Lawrence Berkeley National Laboratory
Recent Work

Title

A METHOD OF RAPID THIN SAMPLE PREPARATION FOR X-RAY FLUORESCENCE ANALYSIS WITH SEMICONDUCTOR DETECTORS

Permalink

https://escholarship.org/uc/item/4kq3q8cs

Author

Street Jr., K.

Publication Date

1973-02-01

eScholarship.org Powered by the California Digital Library
University of California

Submitted as a Note to
Analytical Chemistry

LBL-601
Preprint

A METHOD OF RAPID THIN SAMPLE PREPARATION FOR X-RAY FLUORESCENCE ANALYSIS WITH SEMICONDUCTOR DETECTORS

A. J. Hebert, H. R. Bowman, and K. Street, Jr.

RECEIVED
LAWRENCE
RADIATION LABORATORY

February 1973

Prepared for the U.S. Atomic Energy Commission
under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

LBL-601

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

A METHOD OF RAPID THIN SAMPLE PREPARATION FOR X-RAY FLUORESCENCE ANALYSIS WITH SEMICONDUCTOR DETECTORS*

A. J. Hebert, H. R. Bowman, and K. Street, Jr.

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

February 1973

ABSTRACT

A method is described for X-ray fluorescence analysis which features the use of clear plastic adhesive tape to support thin films of powdered or finely ground sample. The method requires approximately 50 mg of fine crystals or powder and less than 5 minutes of preparation time per sample. Analyses of six USGS rocks for iron gave results in agreement with published values with an average error of less than 5%. Similar results have been obtained for iron in powdered chemicals, thin iron foils, and in hand ground rock samples. Preliminary experiments indicate that the method may be useful for powdered materials in general and for the analysis of many elements heavier than potassium. Lithium metaborate fusion of rocks reduced matrix effects and increased the accuracy of the analyses.

Many of the problems associated with quantitative analysis by X-ray fluorescence methods are simplified or more easily corrected for if one can work with thin samples. Such samples are readily corrected for self absorption effects.

A homogeneous thin sample of known weight per unit area can be fabricated in a relatively short time in the following manner. Hoops are machined with parallel surfaces from aluminum or plastic tubing. In this work, 2" O.D. by 1/8" wall thickness by 1/8" wide plastic hoops with interior areas of roughly 15.5 cm^2 and weighing roughly 1.5 grams each were used. A clean hoop is brought into contact with the sticky surface of a clear plastic adhesive tape. After firmly pressing the hoop to the tape, the excess tape is carefully trimmed off with a hook blade scalpel. Tape-hoops can be stored in a dust free container.

A tape-hoop is weighed and then dusted with sample powder by spreading the powder with a small clean camel hair brush. Care is taken not to touch the bare tape surface directly with the brush. Excess powder from the interior corners is carefully brushed out and the surface is flushed with a light stream of clean air to remove loose particles. The tape-hoop may then be held up to the light and areas of excess density may be lightly brushed. This is followed by another air flush. The sample is then reweighed and is ready for analysis. Weighing, dusting and reweighing normally takes less than 5 minutes per sample.

Depending upon the fineness of the powder used, calibration standards or unknown samples varying from less than 0.5 to more than 2.5 mg/cm^2 may be prepared. Spot check measurements on areas of 3 cm^2 indicate that homogeniety variations of less than 5% are usually obtained for a 15 cm^2 total area. Sample inhomogenieties are compensated for by rotating the 15 cm^2 sample off axis during analysis over a circular 3 cm^2 irradiated region.

The experimental arrangement for analysis in the present experiments is shown in Figure 1. The X-ray source shown in Figure 1 is similar to that described by Giauque (1) where a primary source of radioactive ^{125}I is used to excite a secondary radiation in a target material. The target X-rays, in this case Zn K X-rays are then used to excite characteristic X-rays in the samples. The cylinder of pure germanium shown was used to insure a flat surface and reproducible sample positions. The Ge cylinder would be unnecessary if the target to sample distance were increased so that slight variations in geometry would be less important. The source strength in the present experiments made it necessary to use rather close geometry in order to hold analysis times to 20 minutes or less. A 200 millicurie ^{125}I source was used to excite an iron free target of ZnO in an epoxy matrix.

The application of semiconductor detectors to non-destructive analysis has been described by Bowman et al. (2). Some more recent advances in detector design are described by Landis et al. (3). The detector used had a resolution of approximately 230 eV FWHM for the iron K_α line. In the present work only the iron K_α line was used to obtain integrated X-ray peak intensities. Background corrections were made on all observed intensities by integrating channels on both sides of the iron lines.

The method used for self absorption corrections was suggested by Giauque (4). It consists of

(1) measuring the X-ray intensity of the element of interest from the sample, I_p (counts/minute).

(2) placing a concentrate of the element of interest on top of the sample, as close to the sample position as possible, (in the case of iron, a

flat 1/8" thick disk of pure iron was used), and measuring the X-ray intensity from the sample plus the concentrate, $I(\frac{\text{counts}}{\text{minute}})$.

(3) placing the concentrate at the sample position on a blank tape and measuring its X-ray intensity, I_o (counts/minute).

(4) subtracting the sample intensity, I_p, from the sample plus concentrate intensity, I, to obtain, I_c, which corresponds to the absorption attenuation of I_o by the thin sample, or,

$$\frac{I_c}{I_o} = e^{-\mu m} \quad ,$$

where μ is the mass absorption coefficient of the sample in cm^2/mg and m is the thickness of the sample in mg/cm^2.

(5) calculating the self absorption corrected sample intensity I_{pc} from the product of I_p and the absorption correction term, $(\mu m)/1\text{-}e^{-\mu m}$, or

$$I_{pc} = I_p \cdot \frac{\mu m}{(1-e^{-\mu m})} \quad .$$

In the present experiments on iron the absorption correction factor $\frac{\mu m}{(1-e^{-\mu m})}$ usually amounted to about a 10% correction for a 1 mg/cm^2 sample.

The procedure is repeated with a rock powder, chemical, or uniform foil of know percentage iron and the % Fe in the unknown calculated from:

$$(\%Fe)_{unknown} = (\%Fe)_{known} \cdot \frac{(I_{pc})_{unknown} \cdot (m)_{known}}{(I_{pc})_{known} \cdot (m)_{unknown}} \quad .$$

The results of analyses on six U.S. Geological Survey standards (5) are shown in Table I. The results for three Columbia River Plateau basalts

previously analyzed by neutron activation analysis (6) are shown in Table II. All analyses were made relative to the USGS BCR-1 standard. Twenty minute analyses gave 2.5% counting statistics, (1σ), in the case of a rock containing 2% Fe, and 1% or better for most samples with greater than 5% Fe. Statistical counting fluctuations for the measured absorption correction intensities were of the order of 0.3% for a 2 minute analysis. The 20 minute analysis time provided a limit of detectability, (3σ), of 1 $\mu gm/cm^2$ or 0.07% iron in rock. This corresponds to a signal to noise ratio of 20 for a sample containing 5% iron.

To determine whether matrix effects were contributing to the analysis error a GSP-1 sample and a BCR-1 sample were fused in $LiBO_2$ (7) with a $LiBO_2$ to sample ratio of 11:1. Each of the two fused glasses was cooled, ground with a mortar and pestle and placed on tapes for analysis. The powders were stored in dessicators prior to dusting the tape to avoid the slight error due to moisture pickup by the powder. The results are shown in Table III. The excellent agreement indicates that this technique may be used to obtain better than 3% values for iron analyses with an increase of a few minutes per set of samples for weighing and fusing. One two-gram fusion yields enough powder for 3 or more samples. With our present system the analysis times were roughly 3 times longer but this could be easily shortened with an x-ray tube source, ($\sim$ 2 minute analysis time), or with a stronger radioactive source.

Figure 2 shows the results of absorption experiments using Zn K X-rays and known weights of $Fe(NH_4SO_4)_2 \cdot 6H_2O$. This suggests the possibility of analyzing very light but similar biological or finely powdered samples without direct weighing by using an absorption experiment to determine sample weights.

0 0 0 0 3 7 0 3 3 9 2

Preliminary experiments were conducted on rock samples of USGS-G2 (3.7%K) to determine the feasibility of a potassium analysis. Calibration standards were made with pure KBr powder. The experiments were performed in air and yielded a better than 10% analysis without self absorption corrections. Absorption corrections could be made by using solid KBr or KCl pellets in the same manner as the solid iron.

Inversion of the detector assembly shown in Figure 1 would allow detection of sample X-rays without tape between the sample and detector. The detector window and an air or a Helium atmosphere would be the only antennuators of radiation. This would provide much greater signal intensities for lighter elements. The tape has a thickness of 7 mg/cm^2 which attenuates potassium X-rays four fold. With proper absorption corrections and the selection of an X-ray source to minimize enhancement effects, one should be able to do a 5% or better analysis for many elements heavier than chlorine. The use of an X-ray tube would allow much shorter analysis times.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Frank Asaro and Robert D. Giauque for many helpful discussions and suggestions. We thank Gardener G. Young for his help in the design and fabrication of the sample rotators, sample hoops and the slide top storage containers.

LITERATURE CITED

*Work performed under the auspices of the U. S. Atomic Energy Commission.

(1) Robert D. Giauque, Anal. Chem., 40, 2075 (1968).

(2) Harry R. Bowman, Earl K. Hyde, Stanley G. Thompson, and Richard C. Jared, Science, 151, 562 (1966).

(3) D. A. Landis, F. S. Goulding, and B. V. Jarrett, LBL-320, September 1971.

(4) Robert D. Giauque, private communication.

(5) F. J. Flanagan, Geochim., Cosmochim. Acta., 33, 81 (1969).

(6) H. R. Bowman, F. Asaro, and I. Perlman, private communication.

(7) K. Norrish and B. W. Chappell, Physical Methods in Determinative Minerology, ed. by J. Zussman, Academic Press, London and New York (1967).

Table I.

USGS Standard	% Fe Observed Values	% Fe Average Values and Standard Deviations	(% Fe USGS) and Deviation, Δ, from USGS (Ref. 5)
DTS-1	A 6.38 B 6.24 C 6.64	6.42 ± 0.19(2.8%)	$\Delta = \frac{(6.19)}{3.7\%}$
GSP-1	A 2.94, B 2.77, C 2.78; D 2.79, E 2.87, F 2.96	2.85 ± 0.08(2.8%)	$\Delta = \frac{(3.03)}{6.3\%}$
BCR-1	A 9.66 B 9.59 C 9.21	9.45 ± 0.22(1.7%)	$\Delta = \frac{(9.45)}{0}$
G-2	A 1.88 B 2.01 C 1.89	1.93 ± 0.07(3.2%)	$\Delta = \frac{(1.94)}{0.05\%}$
AGV-1	A 5.02 B 4.58 C 4.86	4.82 ± 0.14(3.0%)	$\Delta = \frac{(4.76)}{1.3\%}$
PCC-1	A 6.36 B 6.23 C 6.45	6.35 ± 0.11(1.5%)	$\Delta = \frac{(5.97)}{6.4\%}$

Table II.

Columbia River Basalt		%Fe Relative to BCR-1	%Fe Average re USGS BCR-1 and Deviations, Δ, from Neutron Activation
CR 59	A	8.13	8.30 ± 0.15
	B	8.45	
	C	8.32	Δ = 0.36%
Cr 63	A	8.15	8.34 ± 0.16
	B	8.32	
	C	8.54	Δ = 2.3%
CR 70	A	8.81	8.79 ± 0.10
	B	8.68	
	C	8.88	Δ = 5.7%

Table III.

		%Fe Observed Values re USGS BCR-1	Average %Fe and Std. Dev.	%Fe USGS and Deviation, Δ, From USGS
GSP-1	A	3.03		3.03
GSP-1	B	3.04	3.01 ± .04(1.3%)	Δ = 0.66%
GSP-1	C	2.97		

FIGURE CAPTIONS

Fig. 1. Cross-sectional sketch of the experimental arrangement.

Fig. 2. Absorption experiment results for various weights per unit area of $Fe(NH_4SO_4)_2 \cdot 6\ H_2O$ powder on tape.

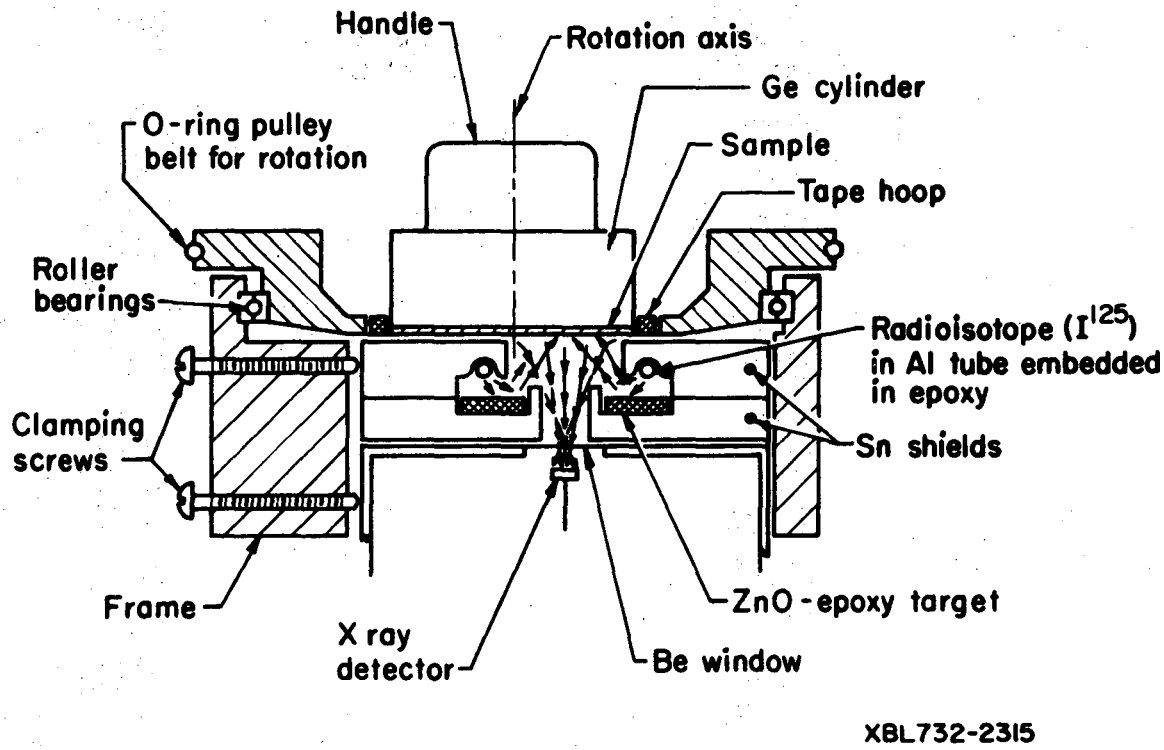
Handle
Rotation axis
Ge cylinder
O-ring pulley belt for rotation
Sample
Tape hoop
Roller bearings
Radioisotope (I^{125}) in Al tube embedded in epoxy
Clamping screws
Sn shields
Frame
ZnO-epoxy target
X ray detector
Be window
XBL732-2315

Fig. 1

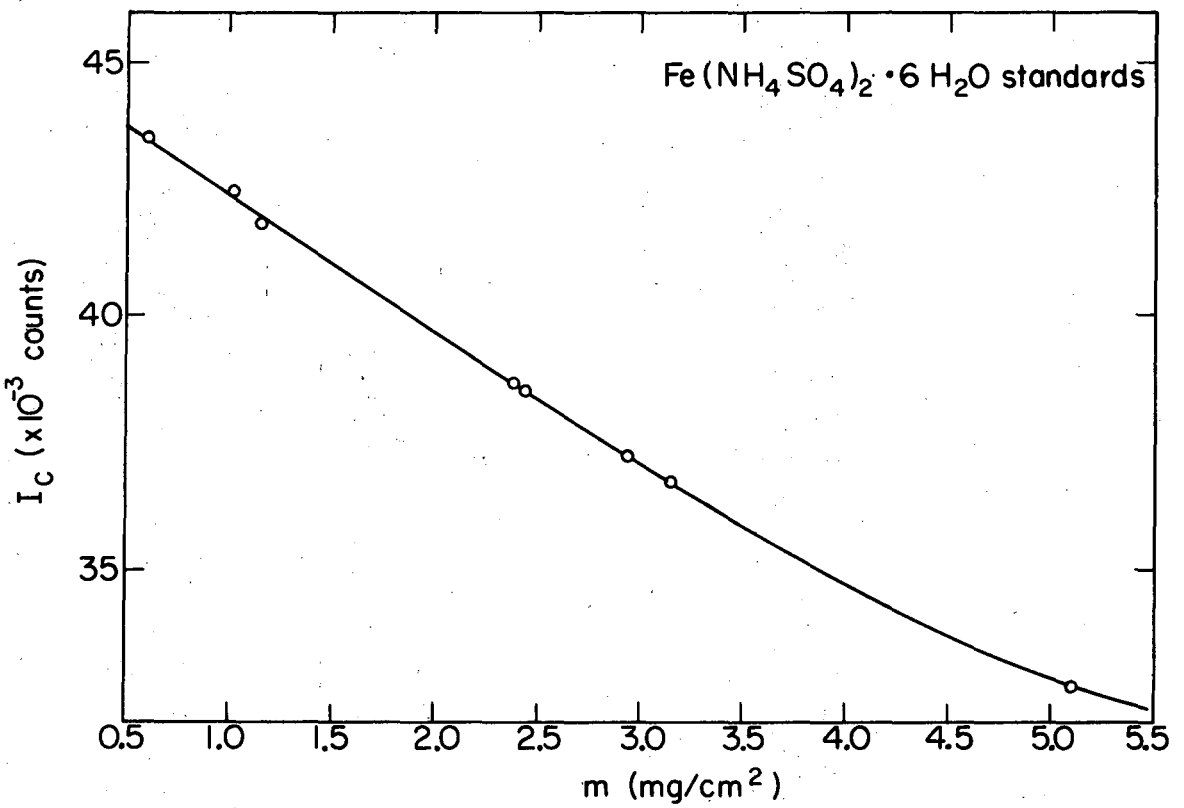
Fe(NH4SO4)2·6 H2O standards
45
40
35
Ic (x10-3 counts)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
m (mg/cm2)
XBL732-2314

Fig. 2

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720