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A Neutron Activation Technique for the Analysis of Cryolite in Core Samples

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Abstract—A short-lived, delayed neutron activation technique has been investigated to determine the content of cryolite (Na_3AlF_6) in core samples, by the detection of fluorine through the fast neutron reaction $^{19}F(n,\alpha)^{16}N$. The resultant γ-rays in the energy range of 2.84–8.14 MeV measured for pure cryolite and background samples, established that cryolite concentrations >13.6 wt% in rock samples could be estimated with uncertainties of about ± 4.3 wt%. The results are very satisfactory for exploration purposes.

1. INTRODUCTION

The mineral cryolite which is used in the production of aluminium is of rare natural occurrence and the deposits in the Amazon region of Brazil are a recent addition to world resources. During exploration, the subsurface core samples exhibit a high degree of fragmentation and present laboratory analyses employ chemical and x-ray techniques. However, neutron activation methods permit a rapid analysis of elemental composition, and are being used increasingly in field analysis, in bore-hole logging and in the mineral processing industry (Schweitzer *et al.*, 1987; Schweitzer, 1991; Shirakawa, 1991). As a result of this interest, a short-lived delayed activation method has been examined for estimating the cryolite content in samples of drill cores, through γ-ray yield measurements.

2. ACTIVATION EXPERIMENT

Considering the composition of cryolite i.e. Na_3AlF_6 (Na = 32.85 wt%, Al = 12.85 wt% and F = 54.30 wt%), the investigation was focussed on the detection of F as a means of measuring the cryolite content in appropriate samples. By using the fast neutron reaction,

$$^{19}F(n,\alpha)^{16}N, \qquad t_{1/2} = 7.14\,s$$

interference from feldspars is avoided and accurate measurements of the intensities of the γ-rays at 6.128 MeV ($\sim 69\%$) and 7.117 MeV ($\sim 5\%$) are possible.

The proposed method was investigated in the laboratory using cyclic neutron activation analysis with a relatively weak $^{241}Am/Be$ source ($\sim 2.5 \times 10^5$ neutrons/s). The mean energy of the neutrons ($\bar{E} = 4.5$ MeV), is highly compatible with the reaction cross-section of F and at the same time any activation of O is marginal due to its high threshold ($E_{th} \sim 9.5$ MeV). The measurement of γ-rays is performed using a 3″ × 3″ diam. NaI(Tl) detector in combination with a standard pulse-processing equipment and a 512 channel pulse height analyser (PHA). The analyser was programmed to permit eight successive 15 s accumulations of γ-ray counts and storage of the data from cyclic exposure experiments. The experiment utilized pure cryolite mineral (PN-A) and background rock (PN-B) formation parts of the core samples for analysis. The samples were previously analyzed using the

reactor at the Instituto de Pesquisas Energticas e Nucleares, São Paulo, SP, to determine the F and Na compositions (Table 1) and the nature of PN-A sample is consistent with the chemical composition of cryolite.

The samples, in powder form (wt ≈ 25 g), were packed in plastic vials and then activated for 60 s and transferred, allowing a lapsed time of 2 s for the start of counting.

3. RESULTS AND DISCUSSION

The γ-ray counts are integrated and stored in five energy bands: 0.253–0.652, 0.652–1.003, 1.003–1.498, 1.498–2.807 and 2.807–8.138 MeV. This division facilitates analysis, since the γ-rays due to F (photo peaks and the associated Compton tail) contribute mainly to the highest energy band of 2.81–8.14 MeV whereas γ-ray contributions due to Na and Al activation and any natural radioactivity of the samples could be present in the lower energy bands.

The average count rate R from ^{16}N in the highest band, can be expressed in relation to the content of element F in the sample by:

$$R = Q.\sigma.G.n.x.f(t_a, t_d, t_m).R_b.\varepsilon$$

where Q is the source strength, σ is the neutron capture cross-section, G is the geometric factor in the irradiation, n is the density of F atoms, x is the average neutron path length (Ozmutlu and Ortaovali, 1976), f is the activation–detection function, R_b is the branching ratio of γ-ray emission and ε represents the total detection system efficiency in the energy band. The function f has the form:

$$f(t_a, t_d, t_m) = (1 - e^{-\lambda t_a}).e^{-\lambda t_d}.(1 - e^{-\lambda t_m})/\lambda t_m$$

where λ is the decay rate and t_a, t_d and t_m are the activation, transfer and measurement durations. The calculations for pure cryolite estimate $\geqslant 710$ counts for the first 15 s duration of the cyclic measurements.

Figure 1 shows the counts in the first two successive 15 s intervals after activation (background subtracted), in the five energy bands, for both PN-A and PN-B samples.

The counts in all the energy bands corresponding to the PN-A sample are generally higher than those from the PN-B sample. Particularly, in the highest energy band of 2.84–8.14 MeV, the counts of PN-B are within 1σ and negligible compared to the two successive PN-A sample counts. The γ-ray counts observed in several successive 4 s accumulations in the case of PN-A (cryolite mineral) gave a half-life decay of 7.16 ± 0.64 s, consistent with ^{16}N. In addition, the observed counts of 946 ± 51 in the first 15 s interval in the case of PN-A sample are consistent with the estimated value and support the positive detection capability of F in the sample.

The observed statistical significance of 18.5σ for γ-ray counts in the energy range 2.81–8.14 MeV and in the first 15 s, for PN-A sample containing 54.3 wt% of F indicates a 3σ accuracy (Shirakawa, 1991) of ± 8.8 wt%. This permits the experimental system to detect any presence of cryolite mineral in formation samples with content > 13.6 wt% with uncertainties in the range of approx. ± 4.3 wt%(1σ). The cryolite content in the PN-B sample can be estimated as $\leqslant 7.8$ wt% from the Na content and the γ-ray flux is expected to be insignificant. By upgrading the source strength by a factor 10, the accuracy of detecting cryolite can be improved to ≈ 4 wt% with an uncertainty of ± 1.3 wt%. In future work, it is envisaged to optimize the source strength, sample geometry and

Table 1. Percentage weight composition (wt%) of Na and Al in the samples

Element	PN-A	PN-B
Na	32 ± 4	2.5 ± 0.4
Al	12 ± 1	7.0 ± 0.6

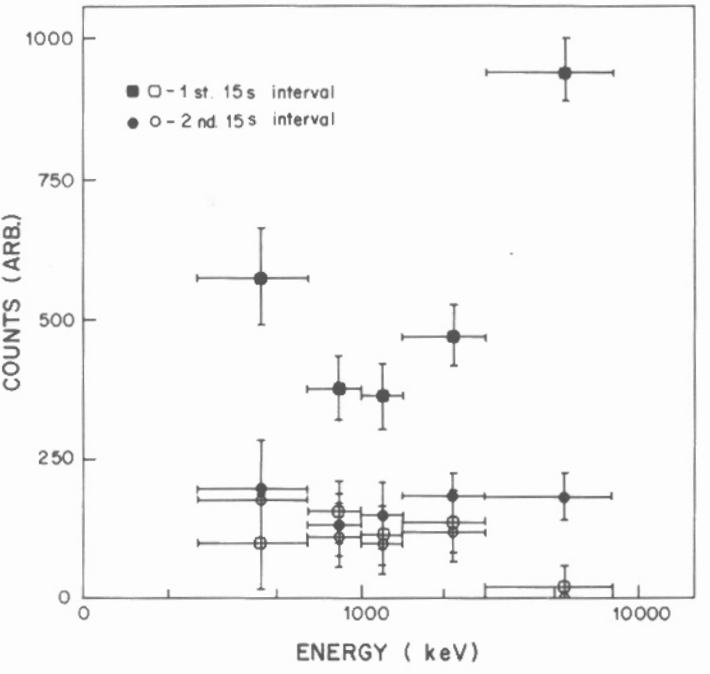

Fig. 1. Gamma-ray counts emitted by cryolite PN-A (filled) and back-ground rock PN-B (open) formation samples, shown as a function of energy in two successive 15 s measurements after neutron irradiation for 60 s.

activation of samples with different mineral contents and also other elements in the construction of a field analysis system.

4. SUMMARY

The suitability of neutron activation as a technique for field analysis of cryolite mineral has been established by laboratory experiments. With an ^{241}Am/Be fast neutron source (2.5×10^5 neutrons/s) and activation times of 60 s, the cyclic exposures of drill core samples of cryolite permitted measurements of γ-rays with a $3'' \times 3''$ dia NaI(Tl) detector. The γ-rays of energy 2.8–8.14 MeV observed at a statistical significance of 18.5σ for pure cryolite samples, establishes that for concentrations of cryolite in rock samples >13.6 wt%, the uncertainties are about ± 4.3 wt%.

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