

CONTRIBUTED PAPERS

ANALYSIS OF ROCKS USING X-RAY FLUORESCENCE SPECTROMETRY

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Introduction

The chemical compositions of rocks are used to solve numerous geological problems, including crystallization history of igneous bodies such as granite or basalt, processes of formation of the sea floor, nature of chemical weathering in various climates, stratigraphic correlation of sedimentary and volcanic rocks, processes of ore generation, and many others. Most rocks are composed primarily of silicate minerals, and over 90% of the composition of most silicate rocks can be characterized by oxides of Si, Ti, Al, Fe, Mg, Ca, Na and K. Minor and trace elements present in rocks include practically every other element, many of which are especially useful for geochemical modelling of geological processes.

X-ray fluorescence spectrometry (XRF) is the technique of choice of most petrologists and geochemists to obtain rock analyses. The XRF analytical technique is far superior to older wet-chemical or atomic absorption because it is rapid and does not require extensive training or experience on the part of the analyst. Early XRF analyses were obtained on finely ground rock powder pressed into coherent pellets; samples prepared this way suffered from surface roughness, grain size and mineralogical effects (see below) and frequent breakage. Approximately thirty years ago sample preparation involving solution of the rock in borate glass was introduced [1]. In a series of landmark papers [2], [3], [4] highly reliable and simple procedures for XRF analysis of all rock types were published. The borate fusion method produces homogeneous samples that are easy to handle, can be analysed many times without deterioration, eliminate grain size and mineralogical effects and reduce differences in mass absorption from sample to sample.

Although energy dispersive XRF spectrometry has improved greatly in the last few years, it is still

generally inadequate for most quantitative geological applications, given that light elements ($Z < 14$) constitute over 87% by weight of the earth's crust. Wavelength dispersive spectrometry, although considerably more costly, is necessary for quantitative rock analyses.

Analytical Standards

To ensure reliable analyses and compatibility of data from laboratories around the world agencies such as the United States Geological Survey (USGS) provide rock standards upon request. The USGS igneous rock standards were the first to be made universally available. Names of these original standards are very familiar to petrologists: W-1

Table 1 Accepted compositions of several USGS standards.

	AGV-1	BCR-1	DTS-1	G-2	PCC-1
SiO ₂	59.61	54.53	40.61	69.22	42.10
TiO ₂	1.06	2.26	0.00?	0.48	0.01
Al ₂ O ₃	17.19	13.72	0.25	15.40	0.73
Fe ₂ O ₃	4.56	3.48	1.02?	1.07	2.54?
FeO	2.03	8.96	6.94?	1.44	5.17?
MnO	0.10	0.18	0.12	0.03	0.12
MgO	1.52	3.48	49.80	0.75	43.50
CaO	4.94	6.97	0.14	1.96	0.55
Na ₂ O	4.32	3.30	0.01?	4.06	0.01
K ₂ O	2.92	1.70	0.00	4.46	0.00
H ₂ O ⁺	0.78	0.67	0/42	0.50	4.70
CO ₂	0.02	0.02	0.07	0.08	0.18
P ₂ O ₅	0.51	0.36	0.00?	0.13	0.01
F	0.04	0.05	0.00	0.12	0.00?
S	0.01?	0.04?	0.00?	0.01?	0.01?
others	0.32?	0.27?	0.93?	0.41?	0.76?
Sum	99.93?	99.99?	100.31?	100.12?	100.39?

Data taken from Abbey, 1980, Table 3.

(dolerite), G-2 (granite), DTS-1 (diorite), AGV-1 (andesite), BCR-1 (basalt), PCC-1 (peridotite), and others (Table 1). They have been analysed many times by many different labs around the world and by many different methods. The original USGS standards have been exhausted, but others have been developed to replace them. In addition, the number and type of standards have been increased. Standard rock powders may be obtained free of charge by writing to Dr F. J. Flanagan, U.S. Geological Survey, Reston, Virginia 22092, U.S.A. Other standards are available from agencies in many other countries. Descriptions of these standards, including the best values to date, addresses from which the standards may be obtained, etc. are published [5]. Standards, membership in the Centre de Recherches Petrographiques et Geochimiques (CRPG), and Geostandards Newsletter can be obtained from K. Govindaraju, CRPG, BP #20, 54501 Vandoeuvre-Nancy, Cedex, France. Membership is \$70 per year.

Precision may be high in individual labs, but without comparative information from other labs accuracy cannot be assured. The universally available rock standards ensures accuracy, without analysts having to reproduce analyses from the other labs. This point is important to geologists because rocks are obtained from the field, commonly at great expense and difficulty, and normally are not available to other analysts. In short, if general petrological and geochemical models are to be possible, research geochemists and petrologists must be able to accept analyses of other labs. Furthermore, natural rock standards greatly simplify and speed up reduction of the data. Standards can be selected such that the unknowns and standard are chemically similar (e.g. BCR-1 with basaltic unknowns), insuring comparable mass absorption coefficients (see below).

A further improvement for rapid, accurate analyses are "secondary standard discs" or "monitors" developed by Dr. K. Norrish. The monitors are artificial rocks with precisely known concentrations of various elements, fused into discs using the flux recipe described below [3], [4]. Mass absorption correction coefficients for different X-ray targets are provided with each disc, and provided the unknown samples are prepared by the same method, acceptable analyses can be obtained directly. If the unknowns are prepared with different flux recipes, it is necessary to recalculate the correction coefficients. In all cases, it is recommended that calibration of the monitor be refined by the analyst using a set of natural standards.

The monitor can then be used as the daily standard and the natural standards safely stored. The monitors are stable over long periods and are easy to handle. Secondary standards are available for purchase from ANUTECH Pty Ltd., GPO Box 4, Canberra ACT 2601, Australia.

Elemental Interference during XRF Analysis

Natural rocks consist of several different minerals of highly variable composition and structure. This affects the behavior of X-rays in highly complex ways. These effects translate directly to complexities in interpreting fluorescence radiation that is detected in the XRF spectrometer. The complexities are collectively known as spectral overlap effects and absorption/enhancement effects. The matrix effects on element i are the combination of absorption/enhancement effects and overlap effects exerted on element i , by all coexisting elements j .

Matrix Effects

Matrix effects result from fluorescence radiation being absorbed by coexisting elements (causing reduced intensity), or enhancement of fluorescence radiation due to secondary radiation from coexisting elements (causing increased intensity). In some cases the effects can be effectively eliminated by proper sample preparation (see below), but corrections can be made in any case. The matrix effect of element j on element i depends on the concentration of element j . A matrix correction for each element i can be made for each coexisting element j . The matrix effect of element j on element i can be determined using several "binary" standards composed of various proportions of i and j (e.g. SiO_2 and Al_2O_3). When the intensity of an "i" X-ray is plotted against the known concentration of i , a calibration curve is obtained. The effect of the concentration of j on the intensity of i can then be obtained. This effect can be expressed in a form such as:

$$W_i = U_i(1 + \sum A_{ij} W_j)$$

where

$$U_i = aI + bI + c$$

$$W_i = \text{weight percent of analyte } i$$

$$W_j = \text{weight percent of } j$$

$$A_{ij} = \text{matrix coefficient}$$

$$I = \text{uncorrected X-ray intensity of } i$$

and a , b and c are the calibration constants.

The matrix coefficient is a small fraction which may be positive or negative. In general, every element exerts an effect on all other elements, but some

are more important than others. Even if A_{ij} is small, a large C_j can result in a strong effect on i . In such cases a correction can be made, or a calibration curve can be calculated without the correction. In the latter case the curve is nonlinear. For an absorbing element present in high concentration and subject to large analytical error, it may be better to forego the correction and calculate a nonlinear calibration curve embodying the absorption.

In applying matrix corrections a complication arises from the fact that the sample in the spectrometer is not just rock but rock plus dilutant (see below). The matrix effect of the weighted fraction of the dilutant must be determined and included in the total correction.

Overlap Effects

Overlap effects result from closely spaced spectral lines causing the net intensity to be non-representative of the concentration of the element of interest. The problem is reduced to one of obtaining greatest resolution (line separation) without undue loss of intensity, and can be optimized by proper selection of collimator-crystal combination. For example, an overlap correction may be necessary in cases where 2θ for the K_α line of element i is close to the 2θ for the K_β line of element j . For example, with the LiF (200) crystal, the 2θ for Zr K_α is 22.54. This peak is near the Sr K_β at 22.44 degrees 2θ . So, the Zr concentrations must be corrected for the presence of Sr.

The overlap correction factor, B_{ij} , may be determined in one of two ways. First, if a series of standards, for example Zr and Sr, exist then a calibration curve may be written of the type:

$$W_i = b \cdot I_i + c - B_{ij} w_j$$

where

- W_i = weight percent of analyte i
- $b+c$ = calibration curve constants
- I_i = uncorrected X-ray intensity of i
- W_j = weight percent of overlapping element j
- B_{ij} = overlap correction constant

The second method does not require a series of i and j standards. If one standard of j exists that does not contain any i then a ratio, α , of the intensity of j at the 2θ of i to the intensity of j of a non overlapped peak may be obtained. This gives an overlap correction equation of the type:

$$W_i = b(I_i - \alpha I_j) + c$$

where W_i , I_i , b and c are defined as above

I_j = intensity of non overlapped peak of j

$$A = I'_j / I_j$$

I'_j = intensity of j at 2θ of i

In practice the corrections discussed above are best applied to calibrate a set of rock standards, from which a curve relating apparent concentration to detected counts is derived. In general this line is quadratic, but if all matrix and overlap corrections are made, the correlation should be linear. Moreover, quadratic equations may be considered linear over short intervals, and prudent selection of standards can ensure a linear calibration curve, even if all corrections are not made. The concentration of an element in an unknown is then determined by applying the measured intensity to the calibration curve.

When all corrections are applied, the following expression allows for the calculation of the corrected concentration of element i , W_i :

$$W_i = U_i \{1 + \sum A_{ij} C_j\} + \sum B_{ij} C_j$$

where U_i is the uncorrected concentration of element i .

The Rigaku 3070 system will perform calculations to correct for overlap and matrix effects, by solving the above equation. To take advantage of this feature, the MATRIX GENERATE mode of PARAMETER JOBS is activated. All A_j are entered as small fractions which will apply directly to the weight percents of elements i and all j . These are calculated theoretically, determined experimentally or obtained from published tables [3]. All significant overlap effects are entered as B_{ij} but their numerical values initially set to zero. This array of all A and B entries is given a matrix code number. A matrix code number is entered during setup of group conditions so that whenever that group is run the designated matrix corrections will be used. Many matrix blocks can be built, and 150 entries can be made in each block.

Standards are established by selection of STD. SAMPLE from the PARAMETER JOBS menu. Then concentrations are entered for each element and a group designated to which this standard will apply. Intensities (I) and apparent concentrations (X) are left at zero. Standards are then run as Std. Sample in AUTO ANALYSIS mode, and the intensities are automatically stored. These intensities are automatically updated every time that standard is run as a Std. Sample.

To calculate a calibration curve from a set of established standards, REGRESSION is selected from the JOB MENU, and a group indicated. Under

REGRESSION the (X) CALCULATION & FILE mode is activated. The program determines the apparent concentrations (X) based on the *A* entries in the appropriate matrix block for that group, and files them in the appropriate standard file opposite the most recent intensities. This is a solution of simultaneous equations, hence there must be at least as many standard samples as *A* entries in the block. Under CALIBRATION WITH OVERLAP mode, the program will search the previously filed peak positions for elemental lines that may overlap with the main line of element *i*, and will calculate *B* values which are filed automatically in the matrix block, and which will be applied to the regression curve.

A batch of unknowns is run by simply designating a group while in AUTO ANALYSIS mode. All elements in that group are run and the regression lines for that group are used to determine concentrations in the unknowns.

Sample Preparation for Major Element Analysis

If the above corrections are to be applied to analysis of complex materials such as rocks, sample preparation must be consistent. The rock sample should be of a size and nature to be representative of the rock mass of interest. For fine-grained rocks such as basalt this may be only 400-500 g, but for coarse grained granite it is not unusual to begin with a sample of 10- 15 kg. The entire sample is crushed, in stages if necessary, in a jaw crusher that can be readily cleaned. The crushed rock is split as many times as necessary to obtain an aliquot of approximately 100 ml. This aliquot is pulverized to a powder, at least fine enough to pass through a 200 mesh screen (74 μm opening size). Theoretically the finer the better, but excessive pulverizing can cause serious contamination. Pulverizing can be accomplished with a mill such as the Shatterbox, available from Spex Industries, 3880 Park Ave., Edison, New Jersey, 08820, U. S. A.

It is critical at this point to guard against contamination. During pulverizing there are three major sources of contamination: (i) the analyst's hand, (ii) the previously pulverized sample, and (iii) the crushing container. Contamination from source (i) can be minimized if the rock and crushing container are handled only with plastic gloves. To minimize contamination from source (ii) two 100 ml aliquots of each sample are run separately, and the first aliquot is discarded. Alternatively, a run of pure silica sand can be made between sample runs, to "clean" the container. This may introduce SiO_2 contamination but it

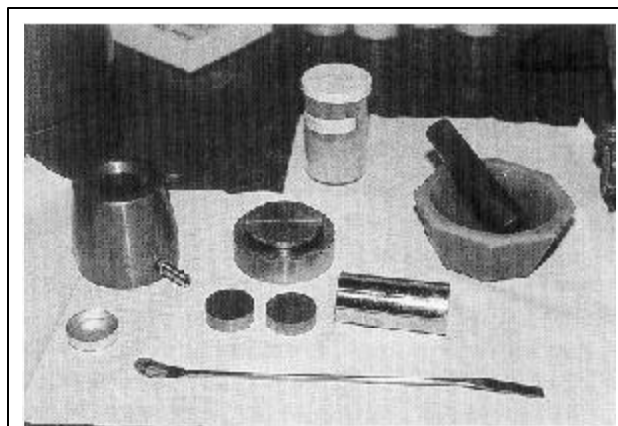


Fig. 1 Apparatus for preparation of pressed powder pellets. Rock powder and binder are mixed in the agate mortar and pestal. The mixture is spooned into a spec cap (lower left) and compressed into the die. The die consists of a cylinder and base, two polished steel pellets and a plunger.

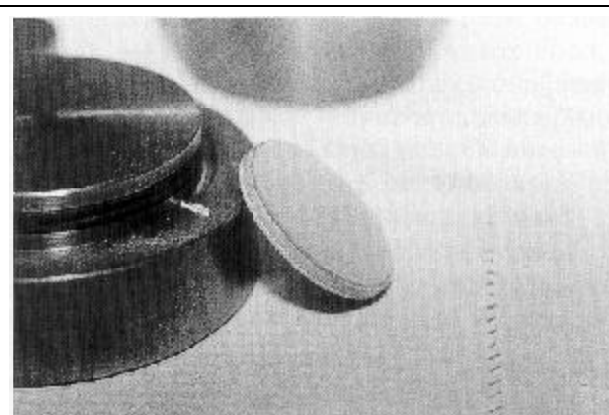


Fig. 2 A properly prepared pressed powder pellet. Final thickness of this pellet is ca. 3 mm.

will normally be a tiny fraction of the total SiO_2 in the rock. Source (iii) cannot be eliminated, but prudent choice of grinding containers can reduce the contamination to elements that are not of great interest. For example, a tungsten carbide container would not be used to pulverise rocks in which W or Co are important to the analyst. Steel containers introduce Fe and Cr errors, ceramic containers cause Si and Al contamination, and agate containers introduce Si contamination. Spex Industries provides data on contamination to be expected from the various grinding containers.

Pressed Powder Pellets

The finely ground rock powder, mixed with a small amount of polyvinyl alcohol dissolved in water, or a small amount of dry cellulose (or other suitable non contaminating binder) can be compressed using a hydraulic press into a coherent briquette or pellet. To

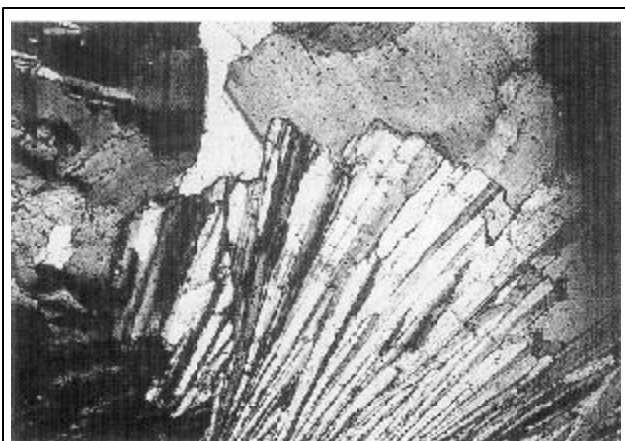


Fig. 3 Thin section photomicrograph of a cluster of chloritoid blades extending into matted chlorite. Although similar in composition, chloritoid and chlorite treat X-rays differently.

enhance sample strength further and facilitate handling, the pellet must be pressed in a thin aluminum container (spec cap) or using crystalline boric acid or cellulose as a backing and rim material [6]. The rock powder is thoroughly mixed in known proportion with the binder, and spooned into a spec cap (Fig. 1). The cap is sandwiched between two stainless steel or tungsten carbide pellets, and the sandwich is compressed in a die at 10 to 30 tons/sq. in. for 2-3 minutes. Pressure is released slowly. Too low pressure or too little time will not produce a coherent pellet, and too high pressure will cause cracking. The optimum combination of binder, pressure and time is determined by trial and error. A properly prepared pellet is shown in Fig. 2.

Pressed powder pellets may be suitable for analysis of heavy elements, but for light elements such Si, Al, Na and Mg these pellets are unsuitable. First, the way in which element *j* interacts with element *i* depends upon the minerals in which the elements reside. For example, Fig. 3 shows radiating blades of chloritoid extending into matted chlorite. Both chloritoid and chlorite are composed primarily of Fe, Mg, Mn, Al, Si and O. But the behavior of these elements in the two minerals is different; hence, the *bulk* absorption effects for the sample cannot routinely apply. This is the mineralogical effect.

Second, attenuation of the fluorescence X-rays emitted by light elements is virtually complete only a short distance below the sample surface. This critical depth of penetration has been determined for the K_{α} line of various elements using USGS standard AVG-1, some of which follow: Na 5 μm , Si 13 μm , Ca 36 μm , Fe 180 μm , Rb 900 μm , La 10600 μm [7]. In-

Table 2 Weight percents of elements in clinopyroxene and plagioclase.

Clinopyroxene	$\text{CaMgSi}_2\text{O}_6$	Plagioclase	$\text{CaNaAl}_{1.5}\text{Si}_{2.5}\text{O}_8$
Ca	18.51%	Ca	13.28%
Mg	11.23%	Na	7.62%
Si	25.94%	Al	13.41%
O	44.32%	Si	23.27%
		O	42.47%

spection shows that analysis of light elements is dominated by the uppermost layer of sample. In the case of a typical 31.5 mm diameter pellet with a sample depth of 4 mm, the critical penetration depth for Na and Si are respectively only 0.12 % and 0.3 % of the sample mass. These cannot be routinely representative of the bulk sample [7].

For example, consider a simplified basalt consisting of 60% clinopyroxene of composition $\text{CaMgSi}_2\text{O}_6$ and 40% plagioclase feldspar of composition $\text{CaNaAl}_{1.5}\text{Si}_{2.5}\text{O}_8$, that we wish to analyse for SiO_2 using Si K_{α} . Shown in Table 1 are the weight percents of elements in each phase and the absorption coefficients for each element on Si K_{α} light [8]. The absorption coefficients for clinopyroxene (CPX) and plagioclase (PL) are the weighted sums of the constituent elements:

$$\text{CPX: } (0.185)(1086) + (0.112)(2824) + (0.259)(327) + (0.443)(965) = 1029$$

$$\text{PL: } (0.133)(1086) + (0.076)(2168) + (0.134)(3493) + (0.233)(327) + (0.424)(965) = 1263$$

The mass absorption coefficient of the rock is the weighted sum of the coefficients of clinopyroxene and plagioclase, namely $0.6 \times 1029 + 0.4 \times 1263 = 1123$. But the grain size of pulverized rock is not strictly uniform, and even finely powdered rock (< 250 mesh) will have the majority of grains much larger than 13 μm [7]. Hence the likelihood of the topmost 13 μm of the pressed powder pellet having clinopyroxene and plagioclase in a 6:4 ratio is low, and the rock mass being analysed would not represent the total rock. This is the grain size effect. Therefore, the calculated mass absorption coefficient for this rock would not strictly apply to the pellet being analysed.

Fused Discs

Properly prepared fused discs are superior to pressed powder pellets for two major reasons. First, fusion destroys the mineral grains and their structures, thus distributing constituent elements homogeneously throughout the mass and eliminating the

grainsize effect and mineralogical effect on mass absorption. Second, dilution greatly reduces errors introduced by mass absorption. The glass discs are prepared in a number of different ways, all of which are basically similar, involving borate glass as a flux. Most mixtures also include other compounds to act as a (i) heavy absorber (further reducing mass absorption effects), (ii) oxidiser to prevent alloying with the crucibles, and (iii) a compound to reduce the surface tension of the melt. The mixture is fused in a crucible of 95% Pt 5% Au at approximately 950° to 1200°C for 10 to 20 minutes to form a homogeneous melt. This may be accomplished in a muffle furnace or on an open blast burner, and stirring may be necessary.

The homogeneous melt is poured into a preheated mold to chill to a thick glass disc, or onto a preheated platen of graphite or duralumin where it is immediately pressed into a thin glass disc using a preheated plunger. The glass discs are allowed to cool slowly to room temperature in a desiccating jar. Cooling rates are critical: if cooled too slowly microcrystals will form, and if cooled too rapidly the disc will crack. Poorly formed discs can be remelted and the process repeated. Pt-Au crucibles and molds are available from Engelhard Corporation, 70 Wood Ave. South, CN 770, Iselin, New Jersey 08830, U.S.A. The hotplate-plunger apparatus is available from Sietronics, Pty Ltd., P.O. Box 521, Fyshwick, ACT 2609, Australia.

The specific fluxing material and proportions used are apparently as varied as the number of labs. Numerous variations of the basic technique are described in detail in [7]. The following method [3], [4] is probably the most widely used. In this method, first the flux is prepared by fusing a mixture of 47% dilithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$), 36.7% lithium carbonate (Li_2CO_3), and 16.3% lanthanum oxide (La_2O_3) (heavy absorber). The melt is chilled to glass, powdered and stored. Second, to promote oxidation sodium nitrate (NaNO_3) or lithium nitrate (LiNO_3) is added to the rock powder in a ratio of one part to fourteen parts rock powder. Third, specimens are prepared for analysis by fusing five parts flux mixture and one part rock-oxidiser mixture by weight. Preprepared flux is marketed as Spectroflux 105, available in the U.S. from Johnson Matthey Aesar Group, 892 Lafayette Rd., P.O. Box 1087, Seabrook, New Hampshire 03874, U.S.A.

In low flux-to-rock mixtures (low dilution), mass absorption effects can be minimized by choosing standards whose bulk compositions are very similar to

that of the unknowns. But this is not always practical. If high flux-to-rock mixtures (high dilution) are used instead, variability in standard compositions become less important. High dilutions minimise mass absorption differences among different rock types as the flux contributes a greater percentage to the total absorption. But high dilutions obviously cause loss of sensitivity and high background-to-peak ratios, and an acceptable balance must be determined by trial and error. With the advent of much better analysing crystals and multilayer semiconductor "crystals" sensitivity is greatly enhanced in modern spectrometers such as the Rigaku 3070. Hence relatively high dilutions have become commonplace in many labs. A ratio by weight of nine flux to one rock, with a heavy absorber, effectively eliminates the need for mass absorption corrections in most cases; however, online computer treatment of data from the Rigaku 3070 makes these corrections routine (see above). Some labs determine trace elements on these high-dilution fused discs, despite the very low concentrations. This may be practical for heavy elements whose lines are strong, but it is probably not a generally recommended practice.

Another practical advantage of using high flux-to-rock ratios is that a greater volume of melt for a given rock volume is produced. For analyses in which limited rock mass is a problem (e.g. ocean floor samples) this is particularly advantageous. Larger melt volumes are easier to handle and can be easily cast in molds rather than pressed into thin glass discs. The casting procedure is faster, easier and safer, and the thick glass disc produced is more durable.

Disadvantages of casting are that more rock powder is generally needed, and the surface tension of them melt must be reduced if the melt is to completely cover the bottom of the mold. This is accomplished



Fig. 4 The Rigaku 3070 sequential X-ray spectrometer at Georgia State University.

by addition of a tiny amount of wetting agent such as ammonium iodide (NH₄I) or lithium iodide (LiI) to the rock powder before fusion.

The XRF as a Regional Analytical Facility

Numerous spectrometers in various configurations are available on the market, and all boast different strengths and limitations. In our case the need for an XRF facility that is both state-of-the-art technologically and adaptable for outside users, made the Rigaku 3070 an ideal choice for geological applications at Georgia State University (Fig. 4). The technological characteristics of the spectrometer are published and are not discussed here.

Each visiting geochemist or petrologist has unique needs. From user to user the rock types, elements of interest, sample preparation methods, etc. may vary. The visiting analyst may have his own set of standards or may simply prefer to do things his own way, based on experience or former training. The Rigaku 3070 has a simple microcomputer with dual floppy disk drives, one drive holding a disk customised for each user. On this floppy disk the standards for regression calibrations can be assigned by the user. Under ELEMENT (QUANT) mode of PARAMETER JOBS, analysing conditions can be set up that meet the specific needs of the user, including counting times, crystal, collimator, number of repeats, etc. In GROUP (QUANT) mode of PARAMETER JOBS the analyst can assign elements to be determined, matrix corrections to be made, etc. In STD. SAMPLE mode the analyst can designate which standards he wishes to use for regression calculations for each element. In short, each user establishes on his own disk all the measuring conditions for his particular needs, none of which affects any other user's measuring conditions. Equally important, each user can be assured that he will not be limited to "official" lab procedures, thus making use of our lab attractive to more potential users.

A drawback to the 3070 system is that the data coming off the spectrometer are sent directly to the printer, without being written to disk. This means that a printer malfunction, ribbon break or paper tear could cause data to be lost. It also means that subsequent data manipulation requires manual re entry of the data into a data file, creating a likely source of error. To solve this problem we are installing a second

complete microcomputer system (IBM PC compatible) with math coprocessor and two floppy disk drives. Through a RC232C serial interface the data can then be written to a file on one of the disks in the second computer, and the disk taken home by the visiting analyst. Moreover, the second computer can be used on site to run data manipulation programs or plot diagrams using the data directly off the spectrometer.

We made a deliberate decision to buy the 3070 and add a second PC with floppy drives, rather than buying the 3370 with a DEC minicomputer. Although less "powerful" overall, the satellite PC system is less expensive and is fully adequate. Moreover, the PC is likely to be similar to systems used for data manipulation in the user's home lab. Hence, the user can bring his programs with him on disk, and use the satellite PC as he would his own. This further enhances the attractiveness to outside users of the XRF facility at Georgia State University.

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