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X-RAY FLUORESCENCE ANALYSIS USING SECONDARY EMITTERS

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THE DETECTION OF LIGHT ELEMENTS BY ENERGY DISPERSIVE
X-RAY FLUORESCENCE ANALYSIS USING SECONDARY EMITTERS*

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Abstract

An energy dispersive X-ray fluorescence analysis system with a Titanium secondary emitter is discussed with respect to its ability to detect the elements Silicon, Phosphorus, Sulfur, Potassium and Calcium at levels ranging from 550 ppm down to 20 ppm for Silicon and Calcium respectively. The efficiency of the system is compared to direct excitation of the same elements in NBS Orchard Leaves and in a synthetic "rock" mixture.

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INTRODUCTION

The detection of light elements by energy dispersive X-ray fluorescence spectroscopy is hindered by their intrinsic low fluorescence yields and the absorption of their soft X-rays by the window of the detector. One solution to the problem of low fluorescent yield is to provide X-rays from a source whose characteristic lines are slightly higher than the K_{α} absorption edge of the element in question. As an example, Hebert and Street² used Mg, Al, and Si as anode material (and also as filters) to detect O, F, Mg, and Al K_{α} lines in a system that also included an ultra-thin aluminum window protecting the Si (Li) detector.

This report is based on the common practice of using secondary emitters composed of light elements, or their compounds, to obtain the soft X-rays needed for efficient excitation with a minimum background. Secondary emitters are easily introduced into a conventional X-ray fluorescence system in such a way that the primary X-ray beam becomes polarized¹, thereby giving a lower background under the peaks of interest.

EXPERIMENTAL

Fluorescence was induced in the sample by bombardment with X-rays from a Tungsten tube after impinging on a secondary emitter. The detector was located perpendicular to the plane containing the source, secondary, and specimen. The dimensions of the system were: 5 cm from X-ray source to secondary; 4.3 cm from secondary to sample; and 3.6 cm from sample to detector; all collimators were 3/8" (0.95 cm) in diameter. A Si (Li) detector and electronic subsystem (0.025 mm Be window, 6 mm in diameter, and 175 eV resolution at 5.9 kev) and a pulse height analyzer completed the system. All measurements were made in vacuum.

The secondary emitters, representing the elements Al, Cl, Ca, K, Br, Ti, and Ag were prepared from the metals (Al, Ti, and Ag) or an appropriate salt (NaCl, Ca (OH)₂, K₂CO₃, KBr); the latter by pelletizing several grams of the salt with about 10% microcrystalline cellulose in a pellet press to 20 tons. In addition a comparison was made with a 1.3 mm thick boron carbide disk as a scatterer.

The power applied to the X-ray tube varied from 450 watts to 875 watts with the limiting factor being a reasonable dead-time in the pulse height analyzer. The analyzer was set to read 0-5.10 keV and counting times of 200 to 1000 seconds were routine.

Peak areas were measured over the range $\pm 10\text{eV}$ from the peak center. Backgrounds were determined by linear interpolation. The minimum detectable levels (MDL's) are calculated as three standard deviations in the background under the peak in a specified length of time divided by the sensitivity:

$$\text{MDL}_{100} = \frac{3 (\text{Background counts})^{1/2} \div 100 \text{ seconds}}{(\text{Analyte Peak Counts/Second}) \div (\text{Analyte concentration})}$$

Two types of specimens were used to evaluate the effectiveness of the various secondaries. One was NBS Orchard Leaves (Standard Reference Material 1571). The specimen was prepared by pressing 5.00 grams of material into a 3.2 cm (1.25") diameter pellet under 20 tons pressure. The resultant pellet had an areal density of $.63\text{g/cm}^2$. The other specimen consisted of a synthetic mixture of common crustal elements. 2.0 grams of the mixture were mixed with 2.0 grams of microcrystalline cellulose binder and pressed as above, giving a pellet with an areal density of 0.51g/cm^2 .

RESULTS

The first objective of this study was to determine if the light element sensitivities could be made great enough and the background low enough by the use of secondary excitation to allow their measurement at relatively low concentrations. A first rough screening of secondaries was made by measuring the intensity of the Al $K\alpha$ line in Al_2O_3 . A boron carbide scatterer was also used in place of the secondaries for comparison purposes. The results are given in Table I. K_2CO_3 , $\text{Ca}(\text{OH})_2$, and Ti secondaries are of almost equal value, with Ti being best. The last column in the Table reflects the different backgrounds produced by the various secondaries.

The next step involved using direct irradiation and irradiation in the presence of a Ti secondary emitter to determine MDL's for Si, S, and Ca in the synthetic "rock" mixture and S, P, Cl, K, and Ca in the Orchard Leaves. In practice all the secondaries were studied but only the results with Ti are reported here because as suspected it gave the best results. See Tables II and III and Figures 1 and 2. The greater sensitivity of the system with a Ti secondary emitter is clear in the figures. However, the sensitivity for P is unrealistically high because of a Ca $K\alpha$ escape peak which appears at nearly the same energy as P $K\alpha$.

DISCUSSION

The results indicate that light elements, Si - Ca, can be detected at low concentrations using an energy dispersive system when secondary emitters are used for excitation. Comparisons may be made with the results of L.T. Kiss², who used a wavelength dispersive instrument to measure the elements Si to Ca in coal. He obtained 100 second detection limits of 6.8 to .34 ppm for these elements. These results for coal may be compared with the results for Orchard Leaves given in Table III. A. J. Hebert and K. Street (3) report MDL's of 160 ppm to 17 ppm (in 100 seconds) for the elements Na to Fe in rock using a variable anode system and guard ring detector. The rock results may be compared with the results for the synthetic mixture given in Table II.

The work reported here gives larger MDL's, as expected, but utilizes an experimental arrangement that is more readily available and generally more economical. In reference to Table I, the difference in efficiency between K_2CO_3 and KBr may be related to differences in density or the weight per-cent of potassium in the two salts. It is also evident from this Table that Ag is less effective than Ti because of the difference in intensities between the Ag $L\alpha$ radiation and the Ti $K\alpha$ radiation.

In electing a system to detect a particular light element one must be selective and choose a secondary that does not emit radiation, either directly or as an escape peak, that will interfere with the element to be studied.

Finally, an attempt was made to extrapolate to MDL's for Mg and Al by irradiating their respective sulfate salts and measuring the peak intensities for the two metals in comparison to that for S in Orchard Leaves. Then a correction was made for the different absorptions in the Be window to give approximate MDL's as 8000 ppm for Mg and 2000 ppm for Al. The number for Mg

is consistent with the experiments because the "Synthetic Mixture" contained 1760 ppm of Mg, which was not detected. Sodium could not be detected in this system and certainly the lightest elements would not be also.

The background spectra of all systems employing secondaries were taken and compared to that with direct irradiation. A photograph of the result with the Ti secondary and then direct irradiation is given in Figure 3. It is apparent that the presence of a secondary produces a flatter background over the 5 kev range studied here.

It may be questioned whether a real comparison between direct excitation and excitation by secondary emitters is valid because the applied voltage is different for each (see Tables II and III). However, the voltage used with the secondary was higher than that with direct excitation. Since background generally increases with voltage, any prejudice in the results is in favor of direct excitation.

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Figure 1. HPS Orchard Leaves. Sensitivity vs Atomic Number

Figure 2. "Synthetic Mixture". Sensitivity vs Atomic Number.

(a)

(b)

Figure 3. Background radiation from a W tube and (a) a Ti secondary and (b) in the absence of the secondary, each at different power levels.

Table I
Al K Intensities in Al₂O₃ Using a W X-Ray Tube
and Different Secondary Emitters

<u>Secondary</u>	<u>Al Kα Intensity (cps)</u>	<u>3 B/S¹⁾ (100 seconds) Relative to Ti Secondary</u>
B ₄ C Scatterer	52	8.4
NaCl Cl-K α	93	7.3
Ag Ag-L α	148	3.5
K Br K K α	105	4.8
K ₂ CO ₃ K K α	207	1.6
Ca(OH) ₂ Ca K α	330	1.2
Ti Ti K α	331	1.0

1) B = background under the peak and S = peak area of the Al K α radiation over 20 eV.

Table II

Minimum detection limits for light elements in synthetic "rock" mixture.¹

	<u>Direct Excitation</u> ²		<u>Ti Secondary</u> ³	
	MDL (ppm)	Rel. Sens.	MDL (ppm)	Rel. Sens.
Si-K α	2330	1.8×10^{-3}	541	3.4×10^{-2}
S -K α	734	6.8×10^{-3}	176	0.13
Ca-K α	151	5.6×10^{-2}	33	1.0

1) "Synthetic Mixture" contains 1.959% Si, 2.101% S, and 3.595% Ca.

2) 15 Kv and 3 Ma, W anode X-ray tube.

3) 35 Kv and 20 Ma, W anode X-ray tube.

Table III

Minimum detection limits for light elements in NBS Orchard Leaves¹.

	<u>Direct Excitation</u> ²		<u>Ti Secondary</u> ³	
	MDL (ppm)	Rel. Sens.	MDL (ppm)	Rel. Sens.
P -K α	304	1.6×10^{-2}	205	4.8×10^{-2}
S -K α	522	9.8×10^{-3}	281	3.8×10^{-2}
Cl-K α	190	2.8×10^{-2}	91.7	0.12
K -K α	31.1	0.18	20.8	0.71
Ca-K α	21.7	0.26	18.7	0.89

1) NBS Orchard Leaves contain 2100 ppm P, 2300 ppm S, 700 ppm Cl, 1.47% K, and 2.09% Ca.

2) 15 Kv and 3 Ma, W anode X-ray tube.

3) 25 Kv and 10 Ma, W anode X-ray tube.

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