

PAPER • OPEN ACCESS

## Express Assessment of the Quality of Fluorite-Containing Raw Materials

To cite this article: T A Glushkova *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **272** 022133

View the [article online](#) for updates and enhancements.

# Express Assessment of the Quality of Fluorite-Containing Raw Materials

T A Glushkova<sup>1</sup>, A G Talalay<sup>1</sup>, I E Shinkaryuk<sup>1</sup>

<sup>1</sup>Ural State Mining University, Street of Kuibyshev, 30, Ekaterinburg, 620144

E-mail: groupnedra@mail.ru

**Abstract.** In the production of fluorspar (fluorite) of various grades, the rapid and accurate determination of fluorite is important. The chemical method is used as a marking method, and neutron activation analysis is used as an express method. Initially, the neutron-activation analysis method for fluorite was used by V. Ya. Bardovski for well logging. Its essence is reduced to the irradiation of rocks containing  $\text{CaF}_2$ , a neutron flux from the polonium-beryllium source, followed by the measurement of induced activity on the short-lived isotopes  $^{16}\text{N}$  and  $^{20}\text{F}$ . This method has the following advantages in comparison with chemical: expressiveness and relatively simple analysis technique, the ability to determine very small amounts of individual elements in rocks and the possibility of element-by-element analysis of rock composition in natural occurrence. The results obtained from the studies indicate that a plutonium-beryllium source should be given preference. According to calculations by E M Filippov [10], 50% of oxygen using a polonium-beryllium source is equivalent to 0.025% fluorine, and for plutonium-beryllium it is 0.0085%.

## 1. Introduction

The quantitative determination of any mineral in the sample can be performed by X-ray diffraction analysis, provided that the given phase (mineral) is contained in an amount not less than a few percent of the total mass, and interference maxima are not superimposed on analytical lines other minerals. Even if these conditions are met, satisfactory results can be obtained only by careful preparation of samples ensuring their sufficient representativeness, since a very small volume participates in the analysis due to the small penetrating ability of X-rays.

A significantly better representation can be obtained by using activation methods of analysis with radioisotope sources, since samples with a mass of 100 or more grams are analyzed. In this case, it is not necessary to thoroughly rub the samples, but it is sufficient to crush them to a size of 3-5 mm. The disadvantage of the activation methods is that they do not determine the content of any mineral, but only the mass fraction of the element being analyzed, regardless of whether it is part of one or several minerals. However, this circumstance does not preclude the use of activation methods for finding the content of the mineral of interest if the element to be determined is concentrated in it, and the content of this element in the rest of the rock remains constant or correlates with the mass fraction of the given mineral. This condition is usually well satisfied for fluorspar deposits, where the bulk of fluorine is associated with fluorite, which led to a fairly wide application of activation methods of analysis in prospecting, exploring and exploiting this type of deposits [1-6].



## 2. Objective

Show the advantages of activation analysis of fluorite ores by the example of two reactions  $^{19}\text{F}(\text{n}, \alpha)^{16}\text{N}$  and  $^{19}\text{F}(\text{n}, \text{p})^{19}\text{O}$ .

## 3. Method of work execution

Natural fluoride consists of one stable isotope  $^{19}\text{F}$ . When irradiated with a neutron flux, nuclear reactions take place, resulting in the formation of radionuclides that radiate nuclear particles when dispersed. The table shows the characteristics of these reactions and the composition of the emerging radiation. The effective cross section of the reaction  $^{19}\text{F}(\text{n}, \gamma)^{20}\text{F}$ , which takes place on thermal neutrons, is 9 millibarns [7].

Comparing the above data, it can be seen that reactions (3) and (4) are of little use for analysis purposes. Reaction (3) has a high threshold and gives rise to annihilation radiation, which will be absorbed by radiation from other nuclides with positron decay. Reaction (4) has a small effective cross section in comparison with other reactions on thermal neutrons, in particular, with the reaction  $^{27}\text{Al}(\text{n}, \gamma)^{28}\text{Al}$  (215 mb). Since the aluminum content in the rock is usually much higher than the fluorine content, and the half-life of  $^{20}\text{F}$  is only an order of magnitude smaller than the half-life of  $^{28}\text{Al}$ , the activity of the latter will always be 1-1.5 orders of magnitude higher, and the fluorine photopeak will be obscured by gamma radiation of aluminum (1, 78 MeV).

**Table 1.** Characteristics of nuclear reactions to fluorine [8-10].

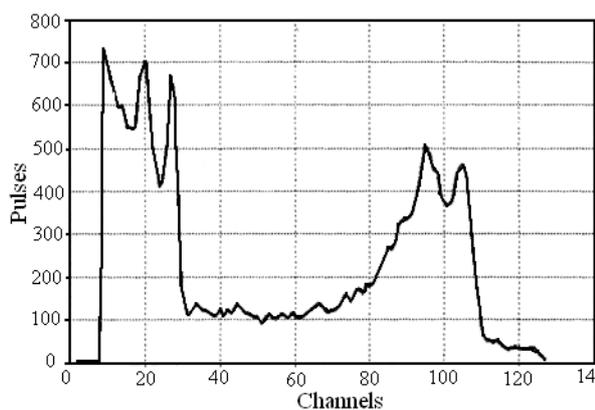
№	Reaction	Threshold, MeV	$T_{1/2}$	Composition of radiation MeV (%)	
				beta	gamma
1	$^{19}\text{F}(\text{n}, \text{p})^{19}\text{O}$	4,2	29,10 s	4,6 (41) 3,25 (59)	1,44 (3,3) 1,36 (5,6) 0,20 (96,7)
2	$^{19}\text{F}(\text{n}, \alpha)^{16}\text{N}$	3,2	7,35 s	10,44 (26) 4,27 (68) 3,30 (4,9)	7,12 (4,9) 6,13 (68)
3	$^{19}\text{F}(\text{n}, 2\text{n})^{18}\text{F}$	10,95	1,87 h	0,65 (97)	0,511 (200)
4	$^{19}\text{F}(\text{n}, \gamma)^{20}\text{F}$	Thermal	11,36 s	5,42 (100)	1,63 (100)

More suitable for analytical purposes are reactions (1) and (2). The  $^{19}\text{O}$  nuclide formed in reaction (1) has a longer half-life, which makes it possible to carry out the analysis without automatic sample transportation. Although low energy emitted by gamma radiation makes it difficult to register, but at a sufficiently high fluorine content, gamma spectrometry makes it possible to measure the amount of its induced activity  $^{28}\text{Al}$ , which is formed from silicon nuclei. EP Vyaznikov and VV Glasson [11] used a source of neutrons with a yield of  $2 \cdot 10^7$  n/s and a detector NaI (T1) 150x150 mm with a well at a sample mass of 25 g. In their estimation, the sensitivity threshold at specified conditions is 0.7% fluorine. Due to the small half-life period, a high performance is achieved - about 5 minutes per sample.

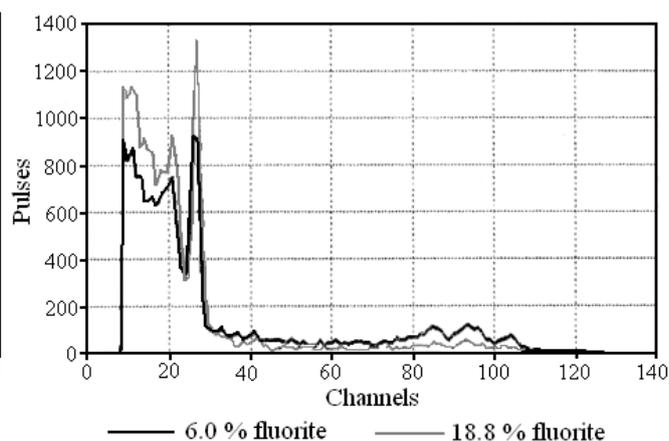
The most widely used in the activation analysis for fluorine are methods based on the reaction (2) [12]. First, this reaction has a significant cross section at a neutron energy of more than 4 MeV, and secondly, the very hard gamma radiation produced during the decay of  $^{16}\text{N}$  nuclei is in the region where there is no natural background, except for the background of cosmic radiation.

Figure 1 shows the apparatus spectrum of the gamma radiation of a fluorite ore, activated by fast neutrons of the Pu-Be source. The spectrum was detected by a detector NaI (T1) 150x100 mm. On the right side of the spectrum, a double peak is seen, due to the origin of the 6.13 MeV line. The right maximum corresponds to the peak of total absorption, the left peak corresponds to the flight of one annihilation quantum. The peak corresponding to the emission of both annihilation quanta is of low

intensity and is not resolved with a half-peak peak, manifesting as a flattening of the left slope of the latter. The peak in channel 20 is associated with the radiation of the nuclide  $^{19}\text{O}$  formed by reaction (1), and in channel 26, the radionuclide of  $^{28}\text{Al}$  nuclide is observed. When the spectrum is registered with a 63x63 mm detector, the probability of emission of both annihilation quanta increases, and the peak on the right side becomes triple (Figure 2). It can be seen that for samples with a lower fluorite content, the relative intensity of the peak is 1.78 MeV. The spectra shown in this figure are obtained at 10 cycles of activation by a plutonium-beryllium source with a yield of  $1, 18 \cdot 10^7$  n / s samples weighing about 200 g. The activation parameters were as follows: activation - 60 s, pause - 7 s, measurement - 12.8 sec.



**Figure 1.** Equipment spectrum of fluorite. Detector NaI (T1) 150x100 mm.



**Figure 2.** Apparatus spectrum of the sample with fluorite. Detector NaI (T1).

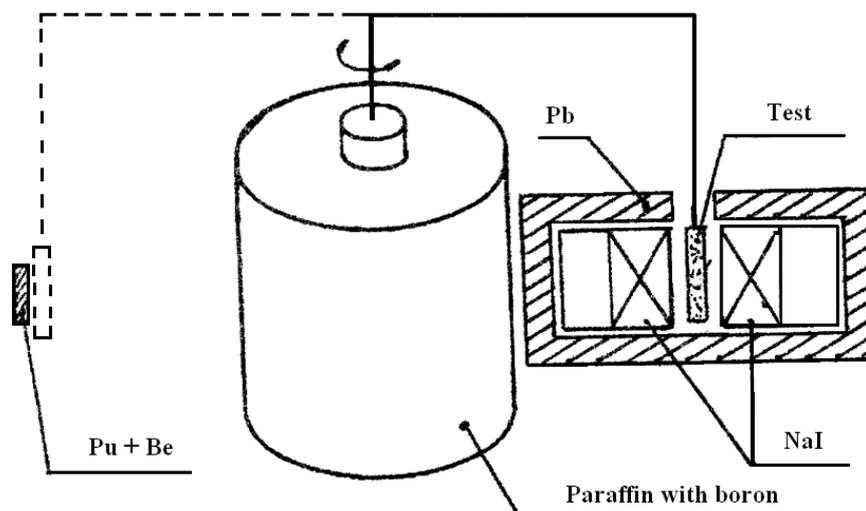
Reaction (2) occurs only at a neutron energy exceeding the threshold value of 3.2 MeV. Although all isotope neutron sources have in their spectrum neutrons whose energy is greater than the indicated value, their fraction is different for sources of different types. Thus, in sources based on the spontaneous  $^{252}\text{Cf}$  fission, the fraction of neutrons with energy above the threshold is about 20% of their total number, and if we take into account that the reaction cross section for neutrons with an energy of less than 4.5 MeV remains small, then actually only 8% of the total number of emitted neutrons can participate in the reaction. It follows that for activation on fluorine it is necessary to use sources with a higher neutron energy. Po-Be and Pu-Be sources have such qualities. Preference should be given to the latter. The fact is that the  $^{16}\text{N}$  nuclei can be formed not only by reaction on fluorine nuclei, but also by the  $^{16}\text{O}(n, p)^{16}\text{N}$  reaction, which has a threshold of 10 MeV. The fraction of neutrons exceeding the threshold of this reaction is smaller in plutonium-beryllium source than in polonium-beryllium. According to E M Filippov's calculations [7], 50% of oxygen using a polonium-beryllium source is equivalent to 0.025% fluorine, and for plutonium-beryllium it is 0.0085%.

Experiments carried out by B S Kamyshev [13] with a plutonium-beryllium source gave even less significance - less than 0.004%.

The small value of the half-lives of the nuclides formed during the reaction of neutrons with fluorine nuclei causes a small number of quanta emitted by the breakdown with a single act of activation. The low efficiency of recording high-energy quanta creates additional difficulties in the number of samples that provide sufficient accuracy of measurements. To reduce the statistical error in the analysis of the samples, a cyclic activation technique is used [14] and larger detectors are used. For example, in a device for activation analysis of samples, described in [13], two 150-100 mm sodium iodide crystals are used, into the gap between which the activated sample is placed (Figure 3).

#### 4. Research results

We have tested the possibility of using detectors with a crystal 63x63 (detector 1). With a detection threshold of 3.0 MeV, the number of pulses recorded from the activated sample (a core of about 7 cm in diameter) located on the end surface of detector 1 turned out to be 6 times smaller than when registered by detector 2 measuring 150x100 mm. This roughly corresponds to the ratio of detector volumes. The background of the unshielded detector 1 at this threshold was at the level of 17 pulses/min, which is also about 6 times smaller than the background of the detector 2. A smaller background partially compensates for the loss in the sensitivity of smaller detectors when working with poor samples.



**Figure 3.** Installation diagram for activation analysis for fluorine [13].

To activate the samples, a container was made, consisting of two interconnected coaxial cylinders, between which a sample was poured.

The diameter of the inner cylinder was 80 mm, external – 100 mm, height – 80 mm. Such dimensions correspond to the size of the sensitive part of the detection unit, allowing the irradiated sample to be as close as possible to the crystal detector. When activated, the neutron source was placed on the axis in the center of the container, ensuring a sufficiently uniform activation of the sample. At the end of the activation, the source dropped into the well at a depth of 0.4 m, and the process was transferred to a detector that was three meters away from the wellhead. The shallow depth of the well did not ensure complete absorption of radiation from the radiation capture of the neutron source, and the background of the detector increased to 50 pulses / min.

With the above time parameters and the power of the source  $1.18 \cdot 10^7$  N/s, the number of pulses per 1 gram of fluorine in 10 cycles was 161 imp/g for a sample with a fluorite content of 18.8% and 182 imp/g for samples containing 6% fluorite. The calibration coefficients given are determined with a relative error of 3%, due to the sampling statistics. The discrepancy of their values, which is slightly more than 10%, can be explained by the error of mineralogical analysis or by the presence of fluorine in other minerals in the amount of about 0.4% of the mass of the sample. Considering that about 250 grams are placed in the container we use, about 1% of the fluorine content accounts for about 20 pulses per activation cycle. BS Kamyshev [13], who used in his installation two detectors 150x100 mm and a source with a yield of  $2 \cdot 10^7$  n / s, with a sample weight of 130 grams recorded a cycle of 260 pulses per 1% of the fluorine content. With the same power of the source and a decrease in the pause of up to 1-2 seconds with a crystal 63x63 mm, it is possible to record about 60-65 quanta per 1% of fluorine per cycle, which is only 4-4.5 times less than in Kamyshev's setup .

## 5. Conclusions

The experimental data allowed estimating the number of cycles needed to ensure the reproducibility of the analysis meeting the requirements for Category 3 methods [15]. Under the conditions of activation and measurement used in the experimental measurements, the required accuracy will be provided for 5 cycles with a fluorite content above 10% and for 8 cycles - with a content of 1 to 2%. Given that the duration of one cycle is less than one and a half minutes, the entire analysis will take 8-12 minutes. Reducing the pause between activation and measurement will allow approximately 2-fold increase in the performance of the analysis.

A short half-life of the fluorine activation products makes it necessary to mechanize the activation of the samples and to detect the induced activity. The neutron source is a powerful source of gamma radiation, including in the hard part of the spectrum, therefore, during the measurement of the induced activity, the detector must be at a sufficient distance from the source and screened both from gamma quanta and neutrons. During activation, the detector should also not approach the source in order to avoid activation of the detector itself. Thus, the problem arises of moving the sample from the neutron source to the detector for 1-3 seconds, so that the activity does not decrease significantly, and then back to the source for the next activation cycle. In the installation [13], shown in Figure 3, the transfer of the sample is made by turning the rocker on which it is fixed. With a large thickness of protection, the installation becomes too cumbersome, therefore it is not possible to achieve full shielding of the detector from the source radiation. With a diameter of the protective block of paraffin with boron 1,2 m background was 4 times higher than natural. It was possible to reduce the background by lowering the source into the well for the measurement period and again raising it at the next activation cycle. In this installation, the flat shape of the container does not ensure homogeneity of the neutron flux across the sample area, which increases the requirements for its homogeneity.

More promising seems to us the use of pre-vehicles, widely used in activation analysis for short-lived nuclides [14]. In this case, the neutron source can permanently be in the well (well), and the sample will be delivered to a detector located at a distance of 1.5-2 meters from its mouth along a pipeline 3-4 meters in length. With an external container diameter of 10 cm, its cross-section is 80 cm<sup>2</sup>, so that an air pressure of 0.1 kg / cm<sup>2</sup> creates a force sufficient to move the container through the pipe. As a supercharger, a conventional vacuum cleaner can be used, which has sufficient capacity. Such an installation will ensure radiation safety and virtually complete shielding of the detector from the radiation of the neutron source. The cylindrical shape of the container ensures a sufficiently uniform activation of the sample material when the source is in the center [16-20].

## 6. References

- [1] Al'bov M N 1975 *Testing of mineral deposits* (Moscow: Nedra) p 232
- [2] Gryaznov O N and Shevkunov I I 1994 Ore-bearing metasomatites of the South Sharni deposit (Middle Urals) *Geology of ore deposits* **36** No 1 pp 48-57
- [3] Kozin V Z 2011 *Probe of mineral raw materials: scientific monograph* (Ekaterinburg: Publishing house of the USMU) p 316
- [4] Korytov F Ya 1976 *Fluorite (resources, patterns of formation and location* ed V P Petrov (Moscow: Nedra) pp 12-14
- [5] Yushkin N P 1991 *Mineralogy of the Urals: Arsenides and Stibnids. Tellurides. Fluorides. Chlorides and bromides* (USSR: Ural Branch of the Russian Academy of Sciences) pp 141-157
- [6] Petrov V P 1976 *Fluorite is an important raw material for the national economy* ed V P Petrov (Moscow: Nauka) pp 5-11
- [7] Filippov E M 1978 *Nuclear Exploration of Minerals* (Kiev: Naukova Dumka) p 586
- [8] Maslov I A and Luknitsky V A 1971 *Handbook of Neutron Activation Analysis* (Leningrad: Nauka) p 312
- [9] Nemets A F and Gofman Yu V 1975 *Handbook of Nuclear Physics* (Kiev: Naukova Dumka) p 415
- [10] 1974 *Handbook on nuclear activation cross-sections* (Vienna: IAEA) p 412

- [11] Dolgirev E I, Potekhin B A, Belov V N, Leipunskaya D I, Dryniki V I, Glasson V V and Vyaznikov E P, e.a 1968 *Neutron Activation Unit* Patent RF no 219707
- [12] Bushkov A P and Prokopchik V I 1966 *To questions about the activation method for the determination of fluorite*. Atomic Energy ed 3 vol 21
- [13] Kamyshev B S 1935 *Nuclear-geophysical methods for prospecting, exploration and development of fluorine-containing raw materials* (Moscow: Nedra) p193
- [14] Ivanov I N and Nikolaenko O K 1987 *Activation analysis for short-lived nuclides* (Moscow: Energoatomizdat) p 119
- [15] Standart 41-08-214-04 *Quality management of analytical work* (Moscow: VIMS) p 92
- [16] Glushkova T A and Talalay A G 2008 Neutron-activation testing of core and sludge (Moscow: IAGO)
- [17] Talalai A G, Makarov A B and Samsonov A V 1995 Fluorite of Shtokverko-Greisen deposits of the Urals *Geology, prospecting and exploration of non-metallic minerals*
- [18] Talalai A G and Makarov A B 1994 Estimation and prognosis of raw materials of the greisen deposits of the Urals for fluorite on the basis of a complex of geological, geophysical and rapid geochemical methods of wells and core studies *Abstracts of the All-Russian Scientific and Technical Meeting* (Perm)
- [19] Talalai A G, Miksevich V N, Zharnikov M Yu, Afonin K V, Ereimeikina O L and Lukashevich O V 1994 On the possibility of using nuclear-petrophysical parameters for quality control of fluorite ores of the Yaroslavsky GOK *Abstracts of the All-Russian Scientific and Technical Meeting* (Perm)
- [20] Talalay A G, Kuznetsov V I and Glushkova TA 2003 Mineral resources of tantalum, niobium, beryllium, zirconium and fluorine of the Ural region: geology, economics, technology *Conf. Mineral resources of tantalum, niobium, beryllium, zirconium and fluorine: geology, economics, technology* (Ust-Kamenogorsk) pp 395-398