PREPRINT UCRL-76751

Conf-750831--4

Lawrence Livermore Laboratory

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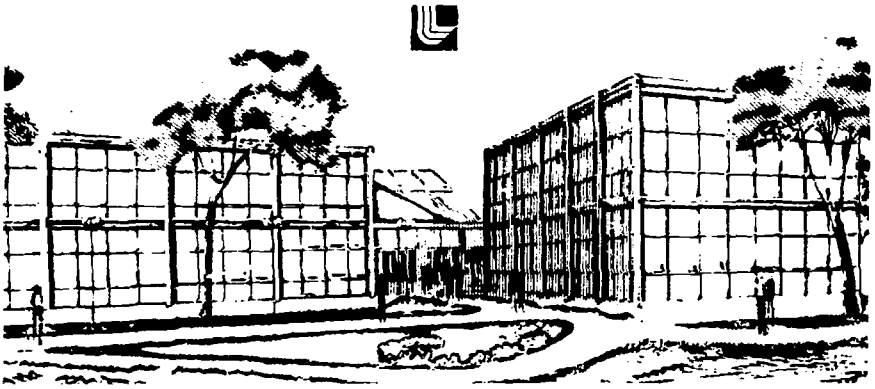
August 29, 1975

This paper has been prepared for submittal to the Proceedings of the 1975 Denver Conference on Applications of X-Ray Analysis



ABSORPTION CORRECTIONS FOR X-RAY FLUORESCENCE ANALYSIS OF ENVIRONMENTAL SAMPLES

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ABSTRACT

The discovery of a very simple and useful relationship between the absorption coefficient of a particular element and the ratio of incoherent to coherent scattering by the sample containing the element is discussed. By measuring the absorption coefficients for a few elements in a few samples, absorption coefficients for many elements in an entire set of similar samples can be obtained.

INTRODUCTION

Absorption corrections in x-ray fluorescence are not negligible and usually must be taken into account if quantitative results are to be obtained. In principle, the absorption corrections can be calculated from published tables of absorption coefficients such as those of Storm and Israel (1), combined with appropriate geometrical factors for the instrument used as described by Bonner, Bazan, and Camp (2). However, the calculation requires a knowledge of the composition of the sample, which is usually not known in sufficient detail when the sample is to be analysed. Thus the usual situation is that absorption coefficients must be measured for each sample.

The purpose of this study was to look for a relationship between sample absorption and some characteristic of the recorded spectrum. Such a relationship would eliminate the necessity of measuring the absorption for each sample.

A remarkably simple relationship has been found. For sets of similar samples, the effective absorption coefficient is a linear function of the ratio of the intensities of the incoherently and coherently scattered exciter radiation. That is,

$$a_i = C_i + B_i \times R,$$

where C_i and B_i are experimentally determined constants; R is the intensity ratio (incoherent peak)/(coherent peak); and a_i is the measured absorption coefficient for element i in the sample.

The utility of this relationship is very clear. Once the constants B_i and C_i have been determined, the absorption coefficient for element i can be calculated from the backscatter ratio, R, with no additional measurements. The only additional information needed to calculate the absorption correction is the sample thickness in g/cm^2.

RESULTS

An obvious place to look for a relationship between absorption and spectral characteristics is the backscatter peaks. The intensities of the coherent and incoherent peaks depend on the amount of absorption in the sample as well as on the atomic number (Z) of the scattering atoms. The absorption coefficient for an x ray is also strongly dependent on Z. From the experimenter's standpoint a ratio of intensities is more convenient than an absolute intensity. Because of this, the first function we looked at was the ratio, R, of the incoherent to the coherent peak integrals for the Ag K_α exciting x ray.

From another study, we had on hand a set of vegetation samples from Eniwetak Atoll. The samples were all 1-in. (2.54 cm) diameter pressed discs each weighing approximately 250 mg. At this thickness, about 50 mg/cm^2, absorption corrections for most elements are appreciable. We measured the effective absorption coefficient, a_{Ni}, for the Ni K_α x ray for these samples. When we plotted a_{Ni} vs R (see Figure 1), the points fell on a straight line within our estimated errors of about 1% in R and 2% in a_{Ni}.

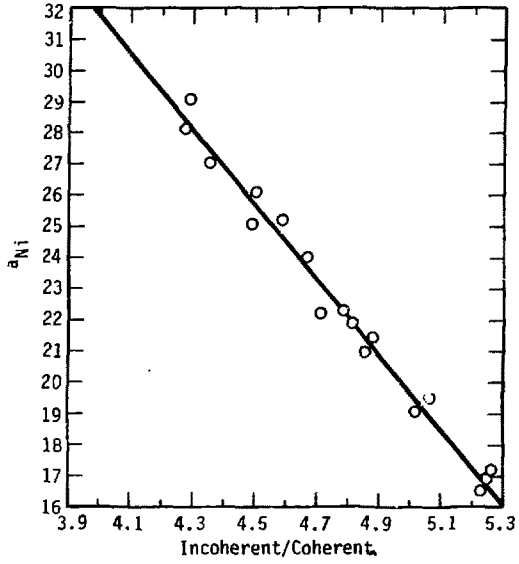

Figure 1 The linear relationship between the absorption coefficient for nickel and the incoherent/coherent ratio for Eniwetak vegetation.

This result was so striking that we decided to prepare some artificial samples of known composition to see how general the result was. Many environmental samples consist of an organic (carbon, hydrogen, oxygen) matrix with admixtures of other low Z elements such as sodium, potassium, silicon, aluminum, and calcium. Our first set of mixtures consisted of cellulose (Avicel*) plus Al_2O_3 and $CaCO_3$, prepared as

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research and Development Administration to the exclusion of others that may be suitable.

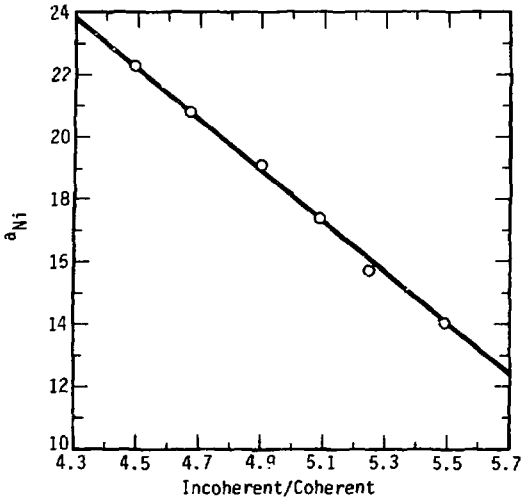

Figure 2 Linear relationship between a_{Ni} and R for cellulose-Al_2O_3 mixtures.

described in the experimental section. In spite of some apparent non-uniformity in the samples, a plot of a_{Ni} vs R gave a very satisfactory straight line as shown in Figure 2. Our second set of mixtures consisted of Avicel plus NaCl and $CaCl_2$. Again a plot of a_{Ni} vs R gave a straight line as shown in Figure 3.

The absorption curves, *ln a vs ln E*, for the NaCl-Avicel samples were straight lines, but the lines for the various samples were not parallel. Figure 4 shows the curves for the two extreme samples. Thus it was possible that the linearity of the a_{Ni} vs R curve might be accidental, and not be valid for other energies. Therefore, we made plots of the a vs R curves for chromium and zinc, the measured elements with the lowest and highest energy x rays. Fortunately, the chromium and zinc plots were also linear, indicating the nickel result is not unique.

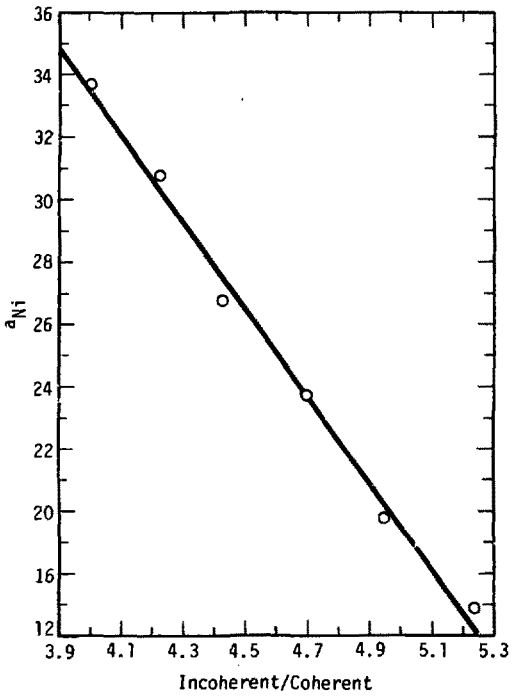

Figure 3 Linear relationship between a_{Ni} and R for cellulose-NaCl mixtures.

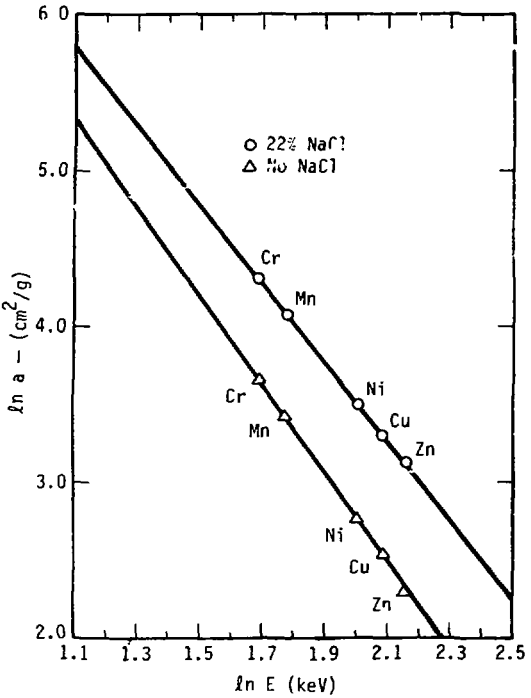

Figure 4 Absorption curves for cellulose-NaCl mixtures.

It should be noted that the a vs R curves for the three sets of samples, Avicel-NaCl, Avicel-Al_2O_3, and Eniwetak vegetation are all different. That is, each set gives a straight line but the sets are not equivalent. This means that for the linear relationship to hold, the set of samples must be similar. We do not yet know what all of the necessary conditions are that make a set sufficiently similar. Chemical

composition seems to be the most critical variable, but we do not know the limits. At present we can only try any given set to see if the relationship holds. It is very encouraging that it holds for a set as varied as the Eniwetak vegetation, which consists of ground leaves and stems from at least three different types of plants. National Bureau of Standard Reference Material 1571 (Orchard Leaves) almost fits the Eniwetak set. The difference between the measured absorption coefficients and the ones calculated from our vegetation curves are about 10%.

As a check of the validity of the method in a situation where extrapolation of the absorption curves is necessary, we used the method in the analysis of a set of milk samples. The calcium absorption coefficients could not be measured directly because the samples contain large amounts of calcium and are essentially infinitely thick to Ca K_α radiation. (Our 50 mg/cm^2 samples attenuate the calcium radiation by a factor of about 400.) We measured the absorption for the usual set of five elements, then extrapolated the curve to the calcium energy. The plot of the resulting a_{Ca} vs R data is shown in Figure 5. Our usual x-ray fluorescence analysis then gave us values of R that we used in conjunction with the curve to get the calcium absorption coefficients. The

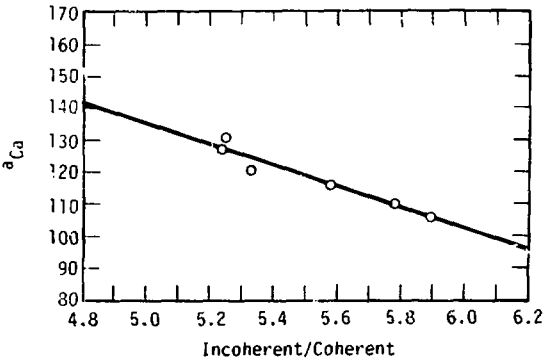

Figure 5 Linear relationship between a_{Ca} and R for milk samples after extrapolation of absorption curves.

Table I. Comparison of x-ray fluorescence and instrumental neutron activation analysis of milk samples.

Sample	Type	Grams of calcium per liter	
		X ray ± σ	INAA ± σ
037	Nonfat	1.25 ± 0.06	1.30 ± 0.05
039	Nonfat	1.06 ± 0.05	1.07 ± 0.05
002	Homogenized	1.04 ± 0.05	1.04 ± 0.04
042	Homogenized	1.22 ± 0.06	1.23 ± 0.05
038	Homogenized	1.12 ± 0.06	1.12 ± 0.05

calcium contents calculated from these data are shown in Table I, which also includes calcium analyses performed by Instrumental Neutron Activation Analysis at Lawrence Livermore Laboratory. The agreement is embarrassingly good, the average difference being about 1%. The error estimates for x-ray fluorescence in the table include only the counting statistics, but our guess is that the uncertainty from the absorption curve extrapolations is about 10%.

EXPERIMENTAL

Counting Procedures

All measurements were made with a nondispersive (energy dispersive) system using a ring-shaped ^{109}Cd exciter and a Si(Li) detector. The scattering angle from exciter to sample to detector is nearly 180°. The system is described in detail in Reference (2).

The coherent and incoherent peak intensities were each sums of channels spanning 325 eV. This includes a reasonable fraction of each peak with minimal overlap. The coherent and incoherent sums were centered at 22.1 and 20.6 keV respectively.

Absorption Measurements

The absorption measurements were made by counting Whatman 41 standards of chromium, manganese, nickel, copper, and zinc with and without an intervening sample. The geometry was such that the sample was in its normal position and the standard was in a reproducible position. (That is, its position did not depend on the presence of the sample.) The absorption coefficient, a, is defined by the equation:

$$I = I_0 \exp(-aD),$$

where I_0 = the net intensity of an x ray from the standard with no absorber; I = the net intensity of the same x ray with the absorber (sample) in place; D = sample thickness in g/cm^2; and a = the effective absorption coefficient for the x ray in cm^2/g.

Note that a is a mass absorption coefficient. We designate it a instead of the usual symbol, μ, to emphasize that it is different from the usual quantity. Our a includes the absorption coefficients for the exciting x rays as well as for the emitted x ray. It also includes the geometric factors resulting from the non-normal paths of the x rays through the sample.

Plots of ln a vs ln E were always straight lines. (E = the energy of the K_α x ray.) The range of our measurements was from 5.41 keV (chromium) to 8.63 keV (zinc). Thus the absorption coefficients for any element with x-ray energies in this range can be obtained by interpolation. It is also possible to extrapolate to some extent, but this is risky as it could generate errors.

Sample Preparation

All samples were pressed in a 1-in. (2.54-cm) diameter steel die with a hydraulic press at 1 to 3 metric tons. This produced flat, smooth, coherent discs with a uniform thickness of about 0.5 mm for our 250-mg samples.

The natural samples were already in powder form and were merely pressed and weighed. The cellulose material in the artificial samples was Avicel, a microcrystalline cellulose with empirical formula CH_2O. The alumina samples were prepared by weighing finely divided Al_2O_3

(levigated alumina), Avicel, and $CaCO_3$ into a glass vial. The samples were homogenized in a mechanical shaker for 5 min. The calcium content was always 2% and the alumina content varied from 0 to 25%. These samples appeared to have segregated to some extent during the pressing procedure. As a result, we prepared a set of Avicel-NaCl samples by a different procedure. Solutions of NaCl and $CaCl_2$ were pipetted into Avicel, and water was added if necessary to make a thin paste. This was well mixed, then dried. The dry powder was ground gently in a mortar and pestle, then pressed into discs and weighed. The NaCl content varied from 0 to 22% and the calcium was kept at 2%.

In these experiments it was unnecessary to know the composition of the mixtures. The purpose of the mixtures was to supply sets of samples with different absorption coefficients and different values of R.

SUMMARY AND CONCLUSIONS

We have demonstrated that a linear relationship exists between absorption coefficients and the incoherent to coherent scattering ratio for sets of similar samples. This relationship can be a very useful tool to the analyst using x-ray fluorescence. If many similar samples are to be analysed, only a few absorption measurements need be made instead of one set per sample. In future work we hope to establish the extent and limitations of the relationships.

ACKNOWLEDGMENT

This work was supported by the U.S. Energy Research and Development Administration.

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