Improvements in the calibration of $^{109}$Cd K x-ray fluorescence systems for measuring bone lead in vivo

A C A Arot, A C Todd, C Amarasingheardenat and H Hut

1 Channing Laboratory, Department of Medicine, Brigham and Women's Hospital, Harvard Medical School, Boston, MA, USA
2 Department of Community Medicine, Mount Sinai Medical Center, New York, NY, USA
3 Occupational Health Program, Department of Environmental Health, Harvard School of Public Health, Boston, MA, USA

Received 6 April 1994, in final form 31 May 1994

Abstract. A $^{109}$Cd K x-ray fluorescence (XRF) system using a point source in a back-scatter geometry is described. The suitability of plaster-of-Paris phantoms as targets for intercalibration standards was evaluated. When the phantom concentrations were measured by inductively-coupled-plasma mass spectrometry (ICP-MS), the calculated phantom concentrations underestimated true concentrations by an average of 15%. Since calculated values are used to calibrate the XRF system, in vivo bone-lead concentrations may be similarly underestimated. The difference between calculated and measured concentrations attributable to the plaster of Paris (e.g. calcium carbonate). The measured concentrations were used to calibrate the XRF system. The same phantoms were also measured as 'unknowns' by a bone-lead measurement system (Abiomed, Danvers, MA, USA). The commercial system overestimated the lowest-concentration phantoms and underestimated the phantoms with concentrations above 15 $\mu$g Pb/g plaster of Paris. The XRF system was compared by measurement of the new phantoms in water. The XRF system exhibited better precision in both solutions. On the basis of this work, we recommend that plaster-of-Paris phantoms used to calibrate XRF measurement systems be analysed by ICP-MS or another valid analytical technique.

1. Introduction

The in vivo x-ray fluorescence (XRF) measurement of bone-lead concentration has emerged as an important technique for future epidemiological studies of long-term lead toxicity. "The technique uses a low-activity source that emits gamma rays to remove an inner-shell electron from a lead atom. Removal of the inner electron leaves the lead atom in an excited state. De-excitation can occur via the emission of one of a series of x-rays whose energy is specific to lead. The x-rays are recorded by a radiation detector, and the number of x-rays is directly proportional to the amount of lead in the bone. The sensitivity of an XRF measurement system is critically dependent upon the choice of fluorescing source energy and source-target-detector geometry. In vivo measurements of lead in bone have been performed with three XRF methods: two fluorescing the K x-rays of lead using a $^{57}$Co source in a 90° geometry (Ahlgren et al 1976, Bloch et al 1977, Price et al 1984) and $^{109}$Cd in a back-scatter geometry and one fluorescing the L x-rays (Wielopolski et al 1981). The $^{109}$Cd K XRF technique was developed at the University of Birmingham (Chettle et al 1991), and has been adopted by other research groups (Jones et al 1991, Erkkila et al 1991, Burger et al 1991, Todd and McNell 1993, Gordon et al 1993, Green et al 1993).
Validation studies comparing K XRF with atomic absorption spectroscopy in cadavers have shown a high degree of accuracy (Somervaille et al 1986, Hu et al 1990).

To our knowledge, there are no reports of direct comparisons of the calibration and precision of different 109Cd K XRF systems. Also, no assessment of the suitability of plaster-of-Paris phantoms as calibration standards have been reported. It is usually assumed that calculated phantom concentrations based on the mass of the initial and final products are adequate. Calculated values are then used to calibrate a K XRF system. Here we describe a K XRF system, the inductively-coupled-plasma mass-spectrometry (ICPMS) protocols used to quantitate phantom-lead concentrations, and a comparison of this system with a commercially available system (Abiomed, Danvers, MA).

2. Methods

2.1. 109Cd K XRF measurements

109Cd emits y-rays of 88.035 keV in 3.6% of its decays. The K-shell absorption edge of lead is 88.005 keV, just 30 eV below the incident y-ray energy; thus there is a high probability of a photoelectric interaction. When a 109Cd y-ray undergoes a photoelectric interaction with a lead K-shell electron, the electron is ejected from the atom. An outer-shell electron can fill the vacancy and, in the transition, release energy as one of a series of K x-rays.

The K XRF system used in these measurements is very similar to other point-source systems and is described in detail elsewhere (Gordon et al 1993, Green et al 1993, Todd and McNeil 1993). A typical MCA spectrum for a 1 14.07 µg Pb/g plaster-of-Paris phantom positioned 2 cm from the 109Cd source is shown in figure 1. Compton scattering is the dominant scattering process and dictates the background magnitude, and therefore the detection limit, of the measurement system. For a high signal-to-noise (K-x-ray) ratio, it is important that the Compton background be located as far as possible from the K XRF signals. Separation increases in parallel with angle of scatter and is maximal at the ideal (but practically impossible) angle of 180°. The maximum in the Compton distribution of figure 1 occurs at 66.1°, which is well below the x-ray peaks (Kα = 72.804 keV, Kβ1 = 74.969 keV, Kβ2 = 83.450 keV, Kβ3 = 84.936 keV, and Kβ4 = 87.300 keV). The mean angle of scatter, calculated from the Compton peak energy, was 157.4°. Figure 1 also shows the other important process of interaction: the elastic scatter peak (88.035 keV). The events (counts) above this peak are due mainly to pulse 'pile-up'.

Of the elastic scatter component 98-99% is due to elements of bone mineral rather than to those of human soft tissue (Chettle et al 1991). In the 109Cd K XRF technique, lead x-rays are normalized to the elastic scatter peak. Normalization yields a unit of measurement of micrograms of lead per gram of bone mineral (µg Pb/g bone mineral). This method of normalization renders the accuracy of measurement insensitive to variations in bone shape, size, and density; to overlying tissue thickness; and to minor subject movement. However, the precision of measurement varies from person to person and depends mainly on the thickness of overlying tissue and the mass of bone mineral sampled.

The effective dose delivered to the subject during an in vivo K XRF measurement is very low as a comparison with natural background radiation demonstrates. In the US the average effective dose rate is around 3 mSv per year (Todd et al 1992a, Todd et al 1992b) described in detail radiation-dosimetry studies involving similar K XRF systems. The effective doses were calculated in accordance with the most recent recommendations of the International Commission on Radiological Protection. The results indicated that the
Improvements in the calibration of $^{109}$Cd K x-rays.

The $K_x$-x-ray system described in this paper is designated $\text{XRFX}$, and we have two other $K_x$-x-ray systems manufactured commercially by Abiomed (Burger et al. 1991). There are several differences between $\text{XRFX}$ and the commercial systems: the most important differences are the dimensions and method of production of the $^{109}$Cd sources. The commercial system uses an 11 mm diameter, reactor-produced source (DuPont, Billerica, MA), whereas $\text{XRFX}$ uses a 3 mm diameter, cyclotron-produced source (Amersham, Chicago, IL). At the time of these measurements, $^{109}$Cd source strengths were 1.08 GBq and 4.82 GBq for the $\text{XRFX}$ and the tested Abiomed system, respectively. Other differences include the mean scattering angle ($\theta_{\text{XRFX}} = 157.4^\circ$ against $\theta_{\text{Abio}} = 150.5^\circ$), where $\theta$ is the mean scattering angle measured from the Compton peak), the peak extraction method, and specific hardware components.

Measurements were made with the phantoms placed in a 9 cm diameter water-filled bottle, with the outer surface of the phantom touching the inner surface of the plastic bottle. Measurements in water approximate count rates found in vivo measurements better than 'in-air' measurements.
2.3. Preparation of calibration standards

2.3.1. Reagents. CaSO₄•1(H₂O) and suprapure HNO₃ were used. A stock solution of Pb (2000 μg/ml⁻¹) was prepared by dissolving 1.8308 ± 0.0001 g of Pb(CH₃COO)₂•3(H₂O) in 50 ml of 1:1 suprapure HNO₃ and diluting to 500 ml with distilled deionized water. Working lead acetate standard solutions (200 μg/ml⁻¹ and 600 μg/ml⁻¹) were prepared by diluting this solution with distilled deionized water. A stock solution was prepared by dissolving the appropriate amount of National Institute of Standards and Technology Standard Reference Material 983 (NIST SRM 983), which is a 206Pb-enriched isotope (1000 μg/ml⁻¹), in 50 ml of 1:1 suprapure HNO₃ on a hot plate (∼100°C). After cooling to room temperature, the solution was diluted to 500 ml with distilled deionized water. Working standard solutions of 206Pb-enriched isotope were prepared by diluting this stock solution.

2.3.2. Phantom preparation. Acrylic tubes (3.2 cm in outer diameter, 2.5 cm in inner diameter; AIN Plastics, Norwood, MA) were cut into 21 cm pieces. Acrylic discs (3 cm in diameter) cut from a flat sheet (thickness, 0.3 cm) were used as lids for the tubes. Both tubes and discs were soaked in a 2% Micro Wash solution (International Products Corporation, Burlington, NJ) for 48 h to remove oil used in machine cutting. Tubes were thoroughly washed with water and soaked in 10% HNO₃ (Curtin Matheson Scientific, Wilmington, MA) for 48 h. Precleaned tubes and discs were thoroughly rinsed with distilled deionized water (Barnstead NANOpure ultrapure water system, Sybron/Barnstead, Boston, MA) and air dried under a class 100 clean hood, After the tubes were dried, the bottom lids were glued with a small amount of acetone, using a glass syringe.

To prepare four replicates of each standard (phantom), 500 ±1 g of CaSO₄•1/2H₂O (calcium sulphate hemihydrate/plaster of Paris, VWR Scientific, Boston, MA) and 250 ml of distilled deionized water/standard Pb acetate solution were mixed thoroughly. The concentration of the standard Pb acetate solution (Puratronic, Johnson Matthey, MA) to be added was calculated by taking into account the weight of the final plaster-of-Paris product CaSO₄•2H₂O, that is, approximately 593 g. The weight of Pb needed to obtain the expected phantom concentrations was calculated as follows:

\[
Pb \text{ needed (μg)} = 593 \text{ g (CaSO}_4 \cdot 1/2\text{H}_2\text{O) } \times \mu\text{g of Pb/g of CaSO}_4 \cdot 1/2\text{H}_2\text{O}.\]

The mixture was stirred with a Teflon spatula for 3 min to obtain homogeneity. It was then poured into four acrylic tubes to a height of approximately 18 cm, yielding a volume of about 91 cm³; an effort was made to exclude air bubbles. The remaining mixture was poured into a precleaned acrylic cup. Both the tubes and the cup were lightly covered with tissue paper (Kimberly Clark, Atlanta, GA) and left to dry in the clean room for 4-5 d. After the samples had dried to a constant weight, the open end of the tubes was sealed, as has been described. For calibration of the K XRF system, a series of plaster-of-Paris phantoms was made, with lead concentrations ranging from 0.30 to 114.07 μg Pb/g plaster of Paris.

2.3.3. ICPMS instrument. The ICPMS instrument used in this study was a Perkin Elmer Sciex Elan 5000 (Perkin Elmer, Norwalk, CT). Before analysis, the mass-spectrometer settings and the nebulizer flow rate were optimized to give a maximal peak intensity for Pb. All samples were analysed by the isotope-dilution technique. This technique provides a unique and highly accurate means of determining the concentration of an element in a sample. Isotope dilution compares the natural abundance of the two isotopes of an element to the abundance occurring in your sample after an enriched-isotope solution (spike) of the sample has been added. The 206Pb-enriched sample was used as a calibration phantom.

2.3.4. Dissolution. Working calibration standards were prepared by adding 206Pb-enriched Pb to the in-house reference material. Samples were mixed thoroughly by sonication and allowed to stand for 5 min. Working solutions were filtered with a 0.22 μm polytetrafluoroethylene (PTFE) membrane filter (VWR Scientific, Boston, MA) to remove any particulate matter. The working solutions were stored at 4°C until analysis, when they were transferred to the ICPMS, using 100 μl aliquots.

2.3.5. Phantoms. A series of K XRF phantoms was prepared with lead concentrations ranging from 0.30 to 114.07 μg Pb/g plaster of Paris. Each phantom was made from 250 mg of the in-house reference material, along with 125 mg of optional contaminant material, and an additional 400 mg of the in-house reference material was added to each sample. For each phantom, a separate 100 μl aliquot of the working solution was used. The phantoms were analyzed for Pb using the ICPMS instrument.
Improvements in the calibration of $^{109}$Cd $K \alpha$

...has been added. Before isotope-dilution analysis, the lead isotope ratio of the lead acetate solution was measured. Data from each determination were averaged over five replicates. A $^{206}$Pb-enriched isotope (NIST SRM 983) was used as the spike for the isotope dilution. The concentration of spike added was determined by the concentration of Pb in the dissolved phantom.

2.3.4. Dissolution of prepared calibration standards. Since there are no standard reference materials available to match the plaster-of-Paris matrix to test the dissolution procedure and the ICPMS instrumental analysis the following recovery study was performed. Five sets of in-house reference standards were prepared by adding a known amount of Pb at different concentration levels into 5 g of plaster of Paris; each set contained five replicates. The whole sample was dissolved and analysed by the ICPMS using the isotope-dilution technique, along with the controls (solution of Pb added to the plaster of Paris). The results of the controls were compared with the data obtained from the in-house reference samples (the Pb contamination contribution from the plaster of Paris was subtracted before the comparison). Recoveries in this study were between 97 and 100%. Accuracy of the Instrumental analysis and the accuracy of the concentration of the spike added was tested by analysing NIST SRM 1643c (trace elements in water) before running any batch of samples.

For each phantom, the remaining lead-doped plaster of Paris in the acrylic cup was ground with an agate mortar and pestle in order to measure the Pb concentration. Five 250 mg portions of the ground sample were weighed and put into leached glass beakers (125 ml capacity). Sufficient spike (NIST SRM 983, $^{206}$Pb enriched) was added to give approximately 100,000 counts in ICPMS analysis. The amount of Pb in the digest was calculated, and the spike was added accordingly. Suprapure HNO$_3$ (5 ml) and distilled deionized water (approximately 20 ml) were then added. The samples were covered with a watch glass and heated on a hot plate for 1 hour at approximately 100°C. Dissolved samples were transferred into volumetric flasks and diluted to 50 ml with distilled deionized water.

Samples were further diluted to give $<500$ ppb of Pb and this solution was analysed by ICPMS, using an isotope-dilution method.

2.3.5. Phantom homogeneity. In order to detect any leadinhomogeneity in the phantoms, a series of $K \alpha$ measurements at different locations were performed on the highest-concentration phantom, that is, $114.07 \mu g$ Pb/g plaster of Paris. Vertical homogeneity was assessed via measurements at the middle position and 4 cm above and below it. Circular homogeneity was assessed via measurements at 0°, 90°, 180°, and 270°. At each position a series of 10 measurements were made, each of 30 min duration.

3. Results and discussion

ICPMS measurements of each phantom concentration (five replicates) are presented in Table 1. ICPMS measurements correlated well ($r^2=0.9998$) with calculated concentrations. However, the measured concentration was, on average, 14.8% higher than was expected for non-blank phantoms. The calculated concentrations of the prepared phantoms were derived from the amount of Pb added assuming that, after the addition of water, CaSO$_4 \cdot 2 $H$_2$O converts completely to CaSO$_4 \cdot 2 $H$_2$O. Impurities (e.g., calcium carbonate) in the plaster of Paris mean that the initial mass is an overestimate of the amount of CaSO$_4 \cdot 2 $H$_2$O and the weight of the final product is consequently less than expected.

Calibration lines (x-ray-to-elastic ratio versus lead concentration) from XRF were obtained using nine phantoms measured by ICPMS for all K-series x-rays. The $\beta_{X \alpha}$ peak
A CA Aro et al

Table 1. Comparison of calculated and ICPMS measured (n=5) phantom concentrations (all units in μgPb/g plaster of Paris).

<table>
<thead>
<tr>
<th>Calculated concentration</th>
<th>ICPMS</th>
<th>measured concentration (μg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.30</td>
<td>(0.01)</td>
</tr>
<tr>
<td>5.06</td>
<td>6.77</td>
<td>(0.10)</td>
</tr>
<tr>
<td>10.12</td>
<td>11.57</td>
<td>(0.05)</td>
</tr>
<tr>
<td>15.18</td>
<td>17.34</td>
<td>(0.40)</td>
</tr>
<tr>
<td>20.24</td>
<td>23.27</td>
<td>(0.77)</td>
</tr>
<tr>
<td>30.35</td>
<td>34.71</td>
<td>(0.37)</td>
</tr>
<tr>
<td>50.50</td>
<td>56.60</td>
<td>(0.06)</td>
</tr>
<tr>
<td>75.90</td>
<td>83.97</td>
<td>(0.94)</td>
</tr>
<tr>
<td>101.18</td>
<td>114.07</td>
<td>(0.79)</td>
</tr>
</tbody>
</table>

was fitted by the peak-extraction program but the peak was not used for calculation of in vivo measurements because of the bremsstrahlung edge from oxygen. The final lead concentration was calculated from the inverse weighted mean of the Kx predictions. The contributions of the different Kx-rays to overall precision are discussed elsewhere (Chuttle et al. 1991).

Table 2: XRF-assessed vertical and circular homogeneity of 114.07 μgPb/g plaster-of-Paris phantom. Mean and SD of 10 measurements (all units in μgPb/g plaster of Paris).

<table>
<thead>
<tr>
<th>Position</th>
<th>Concentration (μg)</th>
<th>Mean</th>
<th>SD (μg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Middle - 4 cm</td>
<td>114.03 ± 0.84</td>
<td>114.03</td>
<td>0.84</td>
</tr>
<tr>
<td>Middle</td>
<td>114.76 ± 0.97</td>
<td>114.76</td>
<td>0.97</td>
</tr>
<tr>
<td>Middle + 4 cm</td>
<td>114.66 ± 0.92</td>
<td>114.66</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Table 3: ICPMS, XRF, Abiomed, and recalibrated Abiomed phantom measurements. Mean and SD of 10 measurements (all units in μgPb/g plaster of Paris).

<table>
<thead>
<tr>
<th>ICPMS</th>
<th>XRF</th>
<th>Abiomed</th>
<th>Recalibrated Abiomed</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.34 (0.91)</td>
<td>0.79 (0.40)</td>
<td>4.43 (1.50)</td>
<td>2.21 (2.42)</td>
</tr>
<tr>
<td>5.77 (1.19)</td>
<td>6.62 (1.46)</td>
<td>7.22 (2.58)</td>
<td>5.63 (2.00)</td>
</tr>
<tr>
<td>11.57 (0.05)</td>
<td>11.08 (0.29)</td>
<td>10.94 (2.36)</td>
<td>11.67 (2.37)</td>
</tr>
<tr>
<td>37.34 (0.40)</td>
<td>37.29 (2.17)</td>
<td>35.62 (1.68)</td>
<td>37.82 (3.05)</td>
</tr>
<tr>
<td>23.27 (0.77)</td>
<td>22.76 (1.67)</td>
<td>18.04 (2.50)</td>
<td>22.35 (2.39)</td>
</tr>
<tr>
<td>34.77 (0.37)</td>
<td>34.08 (0.78)</td>
<td>27.88 (2.33)</td>
<td>34.98 (3.85)</td>
</tr>
<tr>
<td>56.60 (0.96)</td>
<td>56.46 (1.45)</td>
<td>42.53 (2.26)</td>
<td>56.24 (2.89)</td>
</tr>
<tr>
<td>83.97 (0.94)</td>
<td>84.77 (1.83)</td>
<td>64.59 (2.38)</td>
<td>84.59 (2.76)</td>
</tr>
<tr>
<td>114.07 (0.79)</td>
<td>114.34 (1.75)</td>
<td>89.02 (3.65)</td>
<td>114.55 (2.87)</td>
</tr>
</tbody>
</table>

The recalibrated non-linear line by the Birn correlation is close to unit. The unmod phantom, the concentration is worth for xrf3. The properties, a previous in, are made at true levels a'be reanalyse.

4. Conclusion

In vivo K X-ray measurements show a biological measuring that can easily be done.

In this 0.9998 will: approximate, might have
The results of comparisons of the two K \text{XRF} systems and ICMS are presented in table 3. Ten replicate measurements, each of 30 min duration, were made for each phantom. The Abiomed results were analysed with Abiomed software. Subsequently, recalibrated Abiomed results were generated by reanalysing the same raw data with the non-linear least-squares-fitting (Marquardt 1963) technique with fitted functions developed by the Birmingham University group and use of the new ICMS measured phantoms. The correlation between \text{XRF3} and ICMS measurements was good ($r^2 = 0.9998$) with a slope close to unity ($m = 0.9968$) as expected since \text{XRF3} was calibrated against ICMS values. The unmodified Abiomed measurement system overestimated the lowest-concentration phantoms, that is 0 and 5 $\mu g$Pb/g plaster of Paris, and underestimated the phantoms with concentrations above 15 $\mu g$Pb/g plaster of Paris. Modifications solved this problem; but it is noteworthy that the SD for the modified Abiomed system still remained higher than that for \text{XRF3}. These differences are related mainly to geometries, WCd source dimensions and properties, and electronics settings. The immediate implication of this finding is that the previous \textit{in vivo} results obtained with the Abiomed instrument are inaccurate; overestimates are made at true levels below 5 $\mu g$Pb/g plaster of Paris and underestimates are made at true levels above 15 $\mu g$Pb/g plaster of Paris. However, previously measured spectra could be reanalysed with the new methods.

<table>
<thead>
<tr>
<th>ICMS</th>
<th>Abiomed ‘in air’</th>
<th>Abiomed ‘in water’</th>
<th>\text{XRF3}’in air’</th>
<th>\text{XRF3}’in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 (0.02)</td>
<td>4.40 (1.50)</td>
<td>2.34 (0.55)</td>
<td>0.79 (0.40)</td>
<td>2.27 (0.64)</td>
</tr>
<tr>
<td>5.77 (8.10)</td>
<td>7.24 (2.59)</td>
<td>8.41 (4.63)</td>
<td>6.03 (1.44)</td>
<td>6.38 (2.87)</td>
</tr>
<tr>
<td>115.57 (106.35)</td>
<td>10.94 (2.38)</td>
<td>22.22 (3.68)</td>
<td>110.0 (1.29)</td>
<td>9.96 (3.26)</td>
</tr>
<tr>
<td>23.27 (7.77)</td>
<td>15.04 (2.50)</td>
<td>18.77 (5.76)</td>
<td>22.76 (1.67)</td>
<td>22.19 (0.02)</td>
</tr>
<tr>
<td>56.00 (1.96)</td>
<td>42.57 (2.20)</td>
<td>76.18 (5.40)</td>
<td>56.46 (1.45)</td>
<td>50.54 (0.86)</td>
</tr>
</tbody>
</table>

The results of phantom measurements made in air and in water are summarized, for each system, in table 4. The SDs were higher for Abiomed measurements than for \text{XRF3} measurements in both cases. If it is assumed that the minimal detection limit (MDL) is twice the standard deviation of a blank phantom in water, then the MDLs are 13 $\mu g$Pb/g plaster of Paris for Abiomed and 7 $\mu g$Pb/g plaster of Paris for \text{XRF3}, respectively. These results clearly demonstrate that the \text{XRF3} system will be superior in future epidemiological studies of teenagers environmentally exposed to lead, who can be expected to have bone-lead levels that are mostly below 10$\mu g$Pb/g bone mineral (Bellinger \textit{et al} 1994).

4. Conclusions

\textit{In vivo} K \text{XRF} promises to add significantly to our knowledge of lead toxicity by providing a biological marker of lead accumulation. K \text{XRF} is a practical and convenient way of measuring lead stores in the body and requires very little radiation exposure. This system can easily be installed in a mobile facility for field measurements.

In this study, ICMS measurements of plaster-of-Paris phantoms correlated well ($r^2 = 0.9998$) with the calculated concentration. However, the measured concentrations were approximately 15% higher than the calculated concentrations, and \textit{in vivo} lead concentrations might have been underestimated if the expected values had been used to calibrate the
instrument. Since 100% pure plaster of Paris is not available, and the quantity of impurities present is unknown, we strongly recommend that the plaster-of-Paris phantoms used for calibration be measured for lead concentration by ICPMS or another valid analytical technique.

The correlation between the measurements obtained with our K XRF system and those obtained with the ICPMS system were good ($r^2 = 0.9998$), with a slope close to unity ($m = 0.9968$). However, the Abiomed bone-lead system overestimated the lowest-concentration phantoms, that is 0 and $5 \mu \text{g Pb/g plaster of Paris}$, and underestimated those with concentrations above $15 \mu \text{g Pb/g plaster of Paris}$. This problem can be corrected by reanalysing the raw data with a different peak-extraction program and recalibration of the instrument with ICPMS-measured plaster-of-Paris phantoms. This finding implies that previous x-ray fluorescence measurements obtained with an Abiomed instrument could, in principle, be reanalysed to conform with the calibration of XRF (and other instruments).

Acknowledgments

This work was supported by National Institute for Environmental Health Sciences (NIEHS) centre grant 2P30 ES00002, NIEHS R 01-ES 05257-01A1, and NIEHS Superfund P42-ES 05947. Thanks are due to Michael Oh, Nicola Lupoli, and Paul Kandola for their research assistance. We also thank Dr Ramon M Barnes for the use of the clean-room facility at the University of Massachusetts at Amherst.

References

Ahlgren I., Ladh K, Mattsson S and Toppan S 1976 X-ray fluorescence analysis of lead in human skeleton Environ. Health Perspect. 2 82-6
Hu H, Miller F L and Burger D E 1990 X-ray fluorescence measurements of lead burden in subjects with low-level community lead exposure Arch. Environ. Health 45 335-41
the quantity of f-Paris phantoms or valid analytical system and those close to unity were the lowest-estimated those can be corrected by recalibration of Jing implies that cal in principle,


drances (NIEHS) superfund P42-ES or their research in facility at the

human skeleton in bone lead levels

\textit{Iden}tified in situ analysis by K-x-rays with high K x-ray excited bone \textit{In Vivo}Body

\textit{In Vivo} Phys. Med. estimation of bone lead at

\textit{In Vivo} Advances vol 85


for the measurement of lead in bone using L x-ray fluorescence \textit{IEEE Trans. Nucl. Sci.} 28\#1261-74


Todd A C and McNeill F E 1993 \textit{In Vivo} measurements of lead in bone using a \textit{In Vivo}Cd 'spot' source Human Body Composition Studies (New York: Plenum) pp 299-302


Todd A C and McNeil1 F E 1993 \textit{In Vivo} measurements of lead in bone using a \textit{In Vivo}Cd 'spot' source Human Body Composition Studies (New York: Plenum) pp 299-302
