

VIII Analyse - Analysis

Elemental analysis of silicates by instrumental neutron activation analysis.

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SUMMARY

A survey is given of the system for instrumental neutron activation analysis.

The accuracy and precision are compatible with those of the sampling procedure.

Application of cluster-analysis facilitates the interpretation of the data.

1. Introduction

— Elemental analysis is an essential tool in geochemistry. Its usefulness is dependent on three main factors:

- Sample preparation.
- Analytical procedure.
- Data processing.

The application of instrumental neutron activation analysis (INAA) in the classification of geochemical samples is equally governed by these three factors. Let us consider them separately.

— Sample preparation consists of at least three steps:

- Sampling in situ.
- Homogenization and drying.
- Taking of the aliquot for analysis.

The first step is the exclusive responsibility of the geologist. The significance decreases with increasing ratio total mass/sampled amount. A relative standard deviation of a few percents is common. The homogenized sample contains grains of different composition. The moisture content depends on the storage conditions. If there are only two types of grains present, it follows that the relative standard deviation in the total mass of the element of interest, present in the aliquot taken for analysis is given by:

$$\sigma_{rel} \leq \frac{100}{\sqrt{n}} \cdot \frac{\alpha - 1}{\alpha + 1} \% \quad \dots(1)$$

Here n is the number of grains and α the ratio between the concentrations in the two types of grains.

The equality sign applies to equal frequencies of both types.

For the not uncommon case of $n = 1000$ and $\alpha = 2$ this points to $\sigma_{rel} = 1\%$

The variation in the moisture content is usually of the order of 0.5%.

Thus the total uncertainty in the aliquot will be around 1%.

— Analytical procedure

The total statistical error inherent to INAA is 2-5%. This is of the order of the total uncertainty due to sampling and pre-treatment. There is no appreciable systematic error.

— Data processing

The elemental concentrations determined for the various elements can be considered as coordinates in multidimensional space and used as the starting data for cluster analysis. Some criterion for "similarity" is defined and the decrease in clustering with decreasing similarity is plotted. It is obvious that the lower level of this procedure is reached when data from duplicate analyses do not longer fall into the same class.

Cluster techniques are now routines, available in most large computers.

2. A system for routine INAA

The procedure of INAA consists of the following steps:

- Samples of ± 200 mg are weighted into polythene capsules using automatic balances with punch tape output. Small iron rings are mounted to serve as fluxmonitors.
- Ultrapure activated carbon, loaded with known amounts of various elements, serve as standards.
- Irradiation during 12 hours in the rotating facility of the HFR reactor at Petten.
- Return to the laboratory 12 h after the end of irradiation. Transfer to testtubes and counting with a 90 cm³ coaxial Ge (Li) detector, mounted in a sample changer, and connected to a 4000 channel analyzer.

Counting is performed thrice: One day, 3-4 days and 3-4 weeks after the end of the irradiation. Counting time is 1000 or 2000 seconds.

An electronic pulser is used to correct for losses during counting. The gamma-spectra are stored on magnetic tape, together with number, time and duration of the measurement.

- The fluxmonitors are measured with a NaI detector. Data are stored on magnetic tape. Computer processing of the data from these measurements and of the sample-weights and -codes yields punch cards to be used in the sample processing.
- The main computer programme determines the areas under the photopeaks, corrects for flux-difference and counting-conditions identifies the peaks and calculates the count-rates per g. Doublets and triplets are solved by a simple peak-separations programme. The background is interpolated linearly. This may occasionally produce a systematic error.
- A final programme gives the data in $\mu\text{g.g}^{-1}$, plotted in A-4

About 20 elements may be determined in this way. Separate determination using a 1 min pneumatic rabbit irradiation or a 4 hours activation, followed by γ -ray spectrometry yields another 5-8 elements.

With fast neutron activation, Si may be assayed. Photon activation yields Ti, Mg, Ca and Sr.

If we restrict ourselves to INAA the following picture is obtained:

Nearly always	Na, Mg, Al, Cl, K, Ca, Sc, Cr, Mn, Fe,
determinable	Co, Zn, Sr, Sb, Ce, Nd, Sm, Eu, Yb,
	Lu, Hf, Th, U.
Often determinable	Ga, Cs, Ba, Gd, Tb, Dy, Tm.
Sometimes determinable	V, Cu, Br, Ta, Ir, Au.

Some more elements may be obtained by applying computer-programms based on iterative curve-fitting.

3. Results

Two controls are applied:

- Aliquots of a 'home'-standard are processed in each run.
- More sparsely aliquots of one of the USGS and CRPG standards are added.

As 'home'-standards we use Gray Shale 46W-4100. Table I gives the results of the first half year of application.

The data obtained for the USGS standard AGV-1 (andesite) are summarized in table II.

The standard deviation is mainly due to the determination of the area under the photopeaks.

This error may be reduced by the application of iterative computer-programmes.

4. Cluster Processing

The data are fed into the programme CLUSTAN IB, issued by the London University Computer Service. With respect to the plotting of the results, a number of options is available.

The resulting dendograms may be used as a hint for further work.

5. Conclusions

- The present system for INAA of silicate samples gives results which are of a precision comparable to that of the sampling.
- Improvements can be obtained by applying more elaborate computerprogrammes.
- Cluster analysis may be used to interpret the data.

Table I
Measurements of the 'home'-standard Gray Shale 46W-4100

Elements	Concentration	Relative standard deviation (%)
Na	2950 $\mu\text{g}\cdot\text{g}^{-1}$	1.4
Al	9.56 %	1.2
Fe	3.66	1.1
Cr	105.5 $\mu\text{g}\cdot\text{g}^{-1}$	1.0
Co	21.7	1.0
Sc	18.7	0.8
La	38.6	1.3
Ce	95	1.0
Sm	7.2	1.2
As	32.1	1.9
Rb	3.5	3.4
Sc	10.8	2.9
Yb	3.5	3.4
Hf	4.7	3.4
Eu	1.4	3.6
Ba	440	6.1
Sb	2.3	10
Lu	0.8	13
Th	17.4	2.9

Table II
Results for AGV-1

Element	Found	Literature-value
Na	3.14%	3.16%
Al	9.13	9.10
K	2.95	2.40
Sc	10.1 $\mu\text{g}\cdot\text{g}^{-1}$	12.3-13.4 $\mu\text{g}\cdot\text{g}^{-1}$
Cr	11.6	10.2-12.2
Fe	4.73%	4.73%
Co	13.0 $\mu\text{g}\cdot\text{g}^{-1}$	14.1-15.4 $\mu\text{g}\cdot\text{g}^{-1}$
Rb	77	67-78
Sb	4.8	4.3-4.6
Ba	1138	1208
La	41	35-53
Ce	68	67
Sm	6.6	4.9-5.9
Eu	1.6	1.6-1.7
Hf	4.5	5.2

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