CALIBRATION OF ENERGY DISPERSIVE X-RAY

SPECTROMETERS FOR ANALYSIS OF THIN

ENVIRONMENTAL SAMPLES

R. D. Giauque, R. B. Garrett, and L. Y. Goda

Lawrence Berkeley Laboratory

Berkeley, California 94720

INTRODUCTION

The ability to perform quantitative measurements with an x-ray fluorescence spectrometer is limited to the accuracy with which the output, in terms of counts/sec., can be converted to mass concentration, $\mu g/cm^2$. The task of calibrating an x-ray spectrometer involves the determination of sensitivity conversion factors for each element of interest. In analytical programs in which 30 or more elements can routinely be measured, calibration could become a tedious and expensive problem. Fortunately, the multielement detection capabilities of energy dispersive x-ray spectrometers, together with the fact that sensitivity typically varies as a smooth function with atomic number, permit the calibration process to be greatly simplified.

We describe several calibration techniques which can be applied to standardize for analysis of thin environmental specimens. The assumption is made that corrections for self-absorption or enhancement effects are negligible. For analysis of light elements deviations from negligible matrix effects should be treated separately and are not discussed in this paper. The first of the methods to be described for thin-film calibration requires the use of elemental thin-film standards which have been prepared by vacuum vapor deposition of individual elements onto thin substrata. The masses of the standards are determined by weighing. The second method entails the utilization of multielement standard solutions which are nebulized and collected on thin substrata. The deposits are used to determine relative elemental sensitivity factors and absolute calibration of the system is accomplished using an evaporated single element thin-film standard. The third method is a semi-empirical approach which relies upon published photoelectric cross-section and fluorescence yield data to calculate relative excitation efficiencies.

Detector efficiency for various x-ray lines are determined experimentally.
The absolute calibration is again achieved using an evaporated single
element thin-film standard. Finally, a modification of the semi-empirical
approach applicable for thick standards in a few limited cases is
described. The technique can be used in cases when the thin-film criteria
are not easily realized, such as for the very light elements.

CALIBRATION METHODS

To calibrate a spectrometer for analysis of thin environmental
specimens it is necessary to determine the sensitivity of the system for
each of the elements to be analyzed. The sensitivity, S, for an element i
may be expressed:

$$I = S_i m_i \qquad (1)$$

where

I = the intensity, counts/sec., of the x-ray line from an
   elemental thin-film (matrix effects presumed to be negligible).

S_i = the sensitivity in counts/sec. per $\mu g/cm^2$.

m_i = the mass of the elemental thin-film, $\mu g/cm^2$.

Calibration Using Individual Elemental Thin-Film Standards

For some elements calibration has been accomplished using individual
elemental thin-film standards. The standards were prepared by vacuum
vapor deposition of pure elements onto thin high purity substrata. Typical
deposits made were in the range of 50-150 $\mu g/cm^2$. Both aluminum (800 $\mu g/cm^2$ -
prepared by vaporization of 99.99% Al) and Kapton (3 mg/cm^2 polyamide film)
have been used as supporting substrata for the deposits. A distance
of 25 cm between the vapor source and the collection substrate was
maintained during the preparation of the vacuum vapor deposits.

This tended to ensure a uniform deposit over a 5 cm^2 area. The amounts
of deposits collected were determined by weighing, with estimated
accuracies of ±3%. The thin-film standards are stored in a vacuum
desiccator to minimize oxidation of the deposits. Pure elemental thin-
film standards prepared at this laboratory using the vacuum vapor
deposition technique include Cr, Mn, Fe, Ni, Cu, As, Se, Ag, Au, and Pb.
Several elements for which non-uniform deposits were made included Ti, Zn,
and Cd. The lack of uniformity was determined by analyzing various areas
of the deposits. Deposits made of Al and Si on Kapton suffered from x-ray
absorption, which was due to both loading and particle size effects.
Thin-film standards prepared by vacuum vapor deposition of the elements
have been successfully used for calibration by a number of laboratories (1).
The disadvantage of this method is the cost of obtaining standards for
a large number of elements.

Calibration Using Nebulized Multielement Standard Solution Deposits

Calibration for nearly all of the elements to be determined by
x-ray fluorescence analysis can be accomplished by using nebulized multi-
element standard solution deposits on thin filters. The deposits are
analyzed to determine relative elemental sensitivity factors, and absolute
calibration of the system is accomplished using a single element thin-
film standard prepared by vacuum vapor deposition of a pure element.

The multielement standard solutions used in this method contain
from two to five elements, one of which is an internal standard element.
A DeVilbiss glass nebulizer, illustrated in Figure 1, is employed to
generate a very fine mist which is collected on a thin filter. A
distance of approximately 5 cm is maintained between the nebulizer and
the filter, which can be either Nuclepore polycarbonate or cellulose
ester membrane. For deposits of elements which have x-ray energies

of less than 10 keV, cellulose ester membrane filters are not applicable since a small amount of the mist can be absorbed in the filters, which in turn causes some attenuation effects.

The standard solutions are prepared for most elements using a standard weighing form. For example, for many elements pure metals dissolved in acids are used. In some cases, pure compounds are dissolved in water or ammoniacal solutions (i.e., $K_2Cr_2O_7$, As_2O_3, KIO_3). For a standard sulfur solution, H_2SO_4 which has been titrated with a standard NaOH solution is used. Multielement standard solutions are prepared from aliquots of the individual element standard solutions. Mixtures are made only in combinations which will not yield overlapping x-ray lines or produce chemical reactions which will cause the concentration of an element to decrease by the formation of either a precipitate or a volatile compound. The concentration of each element in the mixed solution is in the 100 to 5000 ppm range. Elemental deposits of between 1 to 10 $\mu g/cm^2$ are prepared and require from 50 to 500 ejections from the nebulizer. To prevent large droplet formations on the substrate, a drying period of one minute is allowed between each group of 10 ejections from the nebulizer. For elements which have x-ray energies of less than 3 keV, mixtures of only two elements each are made and the concentration of the elements in solution should not be higher than a few hundred ppm. This permits the mist droplets to evaporate to a smaller particle size and minimizes the possibility of particle size effects. For each element, three separate standard mixed solutions of varying elemental concentration ratios are prepared (the concentration of the internal standard element usually is not varied). Duplicate deposits are made for each standard mixed solution. Relative excitation-

detection calibration factors utilized are the average values determined from the six deposits. Typically, the standard deviations (2σ), for the relative excitation-detection efficiencies we have determined, are 2% or less in nearly every case. Although the deposits are not necessarily uniform over the entire area of deposit, the use of one element as an internal standard compensates for slight non-uniformity. To minimize possible calibration errors for elements which have higher energy K x-rays (>20 keV), where the detector efficiency can be influenced by non-uniformity of the deposit, the internal standard element should have x-rays within the same general energy range (± 5 keV).

To illustrate the relative ease and accuracy with which calibration can be achieved using nebulized multielement standard solution deposits, two separate NBS steel samples, 101c and 121a, were analyzed. 500 mg of each steel, in the form of turnings, were dissolved using a mixture of HNO_3 and HCl acids and brought up to volume. (Note: A very small amount of dark residue remained undissolved and most likely it was composed of Si and C which are present at low levels in these specimens.) Three separate solutions of varying concentrations were made from each of the steel solutions and zinc was added as the internal standard element. Duplicate deposits were made for each solution on polycarbonate filters. Typical loadings corresponded to 3 to 10 $\mu g/cm^2$ of the original steel. The results obtained are shown in Tables 1 and 2. The determined values are the average values obtained from the six deposits made for each steel. The deviations listed are 2σ values. Seven minutes were required to analyze each deposit. The results obtained for the major constituents, Cr, Fe, and Ni, agree to within 2% or better in each case with listed NBS values. Somewhat poorer agreement was obtained for Mn. However, these examples serve to illustrate the ease and capability of the technique of calibration with nebulized multielement standard solution deposits.

Calibration Using a Basic Physical Approach

This method is a semi-emperical approach which relies upon published photoelectric cross section and fluorescence yield data to calculate relative excitation efficiencies. Detector efficiency for various x-ray lines are determined experimentally. Relative elemental sensitivity factors utilized combine the calculated relative excitation efficiencies with the determined detector efficiencies. The absolute calibration of the system is accomplished using an evaporated single element thin-film standard. This semi-emperical approach has been previously described in detail elsewhere (2). The relative elemental sensitivity calibration factors are the product of the relative probabilities of four separate processes, each of which we treat individually.

Calculation of the Relative Ability of the Excitation Radiation to Photoelectrically Produce a Vacancy in a Particular Energy Level

First considered is the probability that a photoelectric interaction will produce a vacancy in a particular inner energy level. The photoelectric mass absorption coefficient for a particular energy level may be expressed:

$$\tau \cdot (1 - \frac{1}{J_{K,L}}) \tag{2}$$

where

τ is the total photoelectric mass absorption coefficient, cm^2/g, of the element for a specific energy level plus all lower energy levels.

$J_{K,L}$ is the ratio (jump ratio) between the photoelectric mass absorption coefficients at the top and the bottom of the absorption edge energy.

For absorption occurring in the K shell, the value of τ is the total

photoelectric mass absorption coefficient for the exciting radiation. However, for the L energy levels the value of τ is obtained by extrapolation of the curve for the particular energy level to the effective exciting radiation energy.

Calculation of the Fraction of the Vacancies Filled by Transitions Which Give Rise to the Emission of a Specific X-Ray Line

Only a fraction of the vacancies created in a particular energy level are filled by transitions which give rise to the direct emission of x-rays. Some vacancies are filled by transitions involving the emission of Auger electrons. The fraction of vacancies filled by transitions which directly yield x-rays is the fluorescence yield value $(\omega_{K,L})$.

Transitions to a particular energy level give rise to the emission of more than one x-ray line since the transitions can originate from different initial energy states. The fraction of a specific x-ray line emitted with respect to the total is referred to as the fractional value (f). Hence, the net fraction of vacancies filled by transitions which give rise to the emission of a specific x-ray line may be expressed:

$$\omega_{K,L} \cdot f \tag{3}$$

Thus, for a particular excitation radiation, x-ray excitation curves may be established for x-ray lines from individual energy levels by multiplying the value of the terms τ, $(1 - \frac{1}{J_{K,L}})$, $\omega_{K,L}$, and f. The value of each of the terms is reported in the literature (3-7). Figure 2 illustrates some calculated curves for the excitation of characteristic $K\alpha$ and $L\alpha$ x-rays with MoK radiation. As shown, the curves are a smooth function of atomic number and one need only plot several points for each curve. Relative excitation factors for this range of

elements can be interpreted to within ±5%.

Calculation of the Fraction of X-Rays Attenuated in the Medium between the Specimen and the Detector

A small proportion of the x-rays excited from the specimen may be attenuated by the air path, if present, and by the beryllium window. The fraction transmitted (T) may be expressed:

$$T = e^{-(\mu_{air} m_{air} + \mu_{Be} m_{Be})} \tag{4}$$

where

μ_{air} and μ_{Be} are the total mass absorption coefficients, cm^2/g, of air and the beryllium window for the fluorescent x-rays, respectively.

m_{air} and m_{Be} are the masses of the air and the beryllium window, g/cm^2, that the flourescent x-rays must traverse.

If the length of the air path is less than 2 cm and if the thickness of the beryllium window is less than 0.03 mm, the value of T would be higher than 0.97 for all x-rays of energy 6 keV and higher. Consequently, for many x-rays attenuation effects are minor or negligible.

Determination of the Detector Efficiency for Specific X-Ray Energies

Due to geometry and detector efficiency considerations, only a fraction of the x-rays which intersect the detector may be detected. The detector efficiency (ε) for radiation intersecting the detector at an angle of 90° near the center of the sensitive region of the detector can be calculated from the mass (m) and the photoelectric mass absorption coefficient of the detector and may be expressed:

$$\varepsilon = 1 - e^{-\tau m} \tag{5}$$

If radiations between 4 and 15 keV strike the detector in the described manner, the efficiency is unity. However, with geometries employed for analysis, a fraction of the radiation intersects the detector at angles

of less than 90° and impinges upon the detector near the periphery of the sensitive region.

To determine the effect of geometry on the detector efficiency, the intensities of characteristic x-rays from thin reference specimens are measured by using, (1) the geometry employed for analysis and (2) a fine long collimator set over the detector so that the x-rays detected approach the detector in the center of the sensitive region at an angle close to 90° as illustrated in Figure 3. Intensity measurements are made for two separate x-ray energies in the two geometries. An x-ray line for which the detector efficiency would be unity in either geometry (i.e., TiKα) is selected as one of the radiations. The detector efficiency for the second radiation may be expressed:

$$\epsilon_2 = \frac{I_2 \times I_1'}{I_1 \times I_2'} \cdot [\ 1 - e^{-\mu_2 m}\ ] \qquad (6)$$

where

I_1, I_1', I_2, and I_2' are the x ray line intensities, counts/sec, for the radiations 1 and 2 in the two geometries.

μ_2 is the total mass absorption coefficient of the detector, cm^2/g, for radiation 2.

m is the mass thickness, g/cm^2, of the detector.

Comparison of Calculated and Determined Relative Excitation-Detection Efficiencies

Table 3 lists a comparison of calculated and determined relative excitation-detection efficiencies for an x-ray system which employs a molybdenum transmission x-ray tube (2). The determined values are the average values ascertained from nebulized standard solution deposits (six for each element) and the errors listed are 2σ values. As shown, the *calculated values for eight of the elements (K, Ca. Cr, Mn, Fe, Ni, Zn and As)*

normalized to the CuKα value agree to within ±4% or better in each case. However, the discrepancies for Rb and Sr are somewhat larger, ±12%. These examples serve to illustrate that relative excitation-detection efficiencies can be calculated fairly accurately using the basic physical approach.

Calibration Using Thick Pure Element Disks

This method is a modification of the semi-empirical approach and has been used to calibrate for analysis of very light elements for which the thin-film criteria are not easily realized. To utilize this approach, (1) the excitation radiation should be a well collimated, near monochromatic x-ray beam and (2) the photoelectric cross section should be a large fraction (over 90%) of the total mass absorption coefficient for the excitation radiation. The mass, m_{thick} (g/cm^2), of the thick element disk may be expressed:

$$m_{thick} = 3.92/(\mu_e \csc\psi_1 + \mu_f \csc\psi_2) \qquad (7)$$

where

> μ_e and μ_f are the total mass absorption coefficients of the element (cm^2/g) for the excitation and fluorescent radiations, respectively.
>
> ψ_1 and ψ_2 are the angles formed by the excitation and fluorescent radiations with the surface of the disk.

Since m_{thick} represents the mass for which only 25% of the radiation (excitation x fluorescence) is not attenuated, the mass of the disk for calibration purposes is $m_{thick}/4.0$.

It is important that the surface of the disk is very smooth when using this method. We have previously applied this approach to calibrate a spectrometer for analyses of three low atomic number elements, Al, Si, and S (8). Calculated relative elemental sensitivity factors agreed to within 5% of the determined values which were ascertained using thick disks for these three elements.

SUMMARY

Four separate techniques for calibrating energy dispersive x-ray spectrometers have been described. They include the use of (1) individual evaporated elemental thin-film standards, (2) nebulized multielement standard solution deposits to determine relative elemental sensitivity factors, (3) a semi-empirical approach to calculate relative elemental sensitivity factors, and (4) thick pure element disks. The first three techniques are applicable for a broad range of elements. The utilization of nebulized multielement standard solution deposits, along with an evaporated single element thin-film standard for absolute system calibration, is the most accurate method of the calibration techniques described.

REFERENCES

1. D.C. Camp and A.L. Van Lehn, "Intercomparison of Trace Element Determinations in Simulated and Real Air Particulate Samples", X-Ray Spect., 4, 123 (1975).

2. R.D. Giauque, F.S. Goulding, J.M. Jaklevic, and R.H. Pehl, "Trace Element Determination with Semiconductor Detector X-Ray Spectrometers", Anal. Chem., 45, 671 (1973).

3. W.H. McMaster, N.K. Del Grande, J.H. Mellett, and J.H. Hubbell, Compilation of X-Ray Cross Sections, UCRL 50174, Sec. II and IV (1969). Available from the National Technical Information Service.

4. W. Bambynek, et al., "X-Ray Fluorescence Yields, Auger and Coster-Kronig Transition Probabilities", Rev. of Mod. Phys. 44, No. 4, 716 (1972).

5. E.J. McGuire, "Atomic L-Shell Coster-Kronig, Auger, and Radiative Rates and Fluorescence Yields for Na-Th", Phys. Rev., A3, 587 (1971).

6. J.S. Hansen, H.U. Freund, and R.W. Fink, "Relative X-Ray Transition Probabilities to the K-Shell", Nucl. Phys., A142, 604 (1970).

7. G.G. Johnson, Jr. and E.W. White, X-Ray Emission Wavelengths and keV Tables for Nondiffractive Analysis, ASTM DS 46, Am. Soc. Testing Mater. (1970).

8. R.D. Giauque, R.B. Garrett, L.Y. Goda, J.M. Jaklevic, and D.F. Malone, "Application of a Low Energy X-Ray Spectrometer to Analyses of Suspended Air Particulate Matter", to be published in Proceedings of the 24th Annual Denver X-Ray Conference, August 1975 (Plenum Press, New York).

Table 1

Analysis of NBS Steel 101c

	Determined	NBS
Cr	18.14%±0.38	18.21%
Mn	0.90%±0.08	0.640%
Fe	70.75%±0.54	(70.7%)
Ni	9.35%±0.24	9.27%

Fe value = 100.0% - (sum of all listed constituents)

Table 2

Analysis of NBS Steel 121a

	Determined	NBS
Cr	18.29%±0.42	18.69%
Mn	1.38%±0.12	1.28%
Fe	68.43%±0.48	(68.2%)
Ni	10.73%±0.12	10.58%

Fe value = 100.0% - (sum of all listed constituents)
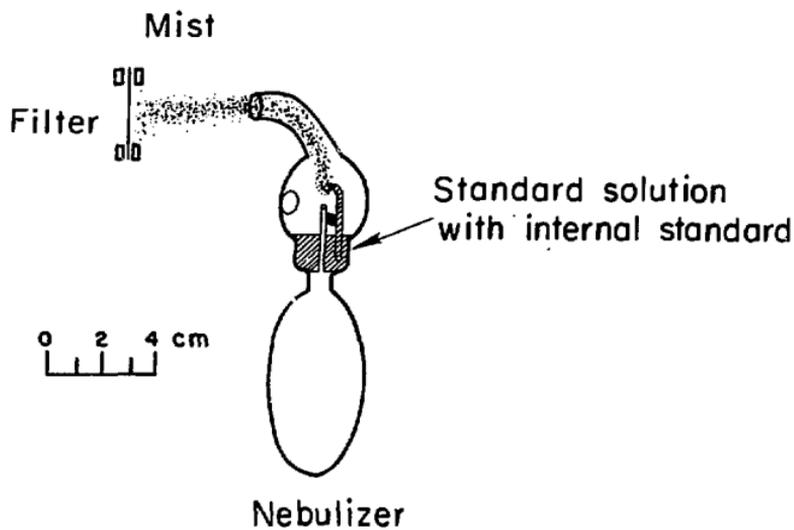
Table 3

Relative Excitation - Detection Efficiencies

Line	Calculated	Determined
KKα	.0622	.0625±.0018
CaKα	.0977	.1005±.0026
CrKα	.339	.346±.006
MnKα	.415	.432±.006
FeKα	.572	.572±.010
NiKα	.815	.817±.006
CuKα	1.000	1.000
ZnKα	1.072	1.078±.008
AsKα	1.467	1.430±.056
RbKα	1.641	1.851±.024
SrKα	1.641	1.848±.014

FIGURE CAPTIONS

Figure 1. Apparatus for preparation of nebulized standard solution deposits.
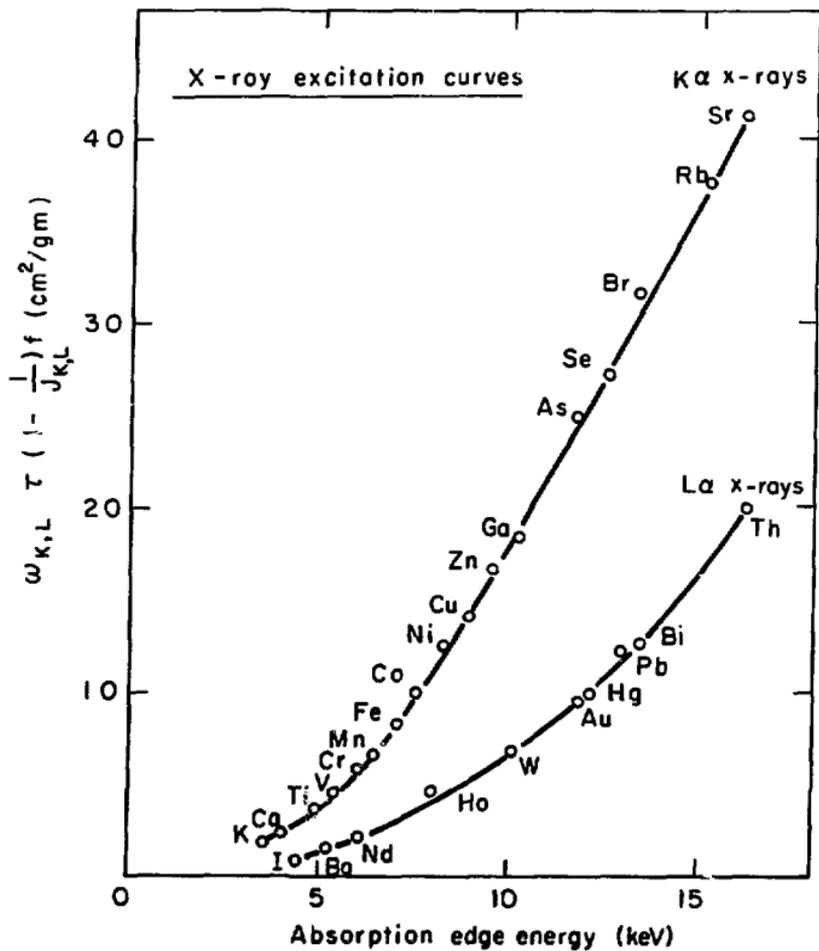
Figure 2. X-ray excitation curves for excitation with molybdenum K radiation.

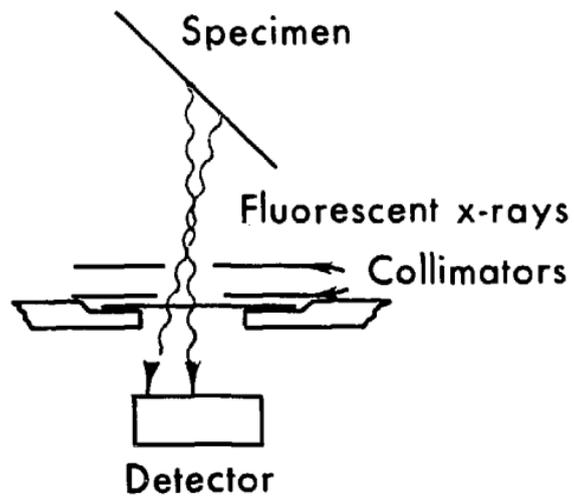Figure 3. Schematic of method used to determine the detector efficiency.

Mist

Filter

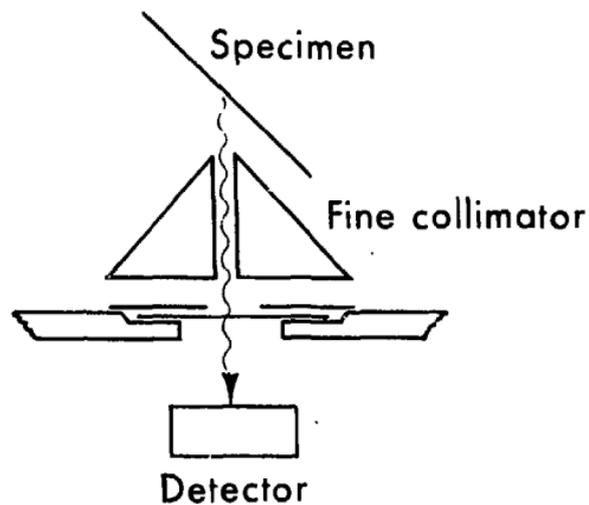Standard solution
with internal standard

0 2 4 cm

Nebulizer

XBL761-2069

Fig. 1

Fig. 2

Measure: I_1 , I_2 I_1' , I_2'

Fig. 3