

An Improved Method for Obtaining Small Pressed Powder Pellets for the Analysis by XRF

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A rapid, very low cost of instrumentation and simple approach to specimen preparation for the analysis by X-ray fluorescence spectrometry is presented. This technique requires a few mg of powdered samples, which are compressed to produce pellets. This procedure is employed for determining major, minor and trace elements in muscovites and K-feldspars. Factors affecting measured intensities, such as particle size and distribution, surface texture, pelletizing pressure, *etc.*, are considered. A description of the new sample preparation device, including technical characteristics, is also given. It is demonstrated that suitable specimen presentation to the X-ray beam is obtained by using our procedure.

Przedstawiono szybką i prostą technikę przygotowywania próbek do analizy rentgenofluorescencyjnej, nie wymagającą drogiego oprzyrządowania. Z kilku miligramów sproszkowanej próbki, którą poddaje się prasowaniu, otrzymuje się pastylki stosowane następnie do oznaczania głównych, mniejszych i śladowych składników muskowitu i skalenia potasowego. Przedyskutowano wpływ następujące czynników na mierzone intensywności: wielkość cząstek i ich rozkład, struktura powierzchni, ciśnienie pastylkowania *etc.* Opisano nowe urządzenie do przygotowywania próbek, włączając charakterystykę techniczną. Otrzymane wyniki udowodniły, że pastylki uzyskane przedstawioną techniką są odpowiednie do analizy rentgenofluorescencyjnej.

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Geochemical prospecting minerals should be representative, regarding their chemical composition, of the different stages of their crystallization. Ionic substitutions taking place at that time and the concentration of the elements reflect the chemical characteristics of the original magma. Analysing these two factors, geologists may characterise rocks and evaluate whether they are economically or technologically exploitable. To achieve this, mineral samples should be both unaltered and free of contamination (coming from inclusions from other minerals).

Muscovites and K-feldspars belong to the final stages of magma crystallization. Consequently they are very abundant and commonly found in granitic pegmatites. Minor and trace elements within their structure may be substituted by potassium. Thus, these minerals are of a great importance in the prospection of granitic pegmatites [1–6].

Before applying any analytical procedure, mineral samples have to be selected, cleaned and prepared. Selection step is often difficult, tedious and slow since the mineral grain selection is carried out by handpicking under a binocular. Therefore, it is desirable to decrease the amount of sample to be analysed.

In geochemical studies by X-ray fluorescence spectrometry (XRF), powdered samples are frequently prepared using binders. Although some authors [7] have suggested the use of small sample pellets weighing 1.5 g, sample amounts usually vary from 4 to 10 g [8–11]. Diminishing the traditional 10 g of powdered mineral to much lower amounts becomes very important.

In the paper we present a significant progress in the sample preparation method reducing the traditional sample amounts to 150 mg. To achieve this we have developed a new stainless steel mould, which has been used to prepare both sample supports and mineral sample films.

Muscovites and K-feldspars samples selected for this study are from San Luis, Córdoba, San Juan and Salta Provinces, Argentina. The following elements were determined: potassium, phosphorus, rubidium, cesium, barium (major constituents); tantalum, niobium, strontium (minor constituents) and gallium (trace element).

In order to evaluate the reliability of our procedure, we have carried out the following tests: application to standard reference materials and standard addition procedure. Data obtained by standard addition procedure were, in turn, compared to the results supplied by XRAL Laboratory. The latter used several analytical techniques, such as inductively coupled plasma optical emission spectrometry (ICP–AES), neutron activation analysis (NAA), atomic absorption spectrometry (AAS) and XRF.

EXPERIMENTAL

XRF instrumentation and experimental conditions

Intensity measurements were carried out using a Philips PW 1400 wavelength-dispersive X-ray spectrometer (3.0 kW–100 mA) with the following experimental conditions: X-ray tube containing a Rh anode, LiF(200) and Ge analyzer crystals, fine collimator (150 μm), flow and scintillation detectors and the appropriate spectrometer mask (14 mm diameter). Since phosphorus determinations need to be carried out in vacuum, measurements were performed under this condition in all cases. Ge analyzer crystal ($2d = 6.532 \text{ \AA}$) was used in the P determinations and LiF(200) crystal ($2d = 4.028 \text{ \AA}$) for the rest. A counting time of 100 s was used in all cases.

Detailed experimental settings corresponding to the measured analytical lines are listed in Table 1.

Table 1. Experimental settings

Line	20 degrees	Detector ^a	Crystal	Potential kV	Current mA
Ta $L\alpha$	44.42	F	LiF (200)	60	40
Nb $K\alpha$	21.40	F	LiF (200)	60	40
P $K\alpha$	141.04	F	Ge	50	50
K $K\alpha$	136.69	F	LiF (200)	50	50
Rb $K\alpha$	26.62	F + S	LiF (200)	60	40
Cs $L\alpha$	91.84	F	LiF (200)	50	50
Sr $K\alpha$	25.15	F + S	LiF (200)	60	40
Ba $L\alpha$	87.17	F	LiF (200)	50	50
Ga $K\alpha$	38.92	F + S	LiF (200)	60	40

^a F = flow detector; S = scintillation detector.

Selection of the most appropriate analytical lines was facilitated by prior qualitative analysis. Most of the analytes selected here exhibited, at least, two intense fluorescent lines for the XRF measurement. As revealed by qualitative analysis of K-feldspars and muscovite samples, no significant spectral-line interferences were present.

RESULTS AND DISCUSSION

New sample preparation device

The ideal sample for presentation to the X-ray beam is homogeneous, flat, infinitely thick with respect to the X-rays and capable of withstanding vacuum. The aim of this

work was to satisfy all of these sample characteristics by using very small amounts of powdered minerals supported by a suitable solid base. Sample supports used in this work consisted of boric acid disks. This material was chosen because of its composition (light elements), which does not produce significant interferences on the samples.

Stainless steel was found to be the most appropriate material to build the mould: it is easy to clean and has suitable hardness to withstand high pressures from a hydraulic press without suffering significant distortions.

On the first attempt, we modified the flat surface of the mould base supplied with the spectrometer. A protuberance was left on the mould base, which, in turn, produced a small cavity of 0.05 cm of depth and 2 cm diameter on one side of the boric acid disk. Figure 1 shows a schematic diagram of the mould described above. It should be noted that the protuberance edge of the mould base is oblique to facilitate the detachment of the disk.

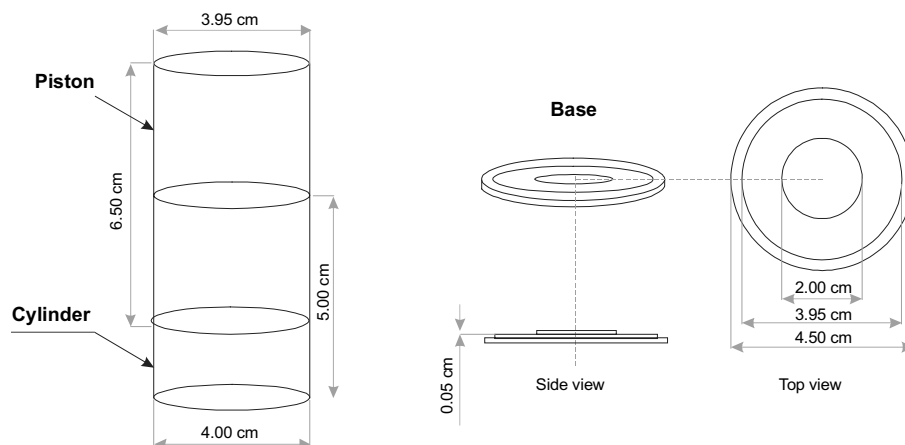


Figure 1. Schematic diagram of the new stainless steel mould used to prepare both sample supports and mineral sample films

About 4 g of boric acid powder were placed into the 4 cm diameter stainless steel mould and pelletized under a pressure of 11 Tcm^{-2} to give a firm disk 5 mm thick. Accurately weighed amounts of sample powder were placed in the cavity and pressed under the same pressure used before. This thin-layer sample assumes, to a certain extent, the nature of a thin film, thus diminishing the effects of particle size and inhomogeneity and absorption-enhancement.

The grain size of the sample powder (less than 0.074 mm) was obtained by grinding it in an agate mortar. Each pellet (support + sample) was covered with a $6 \mu\text{m}$ thick Mylar film to prevent dust from falling into the equipment. This arrangement was found to be very convenient for handling such a small amount of sample. The pellets

suppressed any deformation and so a very flat surface was presented to the X-ray beam. No damages were produced during analysis. Such pellets may be stored for future use.

Decrease and control of sample thickness

A decrease of the sample thickness and, therefore, the sample amount, should be carefully checked since infinitely thick mineral samples are required to be used in the XRF analysis. We propose here the use of very small sample weights that produce infinitely thick samples. To achieve this, the protuberance height of the mould base was systematically decreased. Thus, fluorescent line intensities were measured with every new sample thickness.

Since fluorescent line intensities remain constant when decreasing the sample thickness (or sample weight in the range from 1000 to 100 mg), this guarantees that sample is still infinitely thick (Tab. 2). A sample weight of 150 mg (the lowest sample amount used so far in XRF determinations) still produces infinitely thick samples.

Table 2. Fluorescent line intensities obtained for sample of muscovite (San Elias Pegmatite) amounts ranging from 1000 mg to 100 mg

Sample amount mg	Intensity, counts s ⁻¹								
	Ta L α	Nb K α	P K α	K K α	Rb K α	Cs L α	Sr K α	Ba L α	Ga K α
1000	2572	3587	983	50535	29684	1978	733	933	3751
750	2564	3593	953	50360	29465	2007	739	925	3735
500	2578	3590	962	50489	29703	1983	726	944	3768
250	2583	3595	977	50510	29558	1964	729	928	3743
100	2576	358	960	50431	29612	1969	721	919	3739

Control of sample preparation

In the literature, the sample powder (10 g on average) is often briqueted with a binder or in a shallow aluminium cup [7–8,12]. We propose here the use smaller sample (about 150 mg) ground to extremely fine particle size and supported by a boric acid disk. Thus, thin-layer sample assumes, to a certain extent, the nature of a thin film, which is advantageous since only small amounts of minerals are sometimes available.

Reproducible sample preparation methods are essential. Samples must be in a form that are similar to available standards in terms of analyte concentration, matrix composition, physical form, surface texture and particle size and distribution. Since powdered samples are often pressed into pellets, compression has also to be considered.

Firstly, we considered the influence of pressure on analyte-line intensity. Two sets of pellets were prepared using muscovite and K-feldspars samples and pressures ranging from 4 to 13.5 Tm cm⁻². Every pellet was pressed during 60 s. The same particle size was used in the first attempt.

Secondly, the particle-size effect was taken into account. Muscovite and K-feldspars pellets were prepared using three particle sizes (<44 μm, 44–74 μm and 74–100 μm) and at a constant pressure, which was also maintained for 60 s.

Effects of particle-size and pressure on analyte-line intensity measured from muscovite samples are shown in Figure 2. For a given pressure, the smaller the particle size, the higher is the analyte-line intensity. For a given particle size, the higher the pressure, the higher is the analyte-line intensity. Similar results were obtained when using K-feldspars samples.

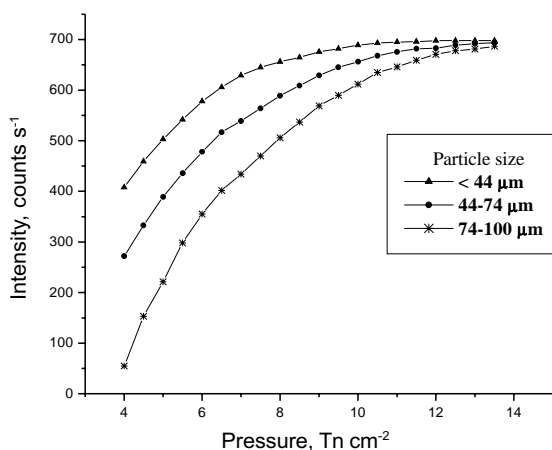


Figure 2. Particle-size and pressure effects on Ta L α intensities (counts s⁻¹) measured from muscovite samples

Surface-texture effect exhibited by sample pellets was negligible since the surfaces of the stainless steel mould (base and piston) were very well polished. Thus, smooth pellet surfaces were exposed to the X-ray beam.

No binders were used in the sample preparation. The same counting time (200 s) was used for both the peak and the background.

Absorption-enhancement effects

From an experimental point of view, the evaluation of the absorption-enhancement effects a specified analyte-matrix system may be subject to is of great importance.

It is well known that major, minor and trace elements in mineral samples may vary within certain limits. Such variations, mainly in major constituents, may change measured intensities of minor and trace elements. To study these variations, we considered advisable to prepare synthetic standards having a composition similar to the mineral samples.

Minerals of the alkali feldspar series (tectosilicates) have similar composition and structure. They have a general formula: $KAlSi_3O_8$ and the following composition (mass percent): SiO_2 , 64.7%; Al_2O_3 , 18.3% and K_2O , 16.9%.

Muscovite (mica group, phyllosilicates) may be represented by $[Si_3AlO_{10}](OH,F)_2Al_2K$ or $K_2Al_4Si_6Al_2O_{20}(OH,F)_4$. It has approximately the following composition (mass percent): SiO_2 , 46%; Al_2O_3 , 36%; K_2O , 10%; H_2O , 6% and F_2O , 2%.

Synthetic standards were prepared using silica, alumina, KCl and boric acid. The latter was used as a complement to major oxides variations. Thus, final compositions (as mass percent) of the synthetic standards varied as follows: SiO_2 35–70%, Al_2O_3 15–40% and K_2O 8–17%. Varying amounts of the analyte were added quantitatively to the set of synthetic specimens according to the expected values. Table 3 shows the results obtained for Ta $L\alpha$ intensities in muscovite-like synthetic matrixes after adding Ta ($1500 \mu g g^{-1}$). Measured Ta $L\alpha$ fluorescent lines remained constant with varying matrix compositions.

Table 3. Synthetic standard composition and Ta $L\alpha$ intensities

Specimen	Synthetic standard composition (mass percent)				Ta added ^a	Ta $L\alpha$ intensities ^b
	SiO_2	Al_2O_3	K_2O	Boric acid		
P1Ta ₂	70	15	8	7	1500	2353020
P2Ta ₂	60	20	12	8	1500	2353202
P3Ta ₂	50	30	14	6	1500	2352780
P4Ta ₂	40	35	16	7	1500	2354280
P5Ta ₂	35	40	17	8	1500	2353987

^a $\mu g g^{-1}$

^b counts $60 s^{-1}$

Limit of detection

In spite of the numerous criteria that have appeared in the literature regarding the definition of limit of detection, we have used here that proposed by Roelandts [13].

Since a linear relationship exists between intensity and concentration, it is easy to calculate the limits of detection, from the analytical curves, for the elements considered in this study. They are ($\mu g g^{-1}$) Ta: 6, Nb: 15, P: 7, K: 8, Rb: 5, Cs: 6, Sr: 8, Ba: 5, Ga: 4.

It should be noted that these detection limits are not definitive and could be lowered by using counting periods longer than the 100 s used in this work.

Standard addition procedure

Standard addition procedure was applied to six splits of mineral samples and fluorescence lines were measured for Ta, Nb, P, K, Rb, Cs, Sr, Ba and Ga in K-feldspars and muscovite samples. Additions were carried out from stock standard solutions according to the expected range of analyte concentrations. Stock standard solutions (P, K, Rb, Cs, Sr, Ba and Ga) were prepared by dissolving accurately weighed amounts of high purity (99.99%) chemicals (Merck products). Ta and Nb stock standard solutions were prepared according to Gibalo's procedure [14]. Working solutions were prepared by appropriate dilution of stock solutions. Known amounts of each analyte were added to solid samples. These were dried in an oven at 80°C for half an hour and finally mixed in an agate mortar to obtain good homogenization.

Calibration curves procedure

K-feldspars and muscovite added samples, which were used in the standard addition procedure, were regarded as standards to ascertain linear calibration curves in all likely concentration ranges of varying analytes. These whole-range calibration curves thus obtained were employed to determine the analyte concentrations in the remaining K-feldspars and muscovite samples.

The short time instrumental drift was taken into account regarding calibration curves linearity.

The same muscovite and K-feldspar samples were analysed by XRAL Laboratories (USA) for comparison purposes. Table 4 shows the results obtained by XRAL Lab. and they are compared to the values we obtained using our procedure.

Table 4. Comparative concentrations in K-feldspars and muscovite samples from Argentinian pegmatitic rocks^a

Element	Sample 1		Sample 2		Sample 3	
	XRAL ^b	this work ^c	XRAL ^b	this work ^c	XRAL ^b	this work ^c
K ₂ O (%)	8.68	10.4	9.16	10.75	8.44	10.39
P ₂ O ₅ (%)	–	0.021	–	0.20	–	0.035
Ta (ppm)	80	87	76	79	59	52
Nb(ppm)	220	220	66	141	260	275
Rb (ppm)	2530	2540	3330	3298	3070	3043

Sr (ppm)	–	26	–	29	–	20
Cs (ppm)	370	379	815	873	314	222
Ba (ppm)	–	114	–	33	–	22
Ga (ppm)	–	83	–	63	–	87
Sc (ppm)	1.99	2.1	0.25	0.18	9.68	9.59
Li (ppm)	150	162	210	185	810	790

^a Sample references: 1 = „La Marta”, 2 = „C72”, 3 = „Las Tapias”.

^b XRAL Laboratories (USA) determinations.

^c Six splits each analysed six times

Application to standard reference materials

The method proposed here was applied to standard reference materials to test its precision and accuracy. Our results compare favourably with the published and accepted values thus showing the reliability of our procedure. Standard reference materials used in this study were the following: FK–N (K-feldspar mineral), GS–N (granite) both provided by ANRT (currently distributed by CRPG, Nancy, France) and AGV–1 (volcanic rock) provided by USGS (United States Geological Survey).

Argentinian K-feldspar minerals used in this work are similar in matrixes to FK–N and GS–N standard materials. AGV–1 standard reference material is a fine-grained volcanic rock of intermediate composition, named andesite. The use of these rocks, in turn, enabled us to test our methodology upon making determinations in similar, although more complex, matrixes.

Tables 5, 6 and 7 show the recommended values [15–16] for the standard reference materials used in this work. They are compared to the concentration values obtained using our procedure.

Table 5. Comparative concentration values of several elements in FK–N (K-feldspar) standard reference material

Method	XRF	ICP OES	AAS	RV ^a	XRF this work ^b	σ , s	Relat. error %
Element							
K ₂ O (%)	–	–	12.90	12.81	12.65	0.13	1.25
P ₂ O ₅ (%)	0.002	0.019	0.093	0.024	0.023	0.001	4.16
Ta (ppm)	–	–	–	0.28	–	–	–
Nb (ppm)	–	–	–	–	–	–	–
Rb (ppm)	845	–	850	860	869	18.45	1.05

Table 5. (continuation)

Sr (ppm)	37	38.9	40	39	42	5.49	7.69
Cs (ppm)	10	-	7.2	7	7.4	1.06	5.7
Ba (ppm)	218	223	210	200	211	6.92	5.5
Ga (ppm)	24.7	17	-	20	19	3.6	5

^a RV = Recommended value according to Govindaraju [15].

^b Concentrations are the mean values of six splits each analysed six times.

Table 6. Comparative concentration values of several elements in GS-N (granite) standard reference material

Method	XRF	ICP OES	AAS	RV ^a	XRF this work ^b	σ , s	Relat. error %
Element							
K ₂ O (%)	4.60	3.96	4.42	4.63	4.71	0.09	1.73
P ₂ O ₅ (%)	0.280	0.280	0.250	0.280	0.27	0.01	3.57
Ta (ppm)	-	-	-	2.6	-	-	-
Nb (ppm)	27.5	-	-	23	22	3	4.35
Rb (ppm)	185	-	178	185	188	6	1.62
Sr (ppm)	556	565	558	570	581	11	1.93
Cs (ppm)	-	-	6	5.7	6	2	5.26
Ba (ppm)	1344	1413	1470	1400	1385	14	1.07
Ga (ppm)	23	13	-	22	23	2	4.54

^a RV = Recommended value according to Govindaraju [15].

^b Concentrations are the mean values of six splits each analysed six times.

Table 7. Comparative concentration values of several elements in AGV-1 (volcanic rock) standard reference material

Method	XRF	ICP OES	AAS	RV ^a	XRF this work ^b	σ , s	Relat. error %
Element							
K ₂ O (%)	2.93	2.84	2.92	2.92	2.80	0.2	4.1
P ₂ O ₅ (%)	0.49	0.47	0.56	0.49	0.52	0.022	6.1
Ta (ppm)	-	-	-	0.9	-	-	-

Table 7. (continuation)

Nb (ppm)	14.3	14.3	–	15	15.3	1	2
Rb (ppm)	64	–	68	67.3	71	9	4.01
Sr (ppm)	689	658	670	662	657	7	0.75
Cs (ppm)	–	–	1.4	1.28	–	–	–
Ba (ppm)	1239	1230	1190	1226	1238	8	0.98
Ga (ppm)	18	–	24.1	20	21	2	5.0

^a RV = Recommended value according to Govindaraju [15].

^b Concentrations are the mean values of six splits each analysed six times.

CONCLUSIONS

A new, rapid and simple approach to specimen preparation for the analysis by XRF is presented. A significant progress is achieved regarding the sample preparation method where traditional sample amounts are reduced to 150 mg. A new stainless steel mould is used to prepare boric acid sample supports where mineral sample powders are placed. The latter are subsequently compressed to produce pellets.

Major, minor and trace elements are determined in pegmatitic muscovites and K-feldspars employing our procedure. Among the geochemical interesting elements successfully determined are: K, P, Rb, Sr, Cs, Ba, Gs, Nb and Ta.

Precision and accuracy obtained for geological reference materials demonstrate the reliability of our XRF procedure. Our results compare favourably with the published and accepted values, thus concluding that a suitable specimen presentation to the X-ray beam is obtained by using our method.

More complex matrixes, such as granites and andesites, can also be geochemically studied by using the procedure here presented.

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