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INTER-LABORATORY EXERCISE
IN THE USE OF MDHS 91;
XRF ANALYSIS OF HARMFUL METALS
ON FILTERS

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FOREWORD

A summary of the findings of the inter-laboratory exercise has already been published as a paper in *Advances in X-ray Analysis, Volume 38 : Proceedings of the 53rd Annual Conference on Applications of X-ray Analysis, Colorado Springs, USA, August 2004*. This report, whilst repeating much of the text of the paper, contains a more detailed record of the analytical performance of the different instrumentation used by laboratories taking part in the exercise. In particular; in Tables 6 and 7, it gives a statistical analysis of the results obtained for each test filter of collected metal fume presented to participating laboratories; in figures 2a-2j, it shows “Result /expected” factors obtained by individual laboratories for all of the test filters analysed and; in Appendix 1, it gives details of the instrumentation used by the laboratories taking part in the exercise and of the instrumental conditions which they adopted.

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EXECUTIVE SUMMARY

Objectives

An inter-laboratory exercise has been carried out to evaluate the analytical performance of *Method for Determining Hazardous Substances: MDHS 91 for determining Metals and metalloids in workplace air by X-ray fluorescence spectrometry*, published by the Health and Safety Executive, UK.

Main Findings

Sets of prepared filter standards were used to “transport” a master calibration established on a X-ray spectrometer at the Health and Safety Laboratory (HSL) to a wide range of makes and types of X-ray spectrometers in over 20 participant laboratories. By subsequent analysis of test filter samples prepared by collection of particulate fume generated from ferrous and non-ferrous alloys, it has been demonstrated that both wavelength-dispersive and high resolution energy-dispersive instruments produced results for masses of most toxic elements of interest to occupational hygiene which were mostly ($p>0.75$) within 10% or 2 μ g, and nearly always ($p>0.9$) within 20% or 3 μ g, of masses previously determined at HSL. Exceptions were elements measured using analytical lines yielding low X-ray count rates / μ g – arsenic (As K β), tin (Sn K α) and antimony (Sb K α). However, even for these elements, over half ($p>0.55$) of the masses reported were within 10% and nearly all ($p>0.9$) were within 20% of masses previously determined, provided these were in excess of 15 μ g. It was not possible, on the basis of the exercise, to make generalisations about the performance of energy-dispersive instruments using Peltier-cooled detectors, because such instruments were poorly represented and because such detectors vary so widely in their sensitivities and energy resolving powers. Nevertheless, those instruments tested, including those using radioactive X-ray sources, performed adequately.

Recommendations

On the basis of these findings, it can be said that MDHS 91, which was developed and validated using a PANalytical PW1480 wavelength-dispersive instrument using an X-ray tube excitation, is equally applicable to a range of X-ray Spectrometers, including wavelength-dispersive instruments, energy-dispersive instruments and those using radioactive source excitation.

1 INTRODUCTION

1.1 BACKGROUND

X-ray fluorescence spectrometry (XRFS) has been used for more than 30 years at the HSL to measure toxic metals in dust and fume collected onto filters from workplace air. However it was only in 1998 that a comprehensive generic XRFS method was published in the HSE Methods for Determining Hazardous Substances Series – :MDHS 91: *Metals and metalloids in workplace air using XRF*.¹ Although this method was developed and validated at the HSL using a wavelength-dispersive X-ray fluorescence spectrometer employing X-ray- tube excitation, it was deliberately drafted in such a way that it could be used by analysts using other instruments, including energy-dispersive spectrometers and those using radioactive source excitation. There was no reason to think that the method would not work equally well for such instruments; however, supporting evidence for this assumption was lacking. In 2000, a study² was carried out at HSL into the feasibility of using a “Sputnik” multiport sampler for generating large batches of calibration and test filters suitable for use with MDHS 91. This being successful, approximately 25 laboratories were recruited to take part in an inter-laboratory exercise using such filters to test the applicability of the MDHS 91 to a wide variety of instruments. This paper gives details of the exercise and attempts to interpret the results obtained.

1.2 MDHS 91

*Method for determining Hazardous Substances MDHS 91: Metals and Metalloids in workplace air using XRFS*¹ takes advantage of the fact that particulate, collected from air onto the surface of a membrane filter, behaves as a thin film in its interactions with X-rays. In thin films, X-ray absorption and enhancement effects are minimised and the measured X-ray fluorescence counting rates of characteristic lines of elements are proportional to the mass collected on the filter. This proportionality holds true provided the particle size and layer depth of the particulate collected on the surface of the filter is small compared with the critical depth of the particulate matrix for the characteristic X-ray wavelength measured. On the basis of considerations on layer depth effects given in a back-up report,³ the MDHS recommends that sampling times and sampled air flow rates be chosen so that there is unlikely to be more than 500 µg (and certainly less than 1000 µg) of particulate collected on a 25 mm diameter filter, or 1000 µg (and certainly less than 2000 µg) on a 37 mm diameter filter. Given these conditions, the method is considered valid for the quantitative determination of elements of atomic number equal to or greater than titanium ($Z \geq 22$) using K lines or lead ($Z \geq 81$) using L lines. Particle size effects are potentially serious. Nevertheless, with the exception of samples of dust of high average particle size, such as that which is generated close to grinding operations or in handling coarse powders, good agreement is generally obtained between results obtained by XRFS and alternative analytical techniques such as atomic absorption spectrometry (AAS) or inductively coupled plasma-atomic emission spectrometry (ICP-AES). These alternative techniques, although unaffected by particle size and particulate layer depth effects require that filters be dissolved in acid before analysis.

The use of MDHS 91 has the advantage that no sample preparation is required. Filters are mounted directly for presentation to the X-ray beam of the spectrometer, either gripped by their edges between metal masks, or trapped between layers of polymer film. Calibration of the spectrometers is achieved using calibration filters which are prepared by collecting particulate from a dust cloud of a pure elemental compound onto the filters in the same way that samples are collected. Calibration curves of X-ray count-rate Vs mass of element on the filter are constructed on the basis of the weight of the elemental compound collected on the filter (assuming its elemental composition is known accurately), or, more reliably, by digesting the

filter after XRF measurement and determining the mass of element on the filter using ICP-AES or AAS.

1.3 AIR SAMPLERS

There are a number of samplers on the market which are used by occupational hygienists to mount filters for collection of particulate from workplace air. These samplers are usually sited in the breathing zone of workers (typically attached to a lapel) and connected by flexible tubing to a small air sampling pump. Samplers fall into two types that mimic the aerosol capture characteristics of the workers respiratory system. They either collect a total inhalable fraction - effectively all particulate inhaled, or the respirable fraction - only those particles which would pass through the trachea and bronchia and enter the air sacks of the lung.

The most commonly employed sampler in the UK is the IOM inhalable dust samplers (SKC Inc., Blandford Forum, Dorset). This sampler, which is based upon a design developed at the Institute of Occupational Medicine, Edinburgh, is commonly employed in the UK, Europe and the USA for collection of aerosols from workplace air. Filter cassettes fitted into this sampler incorporate a truncated cone-shaped cowl. This is intended to simulate the particle collection behaviour of the nose and mouth. Both conductive plastic or stainless steel cassettes are available. However stainless steel cassettes are preferred, since they have been found less likely to remove particulate from the sampled air electrostatically. A 25 mm diameter filter is mounted in the sampler for the collection of dust and fume. In the USA, it is more common to use samplers containing 37mm and 47mm filters. However, these are problematic for use with XRF measurement and more attention is currently being paid to the use of 25 mm filters for this purpose at NIOSH and OSHA.⁴ Dependant on its design, each sampler gives a different distribution of particulate over the surface of the filter. This is of consequence for the use of MDHS 91, since material exposed in the centre of a spectrometer target sample area generally gives a greater X-ray fluorescence yield than that at the edges. Elemental instrumental response is consequently dependent on the sampler used. This is especially marked with those instruments with radioactive or mini-X-ray tube excitation sources, in which only the central area of a filter is irradiated. It is less noticeable for instruments with full-size X-ray tube sources when the whole surface of the filter is irradiated and contributes to the detected X-ray fluorescence.

1.4 FEASIBILITY OF TRANSPORTING CALIBRATIONS

At HSL, we have been exploring the use of aerosols generated from multi-element solutions using an ultrasonic nebulizer in the preparation of filter calibration standards. Ultrasonic nebulizers produce aerosols of great density. Using such aerosols we have been developing the use of a "Sputnik" multiport air sampler to produce batches of nearly identical filter standards. This device was developed at the National Institute for Occupational Health (NIOH), Oslo, Norway, for the mass collection of identical samples of particulate from workplace air and welding fume for use in inter-laboratory analytical quality assurance exercises. By varying the aerosol loading of the filters, it is possible to cover the mass range required for measurement of harmful elements in workplace air; thus enabling sets of multi-element calibration filter standards to be mass-produced. This presents the possibility of "transporting" a "master" primary calibration, obtained using an XRF spectrometer at HSL, to XRF spectrometers in other laboratories. A feasibility study² on the practicality of such a scheme was undertaken in 1999 and proved successful enough to be adopted in this inter-laboratory exercise.

2 EXPERIMENTAL

2.1 EQUIPMENT AND PROCEDURES

2.1.1 Preparation of calibration and test filters

Equipment and procedures were essentially those already fully described for the feasibility study carried out as a prelude to the exercise.³ Only the basic details of the preparation of calibration and test filters are therefore repeated here. They were prepared by using a “Sputnik” multiport sampler, manufactured by the National Institute of Occupational Health, Oslo, Norway, to simultaneously draw aerosol into up to 114 air samplers. The samplers used were intended to mimic the performance and distribution of aerosol on the filter obtained using IOM samplers. They were 25 mm goblet style sampling cassettes with 2 inch long cylindrical barrels made of black conductive polypropylene (SKC, Inc. USA). These were fitted with stainless steel cowls, which were specially fabricated to be essentially identical with those of IOM filter cassettes. The samplers were loaded with 25 mm diameter cellulose ester 0.8 μm pore size membrane filters (Millipore Inc., USA), supported by 25 mm cellulose back-up pads (Millipore Inc. USA). Aerosol for the preparation of calibration filters was generated from 1% solutions of elements using a Cetac U-6000AT⁺ ultrasonic nebulizer marketed for use with ICP-AES instrumentation. Batches of test filters simulating samples of welding and brazing fume were prepared at The Welding Institute (TWI), Cambridge, UK, from aerosols of metal fume generated by electric-arc welding in a special fume box using welding rod-wire consumables composed of a variety of metal alloys. Further batches of test filters were prepared at HSL from aerosol generated in a similar fume box by impinging the torch of a plasma cutter on granular non-ferrous metal reference materials or metal bars.

2.1.2 XRF spectrometric measurements carried out at HSL

XRFS measurements were made at HSL using a PANalytical Model PW1480 wavelength-dispersive sequential XRF spectrometer fitted with a side-window, dual-anode molybdenum/scandium X-ray tube. Only LiF220 or LiF200 diffraction crystals were used for measurements, in combination with a 35 mm mask and a 0.3 mm fine collimator. The instrument was calibrated using filters from the prepared calibration sets. X-ray count-rates were determined, under vacuum path conditions, for the filters gripped by their edges between molybdenum masks to expose them to the X-ray beam, as described in MDHS 91.¹ X-ray count rates were determined for characteristic elemental X-ray fluorescence using the $K\alpha$ line, except arsenic was determined using the $K\beta$ line and lead using the $L\beta$ line. Cr $K\alpha$ count rates were corrected for contributions from the overlapping V $K\beta$ peak. Masses of the elements to be used in the calibration were then determined by analysing the filters using ICP-AES after by digestion in acid. The resulting calibration was then used in the determination of masses of elements on all the collected calibration and test filters used in the exercise. After measurement, the filters were mounted between 5 micron polypropylene film in 32 mm plastic cells of the type normally used for liquid measurements (Chemplex Inc. USA).

2.1.3 Filters supplied to participating laboratories

Each participating laboratory was sent 5 sets of calibration filters (see Table 1), together with a listing of the masses of elements on them, as individually determined at HSL. Participants were asked to calibrate the instrument using the procedures of MDHS 91, interpreting them as best they could to suit their instrumentation. They were then to analyse sets of 11 test filters (See Table 2 for the elements requested.)

2.1.3.1 Calibration Filters

Aerosol for the preparation of calibration filters was generated from 1% solutions of elements using a Cetac U-6000AT⁺ ultrasonic nebulizer marketed for use with ICP-AES instrumentation. Soluble salts used to prepare calibration filters were as follows.

Three multi-element solutions (Co, Cu, Mn, V: As, Cr, Fe, Ni: Cd, Pb, Zn) and two single element solutions (Sb: Sn) were prepared for use with the ultrasonic nebulizer. All were prepared to give a target concentration of 1% of the elements from compatible soluble salts. These were cobalt (II) sulphate heptahydrate (CoSO₄·7H₂O), copper (II) sulphate pentahydrate (CuSO₄·5H₂O), manganese (II) sulphate tetrahydrate (MnSO₄·4H₂O), vanadyl sulphate dihydrate (VO₂SO₄·2H₂O), disodium hydrogen arsenate (Na₂HAsO₄), potassium chromium sulphate docecahydrate (KCr(SO₄)₂·12H₂O), iron (II) sulphate heptahydrate (FeSO₄·7H₂O), nickel (II) sulphate heptahydrate (NiSO₄·7H₂O) and cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O), lead nitrate tetrahydrate (Pb(NO₃)₂·4H₂O), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), tin (IV) chloride pentahydrate (SnCl₄·5H₂O), antimony (II) potassium oxide tartrate sesquihydrate (KSbC₄H₄O₆·0.5H₂O). Salts were all of analytical reagent grade.

Table 1 Sets of calibration filters produced

<i>Set</i>	<i>5 sets, each comprising 6 calibration standards covering the approximate range 20 to 200 µg of each element</i>
1	Co, Cu, Mn, V
2	As, Cr, Fe, Ni
3	Pb, Cd, Zn
4	Sn
5	Sb

2.1.3.2 Test Filters

Batches of test filters simulating samples of welding and brazing fume were prepared at The Welding Institute (TWI), Cambridge, UK, from aerosols of metal fume generated by electric-arc welding in a special fume box using welding rod-wire consumables composed of a variety of metal alloys. Further batches of test filters were prepared at HSL from aerosol generated in a similar fume box by impinging the torch of a plasma cutter on granular non-ferrous metal reference materials or metal bars.

Table 2: Test filters of fume from steels, non-ferrous alloys and solders

<i>Metal generating fume</i>	<i>Metal composition</i>	<i>Analysis requested</i>
Stainless Steel	High chromium steel	Cr, Fe, Mn, Ni
Rima 82	High nickel steel	Cr, Fe, Mn, Ni
Metrode: Cobstel 8	High cobalt steel	Cr, Fe, Mn, Ni, Co
Vanadium steel	4% vanadium steel	Cr, Fe, Mn, V
SIF: phosphor bronze 8	7%Sn/ copper alloy	Cu, Sn, Zn
SIF: phosphor bronze 2	32%Zn/10% Ni/ copper alloy	Cu, Sn, Zn
Leaded bronze	9%Pb/9%Sn/ copper alloy	Cu, Sn, Pb, Zn
Leaded gun metal	4%Pb/3%Zn/7%Sn/ copper alloy	Cu, Sn, Zn, Pb
White metal (with added As)	Pb/Sb copper alloy + 1%As	Cu, Pb,Sb,As
Leaded brass	39%Zn/2%Pb/ copper alloy	Cu, Pb, Zn
Silver solder	Silver/cadmium/zinc solder	Cd, Zn

2.1.4 Laboratories involved in the exercise and their instrumentation

Laboratories were recruited to take part in the exercise, through appeals at analytical conferences, through the Newsletters of the HSL WASP quality Assurance Scheme and through the user-groups of different XRF spectrometer manufacturing companies. Some thirty laboratories volunteered and from these some 23 usable sets of results were obtained. A further two sets of results were obtained using instruments at HSL. A usefully diverse range of laboratories took part. Participant organisations included government institutions, universities, industrial chemical manufacturers, metal founders and assayers. Particularly valuable were the contributions from the applications laboratories of the XRF instrument manufacturers, Bruker AXS, Jordan Valley (USA), Oxford Instruments (UK), PANalytical (UK and Holland) Spectro Analytical (UK and Germany) and Thermo/ARL (UK and Switzerland). Such was the interest expressed by laboratories outside of the UK, that the exercise was extended on a world-wide basis, participant laboratories coming from China, Germany, Holland, Switzerland, Sweden and the USA. A list of participating laboratories and the instruments they used in the exercise is given in Table 3.

Table 3 Volunteering laboratories

<i>No</i>	<i>Laboratory</i>	<i>Instrument</i>	<i>Type</i>
1	Johnson, Matthey, Clitheroe, Lancs., UK	PANalytical MagiXPRO	WD
2	Sheffield Assay Office, Sheffield, UK	Bruker SRS3400	WD
3	Nds Landesamf f Okologie, Hannover, Germany	Bruker S4-Explorer	WD
4	Shanghai Institute of Ceramics, China	PANalytical PW2404	WD
5	Sheffield Hallam University, Sheffield, UK	PANalytical MagiXPRO	WD
6	Thermo ARL, Eclubens, Switzerland	Thermo/ARL Advant'XP	WD
7	Park and Paterson, Marple, Cheshire	Thermo/ARL Advant'XP	WD
8	ESAB, Goteburg, Sweden	PANalytical PW 2404	WD
9	ICI, Redcar, UK	Bruker S4 Pioneer	WD
10	HSL Buxton, Derbyshire, UK	PANalytical PW1480	WD
11	OCE Technologies, Venlo, Holland	PANalytical MagiXPRO	WD
12	Akzo Nobel Decorative Coatings, Lancs., UK	Spectro X-lab2000	ED (LNC)
13	GlaxoSmithKline, Tonbridge, Kent, UK	Oxford ED2000	ED (LNC)
14	QuinetiQ, Bridgewater, Somerset, UK	Baird EX3000	ED (LNC)
15	PANalytical/ Southampton University, UK	PANalytical Epsilon5	ED (LNC)
16	Oxford Instruments, High Wycombe, UK	Oxford ED2000	ED (LNC)
17	Spectro Analytical, Kleve, Germany	Spectro X-lab 2000	ED (LNC)
18	University of St Andrews, Fife, Scotland	Spectro X-lab 2000	ED (LNC)
19	Jordan Valley, Austin, Texas, USA	Jordan EX-6600	ED (LNC)
20	Scientific and Medical Products, Cheadle, UK	Spectro Titan SCD	ED (PC)
21	PANalytical Minipal, Cambridge, UK	PANalytical Minipal2	ED (PC)
22	PANalytical Minipal, Amelo, Holland	PANalytical Minipal2	ED (PC)
23	HSL, Buxton, Derbyshire, UK	NITON XL 700	ED (RAD)
24	NIOSH, Morgantown, WV, USA	NITON XL 701i	ED (RAD)
25	NIOSH, Morgantown, WV, USA (internal calibn.)	NITON XL 701i	ED (RAD)

Key to Instrument Types: WD = Wavelength-dispersive; ED = Energy-dispersive (LNC) = with liquid nitrogen-cooled detector, (PC) = with Peltier-cooled detector (RAD) = with radioactive X-ray source.

2.1.4.1 **Categorisation of Instrumentation**

A listing of the instruments used in the exercise is given in Table 4. In order to compare the performance of different types of X-ray spectrometers, analytical results were categorised according to whether they were obtained using wavelength-dispersive instruments, energy-dispersive instruments with higher resolution liquid nitrogen cooled detectors or energy-dispersive instruments with Peltier-cooled detectors (which might be expected to have lower spectral resolution). A further sub-classification was made for portable instruments using Peltier-cooled detectors in combination with radioactive source excitation.

Table 4 Instruments used in the exercise

<i>Instrument Make</i>	<i>WDXRF</i>	<i>EDXRF with L.N.-cooled detectors</i>	<i>EDXRF with Peltier – cooled detectors</i>
<i>PANalytical</i>	MagiX PRO (3) PW2404 (2) PW1480	Epsilon 5	Minipal 2 (2)
<i>Bruker</i>	S4 Pioneer S4 Explorer SRS 3400		
<i>Spectro</i>		X-Lab 2000 (3)	Titan SCD
<i>Thermo ARL</i>	Advant'XP (2)	Baird EX 3000	
<i>Oxford</i>		ED 2000 (2)	
<i>Others</i>		Jordan Valley EX-6600	NITON XL-700 Series (2)

Note: figures in brackets indicate the number of instruments involved, when this is more than one.

3 RESULTS AND DISCUSSION

3.1 RESULT/EXPECTED FACTORS

Analysis carried out at HSL prior to dispatch, showed that the masses of elements on the test filters supplied to the different laboratories varied significantly; RSDs ranging from 2% to 7%. To compensate for this variability, each reported elemental mass for each individual filter analysed by participant laboratories was divided by the “expected” result, i.e. the mass determined for the same filter at HSL, to obtain a “Result/Expected factor”. The “Result/Expected factors” had two uses. When multiplied by the mean mass of element determined for the set of test filters prior to despatch, they produced normalised results for the mass of element on each individual filter. This normalisation compensated for the difference in the masses of element on the test filters provided and made the results obtained by different laboratories directly comparable. The “Result/Expected factors” were also, in themselves, useful as an indication of the accuracy achieved by different laboratories. Perfect correlation of participant results with those obtained at HSL would correspond to a “Result/Expected factor” of 1. Correlation would be expected to be dependant on: the mass of element on the filter; the wavelength of the analytical lines; characteristics of the instrumentation such as wavelength resolution and sensitivity of detectors and, for high atomic number elements, the maximum kV available for $K\alpha$ excitation and; analytical conditions selected by the analyst, such as the length of counting times.

3.2 DOT, BOX AND WHISKER PLOTS

Dot, box and whisker plots showing the distribution of the result/expected factors calculated for elemental results submitted for a typical steel welding fume and cuprous alloy fume test filter samples are shown in Figure 1.

Boxes represent the limits of the upper and lower quartiles of the factors calculated for results obtained by the different laboratories. The median for the set of results is represented by a line which completely crosses the box, and the mean by a shorter line. The whiskers extend to one and a half times the inter-quartile range from the median value, indicating the range, outside which, points could be considered outliers.

It can be seen, from inspection of the figures, that the median of the sets of results/expected factors for the test filters is close to 1 for all elements. Generally, when elements are present at relatively high mass on the filters ($>15 \mu\text{g}$), most of the result/expected factor points corresponding to the results of individual laboratories and, certainly, their inter-quartile ranges, fall within the range 0.9 and 1.1, indicating that results fall within $\pm 10\%$ of those expected. Further, nearly all factor points fall between 0.8 and 1.2, indicating that results fall within $\pm 20\%$ of those expected. Correlation is not as good for tin and, to a lesser extent, for antimony, no doubt due to the difficulty of exciting the $K\alpha$ fluorescence for these high atomic weight elements. Similarly, correlation is not as good for arsenic, due to the need to measure the weak As $K\beta$ fluorescence. (Because lead was co-present in significant masses in the test samples, it was generally better to measure the $K\beta$ line than to compensate for the strong interference by Pb $L\alpha$ on the As $K\alpha$ line.) Nevertheless, even for these elements, it can be seen that the majority of results fall within $\pm 20\%$ of those expected and, certainly, that the inter-quartile ranges for their factor points fall within 0.8 and 1.2. However, this degree of correlation is evidently lost for all elements as masses on the filter fall. For lower masses of element on the filter ($<10 \mu\text{g}$), it is clear that results vary by an absolute mass of between $\pm 1 \mu\text{g}$ and $\pm 2 \mu\text{g}$ element, rather than $\pm 10\%$ and $\pm 20\%$ of the results.

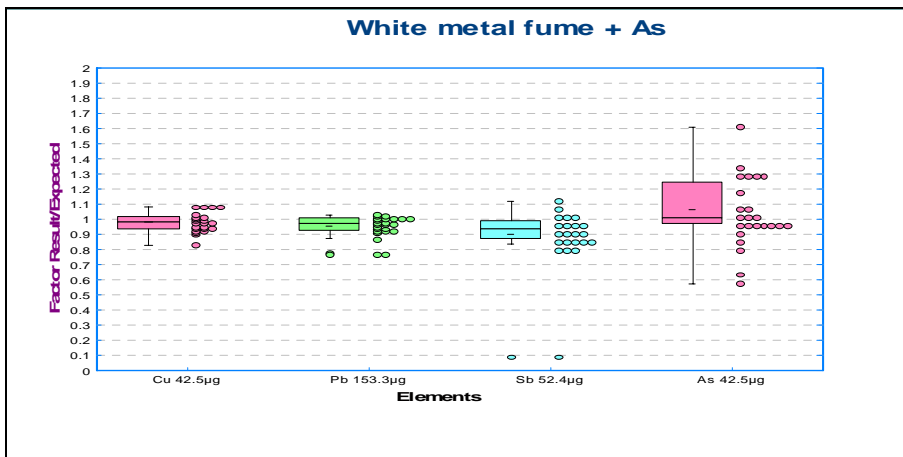
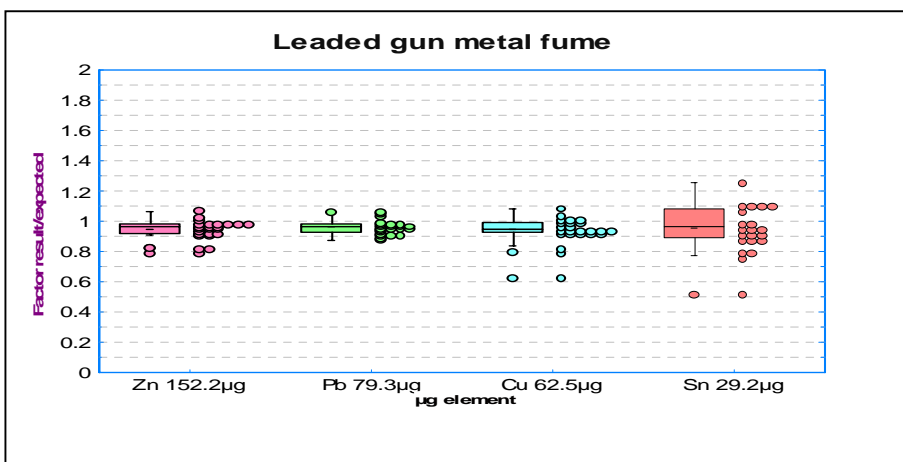
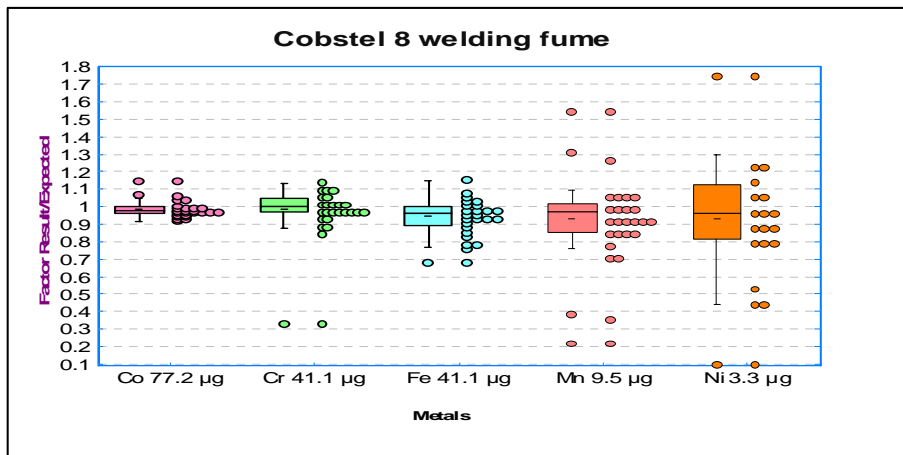


Figure 1 Dot, box and whisker plots for Result/expected factors calculated from results of analysis of test filters reported by participant laboratories
(see text for details)

3.3 RESULTS OF ANALYSIS OF TEST FILTERS

3.3.1 Plots of Result/expected factors

Result/expected factors, calculated for sets of results separated according to the instrument category used, are shown plotted in Figures 2a – 2j for the complete set of welding fume and cuprous alloy fume test filters. Lab numbers refer to results obtained from laboratories taking part in the exercise, numbered as in Table 3. Categories are distinguished by the colour/shading of the bar on the Factor = 1 line. Instrumental categories are displayed from left to right according to decreasing expectations as to wavelength resolution. However, within each classification, the results are displayed in no particular order, i.e. no inference is implied about the expected resolution or performance of any particular instrument. Instrumental details and analytical conditions used are given in Appendix 1.

3.3.1.1 Figures 2a to 2j

Key

WD = Wavelength-dispersive instruments

ED (LNCD) = Energy-dispersive instruments with liquid nitrogen-cooled detectors

ED (PCD) = Energy-dispersive instruments with Peltier-cooled detectors

Rad. Source = Instruments using radioactive sources for fluorescent X-ray excitation

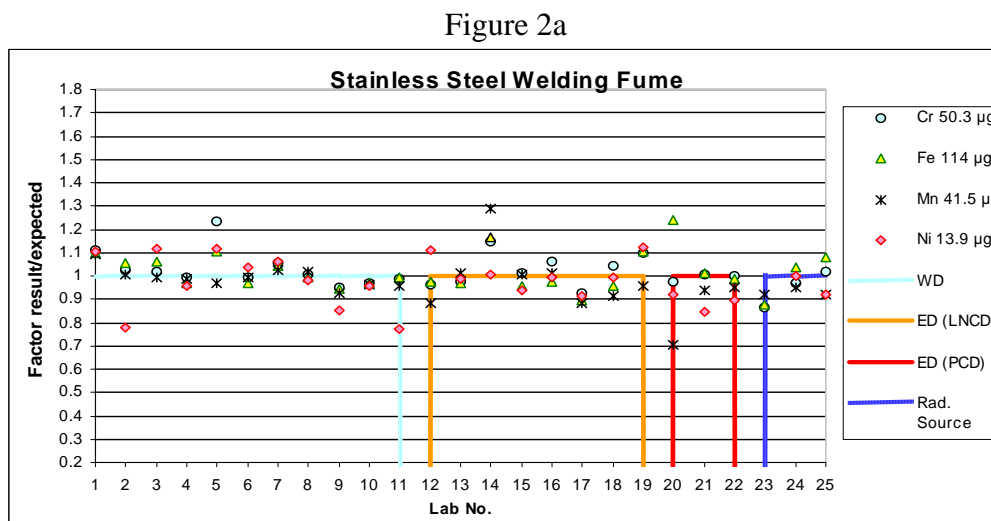


Figure 2a Result/ Expected factors of test filter results reported by participant labs

Figure 2b

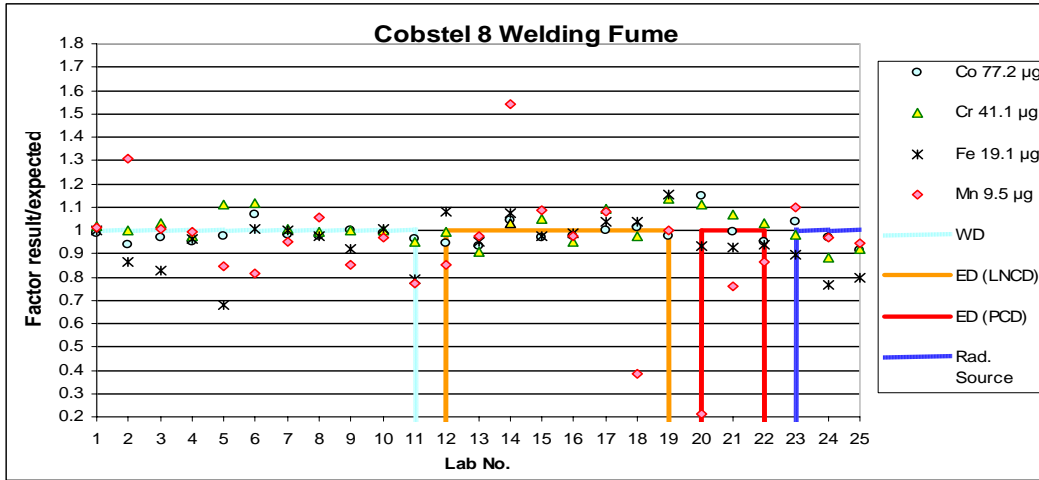


Figure 2c

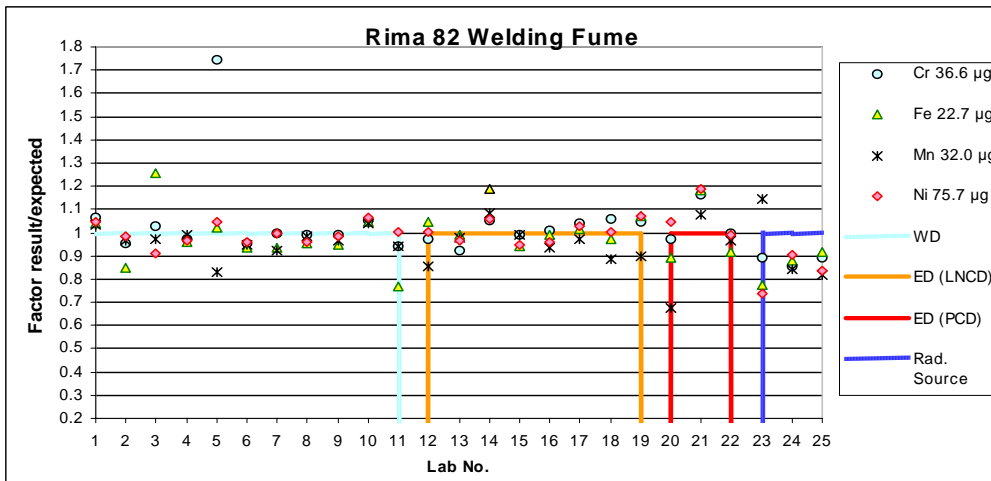
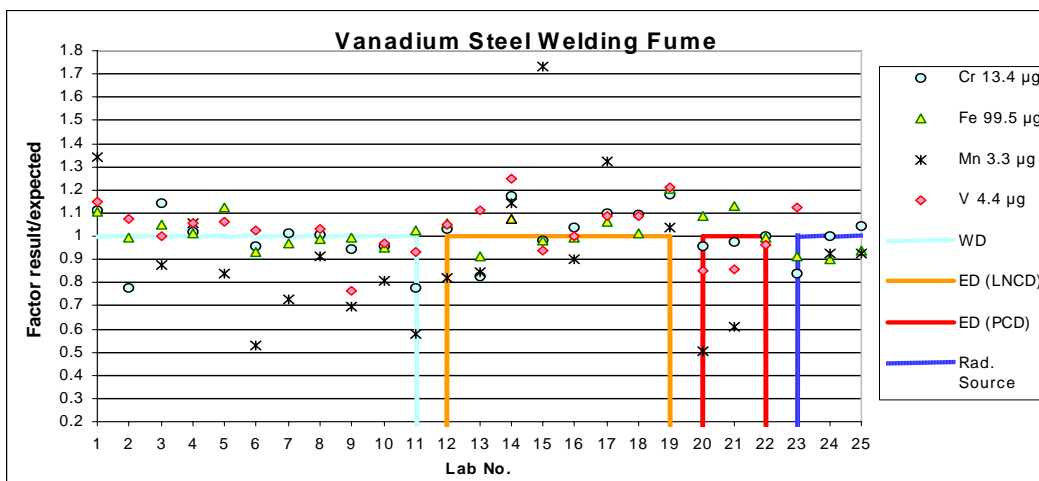


Figure 2d



Figures 2b-2d Result/ Expected factors of test filter results reported by participant labs

Figure 2e

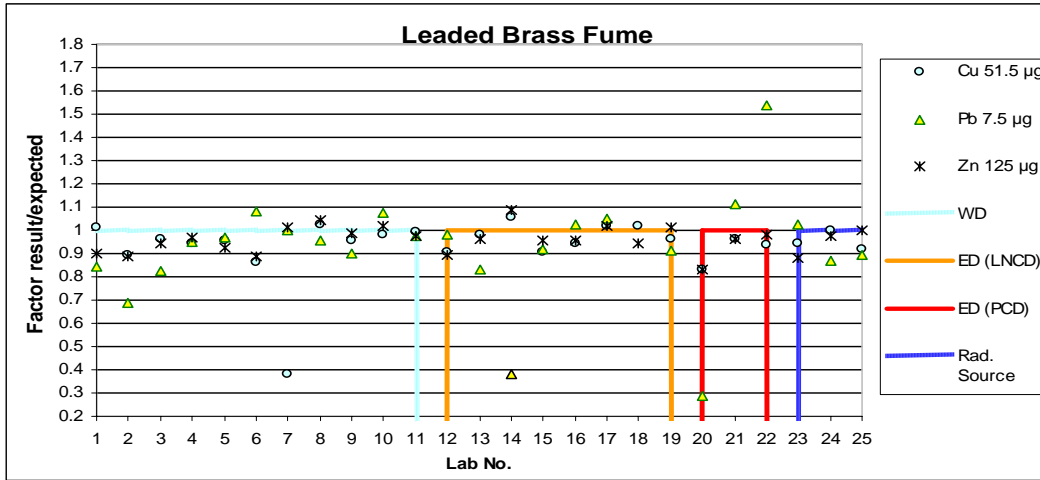


Figure 2f

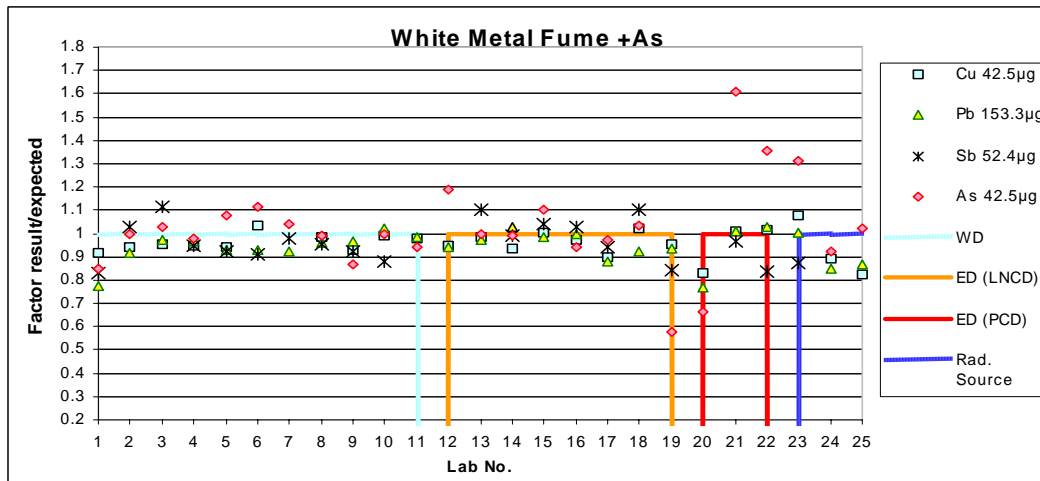
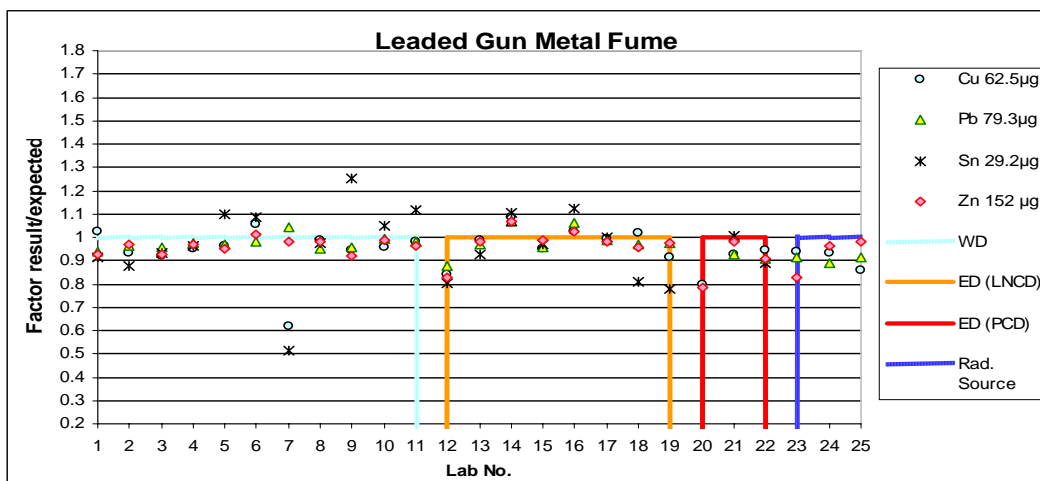


Figure 2g



Figures 2e-2g Result/ Expected factors of test filter results reported by participant labs

Figure 2h

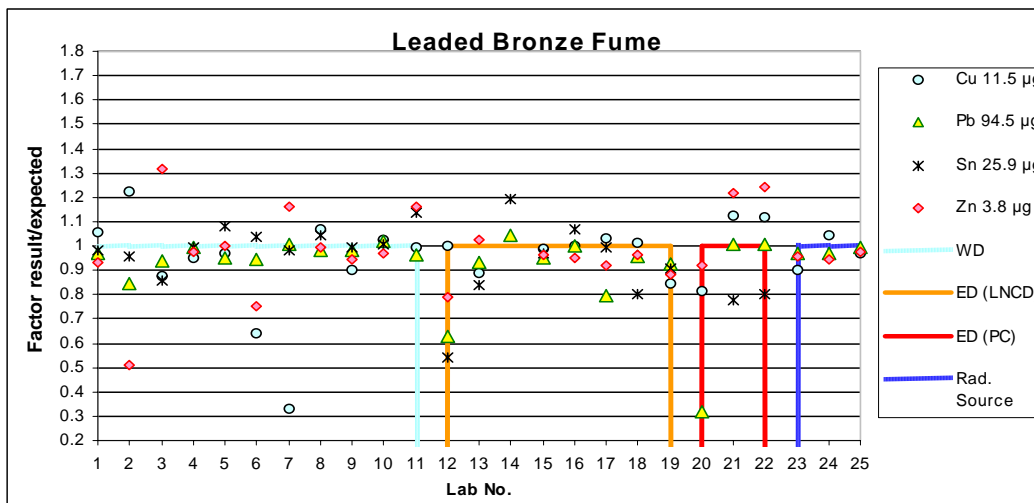


Figure 2i

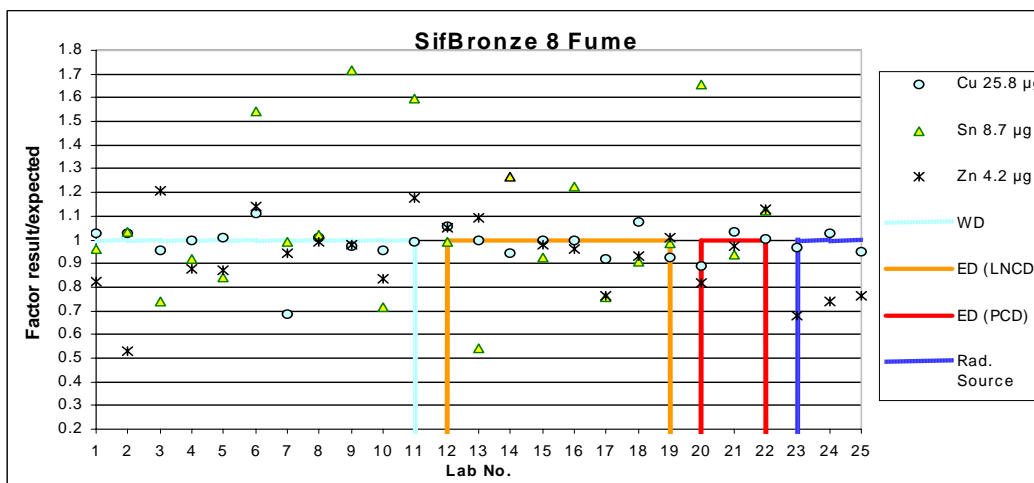
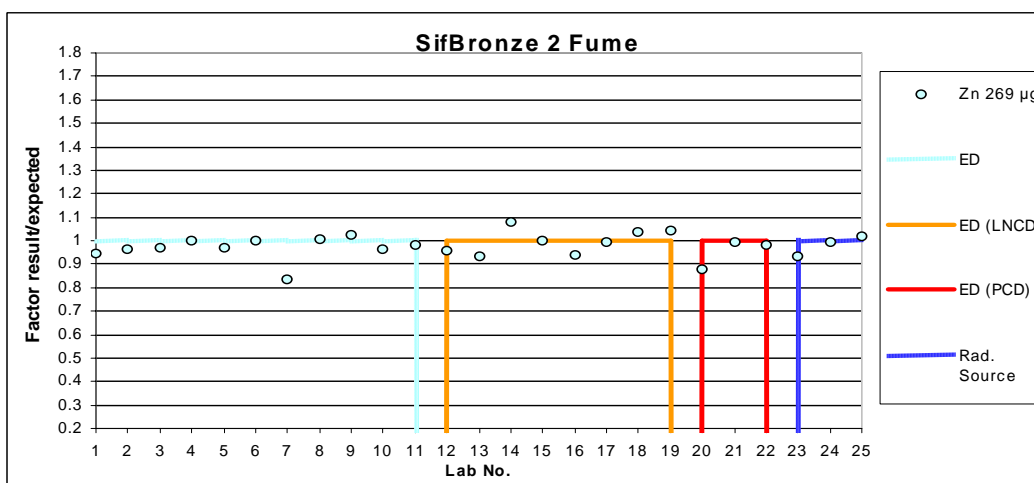


Figure 2j



Figures 2h-2j Result/ Expected factors of test filter results reported by participant labs

It is evident, from visual inspection of Result/expected plots-in Figures 2a-2j, that acceptable results for the masses of most elements on the test filters can be obtained from instruments in all four categories represented in the inter-laboratory exercise. Generally, most elemental results can be seen to be within 10%, and nearly all within 20%, of those expected for masses on the filter which are greater than 10 µg. As might be expected, due to their high wavelength resolving power, most wavelength-dispersive instruments gave consistently good agreement over the whole range of elements. High-resolution energy-dispersive instruments with liquid nitrogen-cooled detectors generally showed nearly as good a performance. Only in certain cases, was there evidence that they did not give as good agreement. Typically, these could be explained by an inaccurately performed line-overlap correction. This would be consistent with the comments of several participants who remarked that the provided calibration filters sets were not ideal for setting up inter-elemental line-overlap corrections on EDXRF instruments, since elements co-present on multi-element calibration filters had been selected to avoid line overlaps. Also, because sets of calibration filters were produced by nebulising the same multi-element solution, the ratio of the elemental masses on the calibration did not vary. Conventional laboratory energy-dispersive instruments with Peltier-cooled detectors were poorly represented in the exercise. Although recently developed Peltier-cooled detectors begin to rival liquid nitrogen-cooled detectors in sensitivity and wavelength resolution, others are markedly inferior. Consequently performance for this category needs to be considered on an instrument by instrument basis. Result sets were only obtained for one Spectro Titan SCD and two PANalytical Minipal 2 instruments, all of which used Si-PIN detectors. Results obtained were generally not as close to expected results as those obtained using the previous two categories of instrument. Even so, results were generally within 20% of those expected and those obtained using the Minipal 2, were mostly within 10%. However, results for some elements, notably arsenic, were widely (>30%) different from those expected (see Figure 2e). Instruments using radioactive X-ray sources and energy-dispersive detectors were only represented by two NITON XL-700 series instruments. The model at HSL had ⁵⁵Fe, ¹⁰⁹Cd and ²⁴¹Am sources, permitting the measurement of all the elements in the exercise. However the NITON model 701i at NIOSH had only a ¹⁰⁹Cd source precluding measurement of Cd, Sb, Sn and V. Given that these instruments are structurally very simple, results were creditable. In spite of the fact that there was sometimes evidence of underestimation of some elements such as lead by 5-10%, results obtained for most elements were, even so, nearly all, within ± 20% of those expected. This was the case, even when the factory-installed internal calibration was used (Set 25) rather than a corrected calibration based on the provided standards (Set 24). Interpretation of results of the exercise is complicated by the fact that the performance of some instruments was adversely affected by the nature of the supplied filters. Participants commented on the asymmetry of deposition of particulate on some of the calibration and test filters. This occurred when the stainless steel cowls, fitted to the samplers, did not give a perfect seal. Such asymmetry would be expected to disadvantage energy-dispersive instruments using mini-X-ray tubes or radioactive sources, since they only excite X-ray fluorescence from particulate on the central portion of the filter, whereas wavelength-dispersive instruments nearly always use full-size X-ray tubes, which irradiate particulate over the whole filter. Asymmetry of particulate deposition on filter surfaces would also be a handicap if an instrument had no sample-spinning facility or if the analyst did not elect to use it. However, even in the cases where instrument lacked a sample-spinning facility (notably NITON XL-700 series and Jordan Valley EX 600 instruments), analysts were able to compensate for asymmetry by averaging two measurements made with filters rotated 90° between them.

3.3.2 Analytical performance statistics

Given the evidently similar performance of wavelength-dispersive instruments and energy-dispersive instruments with liquid nitrogen cooled detectors, it seems reasonable to treat the results of these two categories of instrument together for statistical purposes.

Overall, performance for the analysis of specific elements is summarised in Table 5. A breakdown of the results obtained for analysis of test filters bearing ferrous and non ferrous fume is given in Tables 6 and 7 respectively. The percentage of the supplied results which are within $\pm 10\%$ and $\pm 20\%$ of expected results is shown for test filters on which the determined element is present at a mass greater than $15\ \mu\text{g}$. When elements were present at masses below $15\ \mu\text{g}$, a better measure of correlation was deemed to be whether results were within 1, 2 or $3\ \mu\text{g}$ of the expected results. As can be seen, with the exclusion of only a few extreme outliers, more than 95% or close to 95% ($>92.1\%$) of results for all elements are within 20% of the expected result. Also: more than 90% or close to 90% ($>87.5\%$) of results for elements Cr, Ni, Co, Cu, Pb, Zn and Cd; more than 75% ($>78.9\%$) of results for elements Fe and Mn; more than 65% ($>68.4\%$) of results for the element As and; more than 55% ($>57.2\%$) of results for the elements Sb and Sn are within 10% of the expected result. There are fewer data for elements present at masses below $15\ \mu\text{g}$ on the filters, but: more than 75% ($>76.5\%$) of results for V, Cu, Pb and Zn are within $1\ \mu\text{g}$ of the expected result; more than 85% ($>86.1\%$) of results for Mn and Ni are within $2\ \mu\text{g}$ of the expected result and; more than 75% (78.9%) are within $3\ \mu\text{g}$ of the expected result.

Table 5 Summary statistics of results obtained using either WD-XRF spectrometers or ED-XRF spectrometers with liquid nitrogen-cooled detectors

<i>Results for filters bearing > 15 μg of element</i>							<i>Results for filters bearing < 15 μg of element</i>				
<i>Element</i>	<i>Viable Results</i>	<i>Excluded Outliers</i>	<i>Mean Factor Res./Expd</i>	<i>Overall RSD</i>	<i>Within $\pm 10\%$ of Expd.</i>	<i>Within $\pm 20\%$ of Expd.</i>	<i>Viable Results</i>	<i>Excluded Outliers</i>	<i>Within $\pm 1\ \mu\text{g}$ Expd.</i>	<i>Within $\pm 2\ \mu\text{g}$ Expd.</i>	<i>Within $\pm 3\ \mu\text{g}$ Expd.</i>
Fe	76	0	0.999	9.0%	78.9%	94.7%	0	-	-	-	-
Mn	38	0	1.004	8.9%	81.6%	94.7%	37	1	61.1%	86.1%	94.4%
Cr	57	1	1.030	10.5%	87.5%	96.4%	18	0	50.0%	72.2%	100.0%
Ni	19	0	0.997	4.6%	100.0%	100.0%	35	0	68.6%	88.6%	94.3%
Co	19	0	0.981	3.4%	100.0%	100.0%	0	-	-	-	-
V	0	-	-	-	-	-	19	1	88.9%	100.0%	100.0%
Cu	76	0	0.97	6.8%	89.3%	96.1%	36	1	79.6%	94.1%	97.1%
Pb	57	1	0.96	5.4%	91.0%	96.4%	18	1	76.5%	94.1%	100.0%
Zn	38	0	0.97	5.1%	94.7%	100.0%	55	0	78.2%	98.2%	100.0%
As	19	0	0.98	12.7%	68.4%	94.7%	0	-	-	-	-
Cd	19	0	1.00	8.8%	94.7%	94.7%	0	-	-	-	-
Sn	38	1	0.97	13.2%	57.2%	92.1%	19	0	47.4%	57.9%	78.9%
Sb	19	0	0.96	8.3%	57.9%	94.7%	0	-	-	-	-

Table 6 Breakdown of correlation of results obtained with expected results
for non-ferrous fume test filters

For wavelength dispersive instruments and energy dispersive instruments with liquid nitrogen-cooled detectors

<i>Sample</i>	Mean	RSD	Percentage of results within \pm range of expected							
Element	Mean μg for set	Factor Res./Expd	Viable Results	Excluded Outliers	$\pm<10\%$ Expd.	$\pm<20\%$ Expd.	$\pm<1\mu\text{g}$ Expd.	$\pm<2\mu\text{g}$ Expd.	$\pm<3\mu\text{g}$ Expd.	
<i>White metal fume</i>										
Cu	42.5 μg	0.962	3.6%	19	0	89.5%	94.7%			
Pb	153.3 μg	0.947	5.6%	19	0	89.5%	94.7%			
Sb	52.4 μg	0.964	8.3%	19	0	57.9%	94.7%			
As	42.5 μg	0.983	12.7%	19	0	68.4%	94.7%			
<i>Leaded Gun Metal Fume</i>										
Cu	62.5 μg	0.955	9.8%	19	0	89.5%	94.7%			
Pb	79.3 μg	0.973	4.6%	19	0	94.7%	100.0%			
Sn	29.2 μg	0.954	16.5%	19	0	42.1%	84.2%			
Zn	152.2 μg	0.964	5.1%	19	0	94.7%	100.0%			
<i>Leaded bronze fume</i>										
Cu	11.5 μg	0.951	18.2%	18	1	70.6%	88.2%	64.7%	88.2%	94.1%
Pb	94.5 μg	0.955	5.9%	19	1	88.9%	94.4%			
Sn	25.9 μg	0.991	9.9%	19	1	72.2%	100.0%			
Zn	3.8 μg	0.956	17.2%	18	0	61.1%	77.8%	88.9%	100.0%	100.0%
<i>SifBronze2 Fume</i>										
Cu	1.5 μg	0.995	34.0%	18	0	22.2%	50.0%	94.4%	100.0%	100.0%
Zn	239 μg	0.981	5.2%	19	0	94.7%	100.0%			
<i>SifBronze8 fume</i>										
Cu	25.8 μg	0.981	8.7%	19	0	89.5%	94.7%			
Zn	4.2 μg	0.953	16.2%	18	0	50.0%	83.3%	88.9%	100.0%	100.0%
Sn	8.7 μg	1.035	31.1%	19	0	47.4%	52.6%	47.4%	57.9%	78.9%
<i>Leaded brass Fume</i>										
Cu	51.5 μg	0.966	5.1%	19	1	88.9%	100.0%			
Pb	7.5 μg	0.940	10.2%	18	1	70.6%	94.1%	76.5%	94.1%	100.0%
Zn	124.8 μg	0.968	5.6%	19	0	84.2%	100.0%			
<i>Silver Solder Fume</i>										
Cd	62.7 μg	0.997	8.8%	19	0	94.7%	94.7%			
Zn	8.5 μg	0.954	12.6%	19	0	52.6%	94.7%	57.9%	94.7%	100.0%

Table 7 Breakdown of correlation of results obtained with expected results
for ferrous fume filter samples

For wavelength dispersive instruments and energy dispersive instruments with liquid nitrogen-cooled detectors

<i>Sample</i>	Mean	RSD	Percentage of results within \pm range of expected							
Element	Mean μg for set	Factor Res./Expd	Viable Results	Excluded Outliers	$\pm < 10\%$ Expd.	$\pm < 20\%$ Expd.	$\pm < 1\mu\text{g}$ Expd.	$\pm < 2\mu\text{g}$ Expd.	$\pm < 3\mu\text{g}$ Expd.	
<i>Stainless Steel Welding Fume</i>										
Fe	114.0 μg	1.011	7.0%	19	0	78.9%	100.0%			
Mn	41.4 μg	0.994	8.8%	19	0	84.2%	94.7%			
Cr	50.2 μg	1.031	7.6%	19	0	84.2%	94.7%			
Ni	13.9 μg	0.990	10.8%	19	0	57.9%	89.5%	52.6%	84.2%	89.47%
<i>Cobstel 8 Welding Fume</i>										
Fe	18.6 μg	0.965	11.1%	19	0	73.7%	89.5%			
Mn	9.5 μg	1.005	18.2%	19	1	61.1%	83.3%	61.1%	83.3%	94.44%
Cr	41.1 μg	1.018	6.2%	19	1	83.3%	100.0%			
Ni	3.3 μg	1.037	26.3%	16	0	43.8%	75.0%	87.5%	93.8%	100.00%
Co	77.2 μg	0.981	3.4%	19	0	100.0%	100.0%			
<i>Rima 82 Welding Fume</i>										
Fe	22.7 μg	0.996	10.8%	19	0	78.9%	94.7%			
Mn	32.0 μg	0.958	6.3%	19	0	78.9%	94.7%			
Cr	36.6 μg	1.041	17.6%	19	0	94.7%	94.7%			
Ni	75.7 μg	0.997	4.6%	19	0	100.0%	100.0%			
<i>Vanadium Steel Welding Fume</i>										
Fe	99.5 μg	1.023	7.1%	19	0	84.2%	94.7%			
Mn	3.3 μg	1.028	44.2%	18	0	22.2%	55.6%	61.1%	88.9%	94.44%
Cr	13.4 μg	1.007	12.2%	18	0	55.6%	88.9%	50.0%	72.2%	100.00%
V	4.4 μg	1.148	46.5%	19	1	72.2%	83.3%	88.9%	100.0%	100.00%

3.3.3 Comments on analytical performance

A difference of <10% between determined results and the expected result shows a creditable performance, bearing in mind that this difference is not purely due to error in measurement using a particular instrument, using the conditions selected at the participating laboratory. This error is compounded with the error in determining the “expected” result for the filters at HSL. Further contributions to the difference in results come from the process of transferring the master calibration to the test instrument and from the handling and mounting of the test filters. After mounting between film in plastic cells, calibration filters did not always produce points on a perfect straight calibration line - even when re-measured at HSL. The supplied calibration filters, as already noted, were, apparently, not ideal for setting up line-overlap corrections for energy-dispersive instruments. In spite of the greatest care taken in their preparation, calibration and test filters presented to the participants were not perfect. In some cases, particulate was deposited asymmetrically. There was also the possibility that particulate, on the test filters in particular, could be rubbed off during the processes of measurement and mounting at HSL. It should also be born in mind that; laboratories were carrying out this method for the first time: analysts were adapting the MDHS 91 method to their instrumentation on the basis of their experience, without any opportunity for method development, and that the method of presenting the filters to the instrument was in many cases improvised and not ideal.

3.3.4 Comparison of XRFs performance with other analytical techniques

Analytical accuracy was generally significantly better than that demonstrated in a similar exercise using ICP-AES (inductively coupled - atomic emission spectrometry) and AAS (atomic absorption spectrometry) for the analysis of welding fume filters carried out by laboratories taking part in WASP (HSE’s Workplace Analysis Scheme for Proficiency). This can be seen by comparison of the histogram plots for chromium in stainless steel fume shown in Figure 3. Underestimation of chromium by the laboratories using ICP-AES and AA was almost certainly caused by the of problems in acid-digesting Cr_2O_3 present in the difficultly-soluble rutile form in the welding fume on the WASP test filters, which was produced using an inert gas-shielded welding technique.

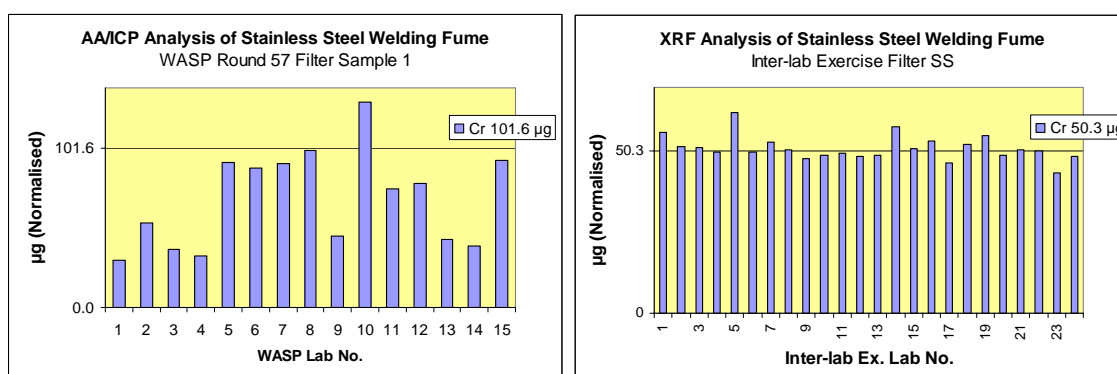


Figure 3 Comparison of lab performances using XRF in the inter-lab exercise with a similar exercise using AAS or ICP-AES for the analysis of Cr in stainless steel fume collected on filters

3.3.5 Alternative use of Ka and La lines

A secondary objective of the exercise was to garner information on whether either K or L X-ray fluorescence measurements could be used to obtain quantitative results using the MDHS 91 method for elements in the atomic number range 48 (Cd) to 51 (Sb). It was requested that laboratories determine cadmium using $K\alpha$ radiation rather than $L\alpha$ radiation, since the latter is strongly affected by particle-size and layer-depth effects⁴. Since Cd $K\alpha$ is difficult to excite, there was doubt over whether some instruments would be able to accurately measure this element. However, this did not prove to be the case (see Figure 4).

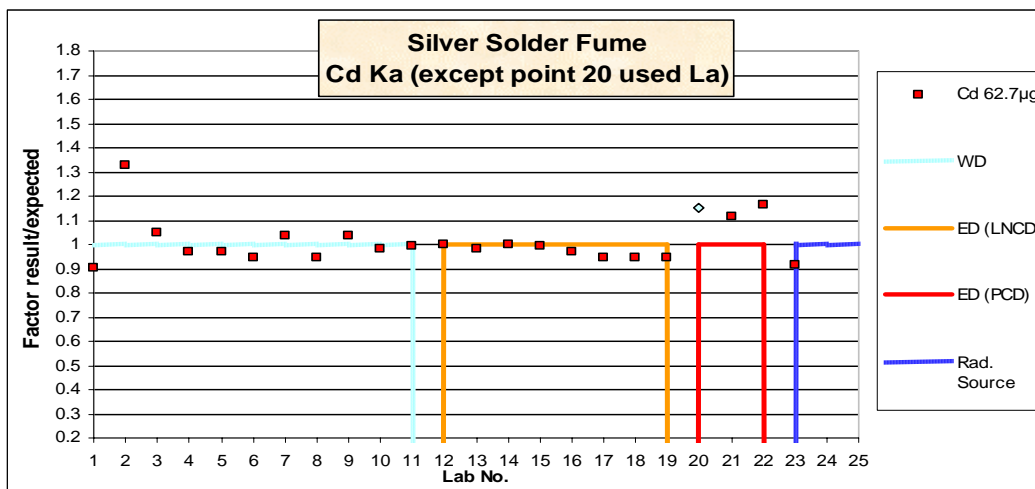


Figure 4 Result/expected factors for lab analysis of cadmium on silver solder fume test filters

If time permitted, it was requested that laboratories attempt to calibrate instruments and determine masses of both tin and antimony using both $K\alpha$ and $L\alpha$ measurements. Disappointingly, only a limited number of results were reported for these elements using $L\alpha$ measurement. Even so, comparison of results with those based on $K\alpha$ measurements were instructive. Examination of Figure 5 reveals that several laboratories obtained more or less identical results using both lines, indicating that depth effects and particle-size effects were not as serious for the $L\alpha$ determinations as feared, even when the filter samples bore significant masses of elements with high X-ray absorption coefficients - notably lead.

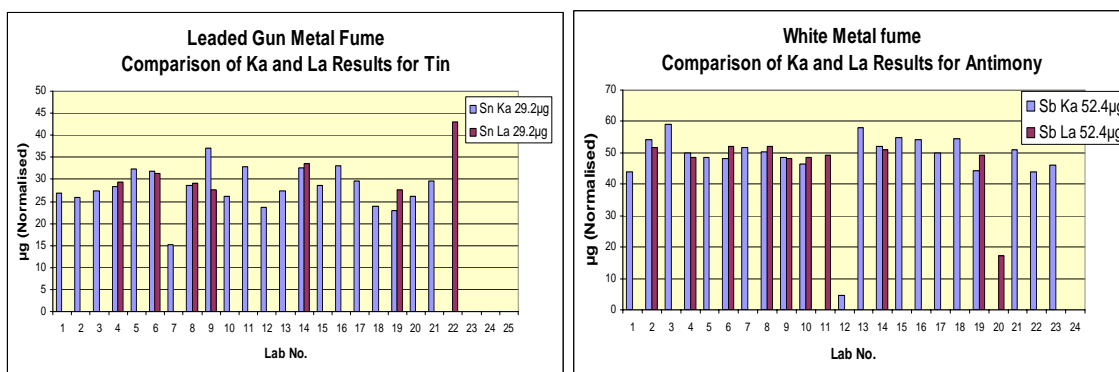


Figure 5 Comparison of result obtained using Ka and La measurements for Sn and Sb

4 CONCLUSIONS

4.1 MAIN CONCLUSIONS

It has been demonstrated, by analysis of test filters prepared from a wide range of metal fumes that, once calibrated, both wavelength-dispersive and high resolution energy-dispersive instruments produced results for masses of most toxic metals of interest to occupational hygiene which were mostly ($p > 0.75$) within 10% or $1\mu\text{g}$, and nearly always ($p > 0.9$) within 20% or $2\mu\text{g}$, of masses previously determined at HSL. The exceptions were the elements arsenic, tin and antimony, these being measured using analytical lines yielding low X-ray count rates $/\mu\text{g}$; As $K\beta$, Sn $K\alpha$ and Sb $L\alpha$ respectively. However, even for these elements, over half the masses reported which were in excess of $15\mu\text{g}$ ($p > 0.55$) were within 10% and nearly all ($p > 0.9$) within 20% of masses previously determined at HSL. It was not possible, on the basis in the exercise, to make generalisations about energy-dispersive instruments using Peltier-cooled detectors because such instruments were poorly represented in the exercise and because such detectors vary so widely in their sensitivities and wavelength resolving powers. Nevertheless, all those tested, and notably the PANalytical Minipal 2 and the NITON XL-700 hand held instrument (with radioactive X-ray source excitation) were shown to be capable of producing results within 20% of those expected for most elements. On the basis of these findings, it can be said that MDHS 91, which was developed and validated using a PANalytical PW1480 wavelength-dispersive instrument using an X-ray tube excitation, is equally applicable to a range of X-ray Spectrometers, including energy-dispersive instruments and those using radiation source excitation.

4.2 SECONDARY OBSERVATIONS

Most instruments were able to obtain quantitative results for cadmium, antimony and tin on metal fume test filters using the difficult-to-excite $K\alpha$ X-ray fluorescence lines. There was some evidence that quantitative results could also be obtained for tin and antimony using alternative $L\alpha$ lines.

4.3 FURTHER INFORMATION

A summary of the findings of the inter-laboratory exercise was presented as a paper at the 53rd Annual Conference on Applications of X-ray Analysis, Colorado Springs, USA, August 2004, which was subsequently published in *Advances in X-ray Analysis, Volume 38*.⁶

5 REFERENCES

- [1] Health and Safety Executive, Methods for determining Hazardous Substances: MDHS 91: Metals and metalloids in workplace air by X-ray fluorescence spectrometry. HSE Books: Sudbury, UK 1998. (www.hse.gov.uk/pubns/pdfs/mdhs/mdhs91.pdf)
- [2] Foster, R D, X-Ray Spectrometry, 2000, 29, 467-474.
- [3] Foster, R D, Read, M L, and Usher, J M, HSL Project report IS/96/03, HSL, Buxton, UK, 1996.
- [4] Harper, M, Hallmark, T S, Andrew, M E & Aaron, J B, Journal of Environmental Monitoring, 2004, 6, 819-826 .
- [5] West, NG, Trends Anal. Chem., 1984, 3, 199-203.
- [6] Foster, R D, Advances in X-ray Analysis, Volume 48, 296-308, International Centre for Diffraction Data, Pennsylvania, USA, ISSN 1097-0002 2005.

6 APPENDICES

6.1 APPENDIX 1 LABORATORY INSTRUMENTATION

Laboratory No. 1: Johnson Matthey Catalysts, Clitheroe, Lancashire, UK

<i>Instrument Details</i>			
Manufacturer: PANalytical		Model No: MagiX Pro	
Instrument Type: Wavelength-dispersive		Measuring Type: Sequential	
Detectors: Scintillation, Duplex (tandem sealed xenon + flow counters)			
X-Ray tube Anode: Rh	Max Watts: 4K	Max kV: 60	Max mA: 125
Secondary Targets: No		Polarised: No	

<i>XRF Measurement Parameters</i>										
<i>Element</i>	<i>XRF Line</i>	<i>Peak count (Secs)</i>	<i>Back grnd (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Crystal</i>	<i>Collim -ation</i>	<i>Detector</i>	<i>PHD Lower Limit</i>	<i>PHD Upper Limit</i>
V	K α	32	4	50	80	LiF200	300 μ m	Duplex	33-	73
Cr	K α	12	2	50	80	LiF200	300 μ m	Duplex	10	70
Mn	K α	20	4	60	66	LiF200	300 μ m	Duplex	12	70
Fe	K α	10	2	60	66	LiF200	300 μ m	Duplex	15	67
Co	K α	16	4	60	66	LiF200	300 μ m	Duplex	16	66
Ni	K α	10	2	60	66	LiF200	300 μ m	Duplex	18	66
Cu	K α	18	2	60	66	LiF200	300 μ m	Duplex	20	66
Zn	K α	14	2	60	66	LiF200	300 μ m	Scintillation	15	80
As	K β	100	28	60	66	LiF200	300 μ m	Scintillation	20	78
Cd	K α	30	30	60	66	LiF200	300 μ m	Scintillation	24	65
Sn	K α	30	30	60	66	LiF200	300 μ m	Scintillation	20	76
Sb	K α	30	30	60	66	LiF200	300 μ m	Scintillation	20	75
Pb	L β	30	30	60	66	LiF200	300 μ m	Scintillation	21	78

Instrument Conditions used:

20mm collimator mask.

300 μ m brass filter used for Cd channel.

Counting times selected for CSE of <0.1%, with a minimum time of 10s on peak and maximum of 100s.

Sample presentation:

Helium path.

Sample cup with 27mm aperture, no extra support film was used.

Problems Encountered:

Some distortion of filters after exposure to X-rays.

Comments on MDHS91:

None received.

Laboratory No. 2: Sheffield Assay Office, Sheffield, Yorkshire, UK

<i>Instrument Details</i>			
Manufacturer: Bruker		Model No: SRS 3400	
Instrument Type: Wavelength -dispersive		Measuring Type: Sequential	
Detectors: Flow counter and scintillation counter and duplex detector			
X-Ray tube Anode: Rh	Max Watts: 4K	Max kV: 60	Max mA: 81
Secondary Targets: No		Polarised: No	

<i>XRF Measurement Parameters</i>										
<i>Element</i>	<i>XRF Line</i>	<i>Peak count (Secs)</i>	<i>Back grnd (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Crystal</i>	<i>Collim -ation</i>	<i>Detector</i>	<i>PHD Lower Limit</i>	<i>PHD Upper Limit</i>
V	K α_1	30	30	50	81	LiF200	0.15°	Flow	-	-
Cr	K α_1	30	30	50	81	LiF200	0.15°	Flow	-	-
Mn	K α_1	30	30	60	67	LiF200	0.15°	Duplex	-	-
Fe	K α_1	30	30	60	67	LiF200	0.15°	Duplex	-	-
Co	K α_1	30	30	60	67	LiF200	0.15°	Duplex	-	-
Ni	K α_1	30	30	60	67	LiF200	0.15°	Duplex	-	-
Cu	K α_1	30	30	60	67	LiF200	0.15°	Duplex	-	-
Zn	K α_1	30	30	60	67	LiF200	0.15°	Duplex	-	-
As	K β_1	30	30	60	67	LiF200	0.15°	Duplex	-	-
Cd	K α_1	30	30	60	67	LiF200	0.15°	Scintillation	-	-
Sn	K α_1	30	30	60	67	LiF200	0.15°	Scintillation	-	-
	L α_1	30	30	50	81	LiF200	0.46°	Flow	-	-
Sb	K α_1	30	30	60	67	LiF200	0.15°	Scintillation	-	-
	L α_1	30	30	50	81	LiF200	0.15°	Flow	-	-
Pb	L β_1	30	30	60	67	LiF200	0.15°	Duplex	-	-

<i>Instrument Conditions used:</i> All lines calibrated using variable alphas. Balance assumed to be carbon.
<i>Sample presentation:</i> Helium path. 23mm aperture gold mask used to present filters to instrument, no extra support film was used.
<i>Problems Encountered:</i> One of the Cr/Fe/Ni/As calibration filters (R24-77) seemed to be off calibration compared to the rest.
<i>Comments on MDHS91:</i> None received.

Laboratory 3: Niedersächsisches Landesamt für Ökologie, Hannover, Germany

<i>Instrument Details</i>			
Manufacturer: Bruker AXS		Model No: S4 Explorer	
Instrument Type: Wavelength-dispersive		Measuring Type: Sequential	
Detectors: Scintillation counter and S4 proportional counter			
X-Ray tube Anode: Rh	Max Watts: 1K	Max kV: 50	Max mA: 20
Secondary Targets: No		Polarised: No	

<i>XRF Measurement Parameters</i>										
<i>Element</i>	<i>XRF Line</i>	<i>Peak count (Secs)</i>	<i>Back grnd (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Crystal</i>	<i>Collim -ation</i>	<i>Detector</i>	<i>PHD Lower Limit</i>	<i>PHD Upper Limit</i>
V	K α	40	40	50	20	LiF220	0.23	S4 Prop	60	140
Cr	K α	40	40	50	20	LiF200	0.23	Scintillation	49	140
Mn	K α	20	20	50	20	LiF200	0.23	Scintillation	48	165
Fe	K α	20	20	50	20	LiF200	0.23	Scintillation	50	167
Co	K α	20	20	50	20	LiF220	0.23	Scintillation	47	159
Ni	K α	20	20	50	20	LiF200	0.23	Scintillation	53	154
Cu	K α	20	20	50	20	LiF200	0.23	Scintillation	48	160
Zn	K α	20	20	50	20	LiF200	0.23	Scintillation	50	155
As	K β	40	40	50	20	LiF220	0.23	Scintillation	60	140
Cd	K α	100	100	50	20	LiF220	0.23	Scintillation	60	140
Sn	K α	100	100	50	20	LiF220	0.23	Scintillation	60	140
Sb	K α	100	100	50	20	LiF220	0.23	Scintillation	60	140
Pb	L β_1	40	40	50	20	LiF200	0.23	Scintillation	60	140

<i>Instrument Conditions used:</i> None stated.
<i>Sample presentation:</i> Helium path. The liquid cells were centred in the normal cups with a plastic ring.
<i>Problems Encountered:</i> None stated.
<i>Comments on MDHS91:</i> None received.

Laboratory 4: Shanghai Institute of Ceramics, Shanghai, China

<i>Instrument Details</i>			
Manufacturer: PANalytical		Model No: PW2404	
Instrument Type: Wavelength-dispersive		Measuring Type: Sequential	
Detectors: Duplex (tandem sealed xenon + flow counters)			
X-Ray tube Anode: Rh	Max Watts: 4K	Max kV: 60	Max mA: 125
Secondary Targets: No		Polarised: Yes	

<i>XRF Measurement Parameters</i>										
<i>Element</i>	<i>XRF Line</i>	<i>Peak count (Secs)</i>	<i>Back grnd (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Crystal</i>	<i>Collim -ation</i>	<i>Detector</i>	<i>PHD Lower Limit</i>	<i>PHD Upper Limit</i>
V	K α	30	8+8	55	70	LiF200	150 μ m	Duplex	11	65
Cr	K α	18	8	55	70	LiF200	150 μ m	Duplex	12	64
Mn	K α	20	6	55	70	LiF200	150 μ m	Duplex	15	64
Fe	K α	16	6	60	65	LiF200	150 μ m	Duplex	15	64
Co	K α	10	4	60	65	LiF200	150 μ m	Duplex	19	64
Ni	K α	10	4	60	65	LiF200	150 μ m	Duplex	18	64
Cu	K α	10	4	60	65	LiF200	150 μ m	Duplex	17	63
Zn	K α	16	6+6	60	65	LiF200	150 μ m	Scintillation	15	77
As	K β	10	4+4	60	65	LiF200	150 μ m	Scintillation	20	78
Cd	K α	100	20+20	60	65	LiF200	150 μ m	Scintillation	28	67
Sn	K α	20	6+6	60	65	LiF200	150 μ m	Scintillation	15	75
	L α	20	8	32	125	LiF200	150 μ m	Flow	18	65
Sb	K α	20	8	60	65	LiF200	150 μ m	Scintillation	15	74
	L α	20	8	32	125	LiF200	150 μ m	Flow	17	65
Pb	L β_1	30	8+8	60	65	LiF200	150 μ m	Scintillation	21	78

Instrument Conditions used:

When measuring Cd K α a 300 μ m brass tube filter was used.

Sample presentation:

Helium path.

27mm diameter gold cups were used.

No support film was used.

Problems Encountered:

Interference with background measurements for K α measurements of Sb and Sn. due to tube lines from the rhodium X-ray tube. It was better to use L α lines for these elements.

Comments on MDHS91:

Suggested that the Compton scattering peak be used to correct results. The Pb L β_1 and Zn K α calibration lines were improved when done like this, but not the Cd K α line

Laboratory 5: Sheffield Hallam University, Sheffield, Yorkshire, UK

<i>Instrument Details</i>			
Manufacturer: PANalytical		Model No: MagiX Pro	
Instrument Type: Wavelength-dispersive		Measuring Type: Sequential	
Detectors: Duplex (tandem sealed xenon + flow counters)			
X-Ray tube Anode: Rh	Max Watts: 4K	Max kV: 66	Max mA: 132
Secondary Targets: No		Polarised: No	

<i>XRF Measurement Parameters</i>										
<i>Element</i>	<i>XRF Line</i>	<i>Peak count (Secs)</i>	<i>Back grnd (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Crystal</i>	<i>Collim -ation</i>	<i>Detector</i>	<i>PHD Lower Limit</i>	<i>PHD Upper Limit</i>
V	K α	60	10	50	80	LiF220	150 μ m	Duplex	11	66
Cr	K α	62	10	50	80	LiF220	150 μ m	Duplex	12	70
Mn	K α	66	12	60	66	LiF220	150 μ m	Duplex	12	68
Fe	K α	58	8	60	66	LiF220	150 μ m	Duplex	15	68
Co	K α	68	10	60	66	LiF220	150 μ m	Duplex	16	69
Ni	K α	56	8	60	66	LiF220	150 μ m	Duplex	14	66
Cu	K α	60	10	60	66	LiF220	150 μ m	Duplex	20	73
Zn	K α	50	10	60	66	LiF220	150 μ m	Scintillation	15	78
As	K β	68	34	60	66	LiF220	150 μ m	Scintillation	20	69
Cd	K α	50	30	60	66	LiF220	150 μ m	Scintillation	28	77
Sn	K α	64	50	60	66	LiF220	150 μ m	Scintillation	24	76
Sb	K α	74	58	60	66	LiF220	150 μ m	Scintillation	22	75
Pb	L β_1	38	22	60	66	LiF200	150 μ m	Scintillation	21	78

Instrument Conditions used:

Cr K α line corrected for line overlap of VK β .

Sample presentation:

Helium path.

27mm diameter aluminium cups were used.

No film was used to support cells.

Problems Encountered:

Disintegration of filters after a number of measurements.

Comments on MDHS91:

Very useful, full of good advice.

Laboratory 6: Thermo Electron, Eclubens, Switzerland

<i>Instrument Details</i>			
Manufacturer: Thermo Electron		Model No: ARL Advant'XP	
Instrument Type: Wavelength-dispersive		Measuring Type: Sequential	
Detectors: Scintillation and flow counters			
X-Ray tube Anode: Rh	Max Watts: 3.6K	Max kV: 60	Max mA: 120
Secondary Targets: No		Polarised: No	

<i>XRF Measurement Parameters</i>										
<i>Element</i>	<i>XRF Line</i>	<i>Peak count (Secs)</i>	<i>Back grnd (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Crystal</i>	<i>Collim -ation</i>	<i>Detector</i>	<i>PHD Lower Limit</i>	<i>PHD Upper Limit</i>
V	K $\alpha_{1,2}$	40	40	50	60	LiF200	0.25	Flow	400	900
Cr	K $\alpha_{1,2}$	40	40	50	60	LiF200	0.25	Flow	400	900
Mn	K $\alpha_{1,2}$	40	40	50	60	LiF200	0.25	Flow	400	900
Fe	K $\alpha_{1,2}$	40	40	50	60	LiF200	0.25	Flow	40	90
Co	K $\alpha_{1,2}$	40	40	50	60	LiF200	0.25	Flow	40	90
Ni	K $\alpha_{1,2}$	40	50	50	60	LiF200	0.25	Scintillation	40	90
Cu	K $\alpha_{1,2}$	40	40	50	60	LiF200	0.25	Scintillation	40	90
Zn	K $\alpha_{1,2}$	40	40	50	60	LiF200	0.25	Scintillation	40	90
As	K β_1	60	60	50	60	LiF200	0.25	Scintillation	40	90
Cd	K $\alpha_{1,2}$	80	80	50	60	LiF200	0.25	Scintillation	40	90
Sn	K $\alpha_{1,2}$	40	40	50	60	LiF200	0.25	Scintillation	40	90
	L α_1	40	40	50	60	LiF200	0.60	Flow	40	90
Sb	K $\alpha_{1,2}$	40	40	50	60	LiF200	0.25	Scintillation	40	90

Instrument Conditions used:

Cd K α line was measured using a Cu primary beam filter.
 Cr analyte has corrections for V as a line-overlapping element.
 Mn analyte has corrections for Cr as a line-overlapping element.
 Fe analyte has corrections for Mn as a line overlapping overlapping element.
 Co analyte has corrections for Fe as a line-overlapping element.

Sample presentation:

Vacuum path. The liquid cells provided were centred using rings in sample cups with a 29 mm opening.

Problems Encountered:

Filters were not always perfectly centred. Sample rotation was used. This fact could have affected sensitivities.

Comments on MDHS91:

The method is comprehensive. It would however be good advice to inform the analyst that, when using synthetic standards where concentrations of most elements are the same, the calibration plots may look very good [but inter-element line overlap effects are not evident]. These may lead to wrong results in unknown samples if matrix effects are present but not taken into account.

Laboratory 7: Park & Paterson Ltd, Marple, Cheshire, UK

<i>Instrument Details</i>			
Manufacturer	Thermo Electron	Model No:	ARL Advant'XP
Instrument Type: Wavelength-dispersive		Measuring Type: Sequential	
Detectors: Flow counter and scintillation counter			
X-Ray tube Anode: Rh	Max Watts: 3.6K	Max kV: 60	Max mA: 120
Secondary Targets: No		Polarised: No	

<i>XRF Measurement Parameters</i>										
<i>Element</i>	<i>XRF Line</i>	<i>Peak count (Secs)</i>	<i>Back grnd (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Crystal</i>	<i>Collim -ation</i>	<i>Detector</i>	<i>PHD Lower Limit</i>	<i>PHD Upper Limit</i>
V	K $\alpha_{1,2}$	3 x 24		30	80	LiF200	0.25	Flow	400	1000
Cr	K $\alpha_{1,2}$	3 x 24		30	80	LiF200	0.25	Flow	400	1000
Mn	K $\alpha_{1,2}$	3 x 24		30	80	LiF200	0.25	Flow	400	1000
Fe	K $\alpha_{1,2}$	3 x 24		30	80	LiF200	0.25	Flow	400	1000
Co	K $\alpha_{1,2}$	3 x 24		30	80	LiF200	0.25	Flow	400	1000
Ni	K $\alpha_{1,2}$	3 x 24		60	40	LiF200	0.25	Scintillation	400	1000
Cu	K $\alpha_{1,2}$	3 x 24		60	40	LiF200	0.25	Scintillation	400	1000
Zn	K $\alpha_{1,2}$	3 x 24		60	40	LiF200	0.25	Scintillation	400	1000
As	K β_1	3 x 24		60	40	LiF200	0.25	Scintillation	400	1000
Cd	K $\alpha_{1,2}$	3 x 40		60	40	LiF200	0.25	Scintillation	400	1000
Sn	K $\alpha_{1,2}$	3 x 24		60	40	LiF200	0.25	Scintillation	400	1000
Sb	K $\alpha_{1,2}$	3 x 24		60	40	LiF200	0.25	Scintillation	400	1000
Pb	L β_1	3 x 24		60	40	LiF200	0.25	Scintillation	400	1000

<i>Instrument Conditions used:</i> None stated.
<i>Sample presentation:</i> Vacuum path. Standard cassette used with 29mm opening and spacing ring. Supplied test and calibration filter cells were mounted between film which had been pin-holed so that they could be analysed under vacuum.
<i>Problems Encountered:</i> Film trapping, test filter "White metal 2" burst under vacuum during analysis (presumably due to not having been adequately pin-holed to let out trapped air).
<i>Comments on MDHS91:</i> None received.

Laboratory 8: ESAB Gothenburg, Sweden

<i>Instrument Details</i>			
<i>Manufacturer</i>	PANalytical	<i>Model No:</i>	PW2404
<i>Instrument Type:</i> Wavelength-dispersive		<i>Measuring Type:</i> Sequential	
<i>Detectors:</i> Sealed Xenon and flow counter			
<i>X-Ray tube Anode:</i> Rh	<i>Max Watts:</i> 4K	<i>Max kV:</i> 60	<i>Max mA:</i> 125
<i>Secondary Targets:</i> No		<i>Polarised:</i> Yes	

<i>XRF Measurement Parameters</i>										
<i>Element</i>	<i>XRF Line</i>	<i>Peak count (Secs)</i>	<i>Back grnd (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Crystal</i>	<i>Collim -ation</i>	<i>Detector</i>	<i>PHD Lower Limit</i>	<i>PHD Upper Limit</i>
V	K α	70	70	50	60	LiF220	150 μ m	Flow	15	72
Cr	K α	70	70	50	60	LiF200	150 μ m	Flow	15	71
Mn	K α	70	70	60	50	LiF220	150 μ m	Flow	15	70
Fe	K α	70	70	60	50	LiF200	150 μ m	Flow	15	70
Co	K α	70	70	60	50	LiF220	150 μ m	Flow	16	69
Ni	K α	70	70	60	50	LiF200	150 μ m	Flow	18	68
Cu	K α	70	70	60	50	LiF200	150 μ m	Flow	20	68
Zn	K α	70	70	60	50	LiF220	150 μ m	Scintillation	15	78
As	K β	70	70	60	50	LiF200	150 μ m	Scintillation	20	78
Cd	K α	70	70	60	50	LiF220	150 μ m	Scintillation	28	77
Sn	K α	70	70	60	50	LiF220	150 μ m	Scintillation	29	76
Sb	K α	70	70	60	50	LiF220	150 μ m	Scintillation	29	75
Pb	L β_1	70	70	60	50	LiF220	150 μ m	Scintillation	21	78

Instrument Conditions used:

Line overlap correction made for V K β on Cr K α and for Cd K α on Sb K α

Sample presentation:

Vacuum path.

27mm diameter steel cups were used.

Supplied test and calibration filter cells were mounted between film which had been pin-holed so that they could be analysed under vacuum.

Problems Encountered:

When running the calibration samples as test samples after the calibration, the results of all elements increased, yet there was no observed drift in the spectrometer response.

Comments on MDHS91:

It is the first time the laboratory has dealt with this type of sample.

Laboratory 9: ICI, Redcar, Yorkshire, UK

<i>Instrument Details</i>			
Manufacturer	Bruker AXS	Model No:	S4 Pioneer
Instrument Type: Wavelength-dispersive		Measuring Type: Sequential	
Detectors: Flow counter and scintillation counters			
X-Ray tube Anode: Rh	Max Watts: 4K	Max kV: 60	Max mA: 67
Secondary Targets: No		Polarised: No	

<i>XRF Measurement Parameters</i>										
<i>Element</i>	<i>XRF Line</i>	<i>Peak count (Secs)</i>	<i>Back grnd (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Crystal</i>	<i>Collim -ation</i>	<i>Detector</i>	<i>PHD Lower Limit</i>	<i>PHD Upper Limit</i>
V	K α_1	50	25	60	40	LiF220	0.23	Flow	60	146
Cr	K α_1	50	25	60	40	LiF200	0.23	Scintillation	35	185
Mn	K α_1	50	25	60	40	LiF220	0.23	Scintillation	42	177
Fe	K α_1	50	25	60	40	LiF200	0.23	Scintillation	48	169
Co	K α_1	50	25	60	40	LiF220	0.23	Scintillation	41	186
Ni	K α_1	50	25	60	40	LiF200	0.23	Scintillation	38	179
Cu	K α_1	50	25	60	40	LiF200	0.23	Scintillation	49	177
Zn	K α_1	50	25	60	40	LiF220	0.23	Scintillation	49	175
As	K β_1	50	25	60	40	LiF200	0.23	Scintillation	45	179
Cd	K α_1	50	25	60	40	LiF220	0.23	Scintillation	60	140
Sn	K α_1	50	25	60	40	LiF220	0.23	Scintillation	60	151
Sn	L α_1	50	25	40	70	LiF200	0.23	Flow	60	140
Sb	K α_1	50	25	60	40	LiF200	0.23	Scintillation	60	141
Sb	L α_1	50	25	40	70	LiF200	0.23	Flow	60	140
Pb	L β_1	50	25	60	40	LiF220	0.23	Scintillation	53	163

Instrument Conditions used:

20mm collimator mask.

300 μ m brass filter used for cadmium channel.

Aimed for CSE of <0.1%, with a minimum time of 10 secs on peak and a maximum of 100 secs.

Sample presentation:

Helium path.

Used 23mm carbon mask insert to support the cells in steel sample cups.

Problems Encountered:

Due to the way the standards were formulated we were unable to counteract the inter element effects of one element from another standard set e.g. Mn on Cr.

Comments on MDHS91:

None received.

Laboratory 10: Health and Safety Laboratory, Buxton, UK

<i>Instrument Details</i>			
Manufacturer	PANalytical	Model No:	PW1480
Instrument Type: Wavelength-dispersive		Measuring Type: Sequential	
Detectors: Flow and scintillation counter.			
X-Ray tube Anode: Mo/Sc	Max Watts: 3K	Max kV: 100	Max mA: 60?
Secondary Targets: No		Polarised: No	

<i>XRF Measurement Parameters</i>										
<i>Element</i>	<i>XRF Line</i>	<i>Peak count (Secs)</i>	<i>Back grnd (Secs)</i>	<i>kV</i>	<i>m A</i>	<i>Crystal</i>	<i>Collim -ation</i>	<i>Detector</i>	<i>PHD Lower Limit</i>	<i>PHD Upper Limit</i>
V	K α	60	60	100	25	LiF200	Fine	FL	30	75
Cr	K α	60	60	100	25	LiF200	Fine	FL	12	70
Mn	K α	60	60	100	25	LiF220	Fine	FL	15	70
Fe	K α	60	60	100	25	LiF200	Fine	F+S	16	70
Co	K α	60	60	100	25	LiF220	Fine	F+S	18	70
Ni	K α	60	60	100	25	LiF200	Fine	F+S	19	75
Cu	K α	60	60	100	25	LiF200	Fine	F+S	20	75
Zn	K α	60	60	100	25	LiF220	Fine	F+S	22	75
As	K β	60	60	100	25	LiF200	Fine	F+S	25	75
Cd	K α	120	120	100	25	LiF220	Fine	F+S	25	70
Sn	K α	120	120	100	25	LiF220	Fine	SC	36	76
Sb	K α	120	120	100	25	LiF220	Fine	SC	25	70
Pb	L β_1	60	60	100	25	LiF220	Fine	SC	22	77

Instrument Conditions used:

28mm collimator mask.

Cells mounted in aluminium cups supported by molybdenum masks described in MDHS 91.

Line overlap correction made for VK β on Cr K α .

Sample presentation:

Helium path

Cells mounted in aluminium cups and supported by molybdenum masks as described in MDHS 91.

Problems Encountered:

None reported.

Comments on MDHS91:

None received.

Laboratory 11:
OCE Technologies b.v., Venlo, Holland

<i>Instrument Details</i>			
Manufacturer	PANalytical	Model No:	MagiX PRO
Instrument Type: Wavelength-dispersive		Measuring Type: Sequential	
Detectors: Flow counter and scintillation counter			
X-Ray tube Anode: Rh	Max Watts: 4K	Max kV: 60	Max mA: 125
Secondary Targets: No		Polarised: No	

<i>XRF Measurement Parameters</i>										
<i>Element</i>	<i>XRF Line</i>	<i>Peak count (Secs)</i>	<i>Back grnd (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Crystal</i>	<i>Collim -ation</i>	<i>Detector</i>	<i>PHD Lower Limit</i>	<i>PHD Upper Limit</i>
V	K α	50	4/4	40	50	LiF200	300 μ m	Flow	15	70
Cr	K α	50	6/6	40	50	LiF200	300 μ m	Flow	15	69
Mn	K α	50	6/6	40	50	LiF200	300 μ m	Flow	15	68
Fe	K α	50	4/4	40	50	LiF200	300 μ m	Flow	15	68
Co	K α	50	6/6	40	50	LiF200	300 μ m	Flow	16	67
Ni	K α	50	6/6	40	50	LiF200	300 μ m	Flow	18	66
Cu	K α	50	8/6	60	66	LiF200	300 μ m	Flow	20	66
Zn	K α	50	8/6	40	50	LiF200	300 μ m	Scintillation	15	78
As	K β	50	18/14	40	50	LiF200	300 μ m	Scintillation	20	78
Cd	K α	50	16/8	40	50	LiF200	300 μ m	Scintillation	28	77
Sn	K α	50	20/26	40	70	LiF200	300 μ m	Scintillation	29	76
Sb	L α	50	8/2	40	70	LiF200	300 μ m	Flow	31	73
Pb	L β	50	20/16	40	50	LiF200	300 μ m	Scintillation	21	78

Instrument Conditions used:

Line overlap correction made for VK β on Cr K α .

Sample presentation:

Helium path.

Normal liquid cup used had a 40mm diameter. Samples were smaller so a self made insert ring was used.

Problems Encountered:

None.

Comments on MDHS91:

None received.

Laboratory 12: Akzo Nobel Research Laboratories, Darwen, Lancashire, UK

<i>Instrument Details</i>			
Manufacturer	Spectro	Model No:	X-Lab 2000
Instrument Type: Energy-dispersive		Measuring Type: Simultaneous	
Detectors: Si (Li) drift, liquid nitrogen-cooled			
X-Ray tube Anode: Pd	Max Watts: 300	Max kV: 50	Max mA: 8.5
Secondary Targets: Pd, Ti		Polarised: Yes	

<i>XRF Measurement Parameters</i>					
<i>Element</i>	<i>XRF Line</i>	<i>Peak Meas Time (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Detector</i>
V	K α	500	35	1.5	Si (Li)
Cr	K α	500	35	1.5	Si (Li)
Mn	K α	500	35	1.5	Si (Li)
Fe	K α	500	35	1.5	Si (Li)
Co	K α	500	35	1.5	Si (Li)
Ni	K α	500	35	1.5	Si (Li)
Cu	K α	500	35	1.5	Si (Li)
Zn	K α	500	35	1.5	Si (Li)
As	K β	500	35	1.5	Si (Li)
Cd	K α	500	49.5	6.0	Si (Li)
Sn	K α	500	49.5	6.0	Si (Li)
Sb	K α	500	49.5	6.0	Si (Li)
Pb	L β	500	35	1.5	Si (Li)

Instrument Conditions used: None stated.
Sample presentation: Nitrogen flush path. Cups fitted into existing X-ray cup holders.
Problems Encountered: Necessary to send calibration data to Spectro in Germany to produce required calibrations, graphs etc.
Comments on MDHS91: None received.

Laboratory 13: Glaxo Smith Kline, Tonbridge, UK

<i>Instrument Details</i>			
Manufacturer	Oxford Instruments	Model No:	ED 2000
Instrument Type: Energy-dispersive		Measuring Type: Simultaneous	
Detectors: Si (Li) drift, liquid nitrogen-cooled			
X-Ray tube Anode: Ag	Max Watts: 50	Max kV: 50	Max mA: 1
Secondary Targets:		Polarised: No	

<i>XRF Measurement Parameters</i>					
<i>Element</i>	<i>XRF Line</i>	<i>Peak Meas Time (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Detector</i>
V	K α	60	35	159	Si (Li)
Cr	K α	60	35	159	Si (Li)
Mn	K α	60	35	159	Si (Li)
Fe	K α	60	35	159	Si (Li)
Co	K α	60	35	159	Si (Li)
Ni	K α	60	35	159	Si (Li)
Cu	K α	60	35	159	Si (Li)
Zn	K α	60	35	159	Si (Li)
As	K β	60	35	159	Si (Li)
Cd	K α	60	50	1000	Si (Li)
Sn	K α	60	50	1000	Si (Li)
Sb	K α	60	50	1000	Si (Li)
Pb	L β	60	35	159	Si (Li)

<i>Instrument Conditions used:</i> Correction made for the overlap of Fe K β on the Co K α , but this was almost insignificant.
<i>Sample presentation:</i> Air path. Samples presented as supplied.
<i>Problems Encountered:</i> Excess film trimmed off the samples to allow them to sit in the carousel. The ED2000 cannot set the units to $\mu\text{g}/\text{filter}$ so the instrument was set to $\mu\text{g}/\text{gramme}$. Concentrations for filter R36 were not supplied, but this caused no real problem.
<i>Comments on MDHS91:</i> Very useful and informative.

Laboratory 14: Qinetiq, Bridgewater, Somerset, UK

<i>Instrument Details</i>			
Manufacturer	Baird Instruments	Model No:	EX 3000
Instrument Type: Energy-dispersive		Measuring Type: Simultaneous	
Detectors: Ge (Li), liquid nitrogen-cooled			
X-Ray tube Anode: Rh	Max Watts:	Max kV: 50	Max mA:
Secondary Targets: No		Polarised: No	

<i>XRF Measurement Parameters</i>					
<i>Element</i>	<i>XRF Line</i>	<i>Peak Meas Time (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Detector</i>
V	K α	300	50	0.5	Ge (Li)
Cr	K α	300	40	0.5	Ge (Li)
Mn	K α	300	50	0.5	Ge (Li)
Fe	K α	300	40	0.5	Ge (Li)
Co	K α	300	50	0.5	Ge (Li)
Ni	K α	300	40	0.5	Ge (Li)
Cu	K α	300	50	0.5	Ge (Li)
Zn	K α	300	50	0.8	Ge (Li)
As	K β	300	40	0.5	Ge (Li)
Cd	K α	300	50	0.8	Ge (Li)
Sn	K α	300	50	1.0	Ge (Li)
Sn	L α	300	50	1.0	Ge (Li)
Sb	K α	300	50	1.0	Ge (Li)
Sb	L α	300	50	1.0	Ge (Li)
Pb	L β	300	50	0.8	Ge (Li)

Instrument Conditions used: None stated.
Sample presentation: Air path.
Problems Encountered: Possible interference of Cr K β on Mn K α accounting for high Mn results. Top standards for Zn Cd and Pb calibrations considered fliers and excluded from calibrations. XRF expert recently retired. Analysis generously carried out by analyst unfamiliar with instrument.
Comments on MDHS91: None received.

Laboratory 15: PANalytical/ Southampton University, UK

<i>Instrument Details</i>			
Manufacturer PANalytical		Model No: Epsilon 5	
Instrument Type: Energy-dispersive		Measuring Type: Sequential/Simultaneous	
Detectors: Ge, liquid nitrogen-cooled			
X-Ray tube Anode: Gd	Max Watts: 600	Max kV: 100	Max mA: 24
Secondary Targets: Fe, Co, Ge, Mo, CsI, CeO ₂ , Al ₂ O ₃		Polarised: Yes	

<i>Element</i>	<i>XRF Line</i>	<i>Peak Meas Time (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Secondary Targets</i>	<i>Detector</i>
V	K α	50	100	Current	Fe	Ge liquid nitrogen-cooled
Cr	K α	50	100	adjusted	Fe	Ge liquid nitrogen-cooled
Mn	K α	50	100	to	Co	Ge liquid nitrogen-cooled
Fe	K α	50	100	optimum	Ge	Ge liquid nitrogen-cooled
Co	K α	50	100		Ge	Ge liquid nitrogen-cooled
Ni	K α	50	100		Ge	Ge liquid nitrogen-cooled
Cu	K α	50	100		Ge	Ge liquid nitrogen-cooled
Zn	K α	50	100		Ge	Ge liquid nitrogen-cooled
As	K α	50	100		KBr	Ge liquid nitrogen-cooled
Cd	K α	50	100		CsI	Ge liquid nitrogen-cooled
Sn	K α	50	100		CeO ₂	Ge liquid nitrogen-cooled
Sb	K α	50	100		CeO ₂	Ge liquid nitrogen-cooled
Pb	L β	50	100		Mo	Ge liquid nitrogen-cooled

Instrument Conditions used:

Line overlap correction for Pb L α on As K α using Pb L β . Ratio Sb to Ce Compton K α line. Correction by deconvolution for residual line overlap interference of: Cu K β on Zn K α ; Ni K β on Cu K α ; Co K β on Ni K α ; Fe K β on Co K α ; Mn K β on Fe K α ; Cr K β on Mn K α , V K β on Cr K α ; Ti K β on V K α .

Sample presentation:

Helium path. Sample was supported on a 32 mm support within a stainless steel holder. A high purity Al cover was then placed over the Chemplex cup to shield it from the stainless steel holder.

Problems Encountered:

Beam size for polarised systems is small. Typically 20mm spot is max. Problems viewing the entire area of the filter meant that any homogeneity problems would be accentuated. So samples were spun. Separation of elements such that standards do not exhibit serious line overlaps means that it is difficult to establish accurate deconvolution for EDXRF systems.

There are some issues with the high loading of the filters. This could lead to a homogeneity problem where there is migration of the elements to the outer edge of the filter. For EDXRF polarised light beam optics, the outer edge of the filter is not seen, thus the calibrations for some elements at high concentration are poor.

Comments on MDHS91:

None received.

Laboratory 16: Oxford Instruments, High Wycombe, Buckinghamshire, UK

<i>Instrument Details</i>			
<i>Manufacturer</i>	Oxford Instruments	<i>Model No:</i>	ED 2000
<i>Instrument Type:</i> Energy-dispersive		<i>Measuring Type:</i> Sequential/Simultaneous	
<i>Detectors:</i> Si (Li) drift, liquid nitrogen-cooled			
<i>X-Ray tube Anode:</i> Ag	<i>Max Watts:</i> 50	<i>Max kV:</i> 50	<i>Max mA:</i> 1
<i>Secondary Targets:</i>		<i>Polarised:</i> No	

<i>XRF Measurement Parameters</i>					
<i>Element</i>	<i>XRF Line</i>	<i>Peak Meas Time (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Detector</i>
V	K α	100	15	Current	Si (Li) drift
Cr	K α	100	15	adjusted	Si (Li) drift
Mn	K α	100	15	to	Si (Li) drift
Fe	K α	100	15	have	Si (Li) drift
Co	K α	100	15	45%	Si (Li) drift
Ni	K α	100	35	dead time	Si (Li) drift
Cu	K α	100	35		Si (Li) drift
Zn	K α	100	35		Si (Li) drift
As	K β	100	35		Si (Li) drift
Cd	K α	100	50		Si (Li) drift
Sn	K α	100	50		Si (Li) drift
Sb	K α	100	50		Si (Li) drift
Pb	L β	100	50		Si (Li) drift

<p><i>Instrument Conditions used:</i> For spectral deconvolution purposes, each element's peaks were included in the method. Most peaks were split as Kα and Kβ, or Lα, Lβ and Lγ</p>
<p><i>Sample presentation:</i> Helium path. Samples were measured as received.</p>
<p><i>Problems Encountered:</i> Suggest, to help spectral deconvolution, that it would be appropriate to have standards containing elements for which the XRF peaks overlap. They are more representative of real samples.</p>
<p><i>Comments on MDHS91:</i> None received.</p>

Laboratory 17: Spectro Analytical, Kleve, Germany

<i>Instrument Details</i>			
Manufacturer	Spectro	Model No:	X-Lab 2000
Instrument Type: Energy-dispersive		Measuring Type: Simultaneous	
Detectors: Si (Li) drift, liquid nitrogen-cooled			
X-Ray tube Anode: Pd	Max Watts: 400	Max kV: 50	Max mA: 15
Secondary Targets: Co, Ti, Al, Mo, HOPG		Polarised: Yes	

<i>Element</i>	<i>XRF Line</i>	<i>Peak Meas Time (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Secondary Targets</i>	<i>Detector</i>
V	K α	100	30	10	Co	Si (Li) drift
Cr	K α	100	30	10	Co	Si (Li) drift
Mn	K α	100	30	10	Co	Si (Li) drift
Fe	K α	100	40	7.5	Mo	Si (Li) drift
Co	K α	100	40	7.5	Mo	Si (Li) drift
Ni	K α	100	40	7.5	Mo	Si (Li) drift
Cu	K α	100	40	7.5	Mo	Si (Li) drift
Zn	K α	100	40	7.5	Mo	Si (Li) drift
As	K β	100	40	7.5	Mo	Si (Li) drift
Cd	K α	200	50	6	Al ₂ O ₃	Si (Li) drift
Sn	K α	200	50	6	Al ₂ O ₃	Si (Li) drift
Sb	K α	200	50	6	Al ₂ O ₃	Si (Li) drift
Pb	L β	100	40	7.5	Mo	Si (Li) drift

Instrument Conditions used:

No line overlap corrections [deconvolution instead].

Mo-Compton/secondary target for elements of atomic number ranges Z= 26-39, 72-90

Al₂O₃-Polarisation target for elements of atomic number ranges Z= 40-58,90

Co-Secondary target for elements of atomic number ranges Z= 19-25

HOPG-crystal for elements of atomic number ranges Z= 11-17

Sample presentation:

Air path.

Used 32mm cups.

No sample rotation.

Problems Encountered:

None stated.

Comments on MDHS91:

None received.

Laboratory 18: University of St Andrews, Fife, Scotland, UK

<i>Instrument Details</i>			
<i>Manufacturer</i>	Spectro	<i>Model No:</i>	X-Lab
<i>Instrument Type:</i> Energy-dispersive		<i>Measuring Type:</i> Simultaneous	
<i>Detectors:</i> Si (Li) drift, liquid nitrogen-cooled			
<i>X-Ray tube Anode:</i> Rh	<i>Max Watts:</i> 3000	<i>Max kV:</i> 60	<i>Max mA:</i> 50
<i>Secondary Targets:</i> Yes		<i>Polarised:</i> Yes	

<i>XRF Measurement Parameters</i>					
<i>Element</i>	<i>XRF Line</i>	<i>Peak Meas Time (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Detector</i>
V	K α	30	Voltage	Current	Si (Li) drift
Cr	K α	30	adjusted	adjusted	Si (Li) drift
Mn	K α	30	to	to	Si (Li) drift
Fe	K α	30	have	have	Si (Li) drift
Co	K α	30	40%	40%	Si (Li) drift
Ni	K α	30	dead time	dead time	Si (Li) drift
Cu	K α	30			Si (Li) drift
Zn	K α	30			Si (Li) drift
As	K β	30			Si (Li) drift
Cd	K α	30			Si (Li) drift
Sn	K α	30			Si (Li) drift
Sb	K α	30			Si (Li) drift
Pb	L β	30			Si (Li) drift

<i>Instrument Conditions used:</i> None stated.
<i>Sample presentation:</i> Air path. Cells placed directly into sample holder; no supporting film used.
<i>Problems Encountered:</i> Three of the sample filters received were not completely flat.
<i>Comments on MDHS91:</i> None received.

Laboratory 19:

Jordan Valley, Austin, Texas, USA

<i>Instrument Details</i>			
Manufacturer Jordan Valley		Model No: EX-6600	
Instrument Type: Energy-dispersive		Measuring Type: Simultaneous	
Detectors: Si (Li) drift, liquid nitrogen-cooled			
X-Ray tube Anode: Rh	Max Watts: 400	Max kV: 60	Max mA: 5
Secondary Targets: Fe, Ge, Zr		Polarised: No	

<i>XRF Measurement Parameters</i>							
<i>Element</i>	<i>XRF Line</i>	<i>Peak Time (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Target or Filter</i>	<i>X-ray path</i>	<i>Detector</i>
V	K α	400	25	3	Ge target	Air	Si (Li)
Cr	K α	400	25	3	Ge target	Air	Si (Li)
Mn	K α	400	25	3	Ge target	Air	Si (Li)
Fe	K α	400	25	3	Ge target	Air	Si (Li)
Co	K α	400	25	3	Ge target	Air	Si (Li)
Ni	K α	400	25	3	Ge target	Air	Si (Li)
Cu	K α	400	25	3	Ge target	Air	Si (Li)
Zn	K α	400	25	3	Ge target	Air	Si (Li)
As	K β	400	30	2.5	Zr target	Air	Si (Li)
Cd	K α	400	55	4	W Filter	Air	Si (Li)
Cd	L α	400	30	4	Fe target	Helium	Si (Li)
Sn	K α	400	55	4	W Filter	Air	Si (Li)
Sn	L α	400	30	4	Fe target	Helium	Si (Li)
Sb	K α	400	55	4	W Filter	Air	Si (Li)
Sb	L α	400	30	4	Fe target	Helium	Si (Li)
Pb	L β	400	30	2.5	Zr target	Air	Si (Li)

Instrument Conditions used:

Peak fitting for steel calibration (V, Cr, Mn, Fe, Co, Ni): Peak fitting for brass calibration (Cu, Zn).
No other overlap correction were required.

Sample presentation:

Air path, except helium used for long wavelength La lines of Sn, Sb, Cd., as per table above.
Sample cups measured as received.
Instrument has no spinner for sample rotation.

Problems Encountered:

Many standards are not uniform [asymmetrically deposited]. Readings from different regions of some filters varied by as much as 20%, so the reading which best fitted to the calibration line was used. One filter was omitted from the calibration because different readings varied by as much as 40% .
Results provided for the analysis of test samples are suspect due to the non-uniformity of standards [and test filters] provided in the study [combined with the fact that the instrument does not incorporate a spinner].

Comments on MDHS91:

Not that useful for EDXRF.

Laboratory 20: Scientific & Medical Products, Cheadle, Cheshire, UK

<i>Instrument Details</i>			
<i>Manufacturer</i>	Spectro	<i>Model No:</i>	Titan SCD
<i>Instrument Type:</i> Energy-dispersive		<i>Measuring Type:</i> Simultaneous	
<i>Detectors:</i> Pin diode – Peltier cooled			
<i>X-Ray tube Anode:</i> Ag	<i>Max Watts:</i> 9	<i>Max kV:</i> 35	<i>Max mA:</i>
<i>Secondary Targets:</i> No <i>Tube filters</i> Fe, Y & Ti		<i>Polarised:</i> No	

<i>XRF Measurement Parameters</i>					
<i>Element</i>	<i>XRF Line</i>	<i>Peak Meas Time (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Detector</i>
V	K α	100	10.7	800	Pin diode
Cr	K α	100	10.7	80	Pin diode
Mn	K α	100	25.6	122	Pin diode
Fe	K α	100	25.6	122	Pin diode
Co	K α	100	25.6	122	Pin diode
Ni	K α	100	25.6	122	Pin diode
Cu	K α	100	25.6	122	Pin diode
Zn	K α	100	25.6	122	Pin diode
As	K β	100	25.6	122	Pin diode
Cd	L α	100	7.4	1100	Pin diode
Sn	L α	100	7.4	1100	Pin diode
Sb	L α	100	7.4	1100	Pin diode
Pb	L	100	25.6	100	Pin diode

Instrument Conditions used:

Note Cd, Sn and Sb analysed using L α rather than K α . Unclear whether L α or L β used for Pb.

Sample presentation:

Air path.

No modification of sample cups was necessary; calibration and sample filters measured in plastic cells as received.

Problems Encountered:

None stated.

Comments on MDHS91:

None received.

Laboratory 21: PANalytical, Cambridge, UK

<i>Instrument Details</i>			
<i>Manufacturer</i>	PANalytical	<i>Model No:</i>	Minipal 2
<i>Instrument Type:</i> Energy-dispersive/ Portable		<i>Measuring Type:</i> Simultaneous	
<i>Detectors:</i> Si PIN Diode, Peltier-cooled			
<i>X-Ray tube Anode:</i> Rh	<i>Max Watts:</i> 9	<i>Max kV:</i> 30	<i>Max mA:</i> 1
<i>Secondary Targets:</i> No		<i>Polarised:</i> No	

<i>XRF Measurement Parameters</i>					
<i>Element</i>	<i>XRF Line</i>	<i>Peak Meas Time (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>Detector</i>
V	K α	400	20	1	Si PIN Diode
Cr	K α	400	20	1	Si PIN Diode
Mn	K α	400	20	1	Si PIN Diode
Fe	K α	400	20	1	Si PIN Diode
Co	K α	400	20	1	Si PIN Diode
Ni	K α	400	20	1	Si PIN Diode
Cu	K α	400	20	1	Si PIN Diode
Zn	K α	400	20	1	Si PIN Diode
As	K β	400	20	1	Si PIN Diode
Cd	L α	400	20	1	Si PIN Diode
Sn	L α	400	20	1	Si PIN Diode
Sb	L α	400	20	1	Si PIN Diode
Pb	L β 1	400	20	1	Si PIN Diode

Instrument Conditions used:

50 μ m Al tube filter was used for all elements

Deconvolution of elemental spectra used instead of line overlap factors.

Cd, Sb and Sn measured using L lines since instrument only goes up to 30kV.

Sample presentation:

Helium path.

Problems Encountered:

Plots of the XRF count-rates obtained for calibration filter standards against micrograms of element on the filter (determined at HSL) in many cases did not fall close to a calibration line produced by linear regression: the top two standards for Ni and As were well below calibration line; the top standard for Cd was well off the plotted line (so deleted); Co Cu V Mn standards seem to plot two lines; the two highest standards for Cr and Sb plotted either side of line; the standards for the Zn calibration plot to curve rather than to a straight line, suggesting critical depth was exceeded for the top standards. Problems were thought by analyst (Steve Davis) to be due to the standards rather than the instrument's performance.

Comments on MDHS91:

None received.

Laboratory 22 : PANalytical, Almelo, Holland

<i>Instrument Details</i>			
Manufacturer	PANalytical	Model No:	Minipal 2
Instrument Type: Energy-dispersive/ Portable		Measuring Type: Simultaneous	
Detectors: Si PIN Diode, Peltier-cooled			
X-Ray tube Anode: Rh	Max Watts: 9	Max kV: 30	Max mA: 1
Secondary Targets: No		Polarised: No	
Tube filters: Al, Mo, Ag, Kapton			

<i>Element</i>	<i>XRF Line</i>	<i>Peak Time (Secs)</i>	<i>kV</i>	<i>mA</i>	<i>X-ray path</i>	<i>Detector</i>
V	K α	100	20	20	Air	Si PIN Diode
Cr	K α	100	20	20	Air	Si PIN Diode
Mn	K α	100	20	20	Air	Si PIN Diode
Fe	K α	100	20	20	Air	Si PIN Diode
Co	K α	100	20	20	Air	Si PIN Diode
Ni	K α	100	20	20	Air	Si PIN Diode
Cu	K α	100	20	20	Air	Si PIN Diode
Zn	K α	100	20	70	Air	Si PIN Diode
As	K β	100	20	20	Air	Si PIN Diode
Cd	L α	100	8	1000	Helium	Si PIN Diode
Sn	L α	100	8	1000	Helium	Si PIN Diode
Sb	L α	100	8	1000	Helium	Si PIN Diode
Pb	L α	100	20	70	Air	Si PIN Diode

Instrument Conditions used:

Sample spin was on.

50 μ m Al tube filter was used for all elements.

Cd, Sb and Sn measured using L lines since instrument only goes up to 30kV. Pb L α used rather than L β .

No matrix corrections were applied.

Sample presentation:

Air path used for all elements except Cd, Sb and Sn, for which helium was used.

No film used; samples were placed directly into sample holder.

Problems Encountered:

The data for Cu in samples R2, R3 and R5 yields different RMS values than R1, R4 and R6. Maybe two different batches were used to produce this set of filter standards..

Comments on MDHS91:

None received.

Laboratory 23: Health and Safety Laboratory, Buxton, UK.

<i>Instrument Details</i>	
Manufacturer Niton	Model No: XL 700
Instrument Type: Energy-dispersive/ Hand held	Measuring Type: Simultaneous
Detectors: Si Pin Diode, Peltier-cooled	
Radioactive X-Ray Source ^{55}Fe : ^{109}Cd : ^{241}Am	

<i>XRF Measurement Parameters</i>					
<i>Element</i>	<i>XRF Line</i>	<i>Peak Meas Time (Secs Nominal)</i>	<i>Source</i>	<i>K eV</i>	<i>Detector</i>
V	K α	120	^{55}Fe	5.9 & 6.4	Si Pin Diode
Cr	K α	180	^{109}Cd	22.1 & 24.9	Si Pin Diode
Mn	K α	180	^{109}Cd	22.1 & 24.9	Si Pin Diode
Fe	K α	180	^{109}Cd	22.1 & 24.9	Si Pin Diode
Co	K α	180	^{109}Cd	22.1 & 24.9	Si Pin Diode
Ni	K α	180	^{109}Cd	22.1 & 24.9	Si Pin Diode
Cu	K α	180	^{109}Cd	22.1 & 24.9	Si Pin Diode
Zn	K α	180	^{109}Cd	22.1 & 24.9	Si Pin Diode
As	K	180	^{109}Cd	22.1 & 24.9	Si Pin Diode
Cd	K α	600	^{241}Am	59.6	Si Pin Diode
Sn	K α	600	^{241}Am	59.6	Si Pin Diode
Sb	K α	600	^{241}Am	59.6	Si Pin Diode
Pb	L	180	^{109}Cd	22.1 & 24.9	Si Pin Diode

Instrument Conditions used:

^{55}Fe used for : V : ^{109}Cd used for Cr, Mn, Fe, Co, Ni, Cu, Zn. As & Pb : ^{241}Am used for Cd Sn & Sb.
Results for test filters obtained from internal calibration (thin film) adjusted by applying correction factors based on linear regressions of results obtained from the sets of supplied calibration standards.

Sample presentation:

Air path.
Filters analysed mounted between film in 32 mm diameter plastic cells.
A Niton 32 mm cell mounting stage was used for presentation of the filters to the instrument.
The filter, in its cell, was rotated 90 degrees between duplicate readings, which were averaged.

Problems Encountered:

Measuring times were automatically extended to compensate for the reduced excitation power of the radioactive sources with time, using an algorithm based upon isotope radioactive half-lives. The sources were several years old, consequently actual measuring times were significantly longer than nominal measuring times.

Comments on MDHS91:

None received.

**Laboratory 24: NIOSH, Morgantown, West Virginia, USA
(Corrected Results)**

<i>Instrument Details</i>	
Manufacturer Niton	Model No: XL 701i
Instrument Type: Energy-dispersive/ Hand held	Measuring Type: Simultaneous
Detectors: Si Pin Diode, Peltier-cooled	
Radioactive X-Ray Source	¹⁰⁹ Cd

<i>XRF Measurement Parameters</i>					
<i>Element</i>	<i>XRF Line</i>	<i>Peak Meas Time (Nominal Secs)</i>	<i>Source</i>	<i>kV</i>	<i>Detector</i>
V	-	Not measured	-	-	-
Cr	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Mn	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Fe	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Co	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Ni	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Cu	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Zn	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
As	K β	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Cd	-	Not measured	-	-	-
Sn	-	Not measured	-	-	-
Sb	-	Not measured	-	-	-
Pb	L β	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode

Instrument Conditions used:

The instrument had only one radioactive source - ¹⁰⁹Cd.
Results for test filters were obtained from factory-installed internal calibration for thin film analysis. These were then adjusted (at HSL) by applying correction factors based on linear regression of results obtained for the sets of supplied calibration standards.

Sample presentation:

Air path.
Calibration and test filters were received un-mounted.
Filters were mounted into NITON 25 mm card mounts covered with Mylar film. These were then presentation to the instrument using a special NITON accessory.[Note this method of presentation does not permit rotation of the filter between readings.]

Problems Encountered:

¹⁰⁹Cd. source is not suitable for excitation of K α of V, Cr, Cd, Sb or Sn, so these elements not measured. One of the Cu/Co/Mn calibration standard read 29% lower than expected, and was considered faulty.

Comments on MDHS91:

Participation in the MDHS 91 inter-laboratory exercise enabled the participant laboratory to conclusively establish a minor instrument calibration issue (a 10% under-read for both Cu and Pb).

Laboratory 25: NIOSH, Morgantown, West Virginia, USA
(Results from factory-installed internal calibration)

<i>Instrument Details</i>	
<i>Manufacturer</i>	Niton
<i>Model No:</i>	XL 701i
<i>Instrument Type:</i> Energy-dispersive/ Hand held	<i>Measuring Type:</i> Simultaneous
<i>Detectors:</i> Si Pin Diode, Peltier-cooled	
<i>Radioactive X-Ray Source</i>	¹⁰⁹ Cd

<i>XRF Measurement Parameters</i>					
<i>Element</i>	<i>XRF Line</i>	<i>Peak Meas Time (Nominal Secs)</i>	<i>Source</i>	<i>kV</i>	<i>Detector</i>
V	-	Not measured	-	-	-
Cr	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Mn	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Fe	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Co	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Ni	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Cu	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Zn	K α	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
As	K β	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode
Cd	-	Not measured	-	-	-
Sn	-	Not measured	-	-	-
Sb	-	Not measured	-	-	-
Pb	L β	240 ns	¹⁰⁹ Cd	22.1 & 24.9	Si-Pin Diode

Instrument Conditions used:

The instrument had only one radioactive source - ¹⁰⁹Cd.
 Results for test filters were obtained from factory installed internal calibration for thin film analysis.
 The results obtained were in $\mu\text{g}/\text{cm}$. A factor of 3.8, based on the 22mm diameter of the particulate deposits was applied to calculate the masses of elements on the test filters.

Sample presentation:

Air path.
 Calibration and test filters were received unmounted.
 Filters were mounted into NITON 25 mm card mounts covered with Mylar film. These were then presentation to the instrument using a special NITON accessory.[Note this method of presentation does not permit rotation of the filter between readings.]

Problems Encountered:

¹⁰⁹Cd. source not suitable for excitation of K α of V, Cr Cd, Sb or Sn, so these elements not measured.
 One of the Cu/Co/Mn calibration standard read 29% lower than expected, and might be faulty.

Comments on MDHS91:

Participation in the MDHS 91 inter-laboratory exercise enabled us to conclusively establish a minor instrument calibration issue (a 10% under-read for both Cu and Pb).