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X-Ray-Fluorescence Analysis Major Elements in Silicate Minerals

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X-RAY FLUORESCENCE ANALYSIS
MAJOR ELEMENTS IN SILICATE MINERALS

by

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ABSTRACT

An automated wavelength-dispersive x-ray fluorescence spectrometer is operational for analysis of major elements in rocks and minerals. Procedures for trace-element analysis are being developed. Sample preparation methods and analytical techniques are similar to those commonly used elsewhere, but data reduction is conducted by the Fundamental Parameters program developed by Criss. Unlike empirically derived calibration curves, this data reduction method considers x-ray absorption and secondary fluorescence, which vary with differences in sample composition. X-ray intensities for each element from several standards are averaged to develop a "theoretical standard" for comparison with samples of unknown composition. Accurate data for samples with wide compositional ranges result from these data reduction and standardization techniques.

I. INTRODUCTION

An automated XRF (x-ray fluorescence) spectrometry system has been put into operation for analysis of major elements in rocks and minerals. The system currently is used for quantitative analysis of the elements sodium, magnesium, aluminum, silicon, phosphorus, potassium, calcium, titanium, manganese, and iron. These are considered major components in silicate rocks and rock-forming minerals and account for 97-99% of the total composition of most rocks. Analysis parameters for the minor and trace elements (less than 0.10%) are being prepared and will be reported at a later date.

The x-ray system is a Rigaku Model 3064 (Fig. 1) (Rigaku, 1979) with a single-channel, wavelength-dispersive, multi-crystal, sequential spectrometer, is computer controlled (DEC LSI11/2), and has automated sample handling (108 samples). The unit is designed to run unattended and samples are commonly analyzed at night.

II. EQUIPMENT

A. X-ray Source

The x-ray tube end window is ultra-thin beryllium (0.126 μm thick). The tube has a rhodium target, cathode grounded, with a maximum power of 3 kW. The operating range of the tube is 20-60 kV, 2-60 mA. The x-ray generator is

Fig. 1
Rigaku Model 3064 x-ray system.

a constant potential voltage source, current stabilized. The generator is not computer controlled and is set at a selected kilovoltage and current setting that is not changed during analysis. X-ray intensity from the sample is computer controlled by means of an absorber wheel. The absorber is a disk with a series of holes to allow 100% or as low as 2% x-ray intensity from the sample. An asborber setting is selected at the time of analysis setup to allow a maximum of fifteen thousand counts per second (15 kcounts/s) to reach the detectors. This reduces dead time corrections to an insignificant number. The sample area analyzed is 30 mm in diameter and masked by copper. Sample spin is selected for the analysis.

B. Spectrometer

The incident angle of the primary x rays into the sample is 90° (vertical); take-off angle for the secondary x rays into the spectrometer is 30° from horizontal. Two Soller slits, selectable by the computer, provide the primary collimation between the sample and the crystals. Secondary collimators are fixed in front of two detectors, a flow proportional counter (P-10 Gas) and a scintillation counter (NaI crystal). The x-ray path is within a vacuum (0.1 torr). The spectrometer is in a cabinet kept at a constant 32°C. Seven crystals, mounted in a rotary holder, cover the x-ray wavelength range for elements carbon through uranium. [Crystals in use are LiF(200) (lithium fluoride 200), LiF(220) (lithium fluoride 220), PET (pentaerythrilol), ADP (ammonium dihydrogen phosphate), Ge (germanium), TAP (thallium acid phthalate), and a special crystal for carbon that is designated by Rigaku as RX-5 that is proprietary in nature.]

C. Automation

The automation is divided into two types, that which is under computer control and that which is not.

The computer controlled automation can be selected by the operator to tailor an analysis setup. This includes spectrometer position, crystal and collimator selection, count time, pulse height analyses, and window settings. Also included are intensity control and loading and unloading of the samples from the 108 sample changer. All analysis parameters are stored in a permanent disk file. The operator selects a file via the computer terminal. Software programs read the file, set the analysis conditions into the spectrometer, load a sample, and perform the analysis. X-ray intensities are corrected for background and printed on a terminal.

The components that are not under computer control such as the x-ray generator, cooling system for the x-ray tube, and a line voltage monitor are designed to sense a fault and automatically turn off the system in a fail-safe mode.

III. X-RAY INTENSITIES

X-ray intensities will drift with time; this drift is classified as short term (minutes-hours) or long term (days-months). Short-term drift is better defined as the analysis time. The analysis time for a 10-element, 6-sample cycle is about 2 1/2 h. A study of this system has shown that short-term drift is negligible. To verify this, a control standard is run every analysis cycle (2 h, 30 min). The intensity values for this control sample are processed through the calibration system and the measured concentration values for the control are checked against the reported value.

Long-term drift is corrected by measuring the intensity values for each element on a reference sample. The reference intensities are permanently stored in the computer program. At the start of an analysis the reference sample is measured, compared to the stored value, and a correction factor is computed. Using this factor, each of the following five samples including the control sample are corrected for long-term drift. A typical 1-element analysis on the 6 samples takes from 8 to 20 min.

Background signal is measured at a high and low two-theta angle relative to the peak of interest and a linear curve fit computes the background signal under the peak. Count time on the background is selectable, but usually equal to the count time on the peak.

Each detector signal is routed to a linking module, which amplifies the signal. The amount of amplification is determined by detector, crystal, spectrometer position, and x-ray order. The output of this module is modified to be constant in gain, allowing nine pulse height analyzer windows to be computer selected around a common centroid. Nine individual count times are available. Counting intervals of 1 to 200 s are available and can be repeated any number of times if longer counting intervals are required.

IV. SAMPLE PREPARATION

Samples (about 10 g) are split to fingernail size and then crushed in a tungsten carbide shatterbox. One gram of sample is weighed (± 0.0005 g) and mixed with 9 grams (9 ± 0.0040 g) of lithium tetraborate flux (all powders and flux are dried at 105°C in a drying oven and cooled in a desiccator before any weighing operation). Ammonium nitrate (0.16 g) is added as an oxidizing agent.

The mix is fused in a platinum alloy crucible (95% Pt, 5% Au) at 1100°C for 20 min over a burner using MAPP gas. The fused mixture is poured into a heated (∿900°C) platinum alloy mold and cooled to room temperature in three steps: 1) allowing to solidify in the mold, 2) turned out of the mold onto a warm hotplate (∿200°C, ∿10 min), and 3) removed from the hot plate and allowed to cool to room temperature. Final samples are 40 mm in diameter by 3 mm thick. Samples are labeled on the back and placed in a plastic container; at no time is the surface to be analyzed allowed to contact any material other than its container.

A separate split of the powdered sample is used to determine sample loss on ignition. About one gram of sample is placed in a preweighed porcelain crucible and the total weight is determined. The crucible is placed in a furnace at 1000°C for 30 min, cooled in a sealed desiccator for a minimum of 1 h, then reweighed to determine material loss.

V. ANALYSIS

Six samples are analyzed as a group, with up to 18 groups in one loading. One sample in each group is an intensity reference. One sample randomly placed in each group is a SRM (standard reference material) used as a control standard. The SRM is selected to be similar in composition to the unknown samples. This SRM standard is treated and reported the same as the four unknown samples. In addition, its reported value is given on the analysis report in a column next to its measured value for that analysis. A typical 10-element analysis takes about 20 min per sample. All SRM reported values used in this report are from a paper by Abbey (1980). The important analysis parameters used are given in Table I.

TABLE I

ANALYSIS PARAMETERS

Element	Crystal	Detector	Time Peak (s)	Time Bkg. (s)	Intensity Asborber
Na_2O	TAP	1	100	80	0
MgO	ADP	1	100	80	0
Al_2O_3	TAP	1	40	40	0
SiO_2	PET	1	40	40	20%
P_2O_5	PET	1	100	80	0
K_2O	LiF200	1	40	40	0
CaO	LiF200	2	40	40	0
TiO_2	LiF200	2	40	40	0
MnO	LiF200	2	100	80	0
FeO	LiF200	2	40	40	20%

Constant: 40 Kvcp, 50 mA
Pulse Height Analyzer, base line 0.6 V window 3.0 V
Collimator, 300 μm (Soller slit)
Detector 1, flow proportional P-10 gas
Detector 2, scintillator NaI crystal

VI. FUNDAMENTAL PARAMETERS

The most commonly used calibration method is to calculate a separate curve for each element of interest. A number of SRMs are run and each element of interest is measured. A plot of measured intensities versus concentrations is made. A curve fit to all the data points averages out minor errors in reported concentrations and measured intensities. The curve is a rapid means of determining the concentration of one or more elements in a matrix of many elements. The curve does not correct for sample matrix effects such as enhancement and absorption. Matrix effects can cause errors of several percent in measured concentration. Matrix corrections are complex and beyond the scope of this paper to cover completely. Briefly stated, x rays produced from light elements are absorbed by heavier elements in the sample, reducing their observed intensity, and x rays produced from heavy elements enhance the observed x-ray intensities of lighter elements by secondary fluorescence. Therefore measured intensity is not directly proportional to concentration. The reader is referred to Zussman (1977).

Fundamental parameters is the most complete matrix correction method in use to date. The method requires that measured values sum as close to 100% in concentration values as possible.

The FPP (Fundamental Parameters Program) is a commercial software program sold by Criss Software Incorporated (Criss 1979) and is a package for computing theoretical predictions of x-ray intensities or concentrations and using these predicted values, along with measured intensities and compositions of SRM, to determine chemical composition of homogeneous samples analyzed by XRF.

FPP (Criss 1980) is a two-part program. Part A characterizes the x-ray system. It calculates the incident spectrum, characteristic lines and continuum. The calculation includes the anode material, operating voltage, beryllium window thickness, incident and exit angles for the x rays, and the sample thickness. All the components of interest are defined and the program calculates an x-ray spectrum and a table of "alpha factors." These are all stored in a disk file for use by part B.

Part B uses the data files and "alpha factors" created by part A to generate quantitative analyses from measured intensities. Compositions and measured intensities for SRMs are used to arrive at a quantitative analysis. Components of interest are input along with the measured intensities for the unknowns and the compositions are calculated. Or, composition of an SRM is input instead of intensities and a set of theoretical intensities can be calculated.

Options that are available in the program include: normalization of the total to 100%, calculation of a component by difference, and calculation of the error expected from counting statistics. Also, components that are fixed in value, such as flux, may be included in the calculation.

VII. CALIBRATION

The FPP stores the composition and measured intensities for up to 20 SRM. The program compares the composition and measured x-ray intensities of the unknown and selects only one of the SRMs for use as a standard. This is a possible source of error, as an error in the standard will be reflected in the calculated unknown composition. An averaged value from many standards reduces the overall error in the final result.

A method for averaging many standards for the FPP is now described. The composition of SRM BCR-1, a U.S. Geological Survey (USGS) material, was selected as a theoretical model. This SRM was chosen because it is well characterized, it has most of the major components in quantity to produce good calculated intensities and its measured intensity can be used to check the final results.

A run was made on the XRF system to collect intensity values for six SRMs, BCR-1 included. For each, the composition and measured intensities were input to the FPP and a set of theoretical intensities was computed for BCR-1 (Table II). An average was determined for components of interest and compared

TABLE II

THEORETICAL INTENSITIES

						BCR-1	
	AGV-1	JB-1	JG-1	NIM-G	G-2	Average	Meas.
Na_2O	146.7	140.1	146.3	145.6	146.4	145.5	141.3
MgO	180.2	180.6	18[illegible].0	177.1	176.8	178.9	175.3
Al_2O_3	4137.4	4122.3	41[illegible].3	4081.2	4071.2	4114.9	4003.9
SiO_2	4093.7	4100.4	4107.6	4081.2	4071.2	4090.8	4080.6
P_2O_5	170.3	178.3	171.4	171.4	161.8	170.6	177.2
K_2O	650.6	628.7	655.1	648.0	649.0	646.3	633.6
CaO	2059.1	2048.6	2065.9	2071.6	2018.4	2052.7	2049.7
TiO_2	890.7	870.0	876.3	893.4	892.7	884.6	886.1
MnO	390.9	410.4	427.1	387.6	431.9	409.6	418.8
FeO	7993.2	7859.8	7785.7	7742.0	7774.6	7831.1	8012.5

Units are counts/second.

to the measured values of BCR-1. The difference between the theoretical model (column 6) and the measured value for BCR-1 (column 7) for silicon, calcium, and titanium was within expected value (± two standard deviations). The remaining seven elements were beyond expected variation indicating that variations were being averaged. Sources of variation are error in reported concentration, measurement, and inclusion of matrix correction into the calculation. This single set of theoretical intensities and the composition of BCR-1 were stored in the FPP. In effect, the program has only one standard to use but the standard is a composite of five SRMs.

This single theoretical standard was checked by running five more SRMs not involved in the calibration and comparing measured results to reported values (Table III). Agreement of measured values to reported values was within expected range for NIM-S, SY-2, and W-1. These three SRMs had

TABLE III

FIVE SRMS RUN AS UNKNOWN

	MRG-1		DTS-1		NIM-S		SY-2		W-1	
Element	Meas.	Rept.	Meas.	Rept.	Meas.	Rept.	Meas.	Rept.	Meas.	Rept.
Na_2O	0.52	0.71	0	0.01	0.49	0.43	4.21	4.34	2.14	2.15
MgO	13.66	13.49	50.25	49.80	0.46	0.46	2.66	2.70	6.66	6.63
Al_2O_3	8.36	8.50	0	0.25	17.08	17.34	12.02	12.12	14.85	15.02
SiO_2	39.11	39.32	40.51	40.61	62.97	63.63	60.03	60.10	52.14	52.72
P_2O_5	0.06	0.06	0.01	0	0.12	0.12	0.44	0.43	0.14	0.14
K_2O	0.11	0.18	0.01	0	14.97	15.35	4.47	4.48	0.58	0.64
CaO	14.80	14.77	0.14	0.14	0.69	0.68	7.96	7.98	10.83	10.98
TiO_2	3.86	3.60	0	0	0.04	0.04	0.14	0.14	1.09	1.07
MnO	0.18	0.17	0.12	0.12	0.01	0.01	0.32	0.32	0.17	0.17
FeO[a]	16.51	16.06	7.90	7.86	1.30	1.26	5.79	5.67	10.03	10.05

Units are concentration as percent.
Rept. = reported (Abbey 1980).

[a] $FeO_{(c)} = 1.28649[Fe_2O_{3(r)} \times 0.69943] + FeO_{(r)}$.

(c) = calculated value.
(r) = reported value.

compositional ranges within that of the calibration group. MRG-1 and DTS-1 both had compositions well outside that of the calibration group yet, with the exception of sodium in MCR-1, all values were within expected range.

Sodium is the most difficult element to measure. The sodium x ray is lowest in energy of the measured group of elements. Absorption effects within the sample matrix are highest for sodium. Sodium is most sensitive to sample preparation errors, surface flatness, and smoothness. A third check was to rerun the five SRMs used in the calibration as unknowns (Table IV), to check for errors. The results of this check showed all values to be within predicted variation.

As with most calibration methods it is wise to use standards as similar in composition as possible to the unknowns. That precaution should be followed when using this method.

TABLE IV

CALIBRATION STANDARDS ANALYZED AS UNKNOWNS

	AGV-1		JB-1		JG-1		NIM-G		G-2	
Element	Meas.	Rept.	Meas.	Rept.	Meas.	Rept.	Meas.	Rept.	Meas.	Rept.
Na_2O	4.32	4.32	2.73	2.79	3.39	3.39	3.38	3.36	4.09	4.06
MgO	1.53	1.52	7.79	7.76	0.77	0.76	0.15	0.06	0.76	0.75
Al_2O_3	17.32	17.19	14.64	14.62	14.29	14.20	12.00	12.08	15.25	15.40
SiO_2	59.62	59.61	52.76	52.60	72.72	72.36	74.85	75.70	68.92	69.22
P_2O_5	0.51	0.51	0.27	0.26	0.09	0.09	0	0.01	0.12	0.13
K_2O	2.92	2.92	1.39	1.42	4.01	3.96	4.94	4.99	4.46	4.46
CaO	4.96	4.94	9.33	9.35	2.19	2.17	0.79	0.78	1.93	1.96
TiO_2	1.07	1.06	1.32	1.34	0.26	0.27	0.09	0.09	0.48	0.48
MnO	0.10	0.10	0.15	0.15	0.06	0.06	0.02	0.02	0.03	0.03
FeO	6.30	6.13	8.22	8.14	1.95	1.95	1.82	1.84	2.39	2.40

Units are concentration as percent.
Rept. = reported (Abbey 1980).

VIII. STATISTICAL EVALUATION

Table V shows the measured values of SRM BCR-1 for 1 run and the average of 10 runs, compared to reported values from the literature (Abbey 1980). The measured values of one run are within acceptable limits (± two standard deviations). The average of 10 runs shows closer agreement of the measured to reported values indicating that if better accuracy were desired it could be gained by longer counting times or averaging several runs. Errors calculated from counting statistics by the method of Jenkins (1978) are shown. Differences in the values also reflect errors in calibration, drift intensity correction, and mechanical system error.

Table VI gives the LLD (lower limits of determination). The analytical level is three times the LLD and is the practical level for routine analysis (Jenkins 1980).

TABLE V

ANALYTICAL ERROR DUE TO COUNTING STATISTICS

Element	Rept.	Error[a]	Meas. 1 Run	Meas. 10 Run
Na	3.30	0.06	3.30	3.21
Mg	3.48	0.06	3.54	3.49
Al	13.72	0.07	13.66	13.30
Si	54.53	0.27	54.83	54.58
P	0.36	0.01	0.38	0.37
K	1.70	0.02	1.72	1.69
Ca	6.97	0.05	7.00	6.97
Ti	2.26	0.02	2.30	2.27
Mn	0.18	0.002	0.19	0.19
Fe	12.30	0.04	12.56	12.47

Units are concentration as a percent.
Rept. = reported (Abbey 1980).

[a] Error (Jenkins 1978).

TABLE VI

LOWER LIMITS OF DETECTION

Element	LLD	Analytical Level
Na	528	1586
Mg	410	1230
Al	299	897
Si	556	1670
P	49	148
K	258	776
Ca	109	330
Ti	92	276
Mn	22	66
Fe	74	222

Units are concentration in ppm.
Sample used is BCR-1(USGS).
LLD calculated using the method of Jenkins (1978).

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