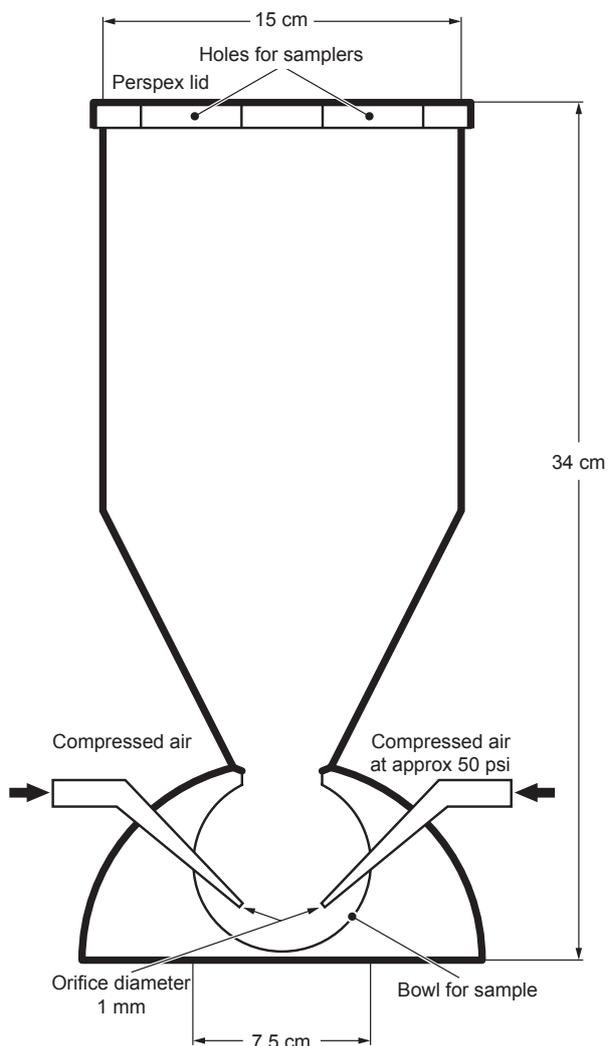
27 Positive displacement micropipettes complying with the requirements of BS EN 8655-6.¹⁰

28 Furnace for drying graphite at $480 \text{ }^\circ\text{C}$.

29 Hydraulic press (20 tonnes applied pressure) for pressing graphite pellets.

30 Dust cloud generator: An apparatus for generating dust clouds from the compounds to be used to prepare the calibration filters. A suitable example is illustrated in Figure 1. It is constructed of 3 mm thick borosilicate glass, apart from the top, which is made of 5 mm clear Perspex. A 2 mm deep groove is machined into the top, which fits onto the rim of the main glass chamber to form a closed system. Four symmetrically spaced holes, through which up to four samplers can be suspended, are drilled in the top. A replacement dummy lid of similar construction should also be available. The dust cloud generation chamber has a bulb at the bottom, into which a small quantity of finely ground compound is placed, and two side arms, through which a **short blast of compressed air is applied to generate the dust cloud.**

Figure 1 Glass chamber for the preparation of calibration standards



31 Microbalance: Calibrated against a primary standard and capable of weighing to a precision of $\pm 0.1 \mu\text{g}$.

X-ray fluorescence spectrometer

32 Either wavelength-dispersive or energy-dispersive spectrometer with adequate sensitivity for the elemental XRF lines of interest, and capable of resolution or deconvolution of these lines from neighbouring lines from other elements present in the sample.

33 X-ray beam collimation: Wavelength-dispersive XRF spectrometers shall be equipped with sets of primary collimator slits which are as fine as possible in order to obtain maximum resolution of wavelengths consistent with obtaining adequate sensitivity.

34 X-ray beam masking: XRF spectrometers shall be fitted with the largest mask available, in order to expose as much of the filter as possible to the X-ray beam, and preferably its entire face. This is because the sample will not necessarily be evenly distributed on the filter. In particular, depending upon the design of the sampler, the sample can often be more heavily deposited in the centre of the filter. If a small mask is used, it is more likely that erroneous results will be obtained in circumstances where the distribution of dust on the sample and calibration filters is not identical.

35 Spectrometer chamber X-ray path conditions: All wavelength-dispersive and some energy-dispersive instruments house the X-ray measurement apparatus in the spectrometer chamber, in which the sample is positioned during measurement. It is recommended they are equipped with a facility to evacuate the spectrometer chamber during measurement, or alternatively a facility to flush it with helium. In order to minimise X-ray absorption, XRFS is best carried out with the spectrometer chamber under vacuum. However, the use of helium atmosphere is acceptable, and preferable for filters mounted between plastic films. There is some loss of sensitivity if an air path is used, especially for X-rays of a long wavelength, but its use is not excluded.

36 Sample spinner: It is recommended that the instrument has a facility to rotate the sample during measurement. Rotation of the sample helps to compensate for any errors introduced by uneven deposition of particulate over the surface of the filter. Some instruments, particularly portable energy-dispersive spectrometers, have no such facility. For these instruments, it is recommended that the filter is measured a second time after rotating it by 90° and a mean result calculated.

37 XRF spectrometer sample cups and masks: Sample cups, equipped with mountings suitable for presenting filters to the XRF spectrometer in such a way that they remain flat during analysis. Ideally, the mountings should be designed so that the entire area of the filter on which the sample is collected is exposed to the X-ray beam. It is recommended that the filter is clamped between two thin masking plates which grip the filter by its edges so that the sample is not disturbed. The masking plates shall be made of a material that will not interfere with the analysis. It is recommended that they are made of the same material as the anode of the X-ray tube used, eg use a molybdenum mask with a dual molybdenum/scandium tube. Alternatively, pure aluminium or metal filler-free polymers may be used.

38 Sample cups manufactured from pure aluminium: Machinable aluminium containing low concentrations (<1%) of manganese, iron, copper, and zinc has been found to be suitable. These elements are still measurable in the sample because the body of the sample cup is screened by the molybdenum mask and

any residual elemental X-ray fluorescence due to the sample cup material is compensated for by blank correction.

39 Liquid cells for mounting filters: Plastic cells designed to present liquid samples to the XRF spectrometer can be used as an alternative means of mounting filter samples when sample loading is high and it appears that particulate could become detached from the filter. In such circumstances, the filter can be retained between two layers of thin polymer film such as 6 µm thick polypropylene or Mylar® film.

Reference analytical method

40 The accuracy of calibrations can be confirmed by re-analysis of calibration filters using a reference analytical method. A reference method is also useful to check and confirm analytical results obtained if there is doubt about the applicability of XRF to the analysis of filter samples generated by a particular process. Either Inductively coupled Plasma – atomic emission spectrometry (ICP-AES) or inductively Coupled Plasma – Mass Spectrometry (ICP-MS) are suitable for this procedure.

Calibration and quality control of the XRF spectrometer

Calibration filters

41 The most accurate analysis is obtained when the calibration filters are prepared in the same way as the samples are collected, ie by collection of dust from an atmosphere using the same samplers. It is therefore easier to obtain accurate calibrations if the amount of the metal or metalloid present on the calibration filters is determined after XRF measurements by analysis using the reference analytical technique.

42 To prepare calibration filters, the filters should be loaded into samplers of the same design used for collection of the field samples. These samplers should be arranged within a standard atmosphere chamber in which the atmosphere to be sampled has been generated from a fine dust (Figure 1). The volumetric flow rate through the samplers should be set to that normally used for collecting samples. Typically, sample masses in the range 0 to 500 µg of dust on the filter for the element(s) of interest are suitable.

43 The dust collected on the sample filters is not usually evenly distributed but is usually concentrated towards the centre of the filter by the orifices of the sampler. Because the X-ray beam of a spectrometer does not impinge evenly over the whole surface of the filter, the central portions of the filter contribute more strongly to XRF emissions. Consequently, it is important to use samplers of the same design used for collection of the samples, as the slope of the calibration line varies according to the type of sampler used.

44 Ideally, the particle size of the dust collected on calibration filters should be the same as that of the particulate collected on sample filters. However, it is not practical to anticipate what this would be. Instead, particle size effects are minimised to negligible levels by preparing calibration filters from dust clouds generated with as small a particle size as possible. However, as a consequence, measurements made on sample filters could have a negative bias if the particle size of the sample is large.

45 Calibration filters may also be prepared using a desolvating nebuliser to generate a dry aerosol from an elemental solution of the metals and metalloids of

interest. This procedure can be used to prepare multi element calibration filters from custom solution blends that can be useful when determining inter elemental interferences

Preparation and use of drift correction monitor standard

46 Weigh 10 g of pelletable graphite into a beaker, and spike it with appropriate volumes of 10 000 $\mu\text{g}\cdot\text{ml}^{-1}$ solutions of each of the metals and metalloids of interest. Elemental masses that give suitable count rates are determined empirically. Add sufficient water to the doped graphite to form a paste, and mix it well to homogenise. Heat the paste to evaporate off the majority of the water and finally dry the doped graphite thoroughly in the furnace at 480 °C overnight.

47 Place the resulting powder in a suitable diameter die, and use a hydraulic press to apply a pressure of 20 tons for 1 minute to form the pellet.

48 Drift in sensitivity of the XRF spectrometer can be compensated for by analysing a drift monitor standard when the instrument is calibrated, and then again when samples are analysed. A factor can then applied to the sample count rates to correct for any change in the count rates obtained for the ratio monitor standard.

49 It is convenient to use a single drift correction monitor standard that contains all the metals and metalloids to be included in the analytical program. However, more than one ratio monitor standard may be required to avoid line overlap effects. A single drift correction monitor standard may be used to correct for a change in the slope of a calibration line, provided that the intercept is small in comparison with the count rate obtained for the ratio monitor standard, and provided that blank correction is applied to the samples. In this case, each metal or metalloid should be included in the ratio monitor standard at a concentration such that its count rate is similar to that which is obtained near the top of the calibration range. More accurate corrections for instrumental drift may be made by using two ratio monitor standards, one of which has a low count rate, and one of which has a count rate similar to that which is obtained near the top of the calibration range. In this case, correction can be made for changes in both the slope and intercept of the calibration. Drift correction monitor standards are commercially available as glass standards.

Quality control samples

50 Quality control samples should be prepared in the same way as the drift correction monitor since mixed cellulose ester filters deteriorate on repeated exposure to X-rays and will eventually disintegrate.

51 Each element should be included in the quality control samples at a concentration such that its count rate is similar to that obtained near the top of the calibration range. A quality control sample should be analysed at the beginning and end of the analytical run.

Sampling

52 Sampling should be carried out in accordance with the procedures described in MDHS14.²

53 After sampling place the exposed filters in labelled transport cassettes before transfer to the laboratory.

54 A minimum of two field blanks should be included with each batch of ten samples. These should be treated identically to the sample filters apart from the actual period of sampling.

Analysis

Sample preparation

55 Mount each calibration and sample filter centrally in the XRF spectrometer sample cup, making sure that the exposed surface is facing the X-ray beam. Ensure that the filter will remain flat during analysis.

56 Provided that less than 1 mg of dust is collected on the filter, there is little risk of dust falling from it, even though, as in the case of most sequential spectrometers, the sample is presented to the X-ray beam face down.

57 If the filter appears to be overloaded it is recommended that they are mounted between two thin sheets of polymer film, eg 6 µm thick polypropylene or Mylar® in the sampling cup. A convenient method for mounting 25 mm diameter filters is to stretch and trap the film across the face of a 31 mm diameter XRF liquid cell using the push-fit rings.

Spectrometer settings

58 Determine the optimum spectrometer settings for the metals and metalloids to be determined, following the advice given in Appendix 1. Conditions suitable for use with the Phillips PW 1480 automatic spectrometer equipped with a molybdenum/scandium anode X-ray tube are given in Table 1 of Appendix 2 for a number of metals and metalloids. However, these conditions might not be appropriate for other instrumentation.

59 Select the best XRF line for measurement of the metal or metalloid and the most suitable voltage and amperage to be applied to the X-ray tube (or alternatively the most suitable radioactive X-ray source, for excitation of X-ray fluorescence for portable instruments).

60 When using a sequential wavelength-dispersive XRF spectrometer, select the most appropriate crystals, detectors, and collimators for the X-ray wavelength to be measured. Also determine the optimum settings for X-ray pulse energy discriminator windows and positioning for background sampling points.

61 Many of the conditions for measuring specific elements may be pre-set for both simultaneous wavelength-dispersive spectrometers and for energy-dispersive spectrometers. Also, energy-dispersive spectrometers normally use deconvolution software for background correction so there is no requirement to measure at specific background points. Similarly, simultaneous XRF spectrometers measure a pre-selected range of elements at fixed XRF wavelengths and usually have no facility to measure background X-ray continuum levels.

62 Establish the X-ray counting time required to achieve acceptable relative standard deviations for the analysis of the metals and metalloids of interest (see Appendix 3).

Sample analysis

63 Set up a calibration program which uses the selected spectrometer settings for the metal or metalloids to be determined.

64 Load the calibration filters into the sample cups and measure the X-ray count rates at the peak and background wavelengths for analytes of interest. Calculate the net count rates by subtracting the extrapolated background count rates from the peak count rates (most modern instruments do this automatically).

65 Measure the count rate of the ratio monitor standard(s) containing the metal or metalloid of interest.

66 Input the mass of the metal or metalloid on the calibration filters into the computer. This may be calculated from the accurately determined weight of the elemental compound collected on the filter, or it may be determined subsequent to XRF determinations by analysis using an alternative reference technique. Then plot the calibration curve.

67 The curve should be very close to linear and is normally treated as a straight line by the software. Calculate the slope (m) for the line, expressed in X-ray counts per second per microgram of element on the filter, and the intercept (c). The slope and intercept of the calibration curve can then be used as a basis for subsequent analysis of unknown filter samples.

68 Sensitivity drift which occurs due to instrumental changes can be corrected for by applying a factor based upon changes in the count rate obtained for the drift monitor standard. It is acceptable to use a single monitor standard to correct the slope of a calibration, provided that the intercept is very small in comparison with the count rate obtained for the ratio monitor standard, and provided that blank correction is applied. More accurate corrections for instrumental drift may be made using two ratio monitor standards, one of which is of low concentration and one of which is high. In this case, correction for both changes in the slope and intercept can be made.

69 Set up the spectrometer to measure all the metals and metalloids of interest by assembling an analytical program containing the spectrometer settings and calibration curves for each of the metals and metalloids concerned.

70 Open the filter transport cassettes, sampler filter cassettes or samplers and mount each filter in a sample cup using flat-tipped tweezers. Follow the same procedure for the blanks. 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, retain the filter cassette or sampler for further analysis, if necessary.

71 Analyse the drift correction monitor standard(s) for all metals and metalloids of interest using an appropriate analytical programme, and calculate the net count rates for each element by subtracting the extrapolated background count rates from the peak count rates. Compare the net count rate with the value which was obtained at the time the calibration was carried out. Calculate the ratio by which the sensitivity of the instrument has drifted for each of the elements being measured. Apply this drift correction factor to the slope of the calibration graph to correct the calibration. (This is normally done automatically by the instrument software.)

72 If the drift correction factor is greater than 1.1 or less than 0.9, significant instrument drift has occurred since the original calibration of the program and consideration should be given to whether the instrument requires servicing. If the ratio is greater than 1.2 or less than 0.8, the instrument should be overhauled or calibration for the analytical program repeated.

73 Analyse the samples and blanks and the quality control samples for all metals and metalloids of interest using the selected analytical programme. Calculate the net count rates for each metal or metalloid of interest by subtracting the extrapolated background count rates from the peak count rates. Alternatively, use line-overlap or peak deconvolution functions to achieve the same effect. Use the stored internal calibration functions (resloped according to the drift factors) to calculate the mass of each metal or metalloid on the filters.

74 It is good practice to analyse quality control samples immediately before and after the batch of samples. Results obtained for the first quality control sample should preferably be inspected before analysing the samples to avoid the need to reanalyse samples if quality control criteria are not met.

Quality control

75 Analyse the quality control sample or samples a suitable number of times (eg 20), on separate occasions, and calculate the mean and standard deviation of the measured readings. Assuming that the distribution of these values is Gaussian, construct a Shewart chart for each quality control sample with warning and action limits at ± 2 SD and ± 3 SD respectively. Subsequently plot the results obtained for the quality control samples with each analytical batch on the Shewart chart. Compare the internal quality control result with the target value and take appropriate action if the warning or action limits are exceeded. In practice, until it is considered that sufficient data have been obtained to establish Shewart charts, sample results should be considered to be acceptable if quality control results are within $\pm 5\%$ of the running mean.

Calculations

Volume of air sample

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

Concentration of metal or metalloid in air

77 Calculate the concentration of metal or metalloid in air, $\rho(E)$, in milligrams per cubic metre ($\text{mg}\cdot\text{m}^{-3}$), using equation 1:

$$\rho(E) = \frac{[m(E)_1 - m(E)_0]}{V} \quad \text{Equation 1}$$

Where $m(E)_1$ is the mass, in micrograms (μg), of metal or metalloid on the sample filter

$m(E)_0$ is the mean mass, in micrograms (μg), of metal or metalloid on the blank filters

and

V is the volume of the air sample, in litres

Detection limits

78 Detection limits are dependent on several factors, including the type of spectrometer used, the analytical parameters selected, the presence of additional phases in the sample, and the particle size of the sample.

79 For samples deposited on filters as thin layers, the precision of XRFS measurements is related to the square root of the number of X-rays counted per unit mass of the element at the wavelength peak, and to the background level of X-ray counts (see Appendix 3). Detection limits can therefore be reduced by counting for longer periods, but this increases analysis time, which can be especially significant if several metals and metalloids are to be determined.

80 Typical qualitative and quantitative detection limits, defined as three times and ten times the standard deviation of a blank measurement, have been determined¹¹ for the XRF lines of a range of metals and metalloids using a wavelength dispersive XRF spectrometer with a molybdenum/scandium anode X-ray tube. Measurements were made under the conditions given in Table 1 of Appendix 2, using a 50-second counting time at the wavelength peak and a total of 50-seconds counting time at the background positions. The detection limits obtained, which are typical of those that can be obtained by XRFS, are given in Table 2 of Appendix 2.

Analytical bias

81 Particle size and depth effects can occur when analysing a sample by XRFS. On the basis of theoretical calculations and supporting experimental work,¹ the following conclusions (which apply to XRFS measurements of particulate collected on 25 mm diameter membrane filters made when K lines are used for elements for atomic number 22 to 60 and when L lines are used for elements of atomic number greater than 60) have been reached:

- Provided that the average physical particle size does not exceed 2.5 μm , the negative bias caused by particle size effects will normally be less than 10%, provided K lines are used for elements of atomic number greater than or equal to that of titanium ($Z \leq 22$), or L lines are used for elements of atomic number greater than or equal to that of lead.
- Provided that less than 500 μg of sample is collected, the negative bias caused by the depth of the layer of particulate collected will normally be less than 10%.

82 For a thin layer of particulate of very small physical diameter, the errors introduced by particle size and depth effects are not simply additive. However, provided that the above criteria are met, the negative bias of the XRFS analysis is unlikely to exceed 10%.

83 Particle size and depth effects are caused by absorption of exciting and fluorescence X-rays by the sample matrix. Only high energy X-rays penetrate solids to a depth of more than about 20 μm . It is therefore of concern that aerodynamic diameters of particles collected from workplace air are often of this order. However, the physical diameters of the particles are evidently very much smaller, since in practice results obtained for such samples using XRFS generally agree well with those obtained using other analytical techniques.^{12,13} Significant underestimation (>10%) due to particle size effects only tends to occur when the absorption coefficient of the sample is particularly high for the fluorescence X-rays being measured. This is most likely to be the case when the fluorescence X-ray wavelength is of low energy. On the basis of X-ray absorption theory,¹⁴ loss of

XRFS sensitivity due to particle size effects can be shown to be much more severe for L lines than for K lines. This is because L line X-rays are of much lower energy than K line X-rays for the same element. Also, because elements for which L line measurements are suitable are those of greatest atomic mass, they are much denser and likely to re-absorb the fluorescence X-rays.

84 Recommendations for the quantitative use of elemental lines are based on the following observations: Lead results obtained using the Pb L β XRF line for real samples from a range of industries showed good agreement with results obtained using atomic spectrometry.^{12,13} This provides evidence that particle size effects are not significant when L line XRFS measurements are made for elements of atomic weight greater than or equal to that of lead ($Z \geq 82$). However, L line XRFS measurements seriously underestimated cadmium ($Z = 48$). Application of XRF particle size theory¹ to lead oxide suggests that for particles of average physical size 2.5 μm , equivalent to an aerodynamic diameter of approximately 7.5 μm , particle size effects would result in a 10% attenuation of the XRF signal, and corresponding low results. Particle size effects should be no more serious than this for K line XRFS measurements made for elements of atomic weight greater than or equal to that of titanium ($Z \geq 22$).

85 Particles of large aerodynamic particle size often prove, on microscopic examination, to be composed of aggregates of particles of much smaller physical particle size. This is especially true of particles formed by condensation of fume, eg from smelting, welding or brazing. Also, particles of compounds originating from flocculation often contain large void spaces with as little as 10% solid material. Samples composed of solid particles of large physical diameter are only likely to be collected if sampling is carried out very close to processes involving milling and grinding materials or handling coarse powders. However, this is difficult to confirm because there is a dearth of data on the physical rather than aerodynamic particle sizes for dust collected from different processes. If it is suspected that errors could be introduced due to particle size effects for a particular batch of samples, it is recommended that the validity of results is tested by re-analysing some samples by ICP-AES or AAS.

Expanded uncertainty

86 It has been shown¹¹ that the expanded uncertainty requirements of BS EN 482¹⁵ can be met, provided a long enough sampling time and/or X-ray counting time is used (see Table 3). For most of the metals and metalloids investigated, using an X-ray peak counting time of 50 seconds the expanded uncertainty requirements will be met for an air volume of at least 60 litres, corresponding to a sampling time of 30 minutes at 2 l.min⁻¹. However, for the expanded uncertainty requirements to be met using an X-ray peak counting time of 50 seconds, an air volume of at least 240 litres, corresponding to a sampling time of 2 hours at 2 l.min⁻¹ was required for the measurement of arsenic (using the K β line) and antimony (using the K α line); and an air volume of at least 960 litres, corresponding to a sampling time of 8 hours at 2 l.min⁻¹, was required for the measurement of barium (using the K α line). An extension of the X-ray peak counting time to 120 seconds, in addition to a volume of at least 960 litres, corresponding to a sampling time of 8 hours at 2 l.min⁻¹, was required for measurement of cadmium (using the K α line).

87 The imprecision of XRFS measurements depends statistically on the square root of the number of X-rays counted (see Appendix 3). Consequently, by increasing counting times, it is generally possible to meet the expanded uncertainty requirements given in BS EN 482¹⁵ by using smaller sample volumes than those given in Table 3. However, significant increases in the counting times are required

to have much effect. For instance, to halve the required sample volume would require that the counting time be increased by more than a factor of four. Counting times cannot be increased indefinitely, otherwise total analysis time would become too long for use in a practicable analytical method. The total counting time which can be used to measure all metals and metalloids of interest is also limited because the exposure of membrane filters to an X-ray beam for periods longer than 30 minutes is likely to cause them to disintegrate.

Interferences

88 Errors can occur if XRF lines are coincidental or overlap. This situation is particularly encountered with energy dispersive spectrometers, which lack the high peak resolution of wavelength dispersive instruments. However, software incorporated in modern systems usually has the capacity to deconvolute any overlapping peaks. Wavelength dispersive systems can compensate for the contribution from the overlap of the interfering element by measuring the intensity of an unaffected XRF line of the interfering element and applying line overlap factors. Nevertheless, it is generally better to avoid the problem by selecting an alternative, interference-free XRF line, by using a dispersive crystal with a high resolving power for the X-ray wavelengths being measured, or in the case of interference between peaks of different orders of diffraction, by careful setting of the energy discrimination window of the X-ray detection system used. Where background corrections are made, it is essential to select background measurement positions that are not influenced by nearby XRF lines.

89 Selection of XRF lines and measurement conditions should be based upon knowledge of the metals and metalloids likely to be present in the sample and tables of elemental XRF lines. This is assisted in the software of most modern XRFS systems by the incorporation of warning information on possible interfering XRF lines in the wavelength region of the elemental XRF line selected.

90 Commonly occurring interferences include:

As $K\alpha$ and Pb $L\alpha$: It is recommended that the As $K\beta$ and Pb $L\beta_1$ lines are measured in preference to the As $K\alpha$ and Pb $L\alpha$ lines.

Interference of second order Sn with Pb $L\beta_1$: the energy discrimination of the detector system should be set to exclude the higher energy Sn X-ray pulses.

Ti $K\beta$ on V $K\alpha$: this overlap should be corrected for, if high levels of titanium are present.

V $K\beta$ on Cr $K\alpha$: this overlap should be corrected for, if high levels of vanadium are present.

Cr $K\beta$ on Mn $K\alpha$: interference between these two lines can usually be avoided with wavelength dispersive systems by the use of high-resolution crystals, eg LiF220. However, the position of background correction points should be carefully selected to avoid the Cr $K\beta$ line.

Mn $K\beta$ on Fe $K\alpha$: the position of background correction points should be carefully selected to avoid the Mn $K\beta$ line.

Pb M_2-N_4 and Ag $K\beta$ on Cd $L\alpha$: it is preferable to use the Cd $K\alpha$ line if the necessary sensitivity can be obtained. Use of the Cd $L\alpha$ line can only be regarded as semi quantitative. If the use of the Cd $L\alpha$ line is unavoidable, and it is suspected that high concentrations of lead or silver could be present in the sample, then the

necessary line overlap corrections need to be made based upon the intensities of the Pb $M\alpha$ and Ag $L\alpha$ lines..

Sr $K\beta$ on Zr $K\alpha$: it is advisable to routinely make line overlap corrections based upon the intensity of the Sr $K\alpha$ line.

Ni $K\beta$ on W $L\alpha$: it is necessary to make line overlap corrections when tungsten is measured in the presence of high levels of nickel, eg in the case of particulate from hard metal grinding.

Appendix 1: Selection and determination of conditions for the determination of specific metals and metalloids

Choice of XRF lines

1 Measurement conditions for a number of metals and metalloids are given in Appendix 2. In some cases, conditions for making both K and L line measurements are given. However, wherever possible, it is better to use K lines for elements of lower atomic number than lead ($Z < 82$), unless it is possible to demonstrate that L lines can be used quantitatively.

2 L lines are much more prone to self-absorption than K lines, and hence to particle size and depth effects. Their use is therefore normally best regarded as semi-quantitative. A notable exception is the lead $L\beta$ line, which it has been demonstrated gives quantitative results for lead in air.^{12,13} Similar evidence has not been obtained for other elements. In fact, in the case of cadmium, measurements using L lines have been shown to seriously underestimate the mass of cadmium on the filter, whilst measurements using K lines have shown good agreement with subsequent AAS measurements.

3 $K\alpha$ or $L\alpha$ lines are normally used for XRF measurements, since these are the most intense lines. However, in a number of significant cases $K\alpha$ or $L\alpha$ lines are used in preference. This is because of possible line overlap effects due to the presence of other elements in the sample. For instance, the Pb $L\alpha$ line coincides with the As $K\alpha$ line. Therefore, since these elements are quite commonly found together, e.g. in samples from lead refineries, they are usually measured using the $L\alpha$ and $K\alpha$ lines, respectively. However, if instruments have computer software that is capable of making very accurate line overlap or peak deconvolution corrections, use of the As $K\alpha$ and Pb $L\alpha$ lines is possible.

Setting wavelength-dispersive detector discrimination

4 Most wavelength-dispersive XRF spectrometers use tandem detectors. A flow counter is used to measure low-energy X-rays and a scintillation counter is used to measure high-energy X-rays. However, some wavelength-dispersive XRF spectrometers use a xenon detector. In all cases, second order and multiple order wavelengths are excluded by energy discrimination carried out on the pulses obtained from the detectors. Depending on the measured XRF wavelength, energy windows are set either to include or exclude the escape peak. A typical setting is 25% to 75% of the energy of the XRF wavelength measured. A notable exception is the Pb $L\alpha$ line, for which the windows are set differently in order to exclude third order tin lines which would otherwise interfere.

Choosing background correction points

5 The count rate measured at the elemental XRF wavelength is corrected for the back-scattered background continuum of the X-ray tube. In wavelength-dispersive XRFs the background count rate at the peak wavelength is estimated by measuring the background count rate close to the peak. This is usually achieved by extrapolation of measurements made either side of the peak, but when the background varies very little with wavelength a single measurement is sometimes made. It is important that the position of these background measurements is selected with care, so that they do not coincide with the positions of XRF lines of other elements which could be present in the sample. Particular care has to be taken with the first row transition metals, since for these elements the $K\alpha$ lines often encroach upon the $K\alpha$ lines of neighbouring elements in the periodic table. Published tables for the diffraction crystal in use should be scrutinised to check for possible interfering lines. If it is not possible to measure the background on both sides of the peak, it is necessary to correct on the basis of only one background measurement.

Selecting counting times

6 The counting time should be long enough to enable a satisfactory relative standard deviation to be obtained for the lowest mass of the metal or metalloid to be determined, in order that the overall uncertainty requirements of BS EN 482¹⁵ can be met. A way of calculating a minimum counting time is given in Appendix C.

7 A 50-second counting time at the peak has generally been found to be more than adequate using a Philips PW 1480 wavelength-dispersive sequential XRF spectrometer, and this counting time is routinely used at HSL. Longer counting times might be necessary in some cases, especially when K lines are measured for high atomic number elements with X-ray tubes which have a low maximum kV capability. As a general principle, the combined counting time at the background correction positions should be equal to the counting time at the peak.

Choosing power settings

8 Low kV, high current settings are generally used to measure K lines of elements of relatively low atomic number and high kV settings are used to measure the lines of elements of high atomic number.

Appendix 2

Table 1 Typical XRF operating conditions for some metals and metalloids using wavelength dispersive XRF*

Element	X-ray line	Tube power		Collimator	Crystal	Peak angle	Background		Detector	Pulse height discriminator	
		kV	mA				+ offset	- offset		Lower	Upper
As	K β	100	25	Fine	LiF200	30.44	0.74	0.74	FS	25	75
Ba	K α	100	25	Fine	LiF220	15.51	0.80	0.80	SC	25	75
Ba	L β	100	25	Fine	LiF200	79.275	2.00		FL	28	75
Cd	K α	100	25	Fine	LiF220	21.63	0.70	0.70	FS	25	70
Cd	L α	40	70	Coarse	PE	53.795	1.40	1.40	FL	25	75
Co	K α	100	25	Fine	LiF220	77.885	1.70		FS	18	70
Cr	K α	100	25	Fine	LiF200	69.37	1.30		FL	12	70
Cu	K α	100	25	Fine	LiF200	45.025	1.50		FS	20	75
Fe	K α	100	25	Fine	LiF200	57.525	1.40		FS	16	70
Mn	K α	100	25	Fine	LiF220	95.255	1.72		FL	15	70
Ni	K α	100	25	Fine	LiF200	48.67	1.30		FS	19	75
Pb	L β	100	25	Fine	LiF220	40.355	0.60		SC	22	77
Sb	K α	100	25	Fine	LiF220	18.99	0.50	0.50	SC	25	70
Sb	L β	40	70	Fine	LiF200	106.485	1.10	1.10	FL	25	75
Sn	K α	100	25	Fine	LiF220	19.81	0.86	0.86	SC	25	70
Sn	L α	40	70	Fine	LiF200	126.815		2.60	FL	25	75
Sr	K α	100	25	Fine	LiF220	35.785	0.80	0.80	SC	25	75
Zn	K α	100	25	Fine	LiF220	60.53	1.10		FS	22	75

FL = Flow counter, SC = Scintillation counter, FS = Flow counter + scintillation counter.

PE Pentaerythritol

* Typical instrument settings for a Philips PW 1480 wavelength-dispersive sequential XRF spectrometer fitted with a dual anode molybdenum/scandium tube, a 35 mm mask, a 0.3 mm fine collimator and a 4.0 mm coarse collimator.

Table 2 Typical detection limits and sensitivity for a range of metals and metalloids using a wavelength dispersive XRF spectrometer*

Element	X-ray line	Qualitative det. Limit (μg)	Quantitative det. Limit (μg)	Sensitivity (kcts/sec/ μg)
As	K β	0.3	1	0.02
Ba	K α	5	15	0.02
Ba	L β	0.2	0.7	0.008
Cd	K α	1	4	0.006
Cd	L α	0.005	0.02	0.9
Co	K α	0.09	0.3	0.03
Cr	K α	0.05	0.2	0.06
Cu	K α	0.06	0.2	0.1
Fe	K α	0.2	0.5	0.08
Mn	K α	0.4	1	0.02
Ni	K α	0.05	0.2	0.1
Pb	L β	0.3	1	0.01
Sb	K α	2	5	0.004
Sb	L β	0.3	1	0.02
Sn	K α	1	5	0.005
Sn	L α	0.02	0.05	0.2
Sr	K α	0.1	0.4	0.03
Zn	K α	0.2	0.6	0.03

* Based upon 50 second counting times

Table 3 Analytical relative standard deviation and typical expanded uncertainty for target values of metals and metalloids*

Element of interest	XRF line	Target value for elements* (mg.m-3)	0.1x to 0.5x target value			0.5x to 2x target value		
			Minimum sample volume (litres)	Maximum RSD analysis	Maximum overall uncertainty (%)	Minimum sample volume (litres)	Maximum RSD analysis	Maximum overall uncertainty (%)
Arsenic and compound	K β	0.1	240	7.0	32.0	240	2.0	25.8
Barium compounds (soluble)	K α	0.5	960	5.6	29.9	960	2.6	26.3
Barium sulphate	K α	2	240	5.6	29.9	240	2.6	26.3
Cadmium and compounds**	K α	0.025	960	15.8	47.7	960	3.4	27.0
Cadmium and compounds	La	0.025	60	11.8	40.4	60	2.5	26.2
Cadmium sulphide	K α	0.04	960	15.9	48.0	960	3.5	27.2
Cadmium sulphide	La	0.04	60	7.4	32.7	60	1.8	25.5
Cobalt and compounds	K α	0.1	60	9.6	36.4	60	2.6	26.2
Chromium and compounds	K α	0.5	60	1.9	25.7	60	1.4	25.4
Copper fume	K α	0.2	60	4.2	28.0	60	1.1	25.3
Copper dust	K α	1	60	1.1	25.3	60	0.6	25.1
Iron oxide fume	K α	5	60	3.8	27.5	60	3.7	27.4
Iron salts	K α	1	60	5.2	29.4	60	3.8	27.5
Manganese and compounds	K α	1	60	5.3	29.5	60	1.2	25.3
Insoluble Nickel compounds	K α	0.5	60	2.2	25.9	60	2.0	25.8
Soluble Nickel compounds	K α	0.1	60	4.8	28.8	60	2.2	25.9
Lead and compounds	L β	0.15	60	16.9	49.9	60	3.8	27.5
Antimony and compounds	K α	0.5	240	8.2	34.0	240	4.5	28.3

Element of interest	XRF line	Target value for elements* (mg.m-3)	0.1x to 0.5x target value			0.5x to 2x target value		
			Minimum sample volume (litres)	Maximum RSD analysis	Maximum overall uncertainty (%)	Minimum sample volume (litres)	Maximum RSD analysis	Maximum overall uncertainty (%)
Antimony and compounds	Lβ	0.5	60	6.1	30.6	60	3.1	26.7
Tin compounds	Kα	2	60	6.0	30.5	60	1.7	25.6
Tin compounds	Lα	2	60	1.0	25.2	60	0.9	25.2
Zinc chloride fume	Kα	1	60	2.5	26.1	60	1.7	25.6

* These values may no longer represent current workplace exposure limit values (WELs) but demonstrate the typical expanded uncertainty (EU) values which could be expected at these target levels as determined using BS EN 482.¹⁵ Users must determine EU according to the most recent version of BS EN 482 and the current WEL or other appropriate target value.

** Based upon a 120 second counting time as opposed to the standard 50 seconds.

Appendix 3: Estimation of the analytical relative standard deviation and minimum XRFs counting time

9 A programme for the calculation of the relative standard deviation of XRFs measurements is generally included in instrument software. However, if such a programme is not available, relative standard deviations may be derived from basic X-ray counting theory, using Equation 5.

10 The measured or calculated relative standard deviations may be used to establish the minimum X-ray count times and/or sample volumes that will enable the expanded uncertainty requirements of BS EN 482¹⁵ to be met for the metals and metalloids of interest.

11 From Poisson statistics the standard deviation in the measured number of X-ray counts, σN , is given by:

$$\sigma N = \sqrt{N} \quad \text{Equation 2}$$

Where N = the number of counts.

Equation 2 can be rewritten as:

$$\sigma N = \sqrt{R \times T} \quad \text{Equation 3}$$

Where R = the count rate, in counts per second; and

T = the measuring time, in seconds.

12 When an element is measured using wavelength-dispersive XRFs, the net count rate, R_{net} , is found by subtracting the background count rate, R_{bg} , from the peak count rate, R_p . The net count rate is then converted into a concentration using the equation:

$$Y = mX + c \quad \text{Equation 4}$$

Where Y = the net count rate, R_{net} , in counts per second;

M = the slope of the calibration line in counts per second per μg ;

X = the mass on filter, in μg ; and

c = the intercept of calibration, in counts per second.

13 The relative standard deviation of the XRFs measurement due to imprecision in the measurement of the peak and background countrates, RSD_{XRF} is given by the equation:

$$RSD_{XRF} = \frac{1}{m} \times \sqrt{\frac{(mX + c + 2R_{bg})}{T_p + X^2}} \quad \text{Equation 5}$$

14 The relative standard deviation of the analysis, $RSD_{analysis}$, may be taken as equal to, RSD_{XRF} , provided that sufficient calibration filters are analysed to accurately determine the slope of the calibration, and provided that a sufficient number of blanks are used to render the error due to blank correction negligible.

15 As a general rule, the expanded uncertainty requirements of BS EN 482¹⁵ are met over the entire range from 0.1 to 2.0 times the limit value, provided that the relative standard deviation of the XRFs measurement, RSD_{XRF} , is < 5% for the mass of element which would be collected on the filter if the element was sampled at 0.5 times the limit value.

16 This general rule holds, provided R_p/R_{bg} is ≥ 5 ; that the calibration line has a relative standard deviation of <2%; and that the error due to blank correction is negligible. The minimum counting time, T_{Pmin} , can then be estimated using Equation 6:

$$T_{Pmin} = \frac{mX + c + 2R_{bg}}{0.0025 \times m^2 \times X_{0.5LV}^2} \quad \text{Equation 6}$$

17 If the general rule does not apply, the minimum counting time may be estimated by substituting increasing values of T_p in Equation 9 to reduce $RSD_{analysis}$ until the expanded uncertainty requirements of BS EN 482,15 as interpreted in Equations 7 and 8, are met:

Overall uncertainty from 0.1 to 0.5 LV < 50%

$$0.145 + 2 \times \sqrt{0.00278 + RSD_{analysis\ 0.1LV}^2} \leq 0.5 \quad \text{Equation 7}$$

Overall uncertainty from 0.5 to 2.0 LV < 30%

$$0.145 + 2 \times \sqrt{0.00278 + RSD_{analysis\ 0.5LV}^2} \leq 0.3 \quad \text{Equation 8}$$

References

- 1 Foster R D Read M L and Usher J M *Particle size and depth effect errors in the XRF determination of elements in aerosol collected on filters* HSL Internal Report IS/96/03 HSL 1996
- 2 *Monitoring strategies for toxic substances* HSG173 (Second edition) HSE Books 2006 www.hse.gov.uk/pubns/books/hsg173.htm
- 3 EH40/2005 *Workplace exposure limits: Containing the list of workplace exposure limits for use with the Control of Substances Hazardous to Health Regulations 2002 (as amended)* Environmental Hygiene Guidance Note EH40 (Second edition) HSE Books 2011 ISBN 978 0 7176 6446 7 www.hse.gov.uk/pubns/books/EH40.htm
- 4 *General methods for sampling and gravimetric analysis of respirable, thoracic and inhalable aerosols* MDHS14/4 HSE 2014 www.hse.gov.uk/pubns/mdhs/index.htm
- 5 PD CEN/TR 15230:2005 *Workplace atmospheres: Guidance for sampling of inhalable, thoracic and respirable aerosol fractions* British Standards Institution
- 6 Ionising Radiation Regulations 1999 SI 1999/3232 www.legislation.gov.uk
- 7 *Work with ionising radiation: Ionising Radiations Regulations 1999: Approved Code of Practice and guidance* L121 HSE Books 2000 ISBN 978 0 7176 1746 3 www.hse.gov.uk/pubns/books/l121.htm
- 8 BS EN ISO 13137:2013 *Workplace atmospheres: Pumps for personal sampling of chemical and biological agents. Requirements and test methods* British Standards Institution
- 9 BS EN ISO 3696:1995 *Water for analytical laboratory use. Specification and test methods* British Standards Institution
- 10 BS EN ISO 8655-6:2002 *Piston operated volumetric apparatus. Gravimetric methods for the determination of measurement error* British Standards Institution
- 11 Read M L Foster R D and Howe A M *Metals and metalloids in workplace air by X-ray fluorescence spectrometry: backup data report for MDHS HSL Project Report IS/97/07* HSL 1997
- 12 West N G 'X-ray fluorescence spectrometry applied to the analysis of environmental samples' *Trends in analytical chemistry* 1984 3 (8) 199–204
- 13 Withers E *X-ray fluorescence and X-ray diffraction studies of airborne toxic metal particulates in the field of occupational hygiene* MPhil thesis University of Surrey 1984
- 14 Quisefit J P de Chateaubourg P Garivait S Steiner E 'Quantitative analysis of aerosol filters by wavelength dispersive X-ray spectrometry from bulk reference samples X-ray' *Spectrometry* 1994 23 59–64
- 15 BS EN 482:2012 *Workplace exposure: General requirements for the*

performance of procedures for the measurement of chemical agents British Standards Institution

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