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X-RAY SPECTROCHEMICAL ANALYSIS: AN APPLICATION TO CERTAIN LIGHT ELEMENTS IN CLAY MINERALS AND VOLCANIC GLASS

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ABSTRACT

Recent developments in instrumentation have extended the range of *x*-ray spectrochemical analysis (*x*-ray fluorescence) to the lighter elements in the range of atomic number 12 to 22. This includes the significant rock-forming elements aluminum, silicon, potassium and calcium, in addition to phosphorus, sulfur, and titanium. Improved procedure provides a rapid, non-destructive, quantitative, semiquantitative, and qualitative analytical method useful in the examination of aluminosilicate minerals and mineraloids. It is also capable of wider application.

The analytical method has been applied to volcanic and related materials from the Marysvale, Utah, uranium area. The *x*-ray instrument has been calibrated through the use of artificial mixtures of chemical compounds containing the constituent elements. Previously analyzed reference clay minerals of the American Petroleum Institute Research Project 49 have served to establish the calibration. *X*-ray analytical data have been obtained for a selection of specimens from the Mt. Belknap Series which forms part of the Late Tertiary volcanic cover of the Marysvale region. The materials examined include rhyolitic obsidian, volcanic ash, granular igneous rocks and argillitic alteration specimens. *X*-ray spectrochemical analyses of the Mt. Belknap Series show a limited compositional range. This indicates that the tuffs, glasses and rhyolites of this series are derived from a uniform magma.

INTRODUCTION

The objective of this study has been twofold: (1) to explore what appears to be a rapid *x*-ray method for the approximate analysis of the important rock- and ore-forming elements, and (2) to apply a considerable group of approximate analyses obtained by the *x*-ray method to the interpretation of a mineralogic-geologic field problem.

The investigation has concentrated on the extent to which *x*-ray spectrochemical analysis may be utilized for rapid analysis of minerals which contain elements with atomic numbers greater than magnesium ($Z=12$). It involves the application of the *x*-ray spectrochemical method

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as one phase in the field study of a sequence of Tertiary tuffs and glasses of the Mt. Belknap Volcanic Series near Marysvale, Utah.

The term *x*-ray spectrochemical analysis has been used by Parrish (1956*a*) to describe qualitative and quantitative analysis using the emission spectra of elements in the *x*-ray wavelength region (0.1 to 100 Å). The name emphasizes the similarity of the method to spectrochemical analysis utilizing the emission spectra of elements in the optical wavelength region. "*X*-ray spectrochemical analysis" is preferable to "*x*-ray spectroscopy," a somewhat misused term first applied to *x*-ray powder diffraction using the diffractometer. The terms "*x*-ray fluorescence spectroscopy," "*x*-ray emission spectroscopy" or "fluorescent *x*-ray spectrographic analysis" are also less desirable. All of these seek to express, in the words of von Hevesy (1932), "chemical analysis by *x*-rays."

The discovery by Barkla (1908–1911) of the "characteristic" nature of *x*-rays emitted by different elements furnished the basis for *x*-ray spectrochemical analysis. Although initial successes, such as the discovery of the element hafnium (von Hevesy, 1932) proved the utility of the method, it was not generally accepted as a means of chemical analysis until recently developed electronic devices replaced earlier photographic methods of intensity measurement.

With the introduction of automatic programing in 1956, *x*-ray spectrochemical instruments have found application on the production line as well as in the laboratory. In the important field of metallurgical alloys (Brissey, Liebhafsky and Pfeiffer, 1953; Whittig, 1959) this development has had special significance. The application of *x*-ray spectrochemical analysis to mineralogical problems has been somewhat delayed. This has been caused primarily by the relatively recent development of reliable instrumentation, and the limitation of the analysis to elements with atomic numbers greater than 22. The last factor has been the most serious; although 80 of the 102 known elements could be analyzed, those which could not, include the important rock-forming elements C, O, Na, Mg, Al, Si, P, S, Cl, K, Ca and Ti. Within the past two years the range of analysis has been extended to Mg, leaving only C, O and Na as rock-forming elements still beyond reach. It is worthy of mention, however, that Siegbahn, using a vacuum *x*-ray spectrograph, has analyzed metals as light as Li ($Z=3$).

The basic theory of *x*-ray spectrochemical analysis has been covered in particular by Compton and Allison (1935), von Hevesy (1932), the Symposium of the American Society for Testing Materials (Friedman, Birks and Brooks, 1954) and in papers by Parrish (1956a). The immediate problem has concerned the modification of the standard *x*-ray spectrograph to permit the detection of light elements, and the application of the modified instrument to the analysis of materials such as clay minerals and volcanic glass.

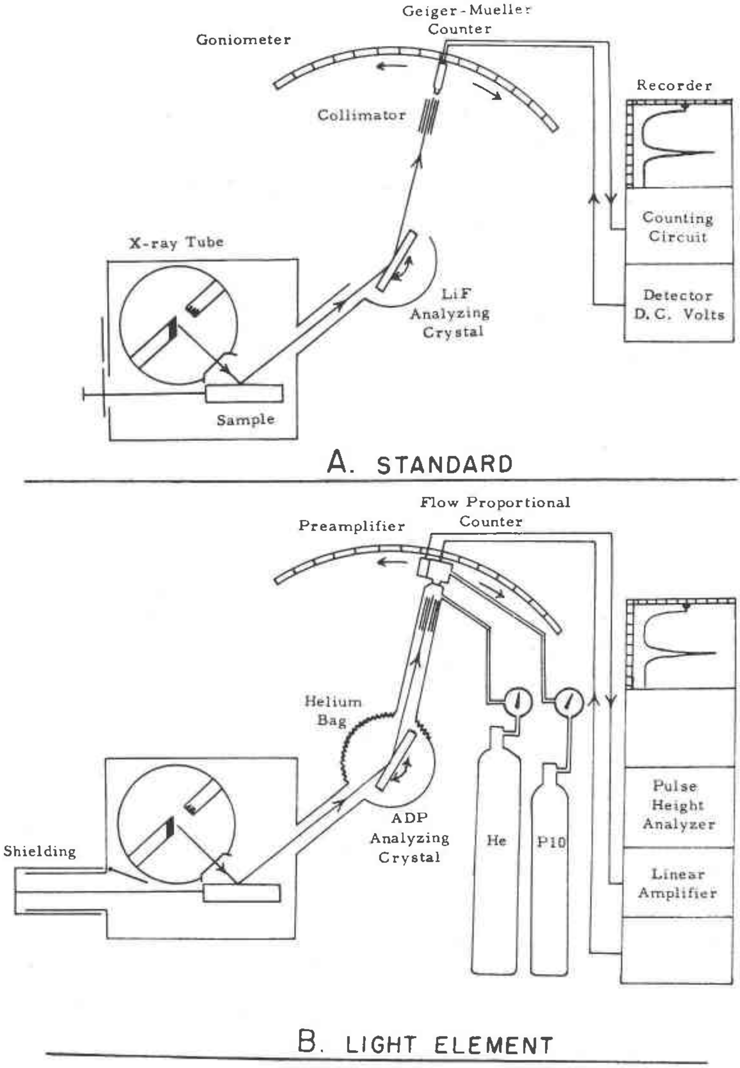
INSTRUMENTATION

Complete absorption of Al Kα radiation ($\lambda = 8.3$ Å) occurs in the 34 cm. air path used in the standard Norelco spectrograph. However, enclosure of the system with a flexible rubber bag permits replacement of the air with helium, which in turn allows 85 per cent transmission of the same radiation. Diffraction of such long wavelength radiation may be accomplished by the use of large single crystals of ammonium dihydrogen phosphate (ADP) which are cleaved along the reflecting plane, $2d = 10.6$ Å. ADP crystals diffract Al Kα radiation within goniometer range with greater efficiency than gypsum ($2d = 15.2$ Å) and mica ($2d = 19.9$ Å). The flow proportional counter developed by Hendee, Fine and Brown (1956) provides a one hundred-fold increase in peak to background ratio over the most sensitive Geiger-Müller counter developed for use in the soft *x*-ray region. The least absorptive window for the flow proportional counter is 0.1 mm. mylar, which transmits 55 per cent Al Kα radiation.

Other items in the standard Norelco spectrograph are the tungsten target *x*-ray tube and the collimator. The former, normally operated at 35 Kv. and 27 Ma. for the detection of heavier elements, is given the heaviest possible loading without excessive overheating (50 Kv. and 40 Ma.) when working with light elements. A 100 Kv. tube has recently been manufactured, but this requires a more powerful basic unit which has not been available for this study. In the case of the collimation, a four-fold increase in counting rate can be obtained by substituting a bundle of coarse nickel tubes for the closely spaced nickel foil collimator. The corresponding loss in resolution is not critical for the widely spaced reflections in the long wavelength region, but for the closely spaced reflections of elements heavier than titanium, such resolution loss cannot be tolerated. For this reason, the standard collimation was retained, thus avoiding realignment of the instrument upon transfer from light to heavy element determinations.

Operational requirements include helium for the instrument path, methane-argon gas (P10) and a linear amplifier for the flow proportional counter, and electronic pulse discrimination by means of a Pulse Height Analyzer. The linear amplifier preserves the energy to pulse height relationship resolved by the detector while amplifying the pulse by a factor of several thousand. The Pulse Height Analyzer consists of a single channel or window of variable width, which can be set to accept pulses with energy corresponding to that of the radiation being studied while rejecting all others including hard background radiation and detector tube noise.

Modifications of the standard x-ray spectrograph for light element detection are summarized in Fig. 1.



A. STANDARD

B. LIGHT ELEMENT

FIG. 1. Schematic diagram of equipment.
A. The standard x-ray spectrograph.
B. Modifications of the x-ray spectrograph for "light element" ($Z=12$ to 29) detection.

MATRIX EFFECTS

If problems caused by the presence of the matrix could be overlooked, *x*-ray spectrochemical analysis of a sample could be limited to an initial calibration, and a routine scan for detection. However, the associated matrix elements and the physical-chemical form of the specimen affect both qualitative and quantitative measurements. Physical state, particle size, and sample preparation must first be standardized. The major and minor associated elements in the sample are then ascertained to determine the importance of inter-element interferences. These interferences have been summarized (Molloy, 1959) in terms of *x*-ray emission and absorption interactions of three types: emission absorption, emission enhancement, and competitive absorption.

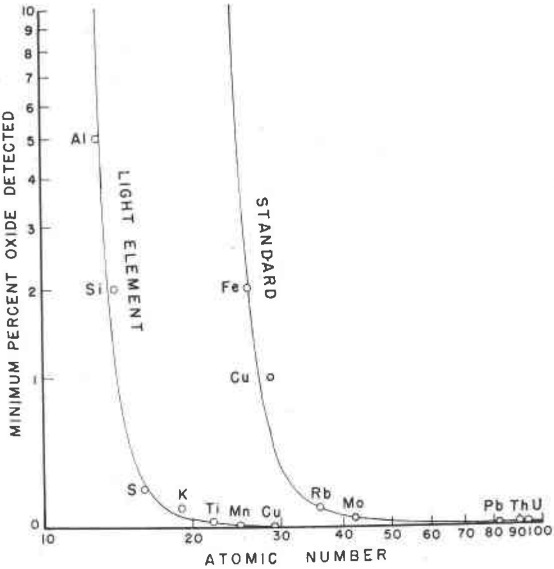


FIG. 2. Estimated limits of minimum detection.

In emission absorption the intensity of a wavelength emitted by one element is decreased by the selective absorption of that wavelength by another element present in the sample. Emission enhancement may be caused either by the overlap of adjacent emission lines, or the absorption of additional energy by one element in the range in which another element is emitting. Competitive absorption may occur with insufficient excitation potential, in which case a decrease in emission intensity may be noted if two or more elements absorb energy in the same range.

The basic limitation in analysis with the *x*-ray spectrograph is the minimum amount of an element that can be detected (Fig. 2). If the element exceeds this minimum, analysis is possible.

The intensity of the secondary radiation emitted by the sample is a direct measurement of the amount of the element present. Quantitative analysis is therefore possible, but, in all except simple systems, this intensity must be corrected for inter-element interferences. Thus the adjustment of intensity measurements to a standard calibration curve becomes the major problem in quantitative *x*-ray spectrochemical analysis.

The accuracy of quantitative analysis is limited, therefore, by the amount of the element present, the atomic number and amount of interfering elements in the sample, the sensitivity of the instrument, and the nature of the detector. At the threshold of light element analysis, only large amounts of Mg and Al can be detected, and with only semi-quantitative accuracy. In the neighborhood of titanium, 0.01 weight per cent oxide may be determined with quantitative accuracy. Titanium is at the threshold of the standard spectrograph, and normally this instrument will not detect less than 1% TiO_2 with the scintillation counter.

MATRIX CORRECTIONS

Hower (1959) and others have pointed out that the matrix corrections for most elements in the trace element analysis of rocks and minerals are satisfied by the correction of the gross *x*-ray absorption coefficient of the sample with reference to a standard. This gross absorption coefficient is essentially dependent on the bulk element composition, and may be expressed in terms of the mass absorption coefficient of the sample calibrated against a standard. Corrections for the major elements are more involved, but may be approximated by the addition of an internal standard which reacts in a manner similar to the element under study. Such theoretical corrections make possible precise, quantitative *x*-ray spectrochemical analysis.

At present, such precise analysis is limited to simple mineral systems, or to restricted applications with well established alloys and chemicals. Bulk analysis of samples with unknown composition is semi-quantitative. However, within a restricted compositional range, certain modifications permit extension of precise, alloy-type analysis to silicate mineral systems.

X-ray spectrochemical analysis of alloys is best accomplished by calibration with previously analyzed standards which are nearly identical in composition to the samples. For each significant change in the proportions of the components, a suitable standard must be prepared. In an instrument such as the Autrometer (Behr, 1956), an automatic *x*-ray comparison spectrometer, the alloy sample and a suitable standard are alternately placed in the detection position as a record is made of element intensities. This immediate comparison of sample and standard forms the basis of quantitative analysis performed with the *x*-ray spectrograph. Absorption and emission interferences are corrected by the analyzed standard which closely approximates the sample in composition and preparation.

The extreme compositional range of rocks and minerals requires strict limitation in the compositional range of a particular study. An approximate quantitative analysis must be confined to a particular mineral or mineral group, or, at most, a small rock suite. In the quantitative analysis of such groups, two factors must be considered: (1) although synthetic mixtures may approach the mineral or rock in composition, the comparative intensities will probably differ because of slightly differing mass absorption coefficients, and (2) an unrecognized interfering element may destroy the accuracy of the analysis.

INSTRUMENT CALIBRATION

Maximum accuracy in quantitative analysis with the *x*-ray spectrograph may be obtained through the application of counting statistics (Parrish, 1956*b*). However, the large number of analyses desired has led to the use of a more rapid method, which may be described as graphic, continuous stripchart recording. Scanned or oscillated peak heights and corrected peak height (minus background) readings may be used for semi-quantitative estimates, but lack sufficient reproducibility for quantitative work.

An integrated peak height method was developed to provide the necessary accuracy. This involves several steps: the goniometer is set for the maximum intensity of the selected peak, the Pulse Height Analyzer is adjusted if required, the proper scale factor and multiplier are selected to retain the peak within the chart range, the maximum time constant (16 sec.) is chosen to permit integration of the signal, and the recorder is allowed to reach the maximum position and continue running for several minutes. The result is a plateau (Fig. 3) which is smooth when a large number of counts are recorded (ThO_2), and irregular when only a few counts are detected (SiO_2). The Scale Factor (S.F.) notations refer to the settings on the electronic circuit panel of the instrument. Because many instrument settings are required, it is advisable to complete the work with each element, determining the calibration curve with standards and analyzing the unknown specimens, before changing the settings to analyze for another element.

Several stages have been employed in the development of calibration curves: (1) the initial calibration utilizing mixtures of simple chemical compounds or elements, (2) calibration with reference clay minerals and previously analyzed clay and volcanic glass specimens, (3) calibration curves corrected to consider absorption or emission interferences. The third calibration is only required where interferences are encountered. Instrument background has not been removed from the data curves.

Figures 4*a* and 4*b* show the chemical calibration curves for silicon and silica in a matrix of aluminum oxide. The linearity of the points in both cases demonstrates that the determination is proportional to the amount of the element present, and that the integrated peak height method compares favorably with the counting statistics technique. For convenience in comparison with mineral and rock analyses the curves are recorded in terms of oxides.

The *x*-ray spectrograph has been calibrated with standard sample

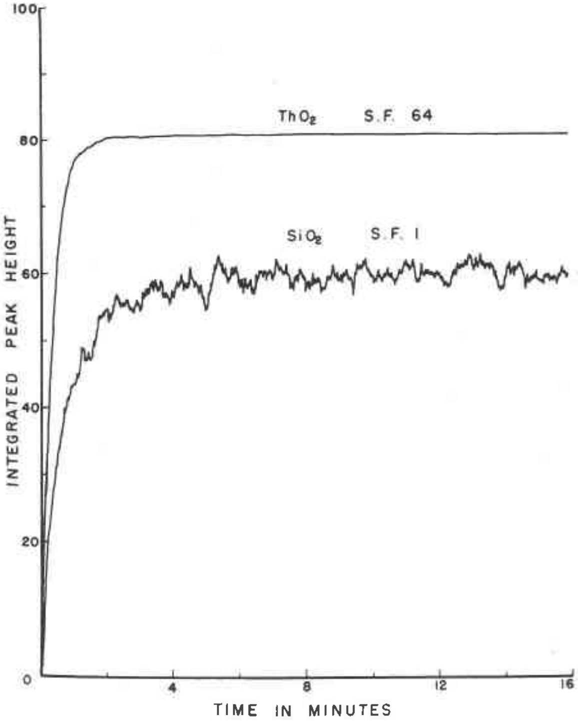


FIG. 3. The integrated peak height method. The upper curve shows the stability obtained with a large number of counts (ThO_2, scale factor 64). The lower curve shows the variation about a mean when only a few counts register (SiO_2, scale factor 1).

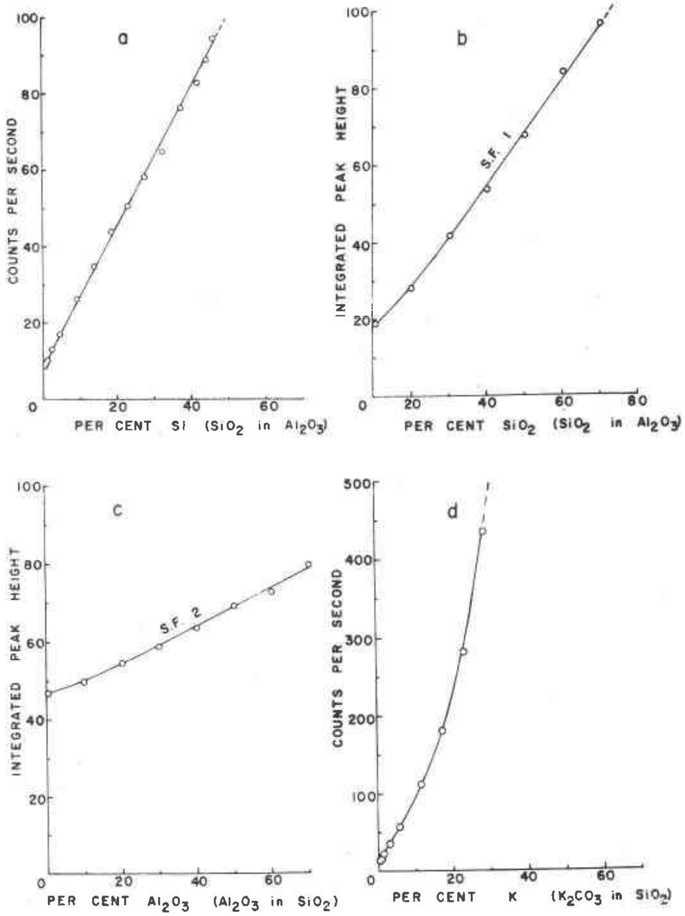


FIG. 4. Chemical calibration curves for mixtures. Weight per cent element or oxide *vs.* counts per second or integrated peak height.

a) Silicon, SiO_2 in Al_2O_3.

b) Silica, SiO_2 in Al_2O_3, scale factor 1.

c) Aluminum oxide, Al_2O_3 in SiO_2, scale factor 2.

d) Potassium, K_2CO_3 in SiO_2.

sequences containing Al_2O_3, K_2CO_3, Fe, Cu, ThO_2 and U_3O_8 in weighed amounts disbursed in finely ground silica. For the calibration of silica, the aluminum oxide set was used. The chemical calibration curves obtained from these preparations illustrate the accuracy and sensitivity of the *x*-ray spectrochemical method for the analysis of simple chemical systems.

Figure 4*c* shows the chemical calibration curve for aluminum oxide in silica, derived from a set consisting of eight prepared mixtures. While the agreement between the points and the curve is good, the slope of the curve is too gradual to provide desirable accuracy. Several factors account for this situation. The long wavelength of aluminum radiation is considerably absorbed by helium; the primary *x*-ray beam is inefficient in the aluminum excitation region; and the detector is relatively insensitive to extremely soft radiation. These three factors combine to reduce the number of counts recorded for each per cent of aluminum oxide in the sample. This in turn results in the gradual slope of the calibration curve over the range of interest (0 to 70% Al_2O_3). In such a case the determinations will have a minimum variation of about ±10% of the amount present, which may be attributed to reproducibility and reading factors alone. This is to be expected for determinations at the threshold of detection of the fluorescence technique.

The chemical calibration curve for silica (Fig. 4*b*) shows a more definitive slope which results from the detection of a much larger number of counts for each per cent silica in the sample. Both the sensitivity and accuracy of the determination benefit from the improved detection.

The large number of counts recorded in the determination of potassium in silica (Fig. 4*d*) shows that the analysis of this element, and others which are greater in atomic number, lies well within the range of maximum sensitivity and accuracy of the instrument. In simple systems detection of less than 1% K_2O is routine, with an accuracy approaching ±5% of the amount present.

Determinations of iron oxide (Fig. 5*a*), copper (Fig. 5*b*), thorium oxide (Fig. 5*c*), and uranium oxide (Figs. 5*d* and 6*a*) in silica are similarly uncomplicated. The accuracy and sensitivity of the determinations improve with the increase in atomic number, again in response to the larger number of counts detected. Figures 5*c* and 5*d* demonstrate the limitation on this increase in sensitivity. When too many counts are available, the detector becomes saturated and fails to record all of the impulses. The curve tends toward a plateau at the upper end, precluding the accurate analysis of samples containing large amounts of these oxides. This is overcome by decreasing the primary *x*-ray beam intensity, thus decreasing the secondary emission from the specimen, and the number of counts recorded by the detector. Figure 6*a* is a small portion of the uranium oxide calibration curve (Fig. 5*d*), recorded with a different Scale Factor, showing the straight line characteristic of a calibration curve over a limited concentration range.

The influence of the mass absorption coefficient of an alumino-silicate matrix and the effect of interfering elements upon these chemical calibration curves have been established by additional calibration with the set of original analyzed specimens of seven reference clay minerals from the American Petroleum Institute Research Project 49 collection. These specimens include kaolinite, halloysite, montmorillonite, and illite, and cover the principal range of clay minerals previously established for the Marysvale, Utah uranium area (Kerr *et al.*, 1957, p. 60). Table 1 lists the chemical analyses for these reference clay minerals.

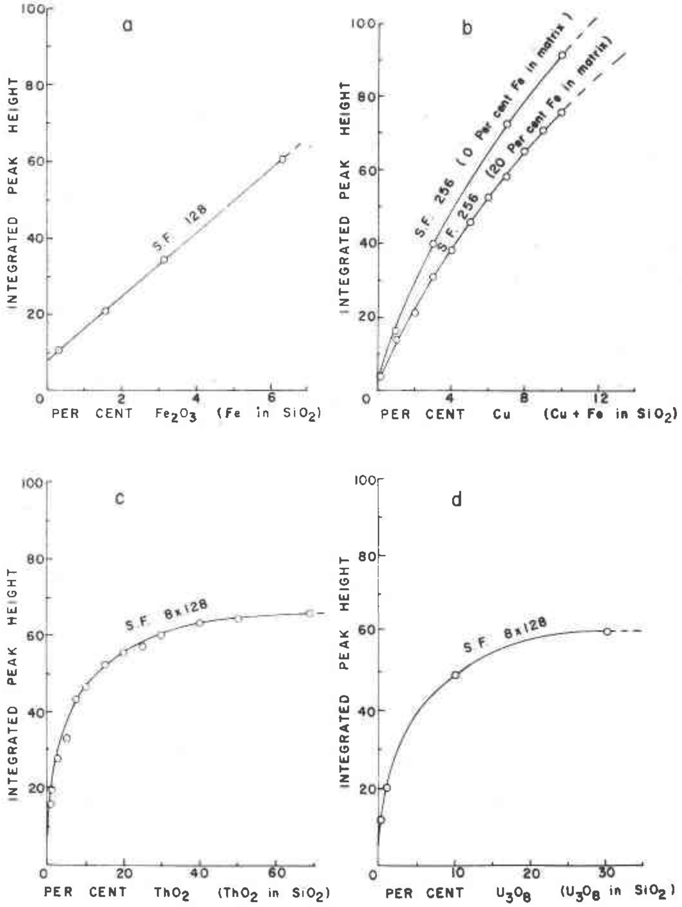


FIG. 5. Chemical calibration curves for mixtures. Weight per cent element or oxide *vs.* integrated peak height.

a) Iron oxide, Fe in SiO_2, scale factor 128.

b) Copper, intensity partly absorbed by iron in matrix, Cu+Fe in SiO_2, scale factor 256.

c) Thorium oxide, saturation of detector is responsible for increasing lack of sensitivity, ThO_2 in SiO_2, scale factor 8×128.

d) Uranium oxide, U_3O_8 in SiO_2, scale factor 8×128.

The curves obtained by plotting the chemical analysis of these standards against the integrated *x*-ray intensity were checked by the *x*-ray spectrochemical analysis of three chemically analyzed specimens of clay and volcanic glass from Marysvale, Utah. These three analyzed specimens were studied in 1953 by Kerr and Hamilton during the previous investigation of vitrophyre ores and alteration in the Central Mining District of the Marysvale Uranium Area. Table 2 shows a comparison of the wet chemical analyses of these Marysvale specimens (by the New Brunswick Laboratory of the U. S. Atomic Energy Commission) and the *x*-ray spectrochemical analyses utilizing the techniques outlined in this study. The agreement between the conventional chemical and *x*-ray spectrochemical analyses was sufficient to encourage proceeding to the analysis of unknown specimens of similar composition, on the basis of the reference clay calibration curves and the analyzed Marysvale specimens.

TABLE 1. CHEMICAL ANALYSES FOR AMERICAN PETROLEUM INSTITUTE REFERENCE CLAY MINERALS*

	Kaolinite		Halloysite	Montmorillonite		Illite	
	API 1a	*API 9a*	*API 13*	*API 19*	*API 23*	*API 35*	*API 36*
	Murfreesboro Ark.	Mesa Alta N. M.	Eureka Utah	Polkville Miss.	Chambers Ariz.	Fithian Ill.	Morris Ill.
SiO_2	45.47%	46.07%	43.98%	50.95%	49.91%	56.91%	57.41%
Al_2O_3	38.84	38.07	38.46	16.54	17.20	18.50	17.96
Fe_2O_3	.19	.33	—	1.36	2.17	4.99	4.99
FeO	—	—	.03	.26	.26	.26	.26
MgO	.17	.01	Trace	4.65	3.45	2.07	2.25
CaO	.24	.38	.32	2.26	2.31	1.59	.64
Na_2O	.24	.27	.14	.17	.14	.43	.15
K_2O	.42	.43	.48	.47	.28	5.10	5.75
H_2O^+	13.66	13.47	14.59	8.28	7.70	5.98	6.70
H_2O^-	.71	.43	2.58	15.01	15.77	2.86	2.97
TiO_2	.86	.50	.01	.32	.24	.81	.82
MnO_2	—	—		.01	.04		
SO_3		Trace					
C		—		.01	Trace		
LiO_2					—		
Impurities	2.81	3.61	7.1				
Absorbed H_2O	.70	.44	2.56				
Total	100.81	99.96	100.59	100.28	99.47	99.50	99.90

* Kerr *et al.*, 1950, Report No. 7, pp. 43, 45, 49, 52, 53, 57.

Table 2. Comparison of Wet Chemical and *X*-ray Spectrochemical Analyses of Three Marysvale, Utah, Standard Clay and Glass Specimens[1]

	Wet Chemical Analysis			*X*-ray Spectrochemical Analysis		
Per cent oxide	Brown glass[2]	Pink clay[3]	Green clay[4]	Brown glass	Pink clay	Green clay
C						
F						
Na	1.88	1.52	.45			
Mg	.32	1.59	3.62			
Al	11.54	14.33	20.24	10.1	15.6	21.9
Si	63.60	56.39	56.02	(65)	(55)	(61)
P						
S	.98	.25	.12	.87	.32	1.20
Cl						
K	3.79	1.09	2.17	3.6	1.5	1.6
Ca	1.76	1.83	.61	1.78	—[5]	.59
Ti	.07	.10	.14	.07	.13	.19
V						
Mn	.05	.02	.02	.04	.03	.02
Fe[6]	5.088	8.061	3.566	(.6)	(3.65)	(1.3)
Cu	.01	.01	.01	.01	.01	.01
Sr						
Mo	.29	.69	.09	.1	.7	.4
Ba						
Pb	.01	.01	.01	.01	.01	.005
U	.42	.02	.02	.02	.02	.02

Semiquantitative data are given in parentheses.

[1] Analyses by New Brunswick Laboratory, U.S. Atomic Energy Commission.

[2] Sample 600-11, brown glass from vitrophyre dike, Bullion Monarch Mine.

[3] Pink clay alteration from same dike.

[4] Greenish clay from same dike.

[5] No determination.

[6] Iron oxides converted to total Fe_2O_3.

On the final calibration curves, the points representing the Marysvale specimens are shown as closed circles.

When the nature of the instrument response to chemical mixtures was considered established by the chemical calibration curves discussed above, preparation of such chemical standards was discontinued. For the final calibration of calcium oxide (Fig. 6*b*), titanium oxide (Fig. 6*c*), and manganese oxide (Fig. 6*d*), the curves obtained from reference clay minerals and checked with the analyzed Marysvale standards were considered sufficient.

For those specimens which had been initially calibrated through the use of standard sets of chemical mixtures, a final calibration was also performed. In these instances, the calibration curves of the chemical mixtures and the reference clay minerals show the same slope for the same element. The displacement that may be noted is caused solely by

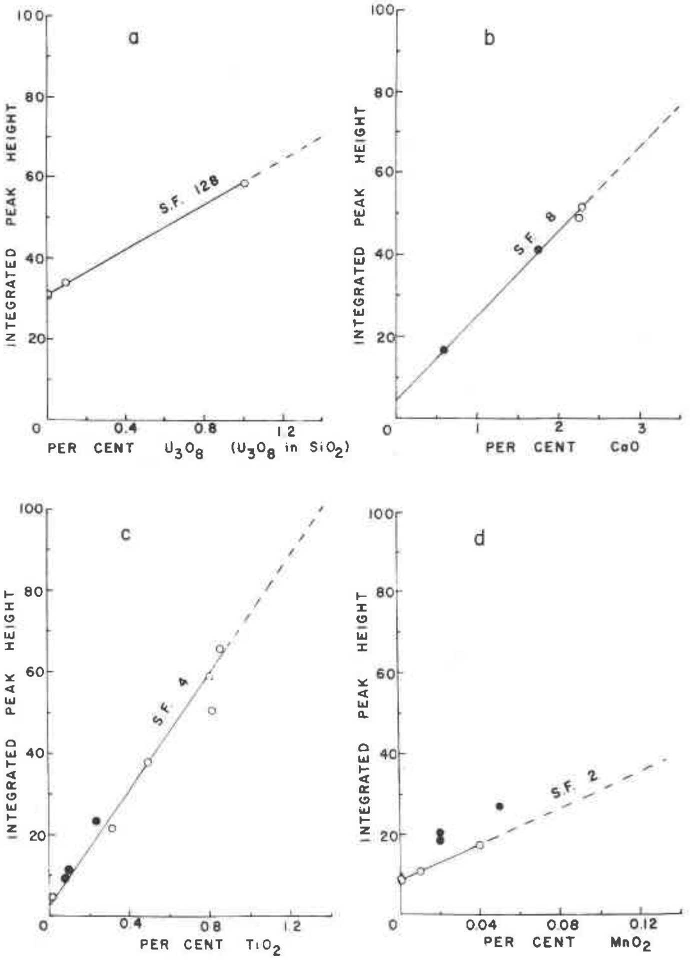


FIG. 6*a*. Chemical calibration curve for a mixture. Weight per cent oxide *vs*. integrated peak height.

a) Uranium oxide, 0 to 1.4 per cent, illustrating the linear character of a short portion of a calibration curve, U_3O_8 in SiO_2, scale factor 128.

6*b*–6*d*. Clay matrix calibration curves. Points represent analyses in Tables 1 and 2.

b) Calcium oxide, scale factor 8.

c) Titalium oxide, scale factor 4.

d) Manganese oxide, scale factor 2.

the difference in mass absorption coefficient between the matrices of the two materials.

Final calibration for aluminum oxide (Fig. 7*a*) met with the same limitations encountered in the initial calibration. At the threshold of detection, the determination of aluminum would be aided by substitution of coarser collimation for the standard nickel foil system. Pulse amplitude discrimination for aluminum radiation would reject most of the increased interference encountered with the coarse collimation, and would result in an appreciably increased signal-to-background ratio. While the selection of chemical standards (Fig. 4*c*) permitted control over the desired range of analyses, the close similarity in aluminum oxide content of the A.P.I. clay specimens (Table 1) and Marysvale standards (Table 2) precluded similar control during the final calibration. Despite the encouraging comparison of the aluminum oxide determinations in Table 2, calibration for aluminum is only slightly better than semi-quantitative, in view of the small number of counts recorded and the poor control afforded by the reference clay standards.

Determination of potassium oxide in the range of interest (0 to 7%) was more successful, as the final calibration curve (Fig. 7*b*) shows.

In the case of the calibration of silica and iron oxide, Figs. 7*c* and 7*d* respectively, the presence of interfering elements caused the displacement of points above and below the calibration curves. This is caused by the enhancement and absorption of the initial radiation. The effect of such emission absorption is seen in Fig. 5*b*, in which the addition of iron to a set of copper standards resulted in the downward displacement of the emission intensities, caused by selective absorption of copper radiation by iron.

Such inter-element interferences may be ascertained from Fig. 8, where the absorption edges and emissions arising from elements encountered in this study have been plotted. The overlap of the emission of copper (Cu $K\alpha_1$, 1.540 Å) and the absorption edge of iron (Fe K_{AB}, 1.740 Å) accounts for the downward displacement of emission intensities encountered in Fig. 5*b*.

A similar displacement is seen in the calibration curve for silica (Fig. 7*c*), and is interpreted as the absorption of silicon emission (Si $K\alpha_1$, 7.125 Å) by aluminum (Al K_{AB}, 7.99 Å). The grouping of the points in the silica plot reflects the aluminum content of the specimens. From left to right the points represent: the first group of three—kaolinites and halloysite; the first pair—montmorillonites; second pair—Marysvale dike clays; third pair—illites; and the last point—Marysvale dike glass. Empirical correction of peak intensities for the amount of interfering aluminum in the specimens is afforded by the correction curve seen on

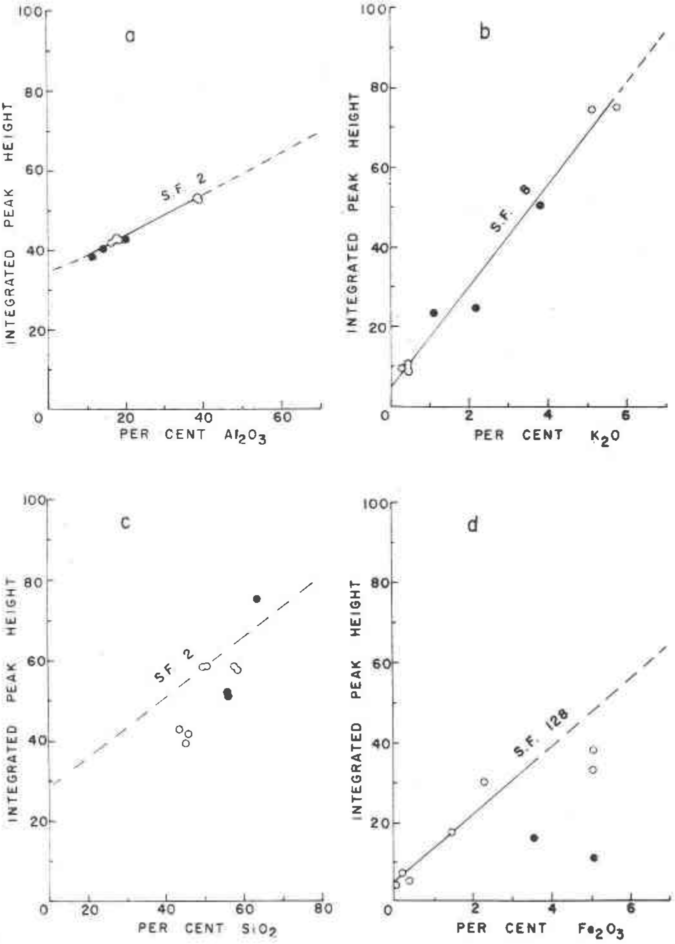


FIG. 7*a*–7*b*. Clay matrix calibration curves. Points represent analyses in Tables 1 and 2.
a) Aluminum oxide, scale factor 2.
b) Potassium oxide, scale factor 8.
7*c*–7*d*. Uncorrected calibration curves. Points represent analyses in Tables 1 and 2.
c) Silica, scale factor 2.
d) Iron oxide, converted to total Fe_2O_3, scale factor 128.

the lower right side of Fig. 9. Application of the correction factor from this plot to the points in Fig. 7*c* results in the corrected per cent SiO_2 final calibration curve of Fig. 9.

A similar grouping of points is not apparent in the calibration curve of iron (Fig. 7*d*). The displacements observed in this plot result from the combined effects of enhancement and absorption. Emission enhancement of Fe radiation by Sr and competitive absorption by Mn are possible, in addition to emission absorption, by traces of V and Cr. In the absence of determinations for Sr, V and Cr from the reference clay minerals, a similar correction could not be established. However, the points from specimens high in Mn are displaced downward, and those high in Ca are displaced upward. The geochemistry of Sr indicates that it is admitted into the structure of Ca minerals in place of the larger radius Ca ion. Strontium would therefore be expected to increase in specimens high in Ca. Indeed, the uncalibrated spectrochemical determinations for Sr in the reference clay minerals show an increase in Sr emission intensity for those specimens high in Ca.

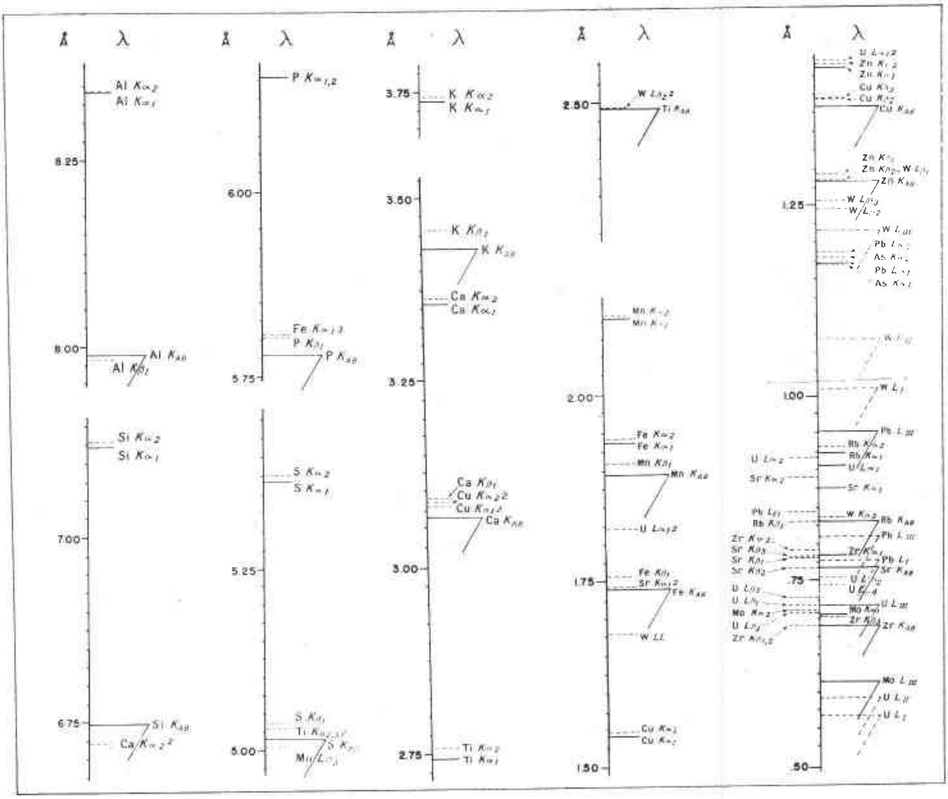


FIG. 8. Plot of inter-element interferences.* The elements chosen are encountered in the x-ray spectrochemical analysis of clay minerals and volcanic glass. The notation used is the following: Cu $K_{\alpha 1}$ represents the alpha 1 emission of the first order of the K series of copper, while Mo L_{III} represents the III absorption edge of the L series of molybdenum.

* Compiled from Fine and Hendee (1954) and Powers (1957).

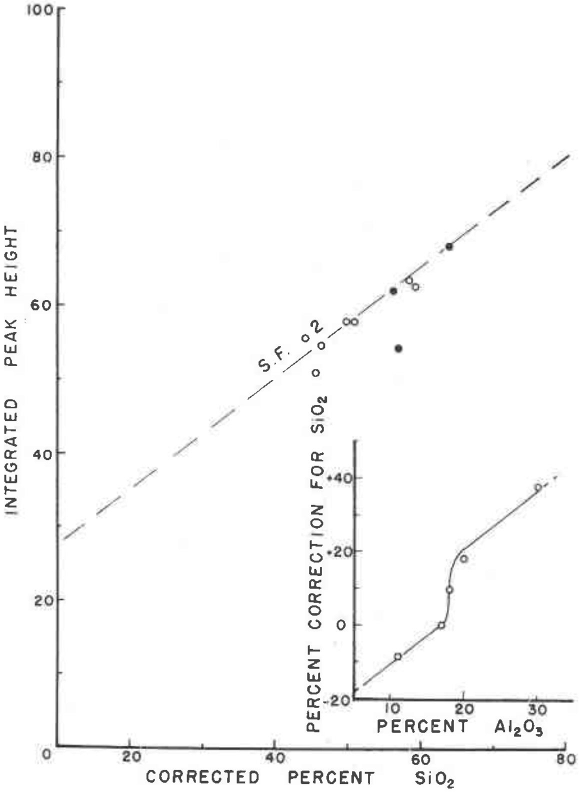


FIG. 9. Clay matrix calibration curve for silica, and correction curve for aluminum interference. Per cent SiO_2 *vs.* integrated peak height, scale factor 2, reference clay minerals. Points represent SiO_2 analyses in Tables 1 and 2, corrected for aluminum absorption.

EVALUATION OF *X*-RAY SPECTROCHEMICAL ANALYSES

Several conventional chemical analyses of clay and glass specimens (Table 2), when compared with *x*-ray spectrochemical analyses, suggest limitations of the *x*-ray method as well as useful applications. Aside from determinations of Na and Mg which lie beyond the present detection range of the *x*-ray spectrograph, some form of analysis was possible for all elements reported.

Determinations for Ca, Ti, Cu and Pb appear reliable, and show a range in minimum sensitivity from 0.01 to 1% in this study. Such determinations would be considered quantitative in accuracy for the purpose of this paper.

S, K, Mo and U analyses showed similar sensitivity to small amounts, but contained a somewhat larger margin of error. These determinations would be considered approximately quantitative in accuracy.

The figures for Al were consistently low by about 10% of the amount present, and those of Mn consistently high by about 50% of the amount present. This indicates a somewhat different mass absorption coefficient for these elements in the Marysvale specimens, in contrast to the reference clay minerals. The calibration curves were therefore corrected by this amount prior to the analysis of the unknown Marysvale samples. These analyses are also considered approximately quantitative. Further study of matrix conditions would probably result in improved analyses for Al and Mn.

Inconsistencies in the analyses of Si and Fe have been discussed. Silicon determinations have been corrected for aluminum absorption, and the figures obtained then lowered by a uniform correction of 10%. The absence of Sr, V, and Cr determinations for the reference clay minerals fails to provide a similar correction for Fe. While the Si analyses are relatively reliable (semi-quantitative in accuracy) those of Fe are unreliable.

X-RAY SPECTROCHEMICAL ANALYSIS OF SPECIMENS FROM THE MT. BELKNAP VOLCANIC SERIES, MARYSVALE, UTAH

The Marysvale, Utah, uranium area (Kerr, Brophy, Dahl, Green and Woolard, 1957) has been under study at intervals by the mineralogy group in the Department of Geology, Columbia University, since the project was begun in 1951 under the auspices of the Division of Raw Materials of the United States Atomic Energy Commission. Initial interest in the association of uranium mineralization and extensive vulcanism has recently become focused on the relation of the mineralization and alteration to glassy dikes which penetrate the uranium mining area (Kerr *et al.*, 1957, pp. 47–48). These glassy dikes are of Late Tertiary age and form part of the Mt. Belknap Series of tuffs, glasses and rhyolites. A study of the Mt. Belknap volcanics in the Tushar Mountains adjoining the area mapped by Kerr *et al.* was begun in 1958. In connection with this work a considerable suite of specimens has been collected, in order to apply *x*-ray spectrochemical analysis to the interpretation of the volcanic sequence, to study the chemical nature of the rock, and to examine the alteration types.

Several factors have served to facilitate this study. Much data have already been established on the compositional nature of the volcanics as well as the mineralization and the alteration (Kerr *et al.*, 1957). Clay minerals and volcanic glass are known to comprise the bulk of the rock suite collected. Hence the *x*-ray spectrograph has been calibrated for the clay-glass compositional range with a set of clay mineral standards

(Kerr *et al.*, 1950), and analyzed clays and glass from the Marysvale area. Standard preparation procedure of samples and standards minimizes differences of a physical nature. Complete scans were made of each specimen in both the light and normal element range (Z=12 to 102) to insure that the effect of inter-element interferences could be considered for each element under analysis. Among the 42 samples studied Al, Si, P, S, K, Ca, Sc, Ti, Mn, Fe, Cu, Zn, Rb, Sr, Zr, Th, and U were found to be significant, and the spectrograph was calibrated for either a quantitative or semi-quantitative determination of each of these elements. The 70 elements which are not reported were either entirely absent, or present in amounts below the minimum sensitivity of the instrument.

Discussion of the analyses of the Marysvale rock suites is limited in the present study to salient points, or to features which are consistent throughout the analyses. A more detailed investigation of minor points which are established by the analyses is planned, and will include a mineralogical study by *x*-ray diffraction, differential thermal, and optical techniques.

Examination of the spectrochemical analyses of the clay specimens (Tables 3A and 3B) shows high Al, Ti, and Fe, occasionally high Ca, low P, and extremely variable Si. These clays were collected from altera-

TABLE 3. CLAY SPECIMENS; MT. BELKNAP VOLCANIC SERIES, MARYSVALE, UTAH

A. Description

M1	Alteration, clay, Beaver Canyon.
M5	Alteration, clay, Phillips 66 tunnel, Beaver Canyon.
M6	Alteration, hematitic clay, Beaver Canyon.
M7	Alteration, clay, Beaver Canyon.
M14	Alteration, hematitic clay, Beaver Canyon.
M15	Alteration, hematitic clay, Beaver Canyon.

*B. X-ray Spectrochemical Analysis**

	Al	Si	K	Ca	Ti	Mn	Fe	Cu	Additional Determinations	Trace
M1	19.8	(66)	5.6	.31	.12	.04	(.7)	.01		P, Rb, Zr
M5	17.9	(62)	5.0	.33	.16	.15	(1.2)	.01		Rb
M6	16.9	(60)	.95	.96	.90	—	(5.7)	.01	1.0 S	Sr
M7	19.3	(37)	4.3	3.2	.76	.08	(6.4)	—		Cr, Rb, Pb
M14	24.2	(58)	5.5	2.8	.82	.02	(5.2)	—		Rb, Sr
M15	22.3	(68)	3.9	.30	.11	.02	(.6)	.01		V, Rb

* In per cent oxide, total iron oxides reported as Fe_2O_3.

TABLE 4. TUFF SPECIMENS; MT. BELKNAP VOLCANIC SERIES, MARYSVALE, UTAH

A. Description

M3	Lithophysae and tuff, Beaver Canyon.
M4	Tuff, slightly radioactive, Nallick claim, Mt. Barrette.
M9	Altered tuff, Beaver Canyon.
M10	Tuff, summit of Gold Mt.
M11	Laminated, weathered tuff, Beaver Canyon.
M13	Columnar welded tuff, Beaver Canyon.
M17	Fragmental tuff, Beaver Canyon.
M19	Joe Lott tuff, upper columnar section, Sam Stowe Canyon.
M20	Joe Lott tuff, dark brown fragmental section, Sam Stowe Canyon.
M31	Fragmental red tuff, south of V.C.A. mine, Marysvale Valley.
M34	Bleached tuff, Beaver Canyon.
M35	Vesicular tuff, Beaver Canyon.
M36	Fragmental tuff, Beaver Canyon.
M41	Red fragmental tuff, Beaver Canyon.

*B. X-ray Spectrochemical Analysis**

	Al	Si	K	Ca	Ti	Mn	Fe	Cu	Additional Determinations	Trace
M3	17.9	(69)	4.9	.30	.17	.08	(1.2)	.01		P, V, Zn, Rb, Zr, Pb
M4	15.1	(68)	5.2	.30	.15	—	(.7)	.01		P, Rb, Zr
M9	20.2	(67)	5.4	.27	.14	—	(.7)	.01		Rb, Zr, Pb
M10	19.2	(72)	4.6	.28	.10	.03	(.2)	.01		Rb
M11	17.8	(70)	6.9	.29	.07	—	(.3)	.01		Rb
M13	13.5	(68)	4.9	.31	.17	—	(.4)	.01		Rb
M17	19.6	(71)	5.1	1.77	.07	.03	(.4)	.01		P, Rb
M19	21.1	(71)	4.3	1.12	.09	.04	(.5)	.01		P, Rb
M20	17.7	(76)	4.5	.71	.08	.03	(.4)	.01		Rb
M31	13.7	(68)	4.4	.68	.09	.07	(.7)	.01		Rb
M34	9.9	(71)	4.7	.27	.14	—	(.6)	.01		P, Rb, Sc
M35	21.0	(69)	4.5	.32	.14	.01	(.8)	.01		Cr, Rb
M36	15.9	(71)	4.7	.28	.01	.02	(.6)	.01		P, Rb
M41	13.1	(68)	4.7	.31	.13	.03	(.9)	.01		Rb, Th

* In per cent oxide, total iron oxides reported as Fe_2O_3.

tion zones, which in the Mt. Belknap Series are localized about fracture systems.

Analyses of the tuff samples (Tables 4A and 4B) are characterized by low Mn, S and Fe, together with consistently high K and a complete absence of Sr. The latter indicates a distinction between the tuffs and local glassy dikes which are high in Sr. Although the glassy dikes and the tuff are closely associated, the spectrochemical data indicate that the dikes were not the source of the major tuff accumulations, which attain a thickness of 3,000 feet in places. Recent field evidence supports this conclusion, indicating that the source of the tuffs was considerably removed from the Marysvale area. In general, the tuff specimens, with their expected homogeneity, are quite similar in spectrochemical analysis, far more so than any other group.

The volcanic glass specimens (Tables 5A and 5B) were among the most interesting examined, both in view of their field occurrence and analyses. The specimens included examples of surficial flow glass and intrusive dike glass, ranging in color from jet black to light brown, and in appearance from obsidian to perlite. Analysis shows frequent traces of strontium and phosphorus, and also distinguishes the dike glasses from the flows. The former (M25 and M29) are lower in K and at the same time higher in Ca, and are thus set apart from the others which are all flow glasses. Field relationships indicate that the glassy flows are

TABLE 5. GLASS SPECIMENS; MT. BELKNAP VOLCANIC SERIES, MARYSVALE, UTAH

A. Description

M22	Gray glass, Deer Creek Canyon.
M23	Gray glass, Teacup Structure (vent), Marysvale Valley.
M24	Black glass, Beaver Hill.
M25	Brown glass from dike, Beaver Canyon.
M26	Gray glass, Beaver Canyon.
M27	Isoclinally folded gray glass, Gray Hills.
M28	Glass from fault zone at mouth of Beaver Creek.
M29	Brown glass from dike, 300 foot level, Prospector mine.
M30	Black glass from Black Knob, Marysvale Valley.

*B. X-ray Spectrochemical Analysis**

	Al	Si	K	Ca	Ti	Mn	Fe	Cu	Additional Determinations	Trace
M22	19.7	(68)	4.3	.62	.09	.05	(.4)	.01		P, Rb, Sr
M23	16.9	(69)	3.5	.97	.20	.03	(1.1)	.01		P, Sr
M24	19.0	(67)	4.7	.37	.13	.06	(.7)	.01		Rb
M25	14.6	(69)	2.1	1.77	.09	.07	(.7)	.01		P, Rb, Sr
M26	19.8	(63)	4.2	1.06	.27	.04	(1.2)	.01		Rb, Sr, Zr
M27	16.0	(68)	4.3	.32	.10	.06	(.8)	.01		P, Rb, Zr
M28	16.5	(75)	4.9	.35	.08	.05	(.6)	.01		P, Rb, Sr, U
M29	17.4	(75)	2.5	1.88	.07	.05	(.5)	.01		V, Rb, Sr, Zr, Pb
M30	14.2	(75)	4.6	.33	.07	.05	(.7)	.01		P, Cr, Rb

* In per cent oxide, total iron oxides reported as Fe_2O_3.

part of the valley sequence of rhyolites and tuffs, associated with local vent structures. The glassy dikes, while also common in the valley area, show a closer relation to both the high mountain tuff sequences and the period of regional mineralization.

As has been pointed out, the rhyolites (Tables 6A and 6B) of the Marysvale area are principally associated with local valley vents. These are the red rhyolites of the lower volcanic sequence, and must be distinguished from the gray rhyolite specimens (M8, M37 and M38) of the upper, high mountain sequence. These gray specimens, as indicated by their characteristic contorted flow-folding, flowed along a regional slope from their original area of deposition in the high mountain region down into the valleys below, building up into a great thickness. A gray flow (M18) from a valley vent structure unrelated to the upper volcanic

TABLE 6. RHYOLITE SPECIMENS; MT. BELKNAP VOLCANIC SERIES, MARYSVALE, UTAH

A. Description

M8	Dense gray flow, Beaver Canyon.
M16	Layered rhyolite from intrusive core, Marysvale Valley.
M18	Gray rhyolite from Teacup Structure (vent), Marysvale Valley.
M21	Red rhyolite, Deer Creek Canyon.
M32	Red rhyolite porphyry, south of V.C.A. mine, Marysvale Valley.
M33	Flow-banded rhyolite, Beaver Canyon.
M37	Flow-banded gray rhyolite, Beaver Canyon.
M38	Gray rhyolite capping, summit of Mt. Belknap.
M40	Red rhyolite, Dome Hill.
M42	Red rhyolite porphyry, Beaver Canyon.

*B. X-ray Spectrochemical Analysis**

	Al	Si	K	Ca	Ti	Mn	Fe	Cu	Additional Determinations	Trace
M8	16.5	(75)	5.4	.26	.10	—	(1.0)	.01		P, Rb, Zr
M16	22.1	(68)	5.6	1.9	.09	.06	(.5)	.01		Rb, Zr
M18	18.0	(63)	3.5	1.02	.90	—	(.2)	.01	6.0 S	Sr
M21	20.1	(72)	3.2	1.18	.09	.06	(.6)	.01		Zn
M32	13.3	(67)	4.7	.36	.11	.04	(.7)	.01		P, Rb
M33	11.3	(63)	6.1	.29	.14	—	(.6)	.01		V, Rb, Cr
M37	16.4	(74)	4.4	.31	.11	.04	(.7)	.01		P, Rb
M38	17.3	(77)	4.6	.32	.12	.01	(.6)	.01		P, Rb
M40	12.6	(63)	4.5	1.37	.09	—	(.6)	.01		Rb
M42	19.6	(73)	5.1	.36	.29	.04	(1.2)	.01		P, Rb

* In per cent oxide, total iron oxides reported as Fe_2O_3.

sequence is distinguished from three other gray rhyolites (M8, M37, and M38) by lower Si and exceptionally high S content. The analyses underline the variability among the rhyolites, which as a group are less homogeneous than any of the others.

Specimens of uranium mineralization, silica and carbonate alteration (Tables 7A and 7B) are sharply distinguished from the normal rock types by spectrochemical analysis. All show a trace of scandium, which, with the exception of a hydrothermally bleached tuff (M34) is found only in specimens associated with mineralization and alteration. Similarly, the uranium ore is unusually high in Fe, Ca, S and U, and low in Al, Si, K, Ti and Rb. M12 represents a zone of silica enrichment surrounding a glassy dike (M25) characterized by 2 to 3 inch lithophysae imbedded in a ground-mass of pink and white perlite and green clay. The lithophysae were almost pure silica, and often showed a central cavity lined with small quartz crystals. Analysis of this material is high in silica, and low in iron, potassium and titanium. Otherwise the composition resembles the tuff specimen (M3) into which this altered material intergrades.

Finally, there is a constant trace of rubidium, copper and titanium in all specimen types.

CONCLUSIONS

The observed sensitivity of *x*-ray spectrochemical analysis in the case of minor amounts of P, S, Sc, Ti, Mn, Cu, Zn, Rb, Sr, Zr, Mo, Pb, Th, and

TABLE 7. OTHER SPECIMENS; MT. BELKNAP VOLCANIC SERIES, MARYSVALE, UTAH

A. Description

M2	Mineralization, uranium ore, Phillips 66 claims, Beaver Canyon.
M12	Alteration, silica nodule from dike, Beaver Canyon.
M39	White alteration, effervescent coating, Beaver Canyon.

*B. X-ray Spectrochemical Analysis**

	Al	Si	K	Ca	Ti	Mn	Fe	Cu	Additional Determinations	Trace
M2	7.8	(5)	.95	9.1+	.02	—	(2.7)	—	.68 S 10.1 U	P, V, Zn, Pb, Sc
M12	15.5	(73)	3.5	.28	.05	.02	(.2)	.01		P, Rb, Sc
M39	6.8	(18)	2.1	21.6+	—	.01	—	—		P, Sr, Sc

* In per cent oxide, total iron oxides reported as Fe_2O_3.

U holds promise for the ultimate quantitative detection of these elements by the *x*-ray spectrographic technique.

Approximate quantitative sensitivity has been developed in complex alumino-silicate systems for K, Ca, Ti, Mn, Cu, Mo, Th, and U in the range from .01 to 10 per cent oxide by weight.

Somewhat larger amounts of Al, Si, and Fe oxides are easily detected, but gross matrix absorption and interelement interferences provide serious problems for precise quantitative analysis. These important elements appear limited at present to semi-quantitative determination, thus restricting conclusions that might otherwise be drawn.

The semi-quantitative analyses for P, S, Sc, V, Cr, Zn, As, Rb, Sr, Zr, and Pb indicate that calibration of the instrument for quantitative determination of these elements should be attempted. For such calibration, a set of previously analyzed standards must be available.

With a capacity for a large number of approximate quantitative determinations, the *x*-ray spectrograph provides a useful supplement for conventional chemical analysis. However, for many determinations where quantitative accuracy is essential, the customary chemical method is preferred. The application of *x*-ray spectrochemical analysis to an increasing number of quantitative determinations shows that further improvement of the method may provide much data now obtained by conventional analyses.

The general uniformity of analyses from the Marysvale specimens emphasizes the homogeneity of the magma which supplied the complex of tuffs, glasses and rhyolites which blanket the region. The analyses also indicate that chemical data may be conveniently assembled with an *x*-ray spectrograph controlled by standards. Several significant relationships are shown by the spectrochemical data: (1) enrichment of Fe, Ti, Al and Ca, and depletion of P in clay alteration zones which follow fracture systems; (2) the chemical distinction between the tuffs and local glassy dikes which might have served as feeder vents; (3) the unusual homogeneity of the tuff specimens; (4) a distinction in K-Ca ratio between flow and dike glasses, indicating that these particular dikes were not feeders for the flow glasses; (5) separation of the red rhyolites of the lower, valley sequence, from the gray rhyolites associated with the tuffs of the upper, high mountain sequence; (6) and finally, the sharp chemical distinction between the carbonate-silica-uranium mineralization and the normal rock types of the Marysvale region.

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