J Math Chem (2010) 48:165–174
DOI 10.1007/s10910-009-9652-z

ORIGINAL PAPER

Mathematical study to improve the sensitivity in the neutron activation analysis of fluorspar

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Received: 30 September 2009 / Accepted: 24 November 2009 / Published online: 7 January 2010

Abstract A mathematical method to design a neutron activation procedure for analyzing a sample of fluorspar from a concentration plant has been created. The neutron activation is used to bombard a sample with neutrons and record the spectrum radioactive produced. The fluorspar grade is directly proportional to the fluorine content of the sample, and this in turn is directly proportional to the amount of 16N, the radioactive product produced in the bombardment. The ratio between both concentrations has been shown but the aim is to determine the activation parameters that increase the sensitivity of the method. This work discusses the mathematical models used and whose use is expected to increase the sensitivity of the reading.

Keywords Neutron activation analysis · Cyclic activation analysis · Fluorspar

1 Introduction

In recent years we have studied [1] the *applicability of the technique of neutron activation using neutrons from an isotopic source of Americium-Beryllium*, in different stages of a mining process. More specifically we have focused the study on the mining of fluorspar.

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The principle of neutron activation analysis is that a neutron induces a nuclear reaction in an atom of a target element. The product of the reaction is detected and quantified by its decay properties, if radioactive [2].

A normal activation measurement is subdivided into two parts: (1) the irradiation of a suitable sample, (2) the counting of the induced activity [3].

In 1960 [4] the reaction $^{19}F\ (n,\alpha)\ N^{16}$ for the determination of fluorine in LiF standard samples was used. The activations were carried out with the epicadmium neutron flux of a Beryllium target irradiated with 2 MeV deuterons from a Van de Graaff accelerator. The sample was packaged in an aerodynamically designed polyethylene rabbit running inside a 35 foot long polyethylene 1/2 inch tube inserted into the system via the air lock located at the 3×3 inch NaI(Tl) scintillation counter.

In addition, the concentrations of metallurgical, biological and geological samples could be determined using long-lived nuclides but the use of short-lived nuclides not only reduces total experiment time but also improves the precision of measurements [5,6]. Therefore, several elements can be determined by neutron activation analysis (NAA) using short-lived nuclides.

The advantages of the described nuclear method of fluorine determination have been reported [6,7], but all the analyses are carried out on metallurgical, biological and industrial samples, using a research reactor as a neutron source, not on fluorspar samples using an isotopic source.

Our experiments have shown that the method of neutron activation with an Americium Beryllium neutron source allows the fluorine content in a sample of fluorspar mineral to be determined, and consequently, the grade of the fluorspar sample, with two interesting advantages: the sample need not be prepared beforehand and the time required to analyze it is very short.

Presently, in this type of research, studies are focused on laboratory analysis of samples. Later, this procedure could be applied in the control of the grade fluorspar in other phases of the mining process: in exploration, mining, and concentration mining. The study includes the following results:

- There is a proportion between the fluorine content and the grade fluorspar in a mineral sample because all the fluorine is present in the fluorspar.
- There is proportionality between fluorine content in the mineral sample and the gamma radiation emitted by the sample bombarded by neutrons which is recorded in a detector of radioactivity.
- The radiation is expressed as the number of radioactive events counted during a given time, also expressed as counts. The number of counts detected in the current tests and with the available device is very low: for a sample with a grade of 60% after being bombarded with neutrons emits 120 counts, the maximum value of counts obtained for a sample with a grade of 97% are 250, and the minimum value for a sample with a grade of 4% are practically negligible. Therefore, one count represents a 0.5% of grade mineral. Figure 1 shows the number of counts detected when neutrons from an isotopic source whose activity is 1Ci bombarded a fluorspar sample. We used a 2"$\times$2" INa detector.
- A mathematical method to design an activation procedure of the fluorspar sample that increases the sensitivity of the method has been developed.

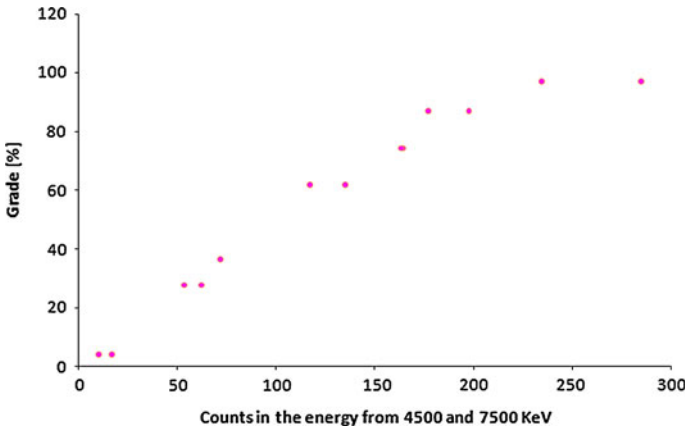

Fig. 1 Relationship between the counts in the energy range from 4,500 and 7,500 keV and the grade in F_2Ca

- This work discusses the mathematical models that have been carried out as well as new working models which are expected to increase the number of counts in reading.

1.1 Neutron activation

Neutron activation is a process by which a sample is irradiated with neutrons from a radioactive source of the type Americium-Beryllium and after irradiation it is possible to read the gamma radiation emitted by the sample. This radiation is produced during a certain time and is characterized by energy and by the time during which it occurs.

In an analysis of the radiation certain elements are found to be present that allow us to quantify its concentration in the sample, because the concentration is directly proportional to the intensity of the radiation. The analysis of the radiation involves the control of three aspects: the energy of the emitted radiation, the amount of radiation emitted and the time during which it emits radiation.

The time during which the source has bombarded the sample with neutrons is known as activation time, while the time during which the sample is read is called reading time. Between the two times the sample has to move from the point of irradiation to the point of detection. This shift represents a time during which the radioactivity of the irradiated sample, is delayed.

This procedure for determining the concentration of a sample of fluorite has been applied. The 16N is a product of interaction between the neutrons from an Americium-Beryllium source and the fluorspar mineral sample. The 16N is a radioactive element that emits a characteristic radiation of energy and time decay which is in contrast when compared with the energies and decay times of the rest of the elements produced in the bombardment.

The activation process [8,9] is controlled by the mathematical equation:

$$g(t) = K * \left(1 - e^{-\lambda t}\right) \tag{1}$$

Where,

- K is a parameter that depends
  - on the concentration of fluorine in the original ore sample,
  - on the neutron flux from the source of Americium-Beryllium and
  - on cross section or probability of occurrence of the neutrons reaction with fluorine,
- λ is the constant half-life of 16N, and is equal to $ln2/T_{1/2}$, where
  - $T_{1/2}$ is the half-time of 16N, 7.13 s, and
- t is the time during which the sample is irradiated.

Moreover, the radioactive products are generated in the irradiation of the sample, according to the following decay law:

$$h(t) = K * \left(1 - e^{-\lambda\tau}\right) * \left(e^{-\lambda(t-\tau)}\right) \tag{2}$$

t refers to the start of irradiation, and τ is the activation time of the sample.

The first step of the experiment is taken ignoring the intensities of gamma radiation emitted by the irradiated sample. Tests performed to date have assumed a single activation process and have read the counts due to the activation for a time on the time decay of 16N.

Figure 2 shows the evolution of the 16N nuclei during the activation process, and during the radioactive decay that occurs while reading radioactivity from the sample irradiated.

X-axis shows the time expressed in seconds, and Y-axis the concentration of 16N present in the sample, and τ represents the activation time. τ expresses the value of time during which the concentration of 16N increases exponentially as shown in Eq. (1). This figure is asymptotic and tends to a value which we call "saturation". In reality, the Y-axis expresses the concentration of 16N in relationship to saturation.

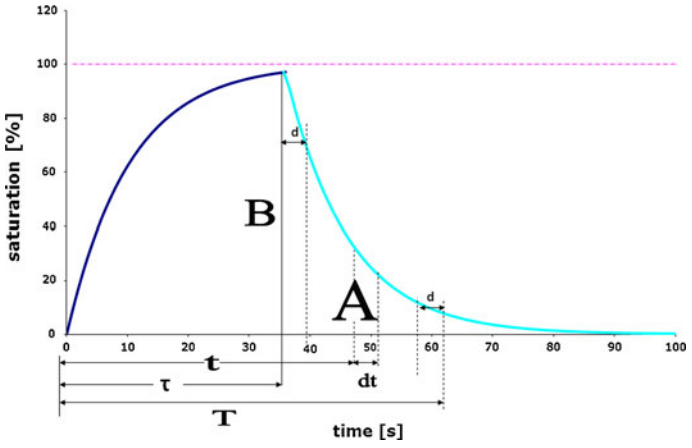

Fig. 2 Evolution of the 16N nuclei in the activating and reading process

At moment τ, the nuclei of 16N decrease following the decay law expressed in Eq. (2). B expresses the highest concentration of 16N nuclei reached during τ s of activation, and in the area marked A represents the measured gamma radiation for a total processing time equal to T.

In mathematics, we can express the area A in function of the above parameters, through the integration of the Eq. (2) from a time between τ and T. The following equation expresses the result of this integral, without transfer time d:

$$A = \frac{K}{\lambda}\left(1 - e^{-\lambda\tau}\right)\left(1 - e^{-\lambda(T-\tau)}\right) \tag{3}$$

Transfer time is the time to move the sample from an activation position to a reading one, or to move the sample from a reading position to an activation one, and it has not been measured in the process. During the transfer time, d, the concentration of 16N decays is not read in the detector. If we consider this parameter as the area obtained in Fig. 2, it is:

$$A^d = -\frac{K}{\lambda}\left(1 - e^{-\lambda\tau}\right)\left(e^{-\lambda(T-\tau-d)} - e^{-\lambda d}\right) \tag{4}$$

Of the correlation with experimental data, the proportionality between grade and area is deduced from mineral grade and area, that is, the low emission of the sample implies a low sensitivity of the analysis method that can be improved by implementation of new procedures for activating and measuring the resulting radioactivity.

1.2 Cyclic activation analysis

Cyclic Activation Analysis (CAA) is a method of elemental analysis in which a sample is irradiated, decayed, counted, then irradiated again, and this process is repeated for a number of cycles [8].

In Neutron Activation Analysis (NAA) based on short-lived radio-nuclides, as in our case, there is high sensibility, precision and accuracy, hence improved detection limits, which can be obtained by Cyclic Activation (CA) of the sample and cumulatively counting the induced activity [10]. CAA was first suggested for the analysis of geological material, but this technique has been used in every field of elemental analysis [11,12]. A computer-controlled system and a program of simulation for the cyclic neutron activation analysis have been developed and the effect of cycling time clearly shown [13,14].

To improve the sensitivity of neutron activation in determining fluorspar samples, the activation and reading times have been repeated several times. In this way the value of A is amplified to the same value of the mineral grade. Our objective is the optimizing process for a specific total time process or ascertaining the value of the number of cycles as well as activation and readings times, which make maximum A.

One procedure is described below, the symmetrical cyclic. In this method, the sample is irradiated for a period of time near to saturation, and after, the radiation emitted is read until the reading is practically zero. This process is repeated again to complete

the process time T. There is a problem to discover the maximum number of cycles for each process time and the proper activation and reading time.

Defining the number of cycles 'n' for each time process involves finding a relationship between activation and reading times. By maximizing the functions defined in Eqs. (3) and (4) with respect to time, the relationship has been found, and the following expressions obtained. (See Table 1).

Where τ_{op} and τ_{op}^{d} are the best activation times to maximize the areas of Figs. 2 and 3 considering or not transfer time.

Knowing the optimum time, it is possible to establish the maximum signal in each case. (See Table 2)

Knowing these signals, it is possible to determine the optimal number of cycles by maximizing functions expressed regarding n, the Eqs. (3) and (4). Expressed by the following equation:

$$e^{\lambda T/2n_{op}} = 1 + \frac{\lambda T}{n_{op}} \tag{5}$$

If we make the change of variable $a = 1 + \frac{\lambda T}{n_{op}}$, the equation will be as follows $e^{a-1/2} = a$ and consequently, the resolution would be simplified because this equa-

Table 1 Activation time τ for activation with symmetrical cycles

	Without transfer time	With transfer time, d
1 cycle	$\tau_{op} = T/2$	$\tau_{op}^{d} = \frac{T}{2} - d$
n cycles	$\tau_{op} = T/2n$	$\tau_{op}^{d} = \frac{T}{2n} - d$

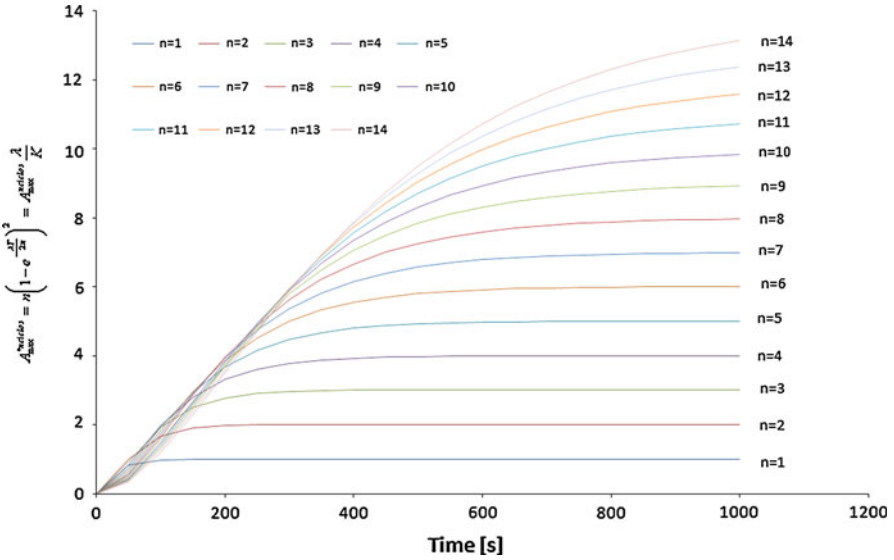

Fig. 3 Representation of function $A_{\max}^{*nciclos} = n\left(1 - e^{-\frac{\lambda T}{2n}}\right) = A_{\max}^{nciclos}\frac{\lambda}{K}$ versus process time T

Table 2 Maximum counting period with the optimal activation time for one or more cycles, and non cyclical and symmetrical model

	Without transfer time	With transfer time, d
1 cycle	$A_{\max} = \frac{K}{\lambda}\left(1 - e^{-\frac{\lambda T}{2}}\right)^2$	$A^{d}_{\max} = \frac{K}{\lambda}\left(1 - e^{-\lambda\left(\frac{T}{2}-d\right)}\right)\left(e^{-\lambda d} - e^{-\lambda\left(\frac{T}{2}\right)}\right)$
n cycles	$A^{nciclos}_{\max} = \frac{nK}{\lambda}\left(1 - e^{-\frac{\lambda T}{2n}}\right)^2$	$A^{dnciclos}_{\max} = n\frac{K}{\lambda}\left(1 - e^{-\lambda\left(\frac{T}{2n}-d\right)}\right)\left(e^{-\lambda d} - e^{-\frac{\lambda T}{2n}}\right)$

tion has a unique solution which is obtained by representing line: $y = a$, and the exponential $y = e^{a-1/2}$, and seeking the cutoff. In this way, we obtain the equation $T = \frac{2{,}51286}{\lambda} n_{op}$ that allows us to obtain T for each n_{op}. It suffers from the disadvantage of not indicating the number of cycles when processing time is within an interval of time. For example, if the process time is between 25.84 s and 51.69, it does not indicate the number of cycles to be carried out so that the signal is optimal. To overcome this drawback, the following process has been designed.

a. Plotting the equation $A^{*nciclos}_{\max} = n\left(l - e^{-\frac{\lambda T}{2n}}\right)^2 = A^{nciclos}_{\max}\frac{\lambda}{K}$ for different process times and different values of n.
b. Observe the family of curves, and thus
c. Deduction for a given T, the value of n in which there is a $A^{*nciclos}_{\max}$ higher value.

This equation is represented in Fig. 3 for values between 1 and 14 cycles. It is observed that for low values of T the curves individually increase exponentially, crossing each other, while in the second part, the curves are parallel and asymptotic for the maximum value of the function $A^{*nciclos}_{\max}$ for each value of n.

We are looking for the upper curves which define the maxima $A^{*nciclos}_{\max}$ for each interval. The upper limit is characterized because the curves corresponding to different

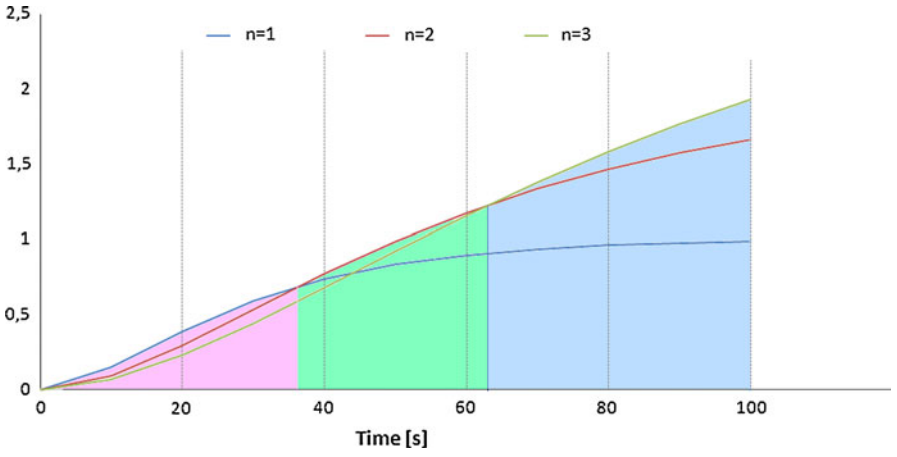

Fig. 4 Fragments of the curves between the points of intersection. Ordinate axis $A^{*nciclos}_{\max}$

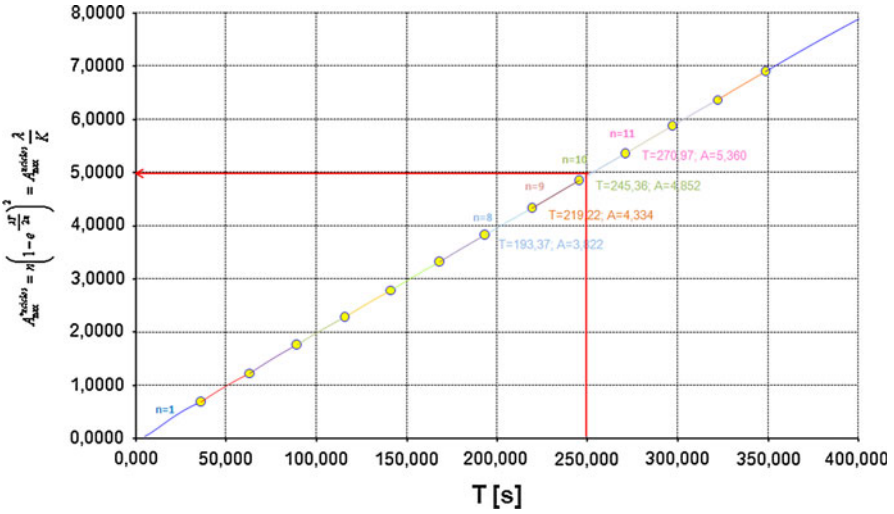

Fig. 5 Relationship between parameters that define the activation process with symmetric cycle

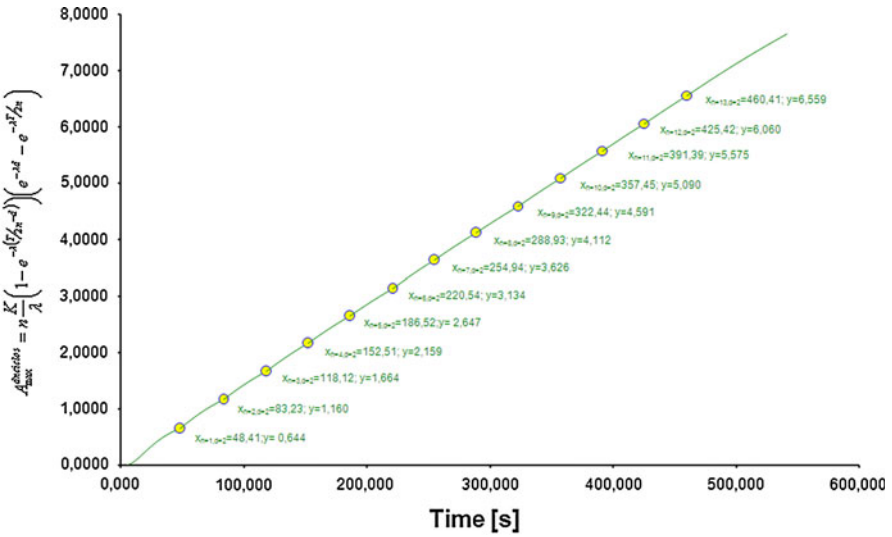

Fig. 6 Relationship between parameters that define the activation process with symmetric cycle $d = 2\,\mathrm{s}$

values of n intersect each other at certain points. If the curves are cut into fragments between points of the intersection we obtain a single curve in which each fragment indicates the number of cycles where the signal value is the highest for this range of times. Figure 4 illustrates this procedure of curve fragmentation which can be seen by the colored areas.

In this way Fig. 5 has been developed. In this Figure the number of cycles for each fragment appears and for greater clarity of the figure every bend in the part that lies below the other curves has been cut.

Figure 6 shows a total processing time ($T = 250$ s), the number of cycles that maximize the signal is 10, its duration is 25.89 s and the signal is 5 times the signal obtained in a single cycle optimized with an activation time equal to a reading time.

Introducing the concept of transfer time and for the same process time, the signal and the number of cycles required decrease with respect to the previous case (Fig. 6), but the reading is still higher compared with the single cycle.

The ^{19}F from reaction ^{19}F (n, α) ^{16}N has been measured. Samples were irradiated for 12 s and counted for 12 s, for a total of 5 cycles without a transfer time between cycles. These measurements are in accordance with previous applications of cyclic neutron activation analysis, for example, in the determination of fluorine as ^{20}F in plastics samples [15] (22-s irradiation, 22-s count, 3 cycles, 25 min between cycles); rubber samples [15] (12-s irradiation, 12-s count, 5 cycles, 25 min between cycles); concentration in the tissues [11–16] (10-s irradiation, 10-s count, 14 cycles, 2 min between cycles); biological materials [5] (namely, cod liver and otolith, fish fluor, bovine liver, and orchard leaves) the timing parameters selected were (10-s irradiation, 10-s count, 12 cycles, 2 S between cycles)

2 Results and discussion

(1) It is possible to perform neutron activation analysis using a neutron source, a detector and detection equipment consisting of a photomultiplier, a source of high voltage, analog to a digital converter, a multichannel analyzer, and software.
(2) The 16N originated in the process is radioactive and decays to produce 16O emitting gamma rays with an energy of 6,128 MeV and half life of 7.13 s.
(3) The most important radioactive element created during the process is the 16N, its advantage being its higher radiation is created in a zone that has a low probability of suffering interference from energies of other elements.
(4) The 16N originated in the process has been found to be from fluorine as well as the proportionality between the fluorspar grade and gamma radiation emitted by the sample. Therefore, all the radiation produced in the order of energies from 4.5 to 6 Mev come from the concentration fluorspar sample.
(5) The development of a symmetrical mathematical model allows defining of the activation and reading times in the process. Manual measure equipment consisting of reading after activation of the sample has been designed.
(6) Because of the low number of counts obtained by this procedure the process was multiplied by n cycles; this new procedure is called the '*cyclic symmetric model*'.
(7) Using the same measurement system, it has been verified that the cyclical symmetric model increases the number of counts in reading.
(8) In view of the results, a new model called 'cyclic asymmetric model', expected to increase the signal obtained, is being developed. In this model the first cycle is different from the other cycles.

Acknowledgments This work has been supported by Mineral Products and Derivatives Company, SA (Minersa), Research grant scheme of the University of Oviedo, Public grant scheme to aid research projects (PCTI). The authors would like to thank the above-mentioned bodies for their collaboration and financial support during this study.

References

1. M.A. Rey-Ronco, Desarrollo de un método rápido basado en técnicas de activación neutrónica para la determinación del contenido en flúor de muestras de mineral de fluorita. Doctoral Thesis, Universidad de Oviedo, 2007. http://www.tesisenred.net/TDR-0802107-133201/index_cs.html
2. R.H. Filby, Isotopic and nuclear analytical techniques in biological systems: a critical study. Neutron activation analysis. Pure Appl. Chem. **67**, 1929–1941 (1995)
3. H. Beer, F. Käppeler, Neutron capture cross sections on ^{138}Ba', ^{140,142}Ce, $^{175-176}$Lu, and ^{181}Ta at 30 keV. Prerequisite for investigation of the ^{176}Lu cosmic clock. Phys. Rev. C. **21**, 534–554 (1980)
4. O.U. Anders, Determination of fluorine by neutron activation. Anal. Chem. **32**, 1368–1369 (1960)
5. A. Chatt, K.N. DeSilva, J. Holzebecher, D.C. Stuart, R.E. Tout, D.E. Ryan, Cyclic neutron activation analysis of biological and metallurgical samples. Can. J. Chem. **59**, 1660–1664 (1981)
6. I.W. Croudace, K. Randle, Fluorine abundances of twenty nine geological and other reference samples using fast-neutron activation analysis. Geostand. Newsl. **17**, 217–218 (1993)
7. I.W. Croudace, K. Randle, A rapid and non-destructive method of fluorine determination using fast-neutron activation analysis. Chem. Geol. **67**, 165–170 (1988)
8. Z.B. Alfassi, *Activation Analysis*, vol. 1–2, (CRC Press, Boca Raton, 1990). pp.179 (vol.1), pp.609 (vol.2)
9. S.J. Parry, *Activation Spectrometry in Chemical Analysis.* vol. 119 (Wiley, New York, 1991), p. 235
10. A.Z. Ortaovali, F. Özek, I. Celenk, N. MSpyrou, Studies on some problems and applications of cyclic activation analysis. J. Radio-Anal. Chem. **61**, 175–182 (1981)
11. H. Xiaolin, in *Cyclic Activation Analysis*, ed. by R.A. Meyers. Encyclopedia of analytical chemistry (Wiley, Chichester, 2000), pp. 12447–12459
12. N. MSypou, Cyclic activation analysis. J. Radio-Anal. Chem. **61**, 211–242 (1981)
13. S.E.B. Nonie, K. Randle, A.G. Blackband, Development of a computer-based system for fast neutron cyclic activation analysis. J. Radio-Anal. Nucl. Chem. **167**, 89–95 (1993)
14. R. Khelifi, Z. Iridi, S. Tobbeche, Simulation and optimization of cyclic activation analysis of short-lived isotopes with 14 MeV neutron generator. Biol. Trace Elem. Res. **43**(45), 679–686 (1994)
15. S.J. Parry, R. Bezing, K.L. Bolstad, E. Steinnes, Epithermal/fast neutron cyclic activation analysis for the determination of fluorine in environmental and industrial materials. J. Radio-Anal. Nucl. Chem. **244**, 67–72 (2000)
16. A.S. Farooqui, W. Arshed, O.A. Aklane, C. Jeynes, N. MSpyrou, Determination in diet samples using cyclic INNA and PIGGE analysis. J. Radio-Anal. Nucl. Chem. **161**, 71–78 (1992)