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RAPID QUANTITATIVE ANALYSIS BY X-RAY SPECTROMETRY

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ABSTRACT

An x-ray fluorescence analysis method applicable to the case of fluorescent spectra excited with monoenergetic x-rays has been developed. The technique employs a minimum number of calibration steps using single element thin film standards and depends upon theoretical cross sections and fluorescent yield data to interpolate from element to element. The samples are treated as thin films and corrections for absorption effects are easily determined. Enhancement effects, if not negligible, are minimized by sample dilution techniques or by selective excitation.
I. INTRODUCTION

The ability to obtain rapid multielement x-ray fluorescence spectra with energy dispersive x-ray spectrometers makes it necessary to have available convenient and accurate methods to convert the spectral intensity data to meaningful element concentrations. Although most present methods employ extensive standard calibration samples,\textsuperscript{1,2} there have been attempts to formulate more general methods based on the calculation of absolute fluorescent intensities.\textsuperscript{3,4} The present method is similar to that of Ref. 3, but is derived as an extension of the technique for the determination of film thickness using monochromatic excitation such as described by Liebhafsky et al.\textsuperscript{5}

In order for the technique to be applicable, it must be possible to prepare the sample in the form of a thin homogeneous specimen of uniform thickness. If monochromatic primary radiation is used to excite the characteristic x-rays from the sample, and if the critical thickness for the characteristic x-ray of energy $E_j$ has not been reached, the problem may be described as shown in Fig. 1. If enhancement effects can be neglected, the probability of exciting the K x-ray of energy $E_j$ from element J in the thickness $dx$ and detecting the x-ray equals the product of three probabilities which may be written as follows:

\begin{equation}
P_1 = \sigma_1 \exp(-\mu_1 \csc \phi_1 px)
\end{equation}

which is the probability the primary radiation will reach a depth $x$

\begin{equation}
P_2 = \tau_j \rho_j \csc \phi_1 [1 - (1/J_K)] \omega_K f dx
\end{equation}

being the probability that element J will absorb the primary radiation in the thickness $dx$ and emit a K x-ray of energy $E_j$.
\[ P_3 = G_2 \exp(-\mu_2 \csc \phi_2 \rho x) A_b \in \] (3)

which in turn is the probability that the K x-ray of energy \( E_j \) will reach the detector and be detected where:

- **\( G_1 \text{ and } G_2 \)** are geometry factors
- **\( \mu_1 \text{ and } \mu_2 \)** are the total mass absorption coefficients \((\text{cm}^2/\text{gm})\) of the sample for the primary and the characteristic, \( E_j \), radiations
- **\( \phi_1 \text{ and } \phi_2 \)** are the angles formed by the primary and the emergent characteristic radiations with the sample surface
- **\( \rho \)** is the density \((\text{gm/cm}^3)\) of the sample
- **\( \rho_j \)** is the density of element \( j \) within the sample considering the entire sample distribution
- **\( \tau_j \)** is the photoelectric mass absorption coefficient of element \( j \) for the primary radiation
- **\( J_K \)** is the ratio between the photoelectric mass absorption coefficients at the top and the bottom of the K absorption edge; \([1 - (1/J_K)]\) is the fraction of photoelectric events which occur in the K shell
- **\( \omega_K \)** is the fluorescent yield for the K x-rays from element \( j \)
- **\( f \)** is the fraction of the K x-rays of energy \( E_j \) with respect to the total K x-rays emitted
- **\( A_b \)** is the absorption for the air path, if present, plus the absorption of the detector window, both of which can be calculated
- **\( \in \)** is the detector efficiency for x-rays of energy \( E_j \).
The values of $\mu_1$, $\mu_2$, $\tau_j$, $J_K$, $\omega_K$, and $f$ can be obtained from literature (Refs. 6,7,8,9). The values of $E$ can be measured or calculated from the detector thickness. In the case of L x-rays the appropriate substitutions for $J_L$, $\omega_L$, etc. can be made.

If the intensity of the primary radiation is $I_o$, then the x-ray intensity due to element $j$ at a depth $x$ is:

$$dI = I_o G \csc \phi_1 \tau_j \rho_j [1 - (1/J_K)] \omega_K f A_b \in [\exp(-apd)] \, dx$$  \hspace{1cm} (4)$$

where

$$G = G_1 G_2 \quad \text{and} \quad \hspace{1cm} (4a)$$

$$a = \mu_1 \csc \phi_1 + \mu_2 \csc \phi_2 \quad \hspace{1cm} (4b)$$

Integrating over the sample thickness $d$ and multiplying the numerator and the denominator by $d$ one obtains:

$$I = I_o G \csc \phi_1 \tau_j \rho_j [1 - (1/J_K)] \omega_K f A_b \in [1 - \exp(-apd)]/apd$$  \hspace{1cm} (5)$$

The value $\rho_j \, d$ is the concentration (gm/cm$^2$) of element $j$ which is to be determined. The quantity $\exp(-apd)$ is the product of the total absorption of the primary radiation ($\mu_1 \csc \phi_1$) and the total absorption of the characteristic radiation ($\mu_2 \csc \phi_2$) in the total sample thickness. The quantity can be determined by measuring the relative intensity with and without the specimen of the K x-ray of a pure target of element $j$ located at a position adjacent to the back of the thin specimen.

Since the values of $\tau$, $J_K$, $\omega_K$, and $f$ are known for each element, the value of $I_o G \csc \phi_1$, may be determined from a single element thin film
standard for which the absorption effects are negligible. (The value \[1 - \exp(-\alpha d)\] essentially equals the value \(\alpha d\) when the value \(\alpha d\) is small.) Thus from a thin film standard, at constant primary radiation intensity and constant geometry, Eq. (5) will reduce to

\[I = CK_j \rho_j d[1 - \exp(-\alpha d)]/\alpha d\]  \hspace{1cm} (6)

where

\[C = I_0 G \csc \phi_1\] and

\[K_j = \text{constant for the element } j\]

In effect, theoretical values of relative excitation and detection efficiencies for various x-ray lines are calculated. The values are calibrated in units of \(gm/cm^2\) using a convenient element for which a thin film standard is available.

Thus using the above procedure, one has an excellent method for determining the concentration of many elements after simply calibrating from a single element thin film standard. Other than determining the intensity of the individual element x-ray lines, only absorption measurement corrections need be made.
II. DISCUSSION

Either characteristic x-ray tubes or radioisotope source-target assemblies are used to provide primary characteristic K x-rays to be employed in the analysis. The primary radiation is treated as two monochromatic x-ray beams corresponding to the Ka and Kβ x-rays. The Ka/Kβ intensity ratio can be easily measured from the spectrum obtained by scattering the primary radiation from light element material.

The experimental x-ray fluorescent yield data commonly are several percent in disagreement with the theoretical fluorescent yield data used in the calculations. To obtain higher accuracy in analysis, thin film standards for each of the elements of interest may be prepared. The standards should be thin enough such that absorption effects are negligible. Using this procedure the values of $K_j$ of Eq. (6) can be determined empirically for the individual elements of interest.

Simultaneous absorption measurements of many elements can often be made by using a multielement uniform reference material. However, to use this procedure, enhancement effects between the sample and the reference material must be negligible. For thin samples with similar element concentrations, repetitive absorption measurements often need not be made if the thin samples prepared are of approximately equal total mass concentrations (gm/cm²). For some thin samples, particularly when using higher energy x-rays for analyses, absorption effects are essentially negligible.

Since matrix enhancement effects are not included in the analysis, it may be necessary to select the primary radiation of energy below the absorption edges of major constituents to eliminate their enhancement effects. Since monoenergetic excitation is used, it is often desirable to use several different incident energies to obtain high excitation efficiencies.
III. EXPERIMENTAL

The data were obtained using a low-background guardring detector\textsuperscript{12} with pulsed light feedback electronics.\textsuperscript{13} The total resolution of the system, FWHM, was approximately 200 eV at 5.9 keV. Excitation was provided with a transmission x-ray tube\textsuperscript{10} with $\phi_1$ and $\phi_2$ equal to approximately $45^\circ$. Due to wide variations in count rates, corrections for both pile-up rejection in the amplifier and the multichannel analyzer dead time were applied. Variations in the tube intensity were taken into account by monitoring the total integrated charge over the duration of the run.

A. Standardization

The thin film standards were prepared by evaporation of the elements onto thin aluminum films. Typically the evaporated layers were in the mass range of 50 to 150 $\mu$ gm/cm$^2$. The aluminum films weighed approximately 800 $\mu$ gm/cm$^2$. Thin film standards may also be prepared by precipitation of the elements on thin filters.\textsuperscript{14} The total area used in standardization and analysis was approximately 2.5 cm$^2$.

B. Sample Preparation

**Biological Specimens**

Weighed samples are either lyophilized or oven dried, reweighed, and pulverized. Thin pellets are pressed at 15,000 p.s.i. and weighed. Typically, the pellets are 1" in diameter, weigh 150 mg, and are approximately 0.03 cm thick. If the prepared specimen is not self-binding, cellulose powder is used as a binding material.
Rock, Glass, and Pottery Specimens

Samples must be pulverized such that particle size effects are negligible for the analyses to be made. For many analyses, grinding the sample to pass through a 325 mesh screen (less than 44 microns) is sufficient. Weighed samples are mixed with weighed amounts of cellulose powder, thin pellets are pressed and weighed. The ratio of cellulose powder to sample specimen should be large enough to minimize possible enhancement effects.

Alloy Specimens and Solutions

A weighed amount of the specimen is put into solution, a fraction of the solution is absorbed on a known weight of cellulose powder, and dried at 80°C. The mixture is weighed, pulverized and a portion of the mixture is pressed into a thin pellet and weighed. To obtain higher sensitivity in analysis one may precipitate the element of interest along with a carrier and collect the element on a filter.

Air Filter Specimens

Since absorption corrections are not necessary for many elements collected on air filters, the contents of these elements may simply be determined by measuring the intensities of the characteristic x-rays. This is also often true when preconcentration procedures have resulted in the material being collected on a filter paper.
IV. RESULTS

The following are some results obtained using a molybdenum transmission x-ray tube to provide the primary radiation. The tube was operated at 42 KV, and 250 μamp. Only one standard, 101 μg Cu/cm², was used for calibration. The fluorescent yield values used in the analyses were the theoretical values.7,8

Table I shows a comparison of the results obtained by x-ray fluorescence and neutron activation on a pottery specimen. 50 mg of pulverized pottery were mixed with 150 mg of cellulose powder, and a 1" diameter pellet was pressed. Total analysis time, including absorption measurements, was 1 hour. The precisions listed are for one standard deviation.

Figure 2 shows the spectrum obtained on a dried plant specimen in 30 minutes. 75 mg of the plant specimen were mixed with 75 mg of cellulose powder and a 1" diameter pellet was pressed. Table II shows a comparison of the results obtained.

Table III shows the results obtained on NBS Steel 121A. After dissolving 125 mg of the sample, 5 mg of the alloy in solution was absorbed on 750 mg of cellulose powder and dried at 80°C. The mixture was weighed, pulverized, and 150 mg was pressed into a 1" diameter pellet. The pellet contained only 1 mg of the original sample. Total analyses time was 45 minutes. The results are slightly high, principally due to enhancement effects caused by scattering of the primary radiation within the pellet.

Figure 3 shows the spectrum and results obtained on an air pollution filter of mass 3 mg/cm². The spectrum was taken in 20 minutes and the results are reported in nanograms/cm².

Figure 4 shows the spectrum and results from a human whole blood specimen which had been lyophilized, pulverized, and of which 150 mg were
pressed into a 1" diameter pellet. Since the concentration factor obtained by lyophilizing the specimen was a factor of five, the concentrations of the elements in the original specimen are one-fifth the reported values. The spectrum was obtained in 30 minutes. The content of lead in this specimen is several times the normal value.

Table IV shows a comparison of the calculated and measured values of relative excitation and detection efficiencies, $K_j$, of various x-ray lines. The calculated values were determined using theoretical fluorescent yield data. The measured values were determined from the average of three thin films of approximate mass 50, 100, and 150 $\mu$g/cm$^2$.

The calibration method used has been successfully applied to trace concentrations in light element matrices. When used in conjunction with low background detector systems and x-ray tube excitation, it can provide rapid and accurate multielement analyses down to less than 1.0 ppm. For a more detailed discussion of detection limits and sensitivities, see Ref. 12.
V. CONCLUSION

The technique of using a single element thin film standard to calibrate for the analysis of many elements is an excellent procedure if the following conditions are met. A thin uniform sample must be prepared. Enhancement effects must be negligible. The critical thicknesses for the x-ray lines to be used in analyses must not have been reached. Absorption correction measurements, if not negligible, must be made.

The analyses of specimens carried out provide good agreement with results obtained by other means of analyses.
VI. ACKNOWLEDGEMENTS

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FOOTNOTES AND REFERENCES

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Table I. Analysis of Pottery

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<tr>
<th></th>
<th>X-ray Fluorescence</th>
<th>Neutron Activation</th>
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<tbody>
<tr>
<td>Ti</td>
<td>.76% ± .02</td>
<td>.78% ± .03</td>
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<tr>
<td>Cr</td>
<td>114 ppm ± 6</td>
<td>115 ppm ± 4</td>
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<tr>
<td>Mn</td>
<td>47 ppm ± 5</td>
<td>40.9 ppm ± 0.5</td>
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<tr>
<td>Fe</td>
<td>1.05% ± .01</td>
<td>1.017% ± .012</td>
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<tr>
<td>Ni</td>
<td>301 ppm ± 6</td>
<td>279 ppm ± 20</td>
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<tr>
<td>Cu</td>
<td>55 ppm ± 2</td>
<td>60 ppm ± 8</td>
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<tr>
<td>Zn</td>
<td>60 ppm ± 2</td>
<td>59 ppm ± 8</td>
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<tr>
<td>Ga</td>
<td>40 ppm ± 2</td>
<td>44 ppm ± 5</td>
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<tr>
<td>As</td>
<td>29 ppm ± 2</td>
<td>30.8 ppm ± 2.2</td>
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<tr>
<td>Rb</td>
<td>58 ppm ± 2</td>
<td>70.0 ppm ± 6.3</td>
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<tr>
<td>Sr</td>
<td>123 ppm ± 3</td>
<td>145 ppm ± 22</td>
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<tr>
<td>Pb</td>
<td>31 ppm ± 2</td>
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Table II. Analysis of Plant Specimen

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<th>Element</th>
<th>X-ray Fluorescence</th>
<th>Neutron Activation</th>
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<tr>
<td>Ti</td>
<td>121 ppm ± 5</td>
<td>&lt; 0.01%</td>
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<tr>
<td>Cr</td>
<td>26 ppm ± 1</td>
<td>23.8 ppm ± 0.9</td>
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<tr>
<td>Mn</td>
<td>60 ppm ± 2</td>
<td>49.3 ppm ± 1.4</td>
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<tr>
<td>Fe</td>
<td>.186% ± 0.002</td>
<td>.201% ± 0.006</td>
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<tr>
<td>Ni</td>
<td>8 ppm ± 1</td>
<td>13.8 ppm ± 3.0</td>
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<tr>
<td>Cu</td>
<td>21 ppm ± 1</td>
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<tr>
<td>Zn</td>
<td>80 ppm ± 1</td>
<td>84 ppm ± 8</td>
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<tr>
<td>Br</td>
<td>48 ppm ± 1</td>
<td>42 ppm ± 1</td>
</tr>
<tr>
<td>Rb</td>
<td>7 ppm ± 1</td>
<td>7.0 ppm ± 1.4</td>
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<tr>
<td>Sr</td>
<td>97 ppm ± 2</td>
<td>236 ppm ± 66</td>
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<tr>
<td>Pb</td>
<td>206 ppm ± 3</td>
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Table III. Analysis of NBS Steel 121A

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<tr>
<th>Element</th>
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<tr>
<td>Ti</td>
<td>0.37% ± 0.05</td>
<td>0.36%</td>
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<tr>
<td>Cr</td>
<td>19.50% ± 0.25</td>
<td>18.69%</td>
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<tr>
<td>Mn</td>
<td>1.43% ± 0.04</td>
<td>1.28%</td>
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<tr>
<td>Ni</td>
<td>10.92% ± 0.13</td>
<td>10.58%</td>
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Table IV. Relative Excitation and Detection Efficiencies

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<th>Line</th>
<th>Calculated</th>
<th>Determined</th>
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<tr>
<td>CrKa</td>
<td>.380</td>
<td>.371 ± .007</td>
</tr>
<tr>
<td>NiKa</td>
<td>.887</td>
<td>.906 ± .009</td>
</tr>
<tr>
<td>CuKa</td>
<td>1.000</td>
<td>1.000 ± .014</td>
</tr>
<tr>
<td>SeKa</td>
<td>1.89</td>
<td>1.78 ± .04</td>
</tr>
<tr>
<td>PbLa</td>
<td>.815</td>
<td>.789 ± .016</td>
</tr>
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FIGURE CAPTIONS

Fig. 1. Schematic diagram of x-ray method.

Fig. 2. Spectrum from dried plant specimen.

Fig. 3. Spectrum from air filter of mass 3 mg/cm². Concentrations listed in nanograms/cm².

Fig. 4. Spectrum from lyophilized whole blood specimen. Concentrations listed are for the lyophilized specimen. This preparation gave a concentration factor of five.
Primary radiation

X-ray excited from sample

\[ \phi_1 \]

\[ \phi_2 \]

\[ dx \]

\[ d \]

Fig. 1
Fig. 2
Fig. 3
LYOPHILIZED WHOLE BLOOD

X-Ray energy (keV)

Fig. 4
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