

## **NOTICE CONCERNING COPYRIGHT RESTRICTIONS**

This document may contain copyrighted materials. These materials have been made available for use in research, teaching, and private study, but may not be used for any commercial purpose. Users may not otherwise copy, reproduce, retransmit, distribute, publish, commercially exploit or otherwise transfer any material.

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specific conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use," that user may be liable for copyright infringement.

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

**SEMIMICRO X-RAY FLUORESCENCE ANALYSIS OF TEKTITES  
USING 50-MILLIGRAM SAMPLES**By HARRY J. ROSE, JR., FRANK CUTTITA, MAXWELL K. CARRON, and  
ROBENA BROWN, Washington, D.C.

*Abstract.*—Semimicro determinations of the major constituents ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , total iron,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ , and  $\text{MnO}$ ) of tektites were made by X-ray fluorescence spectroscopy using 50-milligram samples. The X-ray analytical data are comparable to determinations obtained by conventional chemical techniques.

X-ray fluorescence spectroscopy has been applied to the determination of the major constituents in relatively large samples of materials of geologic interest (Rose and others, 1962, 1963). This technique can also be used for the semimicro analysis of rare mineral specimens or of materials of astrogeologic interest where only very small quantities ( $<100$  mg) of material are available. The analysis of the light elements in tektites has been made possible by advances both in instrumentation and in techniques of sample preparation. It is well known that the intensity of the fluorescent radiation decreases sharply with a decrease in the atomic number ( $Z$ ) of the element being analyzed. This decrease can be attributed to many factors such as diminishing fluorescence yield and absorption of the fluorescent radiation by air, by the sample, by the diffracting crystal, and by the window of the detector. Additionally, as the radiation becomes softer with decreasing atomic number, the depth from which the excited radiation emerges becomes shallower and shallower. Thus the effective radiation involves only those atoms at or near the surface of the sample, a situation that demands precise and reproducible sample preparation.

The elimination of air from the spectrometer by either evacuation of the chamber or by flushing the chamber with helium provides the first necessary step to detecting the radiation. The use of supported thin-film windows (Balis and others, 1962) on the detectors

has resulted in higher intensities by reducing absorption by the window and has extended the useful range of the technique to wavelengths beyond 10 angstroms.

Accurate quantitative determination of the light elements depends primarily on sample preparation and ultimately on the surface of the specimen submitted to the X-ray beam. As mentioned above, the particles at or near the surface provide the effective signal for analysis. Infinite depth, the point beyond which no increase in signal can be observed regardless of increase in sample thickness, is reached for  $\text{CaO}$  in less than 100 microns and for  $\text{MgO}$  in less than  $50\mu$ . It is evident, therefore, that the surface of the prepared specimen must be homogeneous and a true representation of all the layers beneath it.

Fusion of the sample in a mixture of  $\text{Li}_2\text{B}_4\text{O}_7$  eliminates many of the problems inherent in the X-ray fluorescence analysis of powdered samples (Andermann, 1961; Rose and others, 1962), especially those related to particle size and crystal structure. The presence of a strongly absorbing element minimizes absorption differences among samples resulting from variations in matrix, thus obviating the need for absorption corrections or for standards matching the composition of the material under study.  $\text{La}_2\text{O}_3$  was chosen because of its high absorption for the light elements.

The method described initially (Rose and others, 1962) required a 250-milligram sample. Although this amount is considerably less than the quantity used for routine chemical analysis, there are instances when smaller quantities must be analyzed. The effort here was directed toward reducing the sample size to 50 mg by determining the minimum layer of fused sample necessary to maintain the desired signal for the elements being analyzed.

## X-RAY FLUORESCENCE METHOD

The fusion mixture consists of 50 mg of sample, 50 mg  $\text{La}_2\text{O}_3$ , and 340 mg  $\text{Li}_2\text{B}_4\text{O}_7$ . The components are mixed in a boron carbide mortar, transferred to a graphite crucible having a cone-shaped internal base, and fused at  $1,100^\circ\text{C}$  for 10 minutes. The bead is allowed to cool in the graphite crucible. Cooling may be accomplished more rapidly by placing the crucible on a large copper plate, which dissipates the heat more readily. Sufficient boric acid is added to bring the weight to 460 mg. The boric acid compensates for any losses during ignition and acts as a binder during preparation of the pellet. The glass bead is then ground. The grinding vial consists of a lucite cylinder provided with two caps containing tungsten carbide inserts for covering both ends of the cylinder. The bead, which must be crushed before grinding, is placed cone side up in the grinding vial with one of the caps and inserts in place. A  $\frac{1}{2}$ -inch drive pin punch is placed down the cylinder on top of the bead and is then tapped with a hammer. The weighed boric acid is added to the vial along with a  $\frac{1}{4}$ -inch tungsten carbide ball, and the upper cap is placed on the cylinder. The sample is then ground on a mixer grinder for 10 minutes, which reduces the sample to about 325 mesh. The ground powder is then pressed into a pellet 1 inch in diameter. For additional strength the pellet is prepared as a double layer, using boric acid as backing (Rose and Flanagan, 1962). It is essential that the sample layer be spread uniformly on the surface of the boric acid before final pressure is applied. To obtain maximum intensity for Si and Al, pressure in excess of 50,000 pounds per square inch must be used. The preparation of samples must be done consistently with attention to all details to insure the best results.

A single-channel spectrometer was used for this study. The types of crystals, wavelengths, and detectors are given in table 157.1. Because the

fluorescent radiation of elements  $Z \leq 22$  is absorbed by air, the spectrometer chamber is flushed with helium for the determination of these elements. It is generally necessary to flush the chamber for about 1 minute between sample changes to allow the system to come to equilibrium.

Granite G-1, diabase W-1, and an equal mixture of the granite and diabase are used as reference standards. National Bureau of Standards standard samples and other samples analyzed at the U.S. Geological Survey serve as additional reference materials to extend the range of the elements being determined. Several reference standards may be mixed in varying proportions to provide desired points on the calibration curve.

The method has been used recently to analyze six samples of tektites from Java supplied by E. C. T. Chao. The results of both chemical and X-ray fluorescence determinations are given in table 157.2.

TABLE 157.1.—Summary of crystals, detectors, and wavelengths

Element	K (A)	Crystal	Detector or counter <sup>1</sup>	Path
Si	7.125	Gypsum	Proportional	He
Al	8.337	do	do	He
Fe	1.936	LiF <sup>2</sup>	Scintillation	Air
Ca	3.358	Eddt <sup>3</sup>	Proportional	He
K	3.741	Gypsum	do	He
Mn	2.102	LiF <sup>2</sup>	Scintillation	Air
Ti	2.748	LiF <sup>2</sup>	do	He

<sup>1</sup> Pulse-height analysis, channel width 12V, base level 4.5V.

<sup>2</sup> Lithium fluoride.

<sup>3</sup> Ethylene diamine ditartrate substituted for gypsum in samples with high  $\text{K}_2\text{O}$  content.

## CHEMICAL ANALYTICAL METHODS

Six javanites were carefully selected from a collection of about 80 specimens to represent the range of the indices of refraction and specific gravities of the Java tektite collection. The specimens are listed in table 157.2 in order of increasing index of refraction. The tektites were analyzed for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , total iron as

TABLE 157.2.—Comparison of chemical and X-ray analyses of 6 tektites from Java

[Index of refraction (N) in sodium light; X-ray determination made on a single pellet]

	JS-12		JS-9		JS-5		JS-6		JS-3		JS-11	
	Chem.	X-ray	Chem.	X-ray	Chem.	X-ray	Chem.	X-ray	Chem.	X-ray	Chem.	X-ray
$\text{SiO}_2$	74.2	74.4	73.4	73.5	73.8	74.2	74.4	72.7	72.3	72.3	72.5	72.3
$\text{Al}_2\text{O}_3$	11.1	11.6	11.4	11.3	11.3	11.5	11.2	11.3	11.3	11.3	11.4	11.6
$\text{Fe}_2\text{O}_3^1$	5.67	5.70	5.63	5.65	5.28	5.35	5.52	5.66	6.14	6.28	6.17	6.22
CaO	2.25	2.29	2.70	2.70	2.75	2.65	2.36	2.47	2.91	2.97	2.79	2.87
$\text{K}_2\text{O}$	2.24	2.23	2.28	2.27	2.25	2.25	2.29	2.32	2.22	2.22	2.17	2.15
MnO	.11	.10	.10	.11	.09	.10	.10	.11	.11	.10	.11	.11
$\text{TiO}_2$	.67	.68	.68	.68	.67	.66	.69	.69	.70	.70	.69	.68
N <sup>2</sup>	1.5073	----	1.5089	----	1.5102	----	1.5112	----	1.5127	----	1.5141	----
Sp gr. <sup>2,3</sup>	2.443	----	2.464	----	2.439	----	2.426	----	2.469	----	2.483	----

<sup>1</sup> Total Fe as  $\text{Fe}_2\text{O}_3$ .

<sup>2</sup> By Janet Marteka and E. C. T. Chao.

<sup>3</sup> Third place after the decimal not certain.

$\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ , and  $\text{MnO}_2$ . The chemical results are averages of duplicate determinations by the various methods. Using these different techniques, the chemical determinations were closely monitored by similar determinations in granite G-1, diabase W-1, and selected National Bureau of Standards certified samples.

Silica was determined spectrophotometrically using a molybdenum-blue method (Bunting, 1944), gravimetrically by a volatilization-formaldehyde method described by Carron and Cuttitta (1962), and also by a combined gravimetric and photometric procedure (Jeffery and Wilson, 1960). Alumina ( $\text{Al}_2\text{O}_3$ ) was determined by measuring the absorbance of the calcium aluminum alizarin red-S complex in a weakly acidic medium (pH 4.5) at  $485\text{ m}\mu$  (Parker and Goddard, 1950). Interference from iron was eliminated by use of potassium ferricyanide and thioglycolic acid as complexing agents.

Total iron was determined spectrophotometrically with o-phenanthroline (Cuttitta, 1952, and Sandell, 1959) and by a magnetic-susceptibility method developed by Thorpe and others (1963). Calcium oxide was determined by flamephotometry (Kramer, 1957), and by a semimicro, automatic, photometric titration with EDTA in the pH range 12.1–12.3 at  $590\text{ m}\mu$  using murexide as the indicator. Potassium oxide was determined flamephotometrically at  $766\text{ m}\mu$  using an instrument with a photomultiplier attachment. The sample was analyzed by bracketing between the closest potassium standards (Ray, 1956; Willgallis, 1957; Voimovitch and Debras, 1958). Titanium was determined spectrophotometrically with disodium-1, 2-dihydroxybenzene-3, 5-disulfonate (tiron) (Yoe and Armstrong, 1947). The interference of iron was overcome by reduction with ascorbic acid at pH 4.7. The purple permanganate color was utilized for the spectrophotometric determination of manganese. The oxidation was effected with ammonium persulfate (peroxysulfate) at the boiling point in a phosphoric-nitric acid medium in the presence of silver nitrate. Manganese was also determined by Janet D. Fletcher using a quantitative spectrographic method similar to that described by Bastron and others (1960).

#### REFERENCES

Andermann, George, 1961, Improvements in the X-ray emission analysis of cement raw mix: *Anal. Chemistry*, v. 33, 1689–1695.

- Balis, E. W., Bronk, L. B., Pfeiffer, H. G., Welborn, W. W., Winslow, E. H., and Zemany, P. D., 1962, Improved components for the X-ray emission analysis of the light elements: *Anal. Chemistry*, v. 34, p. 1731–1733.
- Bastron, H., Barnett, P. R., and Murata, K. J., 1960, Method for the quantitative spectrochemical analysis of rocks, minerals, ores, and other materials by a powder d-c arc technique: *U.S. Geol. Survey Bull.* 1084-B, p. 165–182.
- Bunting, W. E., 1944, The determination of soluble silica in very low concentration: *Indus. and Eng. Chemistry, Anal. Ed.*, v. 16, p. 612–615.
- Carron, M. K. and Cuttitta, Frank, 1962, Determination of silica in tektites and similar glasses by volatilization: *Art. 30 in U.S. Geol. Survey Prof. Paper* 450-B, p. B78–B79.
- Cuttitta, Frank, 1952, The colorimetric determination of total iron with o-phenanthroline—A spectrophotometric study: *U.S. Geol. Survey TEIR-223* issued by U.S. Atomic Energy Comm. Tech. Info. Service, Oak Ridge, Tenn.
- Jeffery, P. G., and Wilson, A. D., 1960, A combined gravimetric and photometric procedure for determining silica in silicate rocks and minerals: *Analyst*, v. 85, p. 478–485.
- Kramer, H., 1957, Flame photometric determination of calcium in phosphate, carbonate, and silicate rocks: *Anal. Chim. Acta*, v. 17, p. 521.
- Parker, C. A., and Goddard, A. P., 1950, The reaction of aluminum ions with alizarin-3-sulphonate, with particular reference to the effect of calcium ions: *Anal. Chim. Acta*, v. 4, p. 517–536.
- Ray, Norman, 1956, Flame photometric determination of sodium, potassium, calcium, magnesium, and manganese in glass and raw materials. *Anal. Chemistry*, v. 28, p. 34.
- Rose, H. J., Adler, Isidore and Flanagan, F. J., 1962, Use of  $\text{La}_2\text{O}_3$  as a heavy absorber in the X-ray fluorescence analysis of silicate rocks: *Art. 31 in U.S. Geol. Survey Prof. Paper* 450-B, p. B80–B82.
- 1963, X-ray fluorescence analysis of the light elements in rocks and minerals: *Appl. Spec.*, v. 17, no. 4, p. 81–85.
- Rose, H. J., and Flanagan, F. J., 1962, X-ray fluorescence determination of thallium in manganese ores: *Art. 32 in U.S. Geol. Survey Prof. Paper* 450-B, p. B82–B83.
- Sandell, E. B., 1959, *Colorimetric determination of traces of metals*, 3d ed.: New York, Interscience Publishers, Inc., p. 537–542.
- Thorpe, A. N., Senftle, F. E., and Cuttitta, Frank, 1963, Magnetic and chemical investigations of iron in tektites: *Nature*, v. 197, p. 836–840, March 2, 1963.
- Voimovitch, I. A., and Debras, J., 1958, Determination of sodium, potassium, and lithium in silicates by flame photometry: *Indus. Ceramics*, v. 502, p. 321–27.
- Willgallis, A., 1957, Application of flame photometry to alkali analysis of minerals: *Zeitscht. anal. Chemie*, v. 157, p. 249–257.
- Yoe, J. H., and Armstrong, A. R., 1947, Colorimetric determination of titanium with disodium-1, 2-dihydroxybenzene-3, 5-disulfonate: *Anal. Chemistry*, v. 19, p. 100–102.

