

# MDHS

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



# 91

## Metals and metalloids in workplace air by X-ray fluorescence spectrometry

July 1998

### INTRODUCTION

**Note 1:** This MDHS aims to guide those who wish to measure metals and metalloids in air using X-ray fluorescence spectrometry (XRFS) for the purpose of monitoring workplace exposure. It incorporates, improves upon and replaces MDHS 7 'Lead and inorganic compounds of lead in air',<sup>1</sup> MDHS 11 'Cadmium and inorganic compounds of cadmium in air'<sup>2</sup> and MDHS 13 'Chromium and inorganic compounds of chromium in air'.<sup>3</sup>

#### Requirements of the Control of Substances Hazardous to Health (COSHH) Regulations 1994

1 Those who carry out and supervise the procedures described in this MDHS could be exposed to various hazardous substances, and therefore should be aware of the requirements of the COSHH Regulations.<sup>4</sup> These are designed to ensure that the exposure of people at work to substances that could cause health damage is either prevented, or where that is not reasonably practicable, adequately controlled. Employers are required to make an assessment of the health risk created by such work, and to prevent or control exposure to the substances involved. The COSHH Regulations also require that persons who could 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 MDHS.

2 Guidance is given in the Approved Codes of Practices for the Control of Substances Hazardous to Health Regulations (the General COSHH ACOP), the Control of Carcinogenic Substances Regulations (the Carcinogens ACOP) and the Control of Biological Agents Regulations (the Biological Agents ACOP) which are included in a single publication with the COSHH Regulations.<sup>5</sup>

#### Requirements of the Ionising Radiation Regulations 1985

3 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 1985<sup>6</sup> and their associated Approved Code of Practice *The protection of persons against the ionising radiation arising from any work activity*.<sup>7</sup> In particular, the construction of the XRF spectrometer and its use must comply with the Regulations.

#### Occurrence, properties and uses

4 Occurrence, properties and uses of several metals and metalloids and their compounds are covered in guidance notes in HSE's Environmental Hygiene series.<sup>8</sup>

5 Airborne particles containing metals and metalloids and their compounds arise from a number of industrial processes. The nature and size of the particles concerned depends on the process involved and on the parent material which gives rise to them. For example, dust arising from abrasive processes, such as metal grinding, is usually coarse, ie it contains large particles. Similarly, dust produced by handling powders which have been made by milling crystalline compounds generally has a large particle size and consists of separated particles. On the other hand, dust arising from the handling of powders which have been made by precipitative techniques is composed of aggregates of very small particles. Fume produced by the heating and condensation of metal vapour in processes such as welding, brazing and metal refining is also of very small particle size.

#### Health effects

6 The health effects of the more commonly encountered harmful metals and metalloids and their compounds are summarised in HSE's Environmental Hygiene series of guidance notes<sup>8</sup> and are covered more fully in HSE Toxicity Reviews.<sup>9</sup> Further information can be found in industrial hygiene and toxicological reference works.<sup>10,11,12</sup>

7 To reflect the different health effects from different sizes of particles present in industrial dusts two size fractions are specified when setting occupational limits. Total inhalable

dust approximates to the fraction of airborne material that is capable of entering the nose and mouth during breathing and is therefore available for deposition anywhere in the respiratory tract. Respirable dust approximates to the fraction of inhaled dust which is capable of penetrating to the gas-exchange region of the lung. These particle size fractions are defined in BS EN 481.<sup>13</sup>

### Health and safety precautions

8 Information leaflets in HSE's MS(A) series<sup>14</sup> are available for several metals and metalloids. These summarise the risks involved in working with the metals and metalloids and their compounds and what can be done to control them.

9 Guidance notes in HSE's Environmental Hygiene series<sup>8</sup> are also available for several metals and metalloids. These describe measures to prevent and control exposure, emergency procedures and health surveillance for those working with the metals and metalloids and their compounds. Health and safety precautions for lead are fully covered in a specific Approved Code of Practice<sup>15</sup> supporting the Control of Lead at Work (CLAW) Regulations.<sup>16</sup>

### Exposure limits

10 Regulation 7 of the Control of Substances Hazardous to Health Regulations (COSHH) (Amendment) 1996<sup>4</sup> lays down the requirements for the use of maximum exposure limits (MELs) and occupational exposure standards (OESs) for the purpose of achieving adequate control of worker exposure.

11 The Health and Safety Commission has approved OESs and MELs for a number of metals and metalloids in air. These include long-term (8-hour time weighted average) and short-term (usually 15 minutes) exposure limits. Most limits apply to total inhalable dust, although in certain specific cases, eg cadmium sulphide, the limits apply specifically to respirable dust.

12 Occupational exposure standards are published in Table 2 of HSE Guidance Note EH 40.<sup>17</sup> Maximum exposure limits are published in Schedule 1 of the COSHH (Amendment) Regulations 1996<sup>4</sup> and in Table 1 of HSE Guidance Note EH 40.<sup>17</sup> The criteria on which the limits were based are documented in HSE Guidance Notes EH 64<sup>18,19</sup> and EH 65.<sup>20</sup>

13 The occupational exposure limits for lead are a special case. They are set out in regulation 2 of the CLAW Regulations.<sup>16</sup> They are also reproduced in Appendix 5 of HSE Guidance Note EH 40.<sup>17</sup>

14 At the time of publication, the exposure limits for metals and metalloids of atomic number equal to or greater than titanium ( $Z \geq 22$ ) were as summarised in Table D1 of Appendix D of this MDHS. However, they are constantly under scrutiny and subject to revision in the light of new epidemiological evidence. Refer to the most recent version of HSE Guidance Note EH 40,<sup>17</sup> which is updated every year, for current exposure limits.

15 The absence of a specific limit in HSE Guidance Note EH 40<sup>16</sup> does not mean that a metal or metalloid is not harmful. Information on the likely hazard to health of such substances can be found in a number of reference works.<sup>10,11,12</sup> Metals and metal compounds for which no exposure limits are specified are currently subject to the requirements of the COSHH Regulations. These state that a 'dust of any kind' is regarded as hazardous to health when present at a substantial concentration in air. A 'substantial' concentration of dust should be taken as a concentration of 10 mg m<sup>-3</sup> (8-hour time-weighted average) of total inhalable dust or 4 mg m<sup>-3</sup> (8-hour time-weighted average) of respirable dust, where there is no indication of the need for a lower value.

### Analytical methods

16 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.

17 Alternative methods for a number of metals and metalloids have been published in the MDHS series. In particular, methods using atomic absorption spectrometry (AAS) are available for lead,<sup>21</sup> cadmium,<sup>22</sup> chromium,<sup>23</sup> mercury,<sup>24</sup> cobalt,<sup>25</sup> arsenic,<sup>26</sup> nickel<sup>27</sup> and platinum.<sup>28</sup> A generic MDHS using inductively coupled plasma emission spectrometry (ICP-AES) for the measurement of various metals and metalloids is also planned. Information on other methods can be found in HSE's EH40 database.<sup>29</sup> This refers to alternative methods published by ISO,<sup>30</sup> NIOSH<sup>31</sup> and OSHA.<sup>32</sup> However, if any of these methods is used, the sampling procedures described in MDHS 14/2<sup>33</sup> shall be applied.

18 This method has been validated<sup>34,35,36</sup> to demonstrate that it complies with BS EN 482 *Workplace atmospheres - General requirements for the performance of procedures for the measurement of chemical agents*.<sup>37</sup> If an alternative method is used it is necessary to demonstrate that it also meets these performance requirements

**Note 2:** *The method validation<sup>35</sup> does not necessarily apply if the spectrometer or measurement conditions used are substantially different from those used in the validation. In such circumstances, it should be confirmed that the sensitivity of the spectrometer used is adequate for the measuring procedure to meet the overall uncertainty requirements of BS EN 482.<sup>37</sup> Appendix E gives guidance on how this may be achieved.*

### SCOPE

#### Applicability

19 This MDHS describes methods for determination of the concentration of metallic and submetallic elements of

atomic number equal to or greater than that of titanium ( $Z \geq 22$ ). Quantitative analysis can be achieved using K lines for elements of atomic number equal to or greater than that of titanium ( $Z \geq 22$ ) and using L lines for elements of atomic number greater than or equal to that of lead ( $Z \geq 82$ ). Analysis using L lines for elements of atomic number ( $Z$ ) 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.

**Note 3:** *In certain cases, measurements made using XRF lines that are normally suitable for quantitative analysis can only be regarded as semi-quantitative - notably (i) when it is necessary to measure an XRF line which is strongly absorbed by the sample matrix, and (ii) when the particle size of the sample is large.*

20 The method was developed and validated using a sequential wavelength dispersive XRF spectrometer. Much of the text is written assuming that a similar instrument will be used. 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.

21 General recommendations are made for the XRFS measurement of most metals and metalloids ( $Z \geq 22$ ) which are of interest to occupational hygienists. It is not practical to specify exact conditions which would be suitable for all designs of spectrometers and their different exciting X-ray sources. It is assumed, therefore, that spectrometers will be operated or supervised by persons trained in XRFS analysis and able to make best use of the capabilities of the specific instrument used.

22 The XRFS method is suitable for the determination of metals and metalloids in samples weighing up to a maximum of approximately 0.5 mg, when deposited on a 25 mm diameter filter, or 1 mg on a 37 mm diameter filter.

**Note 4:** *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 calculations<sup>36</sup> 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 is reduced to 0.2 mg. Secondly, experience has 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.*

23 Using the XRF lines recommended, the method has also been shown<sup>34,35</sup> to give adequate sensitivity for use for measuring the concentration of the elements As, Ba, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sb, Sn, Sr and Zn when the air sample volume is in the range 120 litres to 960 litres.

24 XRFS analysis requires no sample preparation, and it can therefore be carried out quickly and cheaply. This is a significant advantage over other analytical techniques such as AAS and ICP-AES that require the sample to be taken into solution prior to analysis.

25 Results obtained by XRFS analysis may normally be regarded as quantitative. However, even when measurements are only semi-quantitative (see note 3), the non-destructive nature of the technique makes it suitable for screening air samples to estimate the mass of the metals and metalloids of interest present before repeat analysis, if necessary, using another, more accurate, technique such as AAS or ICP-AES.

## METHOD PERFORMANCE

### Effectiveness of the procedure

26 Over a number of years, experience at the Health and Safety Laboratory (HSL) has shown<sup>38,39</sup> that XRFS is capable of producing reliable results for a range of metals and metalloids in particulate samples collected on filters from workplace air. In most cases, results agree well with those that can be obtained by subsequent analysis using ICP-AES or AAS. Other workers have successfully used XRFS to measure a range of metals and metalloids in workplace air.<sup>40,41,42</sup>

### Detection limits

27 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.

28 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 for unit mass of the element at the wavelength peak, and to the background level of X-ray counts (see Appendix E). Detection limits can therefore be reduced by counting for longer periods, but this increases the analysis time, which can be especially significant if several metals and metalloids are to be determined.

29 Qualitative and quantitative detection limits, defined as three times and ten times the standard deviation of a blank measurement, have been determined<sup>35</sup> 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 C1 of Appendix C, 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 D2 of Appendix D.

30 For comparison purposes, alongside the detection limits in Table D2 are given the masses of the elements concerned that would be collected for a 60-litre sample of air at 1/10 the OEL (corresponding to a 30-minute sample collected at a sampling rate of 2 l min<sup>-1</sup>). Longer sampling times or longer X-ray counting times are clearly required for quantitative measurement when K fluorescence lines are used to measure some metals and metalloids of higher atomic number. The alternative of using L lines, which can be seen to confer much lower detection limits, is not recommended. This is because, except for elements of atomic number greater than or equal to that of lead ( $Z \geq 82$ ), strong absorption by the sample matrix means that results can only be regarded as semi-quantitative.

## Bias

### Sampler bias

31 The bias of inhalable samplers has been shown<sup>13</sup> to vary considerably. However, a bias of less than  $\pm 5\%$  is typical for the samplers recommended in MDHS 14/2.<sup>33</sup> Since the analytical bias is negative (see paragraph 33), a sampler bias of -5% was therefore used when estimating the bias of the measuring procedure as a whole using Equation 1 (see paragraph 34).

### Analytical bias

32 Particle size and depth effects can occur when analysing a sample by XRFS. On the basis of theoretical calculations and supporting experimental work,<sup>36</sup> 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  $\mu\text{m}$ , 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 ( $Z \geq 22$ ), or L lines are used for elements of atomic number greater than or equal to that of lead. See notes 5 and 6.
- Provided that less than 500  $\mu\text{g}$  of sample is collected (see paragraph 22 and note 4), the negative bias caused by the depth of the layer of particulate collected will normally be less than 10%.

33 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%. An analytical bias of -10% was therefore substituted in Equation 1 when estimating the bias of the measuring procedure as a whole.

**Note 5:** 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  $\mu\text{m}$ . 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.<sup>38,39</sup> Serious 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,<sup>41</sup> 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 weight, they are much denser and likely to re-absorb the fluorescence X-rays.

**Note 6:** Recommendations for the quantitative use of elemental lines are based on the following observations. Lead results obtained using the Pb L $\beta$  XRF line for real samples from a range of industries showed good agreement with results obtained using atomic spectrometry.<sup>38,39</sup> This provides evidence that particle size effects are not serious 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 theory<sup>36</sup> to lead oxide suggests that for particles of average physical size 2.5  $\mu\text{m}$ , equivalent to an aerodynamic diameter of approximately 7.5  $\mu\text{m}$ , 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 ( $Z \geq 22$ ).

**Note 7:** 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 precipitation processes are often in the form of a floc with large void spaces and containing as little as 1/10 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.

### Combination of sampling and analytical bias

34 The bias of the measuring procedure as a whole is given by:

$$(1 + bias) = (1 + bias_{sampler}) \times (1 + bias_{analysis}) \quad \text{Equation 1}$$

## Precision

### Imprecision of the aerosol sampling process

35 The imprecision of the aerosol sampling process usually depends strongly on the size distribution of the airborne particles sampled, and it can depend on other factors, such as windspeed. Draft European Standard EN (00137009)<sup>43</sup> suggests calculating approximate values of the imprecision of the sampling process relevant to the workplace atmosphere to be sampled, using information given in the sampler test report.

36 However, this approach is not practicable for assessing the performance of a measuring procedure intended for general application. The results of a study to evaluate the performance of inhalable samplers<sup>44</sup> suggest that the relative standard deviation of the aerosol sampling process is normally less than 5% for inhalable samplers that meet the requirements of draft European Standard EN (00137009).<sup>43</sup> The relative standard deviation of the aerosol sampling process,  $RSD_{sampler}$ , was therefore taken to be 5% when estimating the imprecision of the measuring procedure as a whole using Equation 2 (see paragraph 39).

### Imprecision arising from flow rate variability

37 In the case of aerosol samplers where there is no interaction between particle size selection characteristics and volumetric flow rate, at least for small changes in flow rate, the imprecision arising from flow rate variability can be estimated simply. BS EN 1232 *Workplace atmospheres - Pumps for personal sampling of chemical agents - Requirements and test methods*<sup>45</sup> prescribes a maximum allowable error in the volumetric flow rate of  $\pm 5\%$ . Assuming that this is met on 99% of all occasions, the flow-related relative standard deviation,  $RSD_{flow}$ , is equal to 0.05/3. This value was therefore used when estimating the imprecision of the measuring procedure as a whole using Equation 2.

### Imprecision arising from analytical variability

38 The relative standard deviation of the analytical method,  $RSD_{analysis}$ , depends on the X-ray counting time. Relative standard deviations have been calculated for a number of metals and metalloids using analytical sensitivity data (in counts/ $\mu\text{g sec}$ ) obtained under the measurement conditions given in Table C1 of Appendix C, using a 50-second counting time at the wavelength peak and a total of 50-seconds counting time at the background positions. These calculated relative standard deviations were substituted in Equation 2 to estimate the imprecision of the measuring procedure as a whole.

### Combination of sampling and analytical precision

39 The imprecision of the measuring procedure as a whole is given by:

$$RSD^2 = RSD_{sampler}^2 + RSD_{flow}^2 + RSD_{analysis}^2 \quad \text{Equation 2}$$

## Overall uncertainty

40 The overall uncertainty for a measuring procedure is defined in BS EN 482<sup>37</sup> as 'the quantity used to characterise as a whole the uncertainty of the result given by a measuring procedure', and is expressed in percentage terms, by a combination of bias and precision according to the following equation:

$$OU = \frac{|\bar{x} - x_{ref}| + 2\sigma_{(n-1)}}{x_{ref}} \times 100\% \quad \text{Equation 3}$$

where :  $OU$  is the overall uncertainty of the procedure;

$\bar{x}$  is the mean value of results of n repeated measurements;

$x_{ref}$  is the true or accepted reference value; and

$\sigma_{(n-1)}$  is the standard deviation of n repeated measurements.

41 Equation 3 can be rewritten as:

$$OU = [ |bias| + (2 \times RSD) ] \times 100\% \quad \text{Equation 4}$$

where:  $bias$  is the difference between the mean measured concentration and the true or reference concentration, divided by the true or reference concentration, ie

$$\frac{(\bar{x} - x_{ref})}{x_{ref}}; \text{ and}$$

$RSD$  is the relative standard deviation of n repeated measurements defined as

$$\frac{\sigma_{(n-1)}}{x_{ref}}.$$

42 The overall uncertainty can then be estimated by substituting in Equation 4 the values for bias and relative standard deviation calculated using Equations 1 and 2. Overall uncertainties calculated on this basis are given in table D3 of Appendix D for concentrations ranging from 0.1 to 2 times the limit value, for sampling periods of between 30 minutes and 8 hours, and for a sampling rate of 2 litres/minute.

43 BS EN 482<sup>37</sup> prescribes that the overall uncertainty of procedures for the measurement of chemical agents in workplace air shall be < 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.

44 It has been shown at HSL<sup>35</sup> that the overall uncertainty requirements of BS EN 482<sup>37</sup> can be met, provided a long enough sampling time and/or X-ray counting time is used (see Table D3). For most of the metals and metalloids investigated, using an X-ray peak counting time of 50 seconds the overall uncertainty requirements are met for an air volume of at least

60 litres, corresponding to a sampling time of 30 minutes at 2 litres min<sup>-1</sup>. However, for the overall 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<sup>-1</sup>, was required for the measurement of arsenic (using the K $\beta$  line) and antimony (using the K $\alpha$  line); and an air volume of at least 960 litres, corresponding to a sampling time of 8 hours at 2 l min<sup>-1</sup>, was required for the measurement of barium (using the K $\alpha$  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<sup>-1</sup>, was required for measurement of cadmium (using the K $\alpha$  line), because of its very low limit value of 0.025 mg m<sup>-3</sup>.

**Note 8:** *The imprecision of XRF measurements depends statistically on the square root of the number of X-rays counted (see Appendix E). Consequently, by increasing counting times, it is generally possible to meet the overall uncertainty requirements of BS EN 482<sup>37</sup> by using smaller sample volumes than those given in Table D3. 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. Of course, 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

### Line overlap effects

45 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.

46 Selection of XRF lines and measurement conditions should be based upon a 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 XRF systems by the incorporation of warning information on possible interfering XRF lines in the wavelength region of the elemental XRF line selected.

47 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 semiquantitative. 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.

## PRINCIPLE

48 A measured volume of air is drawn through a filter mounted in an inhalable or respirable dust sampler, as appropriate (see paragraph 11). The dust and fume collected on the filter is then analysed by X-ray fluorescence spectrometry. The XRF spectrometer is calibrated using filters prepared by sampling dust of known composition from an atmosphere generated in a dust chamber. A 'ratio monitor standard' is used to minimise the effects of instrument drift.

## REAGENTS

49 During the analysis, use only reagents of recognised analytical grade. Use only distilled or de-ionised water, or water of equal purity (paragraph 50). Do not pipette by mouth.

### Water

50 Water complying with the requirements of BS 3978<sup>46</sup> grade 2 water (electrical conductivity less than 0.1 mS m<sup>-1</sup> and resistivity greater than 0.01 MΩ.m at 25°C).

### Pure elemental compounds

51 Pure compounds of the metals and metalloids of interest, suitable for preparing filters for calibration of the XRF spectrometer. These shall be in the form of a homogeneous, fine powder of accurately known composition. The first choice in most cases is the oxide, but other compounds might be preferable for some elements. If the compound as supplied is insufficiently fine, it shall be ground to very small particle size (preferably < 5 µm) using a suitable grinding mill.

**Note 9:** *If the mass of the metal or metalloid on the calibration filters is to be confirmed after calibration of the XRF spectrometer using sample dissolution and analysis by ICP-AES or AAS, consideration should be given to the ease of digestion of the compound.*

### Standard elemental solutions, 10 000 µg ml<sup>-1</sup>

52 Use commercially available standard solutions of the metals and metalloids of interest at a concentration of 10 000 µg ml<sup>-1</sup>. Multi-element standard solutions may be suitable in some cases where the XRF lines of the metals and metalloids to be measured do not coincide with any of those other elements in the mixture. Observe the manufacturer's expiry date or recommended shelf life.

53 Alternatively, prepare standard solutions by dissolving pure elemental compounds of known composition in a suitable acid, and then diluting to volume with water (paragraph 50).

### Graphite powder

54 Pelletable graphite powder, suitable for compression in a die to form a solid pellet, for use as a drift correction monitor or quality control sample (see paragraph 118). Elemental impurities shall be as low as possible, and preferably less than 10 µg g<sup>-1</sup>. Ultra-purity electrode carbon has been found to be suitable.

### Reagents for use in a reference analytical method

55 Reagents of recognised analytical reagent grade, as recommended in the reference procedure.

## SAMPLING EQUIPMENT

### Inhalable samplers

56 Samplers designed to collect the inhalable fraction of airborne particles, as defined in BS EN 481,<sup>13</sup> and complying with the provisions of draft European Standard EN (00137009),<sup>43</sup> for use when the exposure limits for metals and metalloids of interest apply to the inhalable fraction of airborne particles. Inhalable samplers suitable for personal sampling are described in MDHS 14/2.<sup>33</sup> Only samplers that collect the inhalable fraction of airborne particles on the filter are suitable for quantitative XRFS analysis (see note 12).

**Note 10:** *In general, personal samplers for collection of the inhalable fraction of airborne particles do not exhibit the same size-selective characteristics if used for static sampling.*

**Note 11:** *Samplers manufactured in non-conducting material have electrostatic properties which can influence representative sampling. Electrostatic influences should be reduced, where possible, by using samplers manufactured from conducting material.*

**Note 12:** *Some inhalable samplers are designed to collect the inhalable fraction of airborne particles on the filter, and any particulate matter deposited on the internal surfaces of the sampler is not of interest. Other inhalable samplers are designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, in which case particulate matter deposited on the internal surfaces of the sampler forms part of the sample. (Samplers of this type generally incorporate an internal filter cassette or cartridge which can be removed from the sampler to enable this material to be easily recovered.) The operating instructions supplied by the manufacturer should be consulted to find out whether particulate matter deposited on the internal surfaces of the sampler forms part of the sample.*

**Note 13:** *Although dust deposited on the internal surfaces of a sampler is usually only a small proportion of the total collected, when this forms part of the sample it prevents XRFS analysis of the filter from giving correct results. In such circumstances, XRFS filter analysis results can only be regarded as suitable for screening purposes, and further analysis will be necessary if high results are obtained.*

### Respirable samplers

57 Samplers designed to collect the respirable fraction of airborne particles, as defined in BS EN 481,<sup>13</sup> and complying with the provisions of draft European Standard EN (00137009),<sup>43</sup> for use when the exposure limits for metals and metalloids of interest apply to the respirable fraction of airborne particles. Cyclone-type respirable dust samplers are described in MDHS 14/2.<sup>33</sup>

## Filters

58 Filters, of a diameter suitable for use in the selected samplers (see paragraph 90), and with a retentivity of not less than 99.5% for particles with a 0.3 µm diffusion diameter (see subclause 2.2 of BS EN 481<sup>13</sup>). Filters of 25 mm diameter are preferable, since the whole filter can be exposed to the X-ray beam. However, the use of 37 mm filters is not excluded (see note 16).

59 The use of membrane filters is recommended, since when these are used the airborne particles are deposited as a thin layer on the surface of the filter. Mixed cellulose ester membrane filters of 0.8 µm mean pore diameter are considered to be the most suitable.

**Note 14:** It is helpful if the filter material can be readily digested in acid if it is intended to characterise calibration filters using ICP-AES or AAS analysis, or if either of these techniques is likely to be used to reanalyse samples after screening by XRFs. In such cases, filters composed of polymers that are not readily decomposed by mineral acids, eg PVC or PTFE, should be avoided.

**Note 15:** Depth effect filters made of glass fibre or paper are not generally considered to be 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. However, they might be suitable for analysis of certain metals and metalloids when using short wavelength XRF lines which are not significantly absorbed by the filter material.

**Note 16:** The method has been validated using 25 mm diameter membrane filters. The use of 37 mm diameter filters has not been investigated, but is not excluded. Indeed, the use of 37 mm diameter filters is recommended in other semi-quantitative XRF methods.<sup>47, 48</sup> However, it is recommended that the validity of results obtained using 37 mm filters is confirmed by re-analysing a representative range of samples using another technique, eg AAS or ICP-AES.

## Sampling pumps

60 Sampling pumps, complying with the provisions of BS EN 1232,<sup>45</sup> and compatible with the samplers used (see paragraph 90).

**Note 17:** Existing users may continue to use sampling pumps that do not comply with all the provisions of BS EN 1232,<sup>45</sup> provided that they take steps to ensure that the required volumetric flow rate (see paragraph 91) is maintained to within ± 5% of the nominal value throughout the sampling period.

61 BS EN 1232<sup>45</sup> requires that sampling pumps have, as a minimum, the following features:

- an automatic control which keeps the volumetric flow rate constant in the case of changing back pressure;
- either a malfunction indicator, which, following

completion of sampling, indicates that the air flow has been reduced or interrupted during sampling; or an automatic cut-out, which stops the pump if the flow rate is reduced or interrupted; and

- a facility for the adjustment of flow rate, such that it can only be actuated with the aid of a tool (eg screw driver) or requires special knowledge for operation (eg via software), so as to preclude inadvertent readjustment of the flow rate during use.

**Note 18:** An integral timer is a highly desirable additional feature.

62 BS EN 1232<sup>45</sup> requires that the performance of the pumps is such that:

- the pulsation of the flow rate does not exceed 10%;
- a flow rate set within the nominal range does not deviate by more than ±5% from the initial value under increasing back pressure;
- within the range of ambient temperatures from 5°C to 40°C, the flow rate measured under operating conditions does not deviate by more than ±5% from the flow rate at 20°C;
- the operating time is at least 2 hours, and preferably 8 hours; and
- the flow rate does not deviate by more than ±5% from the initial value during the operating time.

## Flowmeter

63 Flowmeter, portable, capable of measuring the required volumetric flow rate (see paragraph 91) to within ±1%, and calibrated against a primary standard, ie a flowmeter whose accuracy is traceable to national standards.

**Note 19:** 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 note 36), provided they have adequate sensitivity.

## Ancillary equipment

64 Flexible 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, if required (see paragraph 106), in which to transport samples to the laboratory.

## XRFS INSTRUMENTATION

### XRF spectrometer

Either

65 A wavelength-dispersive XRF spectrometer;

or

66 An energy-dispersive XRF spectrometer of adequate sensitivity for the elemental XRF lines of the metals and metalloids to be measured, and capable of resolution or deconvolution of these lines from neighbouring lines of elements present in the sample.

#### X-ray source

67 The XRF spectrometer shall be equipped with an X-ray source capable of supplying photons of sufficient energy to excite the XRF lines of the metals and metalloids to be measured. This may be an X-ray tube, with a suitable power supply, or a radioactive source.

#### X-ray tube

68 The X-ray tube used shall preferably be a general-purpose X-ray tube capable of exciting a wide range of elements (see note 20). A dual anode molybdenum/scandium X-ray tube has been found to be particularly suitable. At high-voltage settings, typically 100 kV and 25 ma, high-energy XRF lines (eg K lines of elements of high atomic number) can be excited by the high-energy X-ray continuum generated, which is rich in the fluorescence X-rays of the molybdenum atoms of the anode core. At lower voltage, but with similar power settings, typically 60 kV and 40 ma, low-energy XRF lines (eg K lines of elements of low atomic number) are efficiently excited by the low-energy X-ray continuum generated, which is rich in the fluorescence X-rays of the scandium atoms of the anode surface.

69 In decreasing order of performance, the following are examples of other X-ray tubes which may be used:

- molybdenum, rhodium or silver anode tubes (rich in elemental XRF K lines);
- tungsten or gold anode tubes (rich in elemental XRF L lines); or
- chromium or scandium anode tubes, which rely on the general continuum of X-ray emission alone for excitation, can still be used but are not very effective at all.

**Note 20:** For the lowest possible threshold of detection, an X-ray tube with an anode composed of an element which will emit fluorescence X-rays slightly more energetic than the excitation energy of the metal or metalloid to be measured, is ideal.

#### X-ray tube power supply

70 The X-ray tube power supply power shall have the capacity to apply sufficient voltage and wattage to the X-ray tube to ensure that the beam of X-rays produced is capable of exciting the XRF lines of the metals and metalloids to be measured (see note 21).

71 Ideally, the power supply should be capable of achieving a maximum voltage of 100 kV. However, many power supplies have a maximum voltage of 60 kV. When

100 kV cannot be achieved, the excitation of the K lines for elements of higher atomic number will be less efficient. This can be compensated for by using high currents and/or X-ray tubes with end-windows which can be sited closer to the sample.

**Note 21:** When an X-ray tube is used, it is necessary to apply a voltage in excess of the energy of the XRF wavelength for the metal or metalloid to be measured expressed as KeV (listed in most X-ray analysis text books and tables<sup>44</sup>). However, in order to achieve optimum sensitivity, a voltage of three times this value is preferable.

**Note 22:** It is left to the discretion of the user to decide on the current intensity but, the higher it is, the greater the sensitivity obtained. The maximum current applied is, of course, restricted by the acceptable power limits of the X-ray tube used.

**Note 23:** The power supplies of some instruments might not be capable of yielding adequate sensitivity for elements such as Cd, Sn, and Sb using K lines. In this case it might only be possible to measure these elements semi-quantitatively using L lines.

#### Radioactive X-ray sources

72 Radioactive X-ray sources are most commonly used in energy-dispersive XRF spectrometers, particularly portable instruments. Such spectrometers are usually equipped with a number of different sources which emit X-rays of different energies characteristic of the radioactive elements of which they are composed. It is therefore not possible to give specific advice that is applicable to all instruments. Select appropriate sources according to the metals and metalloids to be measured, following recommendations made by the manufacturer. Examples of sources that are typically used are as follows:

- <sup>55</sup>Fe for Ti, Cr
- <sup>109</sup>Cd for Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Zr, Mo, U, Hg, Pb, Th
- <sup>241</sup>Am for Cd, Sn, Sb, Ba, Ag

73 The exciting X-ray wavelength is also sometimes modified by the interposition of a secondary target composed of a different element. For instance, the French Standard NF X 43-027 *Determination of lead in aerosols - X-ray fluorescence spectrometry*<sup>49</sup> recommends, in order of preference:

- either direct excitation by cadmium (<sup>109</sup>Cd); or
- an americium source (<sup>241</sup>Am) with a secondary molybdenum target.

#### Wavelength-dispersive components

##### Wavelength-dispersive crystals

74 Wavelength-dispersive XRF spectrometers shall be equipped with a suitable range of crystals to achieve resolution of the measured XRF lines from other X-rays

emitted or diffracted by the sample. Resolution is achieved by differential diffraction from the crystal lattice according to the wavelength of the X-ray, the d spacing of the atoms in the lattice of the crystal and the angle that the X-ray beam impinges on the crystal.

75 At least one of the crystals shall be of high resolving power, so as to enable line overlap effects to be minimised (see paragraphs 45-47). The crystal faces which are most commonly used for XRF measurement of metals and metalloids are Lithium Fluoride 200 and Lithium Fluoride 220. Other crystal faces of similar d spacing and resolving power are likely to be equally suitable.

#### **X-ray beam collimation**

76 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.

#### **Energy-dispersive components**

77 Energy-dispersive XRF spectrometers shall be equipped with an energy-transponding semiconductor detector, pulse-discrimination circuitry and computer software capable of deconvoluting the measured XRF lines from other X-rays emitted or diffracted by the sample. The resolving power of energy-dispersive systems depends on the quality and construction of their energy-transponding semiconductor detectors. Resolution is not of the same order as that achievable using wavelength dispersion, and therefore line overlaps inevitably occur between neighbouring XRF lines. The suitability of energy-dispersive spectrometers therefore depends to a large extent on the sophistication of their associated deconvoluting computing packages. Most modern instruments can accomplish this adequately, but some older instruments are not as effective.

#### **Spectrometer facilities**

##### **X-ray beam masking**

78 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 incorrect results will be obtained in circumstances where the distribution of dust on the sample and calibration filters is not identical.

##### **Spectrometer chamber X-ray path conditions**

79 All wavelength-dispersive instruments and some energy-dispersive instruments house the X-ray measurement apparatus in the spectrometer chamber, in which the sample is also positioned during measurement. It is recommended that such instruments are equipped with a facility to evacuate the spectrometer chamber during measurement, or alternatively a facility to flush it with helium.

**Note 24:** *In order to minimise X-ray absorption, XRF is best carried out with the spectrometer chamber under vacuum. However, the use of a 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.*

##### **Sample spinner**

80 It is recommended that the instrument has a facility to rotate the sample during measurement.

**Note 25:** *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.*

#### **XRF spectrometer sample cups and masks**

81 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.

82 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.

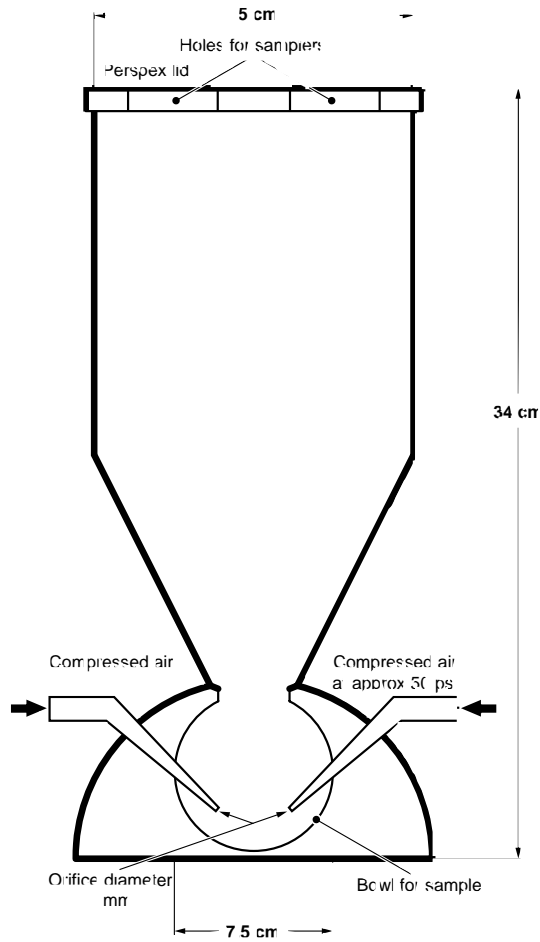
83 A screw-fit sample cup suitable for holding the masking plates is illustrated in Figure 2. This is of a design intended for use in a Philips PW 1480 XRF spectrometer. It is no longer in production, but can relatively easily be fabricated in a well-equipped engineering workshop. Similar cups could be fabricated for other instruments. A special tool (also illustrated in Figure 2) can be made to insert into the circular slits surrounding the central hole to assist the positioning of the filter in the centre of the mask.

**Note 26:** *Ideally, the sample cup would be manufactured of pure aluminium, but this is difficult to machine. Machinable aluminium containing low concentrations (<1%) of manganese, iron, copper, and zinc has been found to be suitable at HSL. These elements are still measurable 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.*

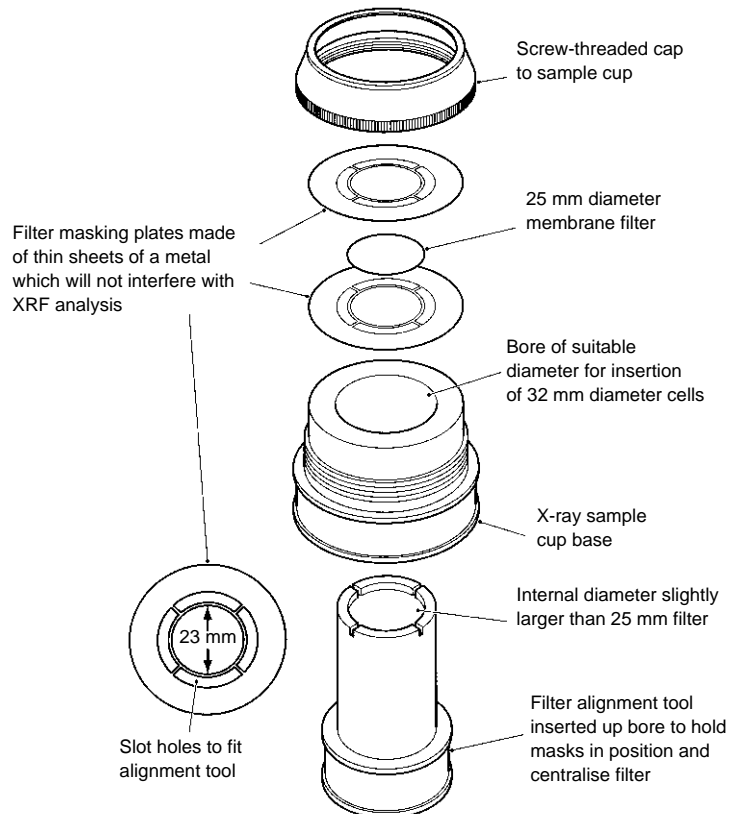
**Note 27:** *The manufacture of sample cups and masks to the design in Figure 2 can be commissioned from HSL workshops.*

##### **Liquid cells for mounting filters**

84 Plastic cells designed to present liquid samples to the XRF spectrometer can be used as an alternative



**Figure 1** Glass chamber for the preparation of calibration standards



**Figure 2** X-ray cup and masks for mounting filters

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 is retained between two layers of thin polymer film.

**Note 28:** 6 µm thick polypropylene film or similar Mylar® film is suitable.

## INSTRUMENTATION FOR A REFERENCE ANALYTICAL METHOD

85 It is recommended that one of the following instruments is available to characterise filters used for calibration of the XRF spectrometer:

- an atomic absorption spectrometer, equipped with appropriate hollow cathode or electrodeless lamps for the range of metals and metalloids of interest;
- an inductively coupled plasma-atomic emission spectrometer; or
- an inductively coupled plasma-mass spectrometer.

**Note 29:** It has been demonstrated<sup>34</sup> that it is possible to successfully calibrate the XRF spectrometer with the aid of a microbalance alone, provided the composition of the calibration standard powder is accurately known. However greater confidence in the accuracy of calibrations is obtained if they are based upon the re-analysis of calibration filters using a reference analytical method. A reference method is also useful to check and confirm results obtained if there is doubt about the applicability of XRFs to the analysis of filter samples generated by a particular process.

## OTHER LABORATORY APPARATUS

### Micro-balance

86 A micro-balance, capable of weighing accurately to ±0.1 µg.

**Note 30:** It would be technically possible to manage without a micro-balance and to calibrate the XRF spectrometer against the analysis obtained for calibration filters by a different analytical technique. However, a micro-balance makes the estimation of the quantity of dust collected on calibration filters much less of a trial-and-error process.

### Dust cloud generation chamber

87 An apparatus for generating dust clouds from the elemental 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 material is placed, and two side arms, through which a short blast of compressed air is applied to generate the dust cloud.

**Note 31:** The manufacture of a dust cloud generation chamber shown in Figure 1 can be commissioned from any reputable glassblowers, eg Farley and Sons Ltd, Enfield.

## Equipment for manufacturing ratio monitor standards and quality control samples

88 The following equipment is required if the recommended procedure for manufacturing ratio monitor standards and quality control samples is adopted (see paragraph 118):

- a set of adjustable micropipettes, complying with the requirements of BS 7653-1 to BS 7653-4;<sup>50-53</sup>
- a furnace, capable of maintaining the temperature necessary for thoroughly drying pelletable graphite;
- a hydraulic press capable of applying 20 tons; and
- a suitable die for pressing pellets of 31 mm diameter (or some other diameter more suitable to the spectrometer).

## Disposable gloves

89 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.

## SAMPLING

### Preliminary considerations

#### Selection and use of samplers

90 Select samplers (paragraph 56 or 57) designed to collect the inhalable or the respirable fraction of airborne particles, as defined in BS EN 481,<sup>13</sup> according to which particle size fraction is applicable to the exposure limits for the metals and metalloids of interest. If more than one particle size fraction is of interest, collect multiple samples.

91 Use the selected samplers (see paragraph 90) at their design flow rate, and in accordance with the instructions provided by the manufacturer, so that they collect the intended fraction of airborne particles.

#### Sampling period

92 Select an appropriate sampling period, taking into account the purpose of the measurement. If sampling is carried out in a dusty environment, the sampling time shall not be so long as to risk overloading the filter. (An 8-hour time weighted average concentration may be derived from the results for two or more consecutive

samples, as described in HSE Guidance Note EH 40.<sup>17)</sup> Advice on monitoring strategies for toxic substances is given in HSE's booklet HSG173.<sup>54</sup>

#### Maximum particulate on filter and sampling periods

**Note 32:** The following comments relate to the use of a 25 mm diameter filter. The quantity of dust which can be collected on filters of different diameters will be in proportion to the relative areas of the surfaces onto which the sample is collected.

93 It is recommended that no more than 500 µg should be collected on the filter unless it is known that the attenuation coefficient for the XRF wavelength measured is low (< 200 cm<sup>2</sup> g<sup>-1</sup>), in which case no more than 1 mg should be collected.

94 In order not to exceed a sample loading of 500 µg, it is recommended that:

- a maximum sampling time of 2 hours is used in most situations when monitoring workplace air against occupational exposure limits;
- a maximum sampling time of 30 minutes is used when monitoring levels of metals and metalloids in dusty workplace air comparable with the hazardous substance threshold for total inhalable dust of 10 mg m<sup>-3</sup>; and
- a maximum sampling time of 1 hour is used when monitoring welding fume for comparison with an occupational exposure limit of 5 mg m<sup>-3</sup> Fe<sub>2</sub>O<sub>3</sub>.

95 A maximum sampling time of 4 hours is recommended when measuring metals or metalloids with a low occupational exposure standard (ie < 0.1 mg m<sup>-3</sup>), provided that dust levels are generally low and the total amount of dust collected on the filter does not exceed 500 µg. It is permitted to extend the sampling time to 8 hours to collect sufficient sample for accurate XRF measurement, but it is preferable to increase X-ray counting times to achieve the same effect.

#### Handling of filters

96 To minimise the risk of damage or contamination, only handle filters using flat-tipped forceps (paragraph 64), in a clean area. Wear disposable gloves (paragraph 89) to prevent the possibility of contamination.

#### Preparation for sampling

##### Cleaning of samplers

97 Clean the samplers (see paragraph 90) before use. Disassemble the samplers, soak in laboratory detergent solution, rinse thoroughly with water (paragraph 50), wipe with absorptive tissue and allow to dry thoroughly before reassembly. Alternatively, use a laboratory washing machine.

##### Loading the samplers with filters

98 Load clean samplers (see paragraphs 97) with filters (paragraphs 58 and 59), label each sampler so that

it can be uniquely identified, and seal with its protective cover to prevent contamination.

#### Setting the volumetric flow rate

Perform the following in a clean area, where the concentration of airborne particles is low:

99 Connect each loaded sampler (see paragraph 98) to a sampling pump (paragraph 60) using flexible tubing (paragraph 64), ensuring that no leaks can occur. Remove the protective cover from each sampler, switch on the sampling pump, attach the calibrated flowmeter (paragraph 63) to the sampler so that it measures the flow through the sampler inlet orifice(s), and set the required volumetric flow rate (see paragraph 91). Switch off the sampling pump and seal the sampler with its protective cover to prevent contamination during transport to the sampling position.

**Note 33:** If necessary, allow the sampling pump operating conditions to stabilise before setting the volumetric flow rate (refer to the manufacturer's instructions).

#### Blanks

100 Retain as blanks, one unused loaded sampler from each batch of ten prepared, subject to a minimum of three. Treat these in the same manner as those used for sampling in respect of storage and transport to and from the sampling position, but draw no air through the filters.

#### Sampling position

101 Position the sampler in the worker's breathing zone, as close to the mouth and nose 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 (paragraph 64) around the waist, or place it in a convenient pocket.

102 Consider 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. If this is the case, make special arrangements to mount the sampler as close as possible to the worker's nose and mouth.

**Note 34:** Examples of the need to make special arrangements to mount the sampler as close as possible to the worker's nose and mouth are:

- in welding and allied processes, when the use of a welder's face shield provides a degree of protection by physically deflecting the plume of welding fume away from the breathing zone, and sampling on the lapel could overestimate exposure (see EN ISO 10882-1),<sup>55</sup> and
- in soldering, when sampling on the lapel could significantly underestimate exposure because the characteristic plume of solder fume rises up past the nose and mouth.

## Collection of samples

103 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.

**Note 35:** *If the temperature or pressure at the sampling position is significantly different from that where the volumetric flow rate was set (see paragraph 99), the volumetric flow rate could change and it might need to be re-adjusted before sampling.*

**Note 36:** *If the sampling pump used does not comply with BS EN 1232<sup>45</sup> (see note 17), monitor its performance frequently, a minimum of once per hour. Measure the flow rate using the calibrated flowmeter (paragraph 63) 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.*

104 At the end of the sampling period (see paragraph 92), record the time and calculate the duration of the sampling period. Check the malfunction indicator and/or the reading on the integral timer, if fitted, 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 (paragraph 63), and record the measured value. Reseal the sampler with its protective cover and disconnect it from the sampling pump.

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

## Transportation

106 For samplers which collect airborne particles on the filter (see note 12), remove the filter from each sampler, place in a labelled filter transport cassette (paragraph 64) and close with a lid. Take particular care to prevent the collected sample from becoming dislodged from heavily loaded filters. Alternatively, transport samples to the laboratory in the samplers in which they were collected.

107 For samplers which have an internal filter cassette (see note 12), remove the filter cassette from each sampler and fasten with its lid or transport clip.

108 For samplers designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, but which do not have an internal filter cassette (see note 12), transport the samples to the laboratory in the samplers in which they were collected.

109 Transport the samples (paragraphs 106-108) to the laboratory in a container which has been designed to prevent damage to the samples in transit and which has been labelled to assure proper handling.

110 When appropriate, ensure that the documentation which accompanies the samples is suitable for a 'chain of custody' to be established.

## ANALYSIS

*Wear disposable gloves (paragraph 89) during analysis to protect the hands from toxic, corrosive and oxidising reagents.*

### Calibration of the XRF spectrometer

#### Manufacture of calibration filters

111 The most accurate analysis is obtained when the calibration filters are produced in the same way as the samples, ie by collection of dust from an atmosphere using the same samplers. Therefore use the dust cloud generation chamber (paragraph 87) to produce dust clouds from pure compounds of each metal or metalloid of interest (paragraph 51), and collect the dust using the same type of samplers (paragraph 90) used to collect the samples.

112 Use a six-figure micro balance (paragraph 86) to pre-weigh sufficient filters (paragraphs 58 and 59) for preparation of the required number of calibration filters and to act as blanks. If the calibration of the instrument is to be based solely upon the weight of elemental compound collected on the filters, leave the filters exposed to the atmosphere to equilibrate for 12 hours before weighing (see note 37).

**Note 37:** *The mass of material deposited on the filter can be determined by weighing the filter before and after sampling. However, mixed cellulose ester membrane filters tend to absorb and desorb moisture from the atmosphere. This can lead to large weighing errors unless the filters are allowed to equilibrate with the atmosphere, and the variation in the weight of the filters due to moisture content is compensated for by comparison with blank filters. 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 some other analytical technique, eg ICP-AES, AAS or ICP-MS. If this is the intention, extremely accurate determination of the weight of elemental compound deposited on the calibration filters is not important, and so the conditioning of filters is unnecessary.*

113 Load pre-weighed filters into samplers of the same design used for collection of the samples (see note 38). Lead flexible tubing from sampling pumps through the Perspex lid of the dust cloud generation chamber (paragraph 87) and connect it to two or three loaded samplers fixed to the underside of the lid. Do not fit the lid at this stage, but set the volumetric flow rate through the samplers, as described in paragraph 99.

**Note 38:** *The particulate collected on the sample filters is not usually evenly distributed, but is typically 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.*

114 Place a few grams of the pure compound of the metal or metalloid of interest (paragraph 51) in the bottom of the dust cloud generation chamber (paragraph 87) and cover it with a dummy lid. Introduce a burst of compressed air through the inlet valves to generate a dust cloud.

115 Halfway through the dust cloud settling time (see note 39), replace the dummy lid with the lid to which the samplers were fixed. When the dust cloud settling time has elapsed, switch on the sampling pumps, using a different sampling time for each sampler in order to obtain different weights of dust on each calibration filter (see note 41).

**Note 39:** Once the cloud has been generated a settling time is introduced so that the large particles in the cloud have a chance to fall under gravity before the cloud is sampled. The penetrating power of XRF radiation emitted by the atoms in a sample is low (typically  $<10\ \mu\text{m}$ ). It can therefore be significantly attenuated if the particle sizes collected are too large. To keep the particle sizes to a minimum the settling time should be as long as possible. However, eventually all the particles settle out and there is no material captured on the filter. The length of settling time is therefore a compromise which is dependent on the compound being used. In practice, times between 1 and 30 minutes have been found necessary.

**Note 40:** Ideally, the particle size of the dust collected on calibration filters would 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 be low if the particle size of the sample is large.

**Note 41:** Most of the dust will be removed from the chamber within the first 30 seconds so the sampling intervals must be very brief.

116 Re-weigh the filters using the six-figure micro-balance (paragraph 86). If the calibration of the instrument is to be based solely upon the weight of elemental compound collected on the filters, leave the filters exposed to the atmosphere to equilibrate for 12 hours before weighing (see note 37). Correct the weights of dust collected for changes in the moisture content of the filters using the average change in weight of at least four blanks. Calculate the weight of metal or metalloid on each calibration filter from the known composition of the powder used to generate the dust cloud.

117 Repeat the process until a spread of weights ranging from 0 to 500  $\mu\text{g}$  of dust on the filter has been obtained.

**Note 42:** Calibration filters may also be prepared using a desolvating nebuliser to generate a dry aerosol from a multi-element solution of the metals and metalloids of interest.<sup>56</sup>

#### **Manufacture of ratio monitor standards and quality control samples**

**Note 43:** Drift in the sensitivity of the XRF spectrometer is compensated for by analysing a ratio monitor standard

when the instrument is calibrated, and then again when samples are analysed. A factor is then applied to the sample count rates to correct for any change in the count rates obtained for the ratio monitor standard.

**Note 44:** It is convenient to use a single ratio monitor standard that contains all the metals and metalloids to be included in the analytical program (see paragraph 132). However, more than one ratio monitor standard might be required to avoid line overlap effects (see paragraphs 45-47).

**Note 45:** A single ratio monitor standard may be used to correct for a change in the slope of a calibration, 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 in an amount 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.

118 Prepare ratio monitor standards, as required (see notes 43-45), using the method described in paragraphs 119-121.

**Note 46:** Ratio monitor standards may be prepared by other methods, eg by impregnating Araldite or cement, but it is important that they are stable.

119 Weigh 10 g of pelletable graphite (paragraph 54) into a beaker, and dope it with appropriate volumes of 10 000  $\mu\text{g ml}^{-1}$  solutions of each of the metals and metalloids of interest (paragraph 52 or 53). Volumes that give suitable count rates (see note 45) are best found by trial and error.

120 Add sufficient water (paragraph 50) to the doped graphite (paragraph 119) to form a paste, and mix it well to ensure that it is homogeneous. Boil off the water and dry the doped graphite thoroughly by placing the beaker in a furnace (paragraph 88) at 480°C overnight.

121 Place the resulting powder in a 31 mm diameter die (paragraph 88), and use a hydraulic press (paragraph 88) to apply a pressure of 20 tons for 5 minutes and produce a pellet.

122 Prepare a quality control sample or samples (see notes 48 and 49) containing the same elements as the ratio monitor standard (see note 44), following the method described in paragraphs 119-121.

**Note 47:** Ideally, quality control samples would be prepared in the same way as calibration filters. However, mixed cellulose ester filters deteriorate on repeated exposure to X-rays and will eventually disintegrate. It is therefore necessary to prepare quality control samples in the form of solid pellets in the same way as ratio monitor standards.

**Note 48:** Each element should be included in the quality control samples in an amount such that its count rate is similar to that which is obtained near the top of the calibration range.

**Note 49:** Preferably, a quality control sample should be analysed at the beginning and end of the analytical run. It might therefore be convenient to prepare two quality control samples for this purpose, but the disadvantage of this is that it will require two separate Shewart charts to be established (see paragraph 136).

#### Mounting filters for loading into the spectrometer

123 Mount each filter centrally in an XRF spectrometer sample cup (see paragraphs 81-83), making sure that the exposed surface is facing the X-ray beam. Ensure that the filter will remain flat during analysis.

**Note 50:** Provided that less than 1 mg of dust is collected on the filter, there is no significant risk of dust falling off in the spectrometer, even though, as in the case of most sequential spectrometers, the sample is presented to the X-ray beam face down. In any case, the sampling time should be limited according to the dustiness of the atmosphere being sampled, with the aim that no more than 0.5 mg is collected (see paragraphs 93-95).

**Note 51:** If the filter appears to be overloaded, the method of mounting described in paragraph 123 is not recommended. In such circumstances, the filters may be mounted in the sampling cup by placing them between two thin sheets of polymer film, eg 6 µm thick polypropylene or Mylar®. A convenient method for mounting 25 mm diameter filters is to stretch and trap the film across the face of 31 mm diameter XRFS liquid cells using the push-fit rings (see paragraph 84). The sample cup illustrated in Figure 2 is designed so that these 31 mm diameter liquid cells can be lowered down the central bore to rest centrally on the masking plate, so exposing the filter surface to the X-ray beam. A similar method for mounting 37 mm filters is described in the qualitative XRFS method OSHA ID-204.<sup>47</sup>

**Note 52:** For accurate analysis when dust has been dislodged from the filter during transportation, the sample filter and dislodged dust should be dissolved and analysed using another technique.

#### Spectrometer settings

124 Determine the optimum settings of the XRF spectrometer for the metals and metalloids to be determined, as described in paragraphs 125-127, following the advice given in Appendix B. Conditions suitable for use with the Phillips PW 1480 automatic spectrometer equipped with a molybdenum/scandium anode X-ray tube are given in Appendix C for a number of commonly analysed metals and metalloids. However, these conditions might not be appropriate for other instrumentation.

125 Select the best XRF line for measurement of the metal or metalloid and the most suitable voltage and amperage to be applied by the power supply (paragraphs 70 and 71) to the X-ray tube (paragraphs 68 and 69), or alternatively the most suitable radioactive X-ray source (paragraphs 72 and 73), for excitation of X-ray fluorescence.

126 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 best settings for X-ray pulse energy discriminator windows and positioning for background sampling points.

**Note 53:** 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.

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

#### Calibration of the XRF spectrometer

**Note 54:** The described method assumes the use of a sequential wavelength dispersive XRF spectrometer, but essentially identical procedures apply to the use of energy-dispersive and simultaneous wavelength-dispersive XRF spectrometers.

**Note 55:** Nearly all modern spectrometers are computer-controlled. This is assumed to be the case in the description of how to calibrate the instrument.

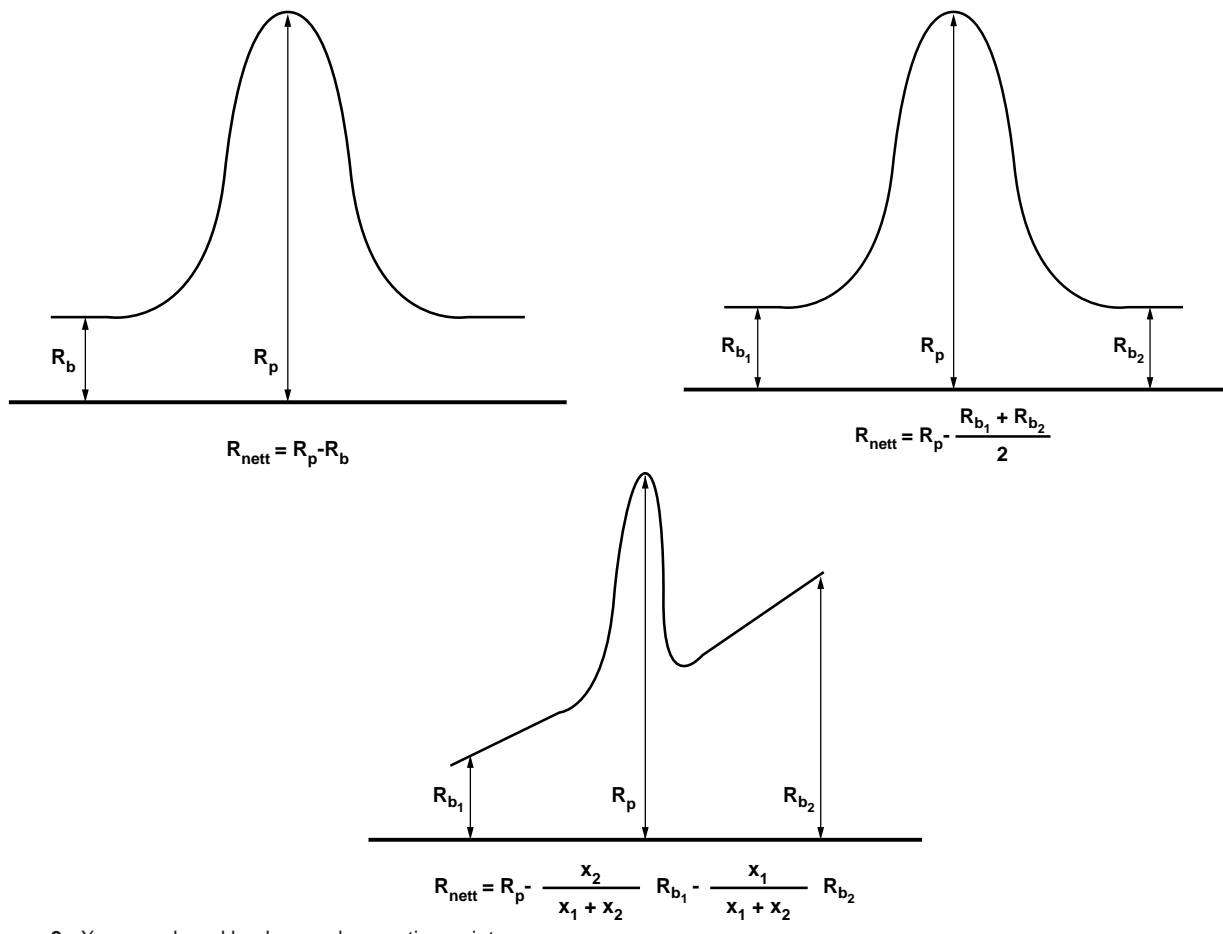
128 Set up a calibration program which uses the selected spectrometer settings for the metal or metalloid for which the spectrometer is to be calibrated (see paragraphs 124-127).

129 Load the calibration filters into the sample cups and measure the X-ray count rates at the peak and background wavelengths for the metal or metalloid of interest, using the calibration program set up in paragraph 128. Calculate the net count rates by subtracting the extrapolated background count rates from the peak count rates, as illustrated in Figure 3.

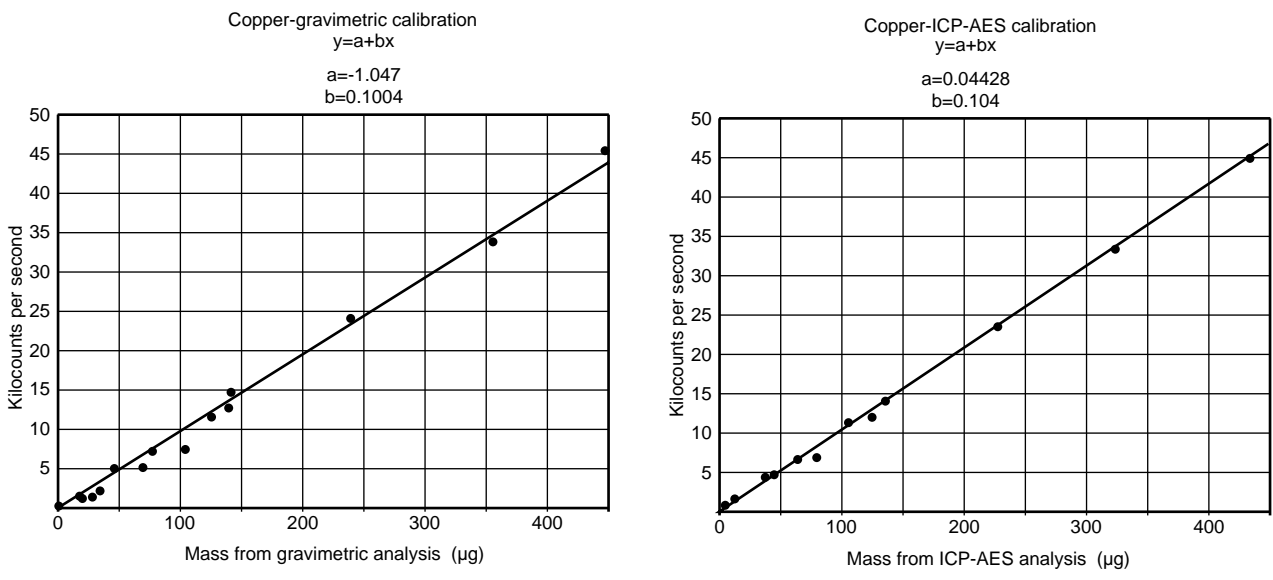
130 Measure the count rate of the ratio monitor standard or ratio monitor standards containing the metal or metalloid of interest (see paragraphs 118-122).

131 Input the weights 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 atomic spectrometry. Then use the computer to produce a calibration curve.

**Note 56:** This curve in fact is very close to linear and is normally treated as a straight line by the software. This will calculate a slope (*m*) for the line, expressed in X-ray counts per second per microgram of element on the filter, and an intercept (*c*). The slope and intercept of the calibration curve is then used as a basis for subsequent analysis of unknown filter samples (see Figure 4).



**Figure 3** X-ray peak and background correction points



**Figure 4** Typical XRF calibration lines

**Note 57:** Sensitivity drift which occurs due to instrumental changes is corrected for by applying a factor based upon changes in the count rate obtained for the ratio monitor standard (see note 43). 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.

### Analytical program

132 Set up the spectrometer to measure all the metals and metalloids of interest by assembling an analytical program containing the spectrometer settings (see paragraphs 124-127) and calibration curves (see paragraph 131) for each of the metals and metalloids concerned.

### Analysis of samples

**Note 58:** The described method assumes the use of a sequential wavelength dispersive XRF spectrometer, but essentially identical procedures apply to the use of energy-dispersive and simultaneous wavelength-dispersive XRF spectrometers.

133 Open the filter transport cassettes (see paragraph 106), sampler filter cassettes (see paragraph 107) or samplers (see paragraph 108) and mount each filter in a sample cup. Follow the same procedure for the blanks (paragraph 100).

**Note 59:** 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 12), retain filter cassette or sampler for further analysis, if necessary (see note 13).

134 Analyse the ratio monitor standard(s) for all metals and metalloids of interest (paragraph 121) using an appropriate analytical programme (see paragraph 132), and calculate the net count rates for each element by subtracting the extrapolated background count rates from the peak count rates, as illustrated in Figure 3. 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.)

**Note 60:** If the ratio 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.

135 Analyse the samples and blanks (paragraph 133) and the quality control samples (paragraph 122) for all metals and metalloids of interest using the selected analytical programme (see paragraph 134). Calculate the

net count rates for each metal or metalloid of interest by subtracting the extrapolated background count rates from the peak count rates, as illustrated in Figure 3. 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 as described in paragraph 134) to calculate the mass of each metal or metalloid on the filters.

**Note 61:** It is best 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

136 Analyse the quality control sample or samples (paragraph 122) 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 Shewhart chart for each quality control sample with warning and action limits at  $\pm 2$  SD and  $\pm 3$  SD respectively. Subsequently plot the results obtained for the quality control samples with each analytical batch and 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.<sup>57</sup>

**Note 62:** 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

137 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 metal or metalloid in air

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

$$\rho(E) = \frac{[m(E)_1 - m(E)_0]}{V} \quad \text{Equation 5}$$

where  $m(E)_1$  is the mass, in micrograms ( $\mu\text{g}$ ), of metal or metalloid on the sample filter (see paragraph 135);

$m(E)_0$  is the mean mass, in micrograms ( $\mu\text{g}$ ), of metal or metalloid on the blank filters (see paragraph 135); and

$V$  is the volume, in litres, of the air sample (see paragraph 137).

## TEST REPORT

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

## QUALITY CONTROL MEASURES

140 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.<sup>57</sup>

141 Internal quality control is an integral part of this method (see paragraph 136).

142 It is strongly recommended that all laboratories undertaking the determination 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). Details of WASP are given in MDHS 71.<sup>57</sup> However, at the time of writing, the WASP scheme only includes two types of membrane filter samples, neither of which is suitable for proficiency testing of XRFS analysis. Filters spotted with solutions do not give correct results using XRFS unless analysed against calibration filters prepared in the same way, and this cannot be done reproducibly. Dust samples are also not amenable to analysis by XRFS, since they are treated to fix particulate in a way which makes them curl and difficult to flatten for presentation to the XRF spectrometer.

## ADVICE

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

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

## APPENDIX A RECOMMENDATIONS FOR THE TEST REPORT

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

- (a) a complete identification of the air sample, including the date of sampling, the place of sampling, and the identity of the individual whose breathing zone was sampled;
- (b) a reference to this MDHS, and a description of any deviation from the procedures described;
- (c) the type and diameter of filter used;
- (d) the type of sampler used;
- (e) the type of sampling pump used;

- (f) the type of flowmeter used, the primary standard against which it was calibrated, and the range of flow rates for which the flowmeter was calibrated;
- (g) the time at the start and at the end of the sampling period, and the sampling time in minutes;
- (h) the volume of air sampled, in litres;
- (i) the name of the person who collected the sample;
- (j) the time-weighted average mass concentration of metal or metalloid found in the air sample, in micrograms per cubic metre;
- (k) the name of the analyst;
- (l) the date of the analysis.

## APPENDIX B ADVICE ON THE SELECTION AND DETERMINATION OF CONDITIONS FOR THE DETERMINATION OF SPECIFIC METALS AND METALLOIDS

### Choice of XRF lines

- B1 Measurement conditions for a number of metals and metalloids are given in Appendix C. 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.
- B2 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<sup>38,39</sup> gives quantitative results for lead in air. 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.
- B3  $K\alpha$  or  $L\alpha$  lines are normally used for XRFS measurements, since these are the most intense lines. However, in a number of significant cases  $K\beta$  or  $L\beta$  lines are used in preference. This is because of possible line overlap effects due to the presence of other elements in the sample (see paragraphs 45-47). For instance, the Pb  $L\alpha$  line coincides with the As  $K\alpha$  line. Therefore, since these elements are quite commonly found together, eg in samples from lead refineries, they are usually measured using the  $L\beta$  and  $K\beta$  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

- B4 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 $\beta$  line, for which the windows are set differently in order to exclude third order tin lines which would otherwise interfere.

### Choosing background correction points

- B5 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 (see Figure 3). 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 $\beta$  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

- B6 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 482<sup>37</sup> can be met. A way of calculating a minimum counting time is given in Appendix E.
- B7 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

- B8 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 C TYPICAL INSTRUMENT OPERATING CONDITIONS FOR DETERMINATION OF COMMONLY MEASURED METALS AND METALLOIDS USING WAVELENGTH-DISPERSIVE XRFs**

**Instrument operating conditions used at HSL**

C1 XRFs measurements are made at HSL using 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. These are typical of conditions that could be used elsewhere.

**Measurement conditions used at HSL for commonly measured metals and metalloids**

C2 Measurement conditions used at HSL are given in Table C1. These are also typical of conditions that could be used elsewhere.

**Table C1 Typical measurement conditions**

Element	X-ray line	Tube power		Collimator	Crystal	Peak angle	Background		Detector	Pulse height discriminator	
		kV	mA				+ offset	- offset		Lower	Upper
As	K $\beta$	100	25	Fine	LiF200	30.44	0.74	0.74	FS	25	75
Ba	K $\alpha$	100	25	Fine	LiF220	15.51	0.80	0.80	SC	25	75
Ba	L $\beta$	100	25	Fine	LiF200	79.275	2.00	-	FL	28	75
Cd	K $\alpha$	100	25	Fine	LiF220	21.630	0.70	0.70	FS	25	70
Cd	L $\alpha$	40	70	Coarse	PE	53.795	1.40	1.40	FL	25	75
Co	K $\alpha$	100	25	Fine	LiF220	77.885	1.70	-	FS	18	70
Cr	K $\alpha$	100	25	Fine	LiF200	69.370	1.30	-	FL	12	70
Cu	K $\alpha$	100	25	Fine	LiF200	45.025	1.50	-	FS	20	75
Fe	K $\alpha$	100	25	Fine	LiF200	57.525	1.40	-	FS	16	70
Mn	K $\alpha$	100	25	Fine	LiF220	95.255	1.72	-	FL	15	70
Ni	K $\alpha$	100	25	Fine	LiF200	48.670	1.30	-	FS	19	75
Pb	L $\beta$	100	25	Fine	LiF220	40.355	0.60	-	SC	22	77
Sb	K $\alpha$	100	25	Fine	LiF220	18.990	0.50	0.50	SC	25	70
Sb	L $\beta$	40	70	Fine	LiF200	106.485	1.10	1.10	FL	25	75
Sn	K $\alpha$	100	25	Fine	LiF220	19.810	0.86	0.86	SC	25	70
Sn	L $\alpha$	40	70	Fine	LiF200	126.815	-	2.60	FL	25	75
Sr	K $\alpha$	100	25	Fine	LiF220	35.785	0.80	0.80	SC	25	75
Zn	K $\alpha$	100	25	Fine	LiF220	60.530	1.10	-	FS	22	75

Key FL Flow counter  
 SC Scintillation counter  
 FS Flow counter + scintillation counter  
 PE Pentaerythritol

**APPENDIX D EXPOSURE LIMITS RELATED TO DETECTION LIMITS, RELATIVE STANDARD DEVIATIONS, AND OVERALL UNCERTAINTIES FOR THE DETERMINATION OF METALS AND METALLOIDS USING XRFs**

**Table D1 Exposure limits for metals and metalloids (Z ≥22), as given in EH 40/97<sup>17</sup>**

Element	Atomic No	Substances	Exposure limits† (in mg.m <sup>-3</sup> )			
			Occupational standards (OESs)		Maximum exposure (MELs)	
			LT	ST	LT	ST
Ti	22	Titanium dioxide (as TiO <sub>2</sub> ), total inhalable dust	10			
		Titanium dioxide (as TiO <sub>2</sub> ), respirable dust	4 <sup>R</sup>			
V	23	Divanadium pentaoxide (as V), total inhalable dust <sup>Table 4d</sup>	0.5			
		Divanadium pentaoxide (as V), fume and respirable dust <sup>Table 4d</sup>	0.04 <sup>R</sup>			
Cr	24	Chromium, Cr(II) compounds (as Cr) and Cr(III) compounds (as Cr)	0.5			
		Cr(VI) compounds (as Cr)			0.05	
Mn	25	Manganese, fume (as Mn)	1	3		
		Manganese and compounds (as Mn)	5			
Fe	26	Iron oxide, fume (as Fe <sub>2</sub> O <sub>3</sub> )	10 <sup>F</sup>	5 <sup>F</sup>		
		Iron salts (as Fe)	1	2		
Co	27	Cobalt and cobalt compounds (as Co)			0.1	
Ni	28	Water-soluble nickel compounds (as Ni)			0.1	
		Nickel and water-insoluble nickel compounds (as Ni)			0.5	
Cu	29	Copper, fume	0.2			
		Copper, dusts and mists (as Cu)	1	2		
Zn	30	Zinc chloride, fume (as ZnCl <sub>2</sub> )	1	2		
		Zinc oxide, fume (as ZnO) <sup>Table 4d</sup>	5	10		
Ga	31	No occupational exposure limits specified				
Ge	32	No occupational exposure limits specified				
As	33	Arsenic and compounds, except arsine (as As)			0.1	
Se	34	Selenium and compounds, except hydrogen selenide (as Se)	0.1			
Rb	37	No occupational exposure limits specified				
Sr	38	No occupational exposure limits specified				
Y	39	Yttrium	1	3		
Zr	40	Zirconium compounds, (as Zr)	5	10		
Nb	41	No occupational exposure limits specified				
Mo	42	Molybdenum, soluble compounds (as Mo)	5	10		
		Molybdenum, insoluble compounds (as Mo)	10	20		
Tc	43	No occupational exposure limits specified				
Ru	44	No occupational exposure limits specified				
Rh	45	Rhodium, metal fume and dust (as Rh)	0.1	0.3		
		Rhodium, soluble salts (as Rh)	0.001	0.003		
Pd	46	No occupational exposure limits specified				

Element	Atomic No	Substances	Exposure limits† (in mg.m <sup>-3</sup> )			
			Occupational standards (OESs)		Maximum exposure (MELs)	
			LT	ST	LT	ST
Ag	47	Silver, metallic <sup>Table 4a</sup>	0.01			
		Silver compounds (as Ag)	0.01			
Cd	48	Cadmium and cadmium compounds, except cadmium oxide fume, cadmium sulphide and cadmium sulphide pigments (as Cd)			0.025	
		Cadmium oxide fume (as Cd)			0.025	0.05
		Cadmium sulphide and cadmium sulphide pigments, respirable dust (as Cd)			0.03 <sup>R</sup>	
In	49	Indium and compounds (as In)	0.1	0.3		
Sn	50	Tin compounds, inorganic, except SnH <sub>4</sub> (as Sn)	2	4		
Sb	51	Antimony and antimony compounds except stibine (as Sb)			0.5	
Te	52	Tellurium and compounds, except hydrogen telluride (as Te)	0.1			
Cs	55	Caesium hydroxide (as CsOH)	2			
Ba	56	<sup>S</sup> applies to soluble salts <sup>R</sup> applies to respirable Ba <sub>2</sub> SO <sub>4</sub>	0.5 <sup>S</sup> 2.0 <sup>R</sup>			
La -	57-71	Lanthanides: No occupational exposure limits specified				
Hf	72	Hafnium	0.5	1.5		
Ta	73	Tantalum	5	10		
W	74	Soluble tungsten compounds (as W)	1	3		
		Tungsten and soluble tungsten compounds (as W)	5	10		
Re	75	No occupational exposure limits specified				
Os	76	No occupational exposure limits specified for particulate osmium				
Ir	77	No occupational exposure limits specified				
Pt	78	Platinum metal	5			
		Platinum compounds, soluble, except certain halogeno-platinum compounds (as Pt)	0.002			
		Halogeno-platinum compounds (complex co-ordination compounds in which the platinum atom is directly co-ordinated to the halide groups) (as Pt)			0.002	
Au	79	No occupational exposure limits specified				
Hg	80	Mercury and its inorganic divalent compounds (as Hg) 0.025				
Tl	81	Thallium, soluble compounds (as Tl)	0.1			
Pb	82	Lead and lead compounds except tetraethyl lead (as Pb)	0.15*			
Bi	83	Dibismuth tritelluride	10	20		
		Dibismuth tritelluride, selenium doped	5	10		
Th	90	No occupational exposure limits specified				
U	92	Uranium compounds, natural, soluble (as U)	0.2	0.6		

#### Key

† Exposure limits apply to total inhalable dust unless otherwise indicated

R Exposure limits apply to respirable dust

R Exposure limits apply to fume and respirable dust

Table 4a Substance for which WATCH is recommending an OES to ACTS

Table 4d Substances on the current ACTS/WATCH work programme

\* Lead is a special case where occupational exposure limits are set out in regulation 2 of the CLAW Regulations<sup>16</sup> and reproduced in Appendix 5 of HSE Guidance Note EH 40.<sup>17</sup>

**Table D2 Detection limits and sensitivity**

<i>Element</i>	<i>X-ray line</i>	<i>OEL (mg m<sup>-3</sup>)</i>	<i>Deposit from 30min sample at 1/10th OEL (µg)</i>	<i>Qualitative det. limit (µg)</i>	<i>Quantitative det. limit (µg)</i>	<i>Sensitivity (kcts/sec/µg)</i>
As	Kβ	0.1	0.6	0.3	1	0.02
Ba	Kα	0.5	3	5	15	0.02
Ba	Lβ	0.5	3	0.2	0.7	0.008
Cd	Kα	0.025	0.2	1	4	0.006
Cd	Lα	0.025	0.2	0.005	0.02	0.9
Co	Kα	0.1	0.6	0.09	0.3	0.03
Cr	Kα	0.05	0.3	0.05	0.2	0.06
Cu	Kα	0.2	1	0.06	0.2	0.1
Fe	Kα	1	6	0.2	0.5	0.08
Mn	Kα	1	6	0.4	1	0.02
Ni	Kα	1	6	0.05	0.2	0.1
Pb	Lβ	0.1	0.6	0.3	1	0.01
Sb	Kα	0.5	3	2	5	0.004
Sb	Lβ	0.5	3	0.3	1	0.02
Sn	Kα	0.1	0.6	1	5	0.005
Sn	Lα	0.1	0.6	0.02	0.05	0.2
Sr	Kα	-	-	0.1	0.4	0.03
Zn	Kα	1	6	0.2	0.6	0.03

Note: Based upon 50-second counting times.

**Table D3 Analytical relative standard deviations and overall uncertainties demonstrating compliance with BS EN 482 in determination of limit values**

Element	XRF line	Occupational exposure limits for elements	0.1x to 0.5x limit value			0.5x to 2x limit value		
			Minimum sample volume (litres)	Maximum RSD <sub>analysis</sub>	Maximum overall uncertainty (%)	Minimum sample volume (litres)	Maximum RSD <sub>analysis</sub>	Maximum overall uncertainty (%)
As	Kβ	arsenic and compounds : 0.1mg m <sup>-3</sup>	240	7.0	32.0	240	2.0	25.8
Ba	Kα	barium compounds (soluble) : 0.5 mg m <sup>-3</sup>	960	5.6	29.9	960	2.6	26.3
Ba	Kα	barium sulphate : 2 mg m <sup>-3</sup>	240	5.6	29.9	240	2.6	26.3
Cd	Kα	cadmium and compounds : 0.025 mg m <sup>-3</sup>	960	15.8*	47.7*	960	3.4*	27.0*
Cd	Lα	cadmium and compounds : 0.025 mg m <sup>-3</sup>	60	11.8	40.4	60	2.5	26.2
Cd	Kα	cadmium sulphide : 0.04 mg m <sup>-3</sup>	960	15.9	48.0	960	3.5	27.2
Cd	Lα	cadmium sulphide : 0.04 mg m <sup>-3</sup>	60	7.4	32.7	60	1.8	25.5
Co	Kα	cobalt and compounds : 0.1 mg m <sup>-3</sup>	60	9.6	36.4	60	2.6	26.2
Cr	Kα	chromium and compounds : 0.5 mg m <sup>-3</sup>	60	1.9	25.7	60	1.4	25.4
Cu	Kα	copper fume : 0.2 mg m <sup>-3</sup>	60	4.2	28.0	60	1.1	25.3
Cu	Kα	copper dust : 1 mg m <sup>-3</sup>	60	1.1	25.3	60	0.6	25.1
Fe	Kα	iron oxide fume : 5 mg m <sup>-3</sup>	60	3.8	27.5	60	3.7	27.4
Fe	Kα	iron salts : 1 mg m <sup>-3</sup>	60	5.2	29.4	60	3.8	27.5
Mn	Kα	manganese and compounds : 5 mg m <sup>-3</sup>	60	1.2	25.3	60	0.5	25.1
Mn	Kα	manganese fume : 1 mg m <sup>-3</sup>	60	5.3	29.5	60	1.2	25.3
Ni	Kα	insoluble nickel compounds : 0.5 mg m <sup>-3</sup>	60	2.2	25.9	60	2.0	25.8
Ni	Kα	soluble nickel compounds : 0.1 mg m <sup>-3</sup>	60	4.8	28.8	60	2.2	25.9
Pb	Lβ	lead and compounds : 0.15 mg m <sup>-3</sup>	60	16.9	49.9	60	3.8	27.5
Sb	Kα	antimony and compounds : 0.5 mg m <sup>-3</sup>	240	8.2	34.0	240	4.5	28.3
Sb	Lα	antimony and compounds : 0.5 mg m <sup>-3</sup>	60	6.1	30.6	60	3.1	26.7
Sn	Kα	tin compounds : 2 mg m <sup>-3</sup>	60	6.0	30.5	60	1.7	25.6
Sn	Lα	tin compounds : 2 mg m <sup>-3</sup>	60	1.0	25.2	60	0.9	25.2
Zn	Kα	zinc oxide fume : 5 mg m <sup>-3</sup>	60	1.7	25.6	60	1.6	25.5
Zn	Kα	zinc chloride fume : 1 mg m <sup>-3</sup>	60	2.5	26.1	60	1.7	25.6

Note: Based upon a 50-second counting time, except where \* denotes 120 seconds.  
Sample volumes considered in establishing a minimum for compliance with BS EN 482 were 60, 240 and 960 litres.

**APPENDIX E ESTIMATION OF THE ANALYTICAL RELATIVE STANDARD DEVIATIONS AND MINIMUM XRF COUNTING TIMES**

- E1 A programme for the calculation of the relative standard deviation of XRF 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 9.
- E2 The measured or calculated relative standard deviations (see paragraph E1) may be used to establish the minimum X-ray count times and/or sample volumes that will enable the overall uncertainty requirements of BS EN 482<sup>37</sup> to be met (see paragraphs 40-44) for the metals and metalloids of interest.
- E3 From Poisson statistics the standard deviation in the measured number of X-ray counts,  $\sigma_N$ , is given by:

$$\sigma_N = \sqrt{N} \quad \text{Equation 6}$$

where  $N$  = the number of counts.

- E4 Equation 6 can be re-written as:

$$\sigma_N = \sqrt{R \times T} \quad \text{Equation 7}$$

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

$T$  = the measuring time, in seconds.

- E5 When an element is measured using wavelength-dispersive XRF, the net count rate,  $R_{net}$ , is found by subtracting the background count rate,  $R_{bg}$ , from the peak count rate,  $R_p$  (see Figure 3). The net count rate is then converted into a concentration using the equation:

$$Y = mX + c \quad \text{Equation 8}$$

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

$m$  = the slope of the calibration line in counts per second per  $\mu\text{g}$ ;

$X$  = the mass on filter, in  $\mu\text{g}$ ; and

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

- E6 The relative standard deviation of the XRF measurement due to imprecision in the measurement of the peak and background countrates,  $RSD_{XRF}$ , is given by the equation:

$$RSD_{XRF} = \frac{1}{m} \times \sqrt{\frac{(mX + c + 2R_{bg})}{T_p \times X^2}} \quad \text{Equation 9}$$

- E7 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.
- E8 As a general rule, the overall certainty requirements of BS EN 482<sup>37</sup> are met over the entire range from 0.1 to 2.0 times the limit value, provided that the relative standard deviation of the XRF 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.
- E9 This general rule holds, provided  $R_p/R_{bg}$  is  $\geq 5$ ; that the calibration line has a relative standard deviation of  $\leq 2\%$ ; and that the error due to blank correction is negligible. The minimum counting time,  $T_{pmin}$ , can then be estimated using the equation:

$$T_{pmin} = \frac{mX + c + 2R_{bg}}{0.0025 \times m^2 \times X_{0.5LV}^2} \quad \text{Equation 10}$$

- E11 If the general rule given in paragraph E9 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 overall uncertainty requirements of BS EN 482, as interpreted in Equations 11 and 12, are met:

Overall uncertainty from 0.1 to 0.5 LV  $< 50\%$

$$0.145 + 2 \times \sqrt{0.00278 + RSD_{analysis0.1LV}^2} \leq 0.5 \quad \text{Equation 11}$$

Overall uncertainty from 0.5 to 2.0 LV  $< 30\%$

$$0.145 + 2 \times \sqrt{0.00278 + RSD_{analysis0.5LV}^2} \leq 0.3$$

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