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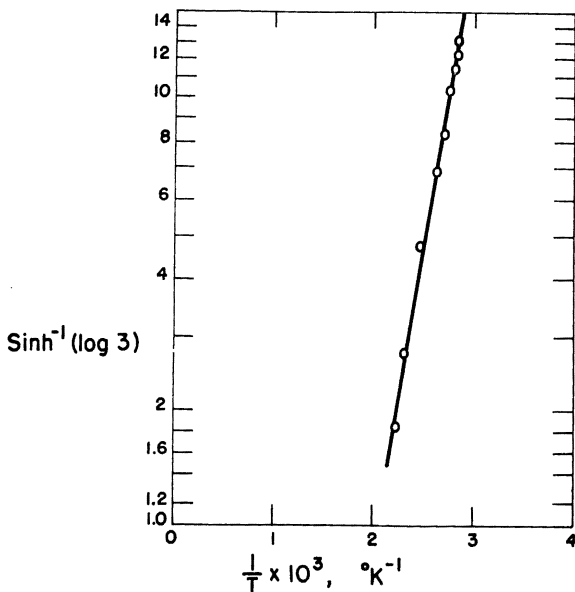Available at: https://scholarworks.uni.edu/pias/vol70/iss1/32

Figure 7. Plot of log visc. versus $\frac{1}{T_0}$ for high polymer on hyperbolic sine graph paper.

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Literature Cited

1. J. D. MacKenzie. J. Am. Cer. Soc. *44*, 598, 1961.
2. J. P. Poole, Glass Industry, *30*, 56. 1949.
3. G. W. Morey, *Properties of Glass*, Reinhold, New York, (1954).
4. Glasstone, H., Laidler, K. J., and Eyring H., *The Theory of Rate Processes*. McGraw-Hill, New York, 1941.

Analysis of Fe_2O_3, TiO_2 and Cr_2O_3 in Mullite by X-Ray Fluorescence[1]

M. O. MARLOWE AND THOMAS D. McGEE

Abstract. The basic theory and methods of X-ray fluorescence are briefly discussed. Pure synthetic mullite was made by mixing aluminum and silicon chlorides in non-aqueous solvent, coprecipitating as hydroxides, calcining to remove solvents and firing to 1600°C. Additions of Fe_2O_3, TiO_2 and Cr_2O_3 to the high purity mullite were used to produce standard calibration curves for use in the analysis of unknowns. Experimental techniques are described and standard curves are presented. The method is rapid and results are comparable in accuracy to those of wet chemical analysis.

Mullite, nominally $Al_6Si_2O_{13}$, is found in many fired ceramic products such as whitewares, structural clay products and fire-clay refractories. The phase equilibrium diagram for the mullite portion of the alumina-silica system has not been accurately determined (1). The range of composition at elevated temperatures and whether mullite melts congruently are still in controversy. Part of the controversy has been ascribed to the effects of transition element impurities on stability and on phase relationships (2).

Wet chemical analysis of mullite is difficult, time consuming and often inaccurate. A method of accurately determining the impurities in mullite is needed. For certain transition elements commonly present in mullite the X-ray spectrofluorescence technique appears suitable. This paper reports the result of undergraduate research directed toward the use of the spectrofluorescence technique for mullite analysis.

LITERATURE REVIEW

When a material is placed in the optical path of X rays, photons which strike inner shell electrons of atoms of the material may, if they possess enough energy, eject electrons from the atoms — producing an excited state (3). An outer shell electron will then collapse to the inner shell; emitting an X-ray photon in the process at a frequency characteristic of the difference in energy between the two electronic states of the particular atom.

The most likely transition is from the L to the K shell and therefore this is the radiation of highest intensity. Each orbital of the L shell has a different energy level so there are actually three slightly different energy levels. Only two transitions are possible and this gives rise to the slightly different characteristic frequencies, $K\alpha_1$ and $K\alpha_2$. The transition from the M to the K shell is less probable but higher in energy (higher frequency). The greater multiplicity of transitions from the M to the K shell gives rise to the $K\beta_1 - K\beta_3$ doublet and the $K\beta_2$ line.

The characteristic wavelengths for each element have been accurately determined. Therefore determining the wavelengths of X-ray fluorescence may result in qualitative analysis of the elements of the sample.

The intensity of the characteristic radiation fluoresced by a sample is directly proportional to the number of atoms present. Therefore measurement of the intensity of any one of the characteristic frequencies may be used to determine the quantity of the atomic species which are present.

The fundamental requirements for quantitative X-ray spectrochemical analysis are: (4)

1. A source of short wave length high intensity X rays to cause the sample to fluoresce.
2. A method of sorting the various characteristic wavelengths such as a standard diffraction crystal and a goniometer for measuring the angle of diffraction.
3. A method of measuring the X ray intensity.

To determine the wavelength of fluorescence the Bragg equation is used to relate angle of diffraction to the lattice spacing of the standard diffraction crystal. Thus, by $n\lambda = 2d \sin \theta$, with a halite crystal of d equal to 2.89 angstroms, by measuring the Bragg angle, θ, one can determine the wavelength, λ, of X radiation for a first order reflection (n equals one).

The incident X-ray beam and the fluorescent X-rays themselves are subject to absorption by the materials which they pass through. According to Beer's law the intensity of radation at any depth x, along a linear path is given by: $I = I_o \, e^{-\mu x}$. Where I_o is initial intensity, I is intensity at any depth of penetration, x, and μ is the linear absorption coefficient, a constant for the particular wavelength of X rays and the absorbing material.

Therefore, in spectroscopic analysis the absorption conditions must be closely controlled. Penetrating X rays are needed to reach and excite many atoms in order to have high intensities for measurement. Atoms with low bonding energies, atomic number less than 13, emit such weak radiation that it is impractical to measure their fluorescence. Elements of atomic number 13 to 20 may be determined only with a vacuum or with a low atomic number gas in the optical path to limit scattering and absorption of the X rays in the optical system.

If a powder sample is not completely homogeneous different grains will absorb and fluoresce to different degrees. This may cause variation in measured intensites from place to place on the sample as well as when the powder grain size is changed. Coarse samples will exhibit greater intensity variation. From a theoretical analysis F. Claisse asserts that inhomogeneous samples cannot be accurately analyzed because present grinding equipment will not grind to sufficient fineness (5). He does assert, however, that accurate analysis is possible if the chemical composition and grain size of the matrix is constant. Matrix dilution is also sometimes helpful (6).

Variation in matrix absorption and in X ray generation and intensity measuring equipment may be partially compensated by the internal standard technique (7). The choice of a standard is difficult because of matrix absorption and excitation effects (8). With this method a known quantity of another element is added to each sample. The ratio of the intensity of an unknown element to that of the internal standard element can be used for analysis.

PROCEDURE

Pure mullite was made by mixing solutions of aluminum chloride and silicon chloride in absolute methanol, co-precipitating the hydroxides by the addition of aqueous ammonia to obtain at pH of 7, dehydrating first at 110°C and then with a Meeker burner, pressing the resultant powder into ½" diameter pellets, and firing the pellets to 1600°C in a gas-fired kiln. This mullite was then leached for 10 minutes with 10% HF at 0°C, filtered, and washed with 5% HCl until the filtrate was free of $Al(OH)_3$ when neutralized with NH_4OH. Parts of this procedure are similar to a method of Wiegmann and Horte (9).
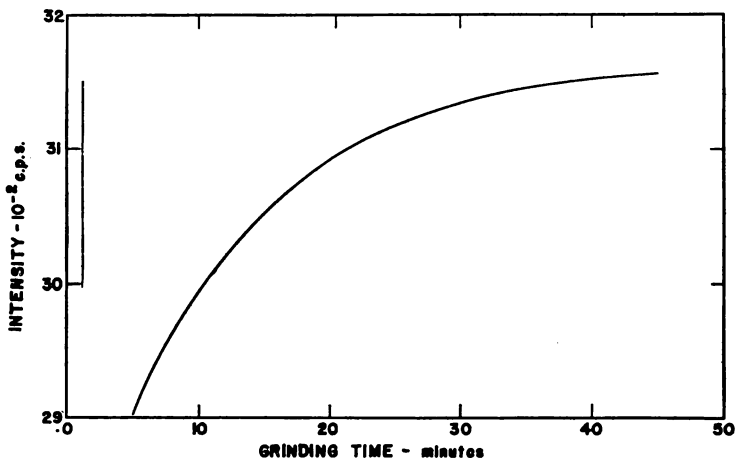

Figure 1.   Effect of grinding time on intensity of fluorescent X rays from mullite sample.

Appropriate quantities of reagent grade Fe_2O_3, TiO_2 and Cr_2O_3 were mixed with the mullite powder with an agate mortar to produce one gram samples ranging in composition from 0 to 15% of each oxide in 3% increments. An additional sample containing 10% Fe_2O_3 was ground for increasing time intervals with an agate mortar until the X ray fluorescent intensity reached a constant value, about 45 minutes (Figure 1). Because intensity was virtually constant at 30 minutes and to reduce grinding time all samples were then ground for 30 minutes in motor driven agate mortar. Samples were packed by hand into ¾" x ¾" x 0.05" recess of a bakelite sample holder.

An XRD-5 General Electric spectrogoniometer arranged for spectrographic technique and equipped with a halite analyzing crystal and a Machlett AEG-50T tungsten tube operated at 50 KV and 50 ma was used. In order to avoid overlapping peaks the various spectra were studied and the angles shown in Table I were selected for analysis.

Table 1.   Angles used for intensity measurement.

Element	Peak 2θ	Background 2θ	
Fe	40.18	38.30	42.60
Cr	47.94	41.40	56.40
Ti	58.35	56.40	62.00

Each peak and background was counted 10 counts of 10 seconds duration. The average background intensity for each peak was substracted from peak intensity. A sample of each pure oxide was prepared and the intensity of each peak, less background, was determined (Table 2). These samples were carefully preserved and were analyzed periodically. The results of intervening analyses were then adjusted appropriately in proportion to the deviation from the values in Table 2 to correct for drift in the generation and intensity measuring equipment.

Table 2.   Intensity of pure oxides.

Oxide	Counts per second
Fe_2O_3	4,115
Cr_2O_3	1,478
TiO_2	199
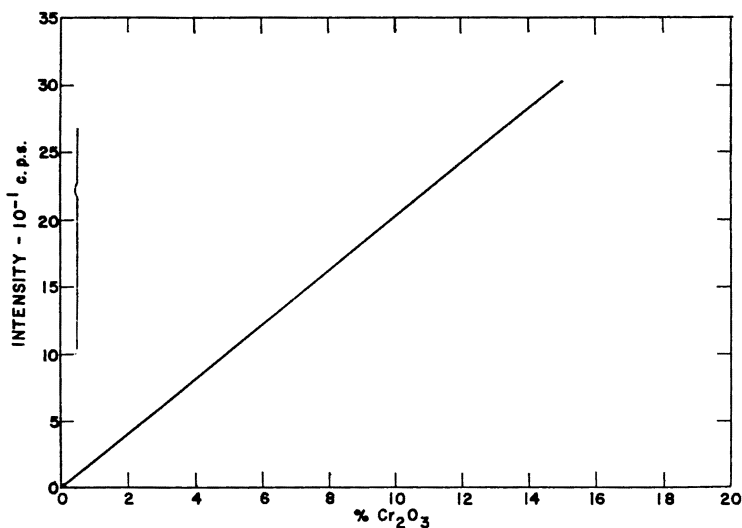
Figure 2.   Standard curve for determination of Cr₂O₃ in multiple samples.

RESULTS

The standard curves, Figures 2, 3 and 4, are typical of X-ray spectrographic analysis without an internal standard. The curvature is caused by the change in the absorption of the samples as the oxide content is varied. The direction of curvature depends upon whether absorption is increased or decreased by addition of an oxide.
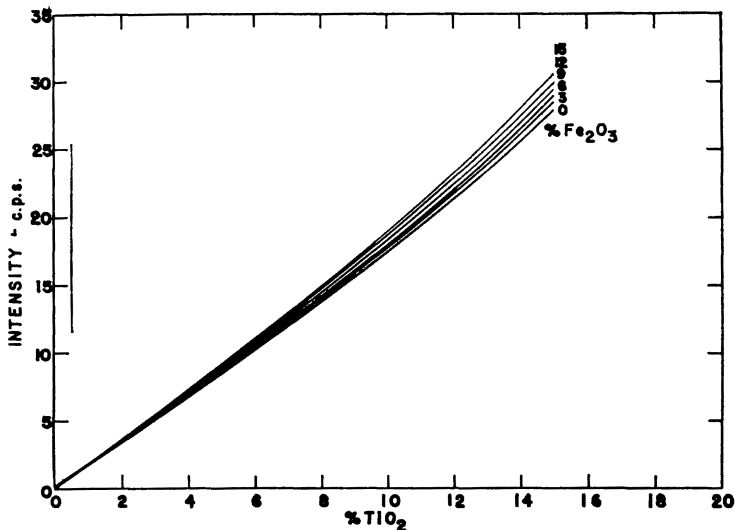
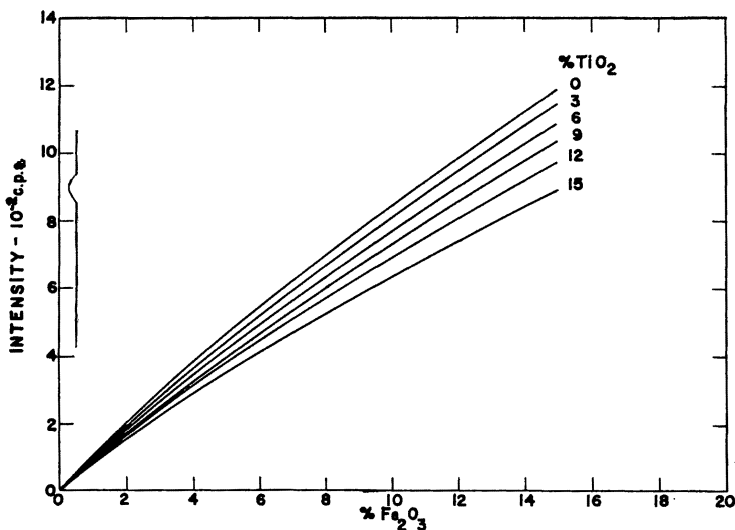Figure 3.   Standard curves for determination of TiO₂ in mullite samples with varying Fe₂O₃ concentration.

Figure 4.   Standard curves for determination of Fe₂O₃ in mullite samples with varying TiO₂ concentration.

To test the standard graphs a series of analyses was made on synthetic samples of known composition using preparation techniques identical with those for the standard curves. Table 3 gives the results of this test.

Table 3.   Comparison of Results

Sample	Actual Composition			X-ray Spectrofluorescent Results		
	%Fe$_2$O$_3$	%TiO$_2$	%Cr$_2$O$_3$	%Fe$_2$O$_3$	%TiO$_2$	%Cr$_2$O$_3$
A......		0.88			0.75	
B......		9.7			10.0	
C......		12.1			11.7	
D......	0.83			0.8		
E......	8.4			8.2		
F......	10.9			10.7		
G......	11.7			11.8		
H......			0.96			0.80
I......			11.6			11.2
J......			8.3			7.9
K......	3.5	6.5		3.7	6.5	
L......	8.5	11.7		8.0	10.8	
M.....	14.2	3.0		13.8	3.0	
N......	3.3	15.3		3.1	15.0	
O......	12.8	11.2		11.9	11.0	

DISCUSSION

The results indicate accuracy approximately the same as is often obtained by wet chemical analysis. Unknown mullites, however, may vary in alumina and silica contents as well as in other impurities. For samples of this nature incorporation of an internal standard to compensate for absorption variations may be necessary. For such mullites the heavier elements can readily be detected by qualitative X-ray spectrochemical analysis.

Grinding the sample for a longer time should reduce the variability of the results. Counting deviations, which are proportional to the square root of the number of counts, could be reduced by counting for longer time periods or, for TiO$_2$, by substituting a light gas such as helium for air in the optical path.

Once a suitable preparation technique is devised and standard curves are prepared analysis is rapid and accurate. As many as 40 samples can be analyzed in an eight hour day.

Literature Cited

1. A C. Cooper, D. A. R. Kay and J. Taylor. Trans. Brit. Cer. Soc. 60, 124. 1961.
2. M. K. Murthy and F. A. Hummel. J. Am. Cer. Soc. 43, 276. 1960.
3. Theoretical aspects may be found in any introductory X-ray text such as B. D. Cullity, *Elements of X-Ray Diffraction*, Addison-Wesley Publishing Co., Inc., Reading, Mass. 1956.
4. A.S.T.M., *Symposium on Fluorescent X-Ray Spectrographic Analysis*. A.S.T.M. Special Publication No. 157., Philadelphia, Pa. 1953.

5. F. Claisse. "Accurate X-Ray Fluorescence Analysis Without Internal Standard." Quebec Dept. Mines, Labs. Branch, Prelim. Reports No. 327 24 pp. 1956.
6. E. L. Gunn. Anal. Chem., 29, 184. 1957.
7. G. L. Lewis, Jr., and E. D. Goldberg. Anal. Chem 28, 1282. 1956.
8. I. Adler and J. M. Axelsod, Spectrochim Acta 7, 91. 1955.
9. J. Wiegmann and C. Horte. Z. Anorg u. alleg. Chem. 286, 268. 1956.

Changes in Training for Teachers Made Necessary by CBA

ANDREW STEVENSON

Abstract. In summary, surveys conducted at the State University of Iowa have revealed the following points that lead to a single conclusion: 1) Science teachers in Iowa are generally eager to improve their courses and their teaching. 2) Science teachers desire help from the colleges in securing appropriate training in order to approach the "new" science courses. 3) New graduates of most colleges and Universities feel wholly inadequate about teaching the new courses. 4) Apparently considerable reorganization of college curricula is necessary to provide certified teachers who would be ready to teach the CBA course (and presumably the other new courses).

The CBA course differs from traditional chemistry in both specific content and method. The content is organized around the main basic theme of the chemical bond and the approach is one of inquiry. These differences suggest needed changes in the training of teachers who will be involved in the teaching of the "new" chemistry.

In 1957 the Svoiet Union announced that they had successfully placed Sputnik I in orbit around the earth. The accomplishment of the Russians had many effects on the people who inhabit the earth. In the United States there was a general concern about the science programs of the country. The need to reevaluate the existing programs was apparent. The Congress of the United States formed the National Science Foundation, which supplied funds to improve scientific training and knowledge, and passed the National Defence Education Act, which allowed schools to buy more and better equipment for their science laboratories. Conferences to study existing science programs and possible revisions were held at different colleges and universities throughout the country with funds provided by the National Science Foundation (NSF) as well as other agencies and the science educational revolution was on.

With the revolution came the Physical Science Study Committee (PSSC) course for physics, the Biological Sciences Curriculum Study (BSCS) presenting several courses in biology, the