ADVANCED INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS FOR GEOLOGICAL RESEARCH

Papadopoulos,N.N.* and Tsagas,N.F.**

* National Center for Scientific Research "Demokritos", 153 10 Ag. Paraskevi, Greece
** Democritus University of Thrace, Xanthi 671 00, Greece

A B S T R A C T

Instrumental neutron activation analysis has been used as a complementary to other methods multielement analytical technique to cover a wide range of geological analytical requirements. High accuracy, sensitivity and selectivity, small matrix interference and simple nondestructive preparation of samples with a wide measurable concentration range are some of its advantages. New developments in short time neutron activation techniques with counting time prolongation by count rate decay compensation, combined with cyclic activation, lead to higher counting statistics and accuracy, permitting higher throughputs and increased detection limits of short-lived nuclides, extending the application range of this nuclear technique.

ΠΡΟΧΩΡΗΜΕΝΗ ΑΝΑΛΥΣΗ ΕΝΟΡΓΑΝΗΣ ΝΕΤΡΟΝΙΚΗΣ ΕΝΕΡΓΟΠΟΙΗΣΗΣ ΓΙΑ ΓΕΩΛΟΓΙΚΗ ΕΡΕΥΝΑ

Παπαδόπουλος,Ν.Ν και Τσάγκας,Ν.Φ.

Π Ε Ρ Ι Λ Η Ψ Η

Ενόργανος ανάλυση με νετρονική ενεργοποίηση έχει χρησιμοποιηθεί σαν συμπληρωματική προς άλλες μεθόδους πολυστοιχειακή αναλυτική τεχνική για να καλύψει ευρύ φάσμα γεωλογικών αναλυτικών απαιτήσεων. Υψηλή ακρίβεια, ευαισθησία και επιλεκτικότητα, μικρή αλληλεπίδραση και απλή προπαρασκευή χωρίς καταστροφή των δειγμάτων με ευρεία περιοχή μετρήσιμων περιεκτικοτήτων είναι μερικά από τα πλεονεκτήματά της. Νέα ανάπτυξη βρυχυχρόνιας ανάλυσης με νετρονική ενεργοποίηση με προέκταση του χρόνου μέτρησης μέσω αντιστάθμισης της πτώσης του ρυθμού κρούσεων σε συνδυασμό με κυκλική επαναληπτική ακτινοβόληση, οδηγεί σε υψηλότερη στατιστική και ακρίβεια μετρήσεων,επιτρέποντας υψηλότερους ρυθμούς μετρήσεων και αυξημένα όρια ανιχνευσιμότητας βραχύβιων ισοτόπων, επεκτείνοντας την περιοχή εφαρμογών αυτής της πυρηνικής τεχνικής.

INTRODUCTION

Instrumental neutron activation analysis has been used in a variety of applications. It is a nuclear physical technique,

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

particularly suitable for elemental analysis of geological samples in geological research because of its significant advantages, such as high accuracy, sensitivity and selectivity, small matrix interference and simple nondestructive sample preparation, capable to cover the determination of elements with a wide concentration range(Hoffman,E.L. and Ernst,P.C.1982) . However for long-lived nuclide analysis the technique is quite time consuming, mainly because of the long waiting time required after irradiation before counting, in order to decrease the short-lived nuclide interference. Therefore, the tendency is to shorten the measurement time by using short-lived isotopes, whenever possible, or to decrease the irradiation, waiting and counting periods even of the long-lived nuclides when their concentration is high enough to distinguish them from the matrix. Since however short counting times decrease the counting statistics and the accuracy and sensitivity of the technique, optimization of the experimental conditions is necessary to obtain the best results.

THE APPLICATION RANGE OF THE TECHNIQUE

One of the main advantages of the instrumental neutron activation analysis is its multielement analytical capability. By thermal neutron activation the following long-lived nuclides, among others, can be analyzed (Vobecky,M.,et al,1970,1972,1979, Frost,J.K., et al,1982) : Ag, As, Au, Ce, Co, Cr, Cs, Cu, Eu, Fe, Ga, Hf, Hg, Ir, K, La, Lu, Na, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, U, W, Yb, Zn. By epithermal neutron activation it is possible to analyse the following elements (Rosenberg,R.J. et al, 1982, Parry,S.J., 1982): Ag, As, Au, Ba, Br, Co, Cr, Cs, Eu, Fe, Lu, Mo, Na, Ni, Sb, Sc, Sm, Sn, Ta, Th, U, Zn. On the other hand, for the radioisotopes ^{28}Al, ^{139}Ba, ^{49}Ca, ^{66}Cu, ^{165}Dy, ^{42}K, ^{27}Mg, ^{56}Mn, ^{24}Na, ^{155}Sm, ^{51}Ti, ^{52}V, ^{239}U and others, short-lived nuclide activation analysis can be applied (Vobecky,M. et al, 1970,1972,1979) . For certain elements, such as Se and Au, both the long and short-lived isotopes can be determined. Especially for U and Th analysis, neutron activation with delayed fission neutron counting is favorable (Papadopoulos,N.N.,1987; Papadopoulos,N.N. and Tsagas,N.F.,1993).

Important are of course also the detection limits which determine the sensitivity of the technique for the various nuclides. Some estimated detection limits, depending however on the matrix and other parameters, are given in Table 1. As can be seen from the Table, the method is highly selective but there is also a need to determine the optimum irradiation, waiting and counting time sequences, as well as the proper thermal or epithermal reactor neutron flux for sample irradiation in order to optimize the results for each element. Usually certain scenarios are applied to determine groups of elements, such as (a) t_i=20s, t_w=2 min, t_c=5 min, (b) t_i=5 min, t_w=30 min, t_c=10 min, (c) t_i=1 h, t_w=12h, t_c=1 h, (d) t_i=30 h, t_w=3 weeks, t_c=3h, (e) t_i=1 week, t_w=1-4 weeks, t_c=1-3 h.

It is obvious that the technique should be complemented by other methods to cover the whole range of analytical requirements.

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

Table 1. Approximate detection limits by INAA

	ppm		ppm		ppm
Al	200	Ge	10	Rb	20
Ag	3	Gd	5	Sb	0.2
As	1	Hf	3	Sc	0.1
Au	0.005	Hg	0.05	Se	4
Ba	100	I	40	Sm	0.1
Br	1	In	0.1	Sn	100
Ca	1000	Ir	0.01	Sr	5
Ce	2	K	2000	Ta	1
Cd	5	La	1	Tb	0.1
Cl	500	Lu	0.1	Te	1
Co	1	Mg	100	Ti	300
Cr	50	Mn	10	Th	0.4
Cs	0.5	Mo	2	U	0.3
Cu	1	Na	250	V	20
Dy	0.5	Nd	5	W	1
Eu	0.1	Ni	40	Yb	0.5
Fe	2000	Pd	1	Zn	100
Ga	0.5	Pt	0.5	Zr	200

THE ANALYTICAL SYSTEM

Special emphasis has been given to short-time instrumental neutron activation analysis, for shorter measurement times and higher throughputs. It is obvious that for this case short-lived nuclides are the most suitable ones, although also long-lived nuclides with relative high element concentration can be considered. The short-time analytical system has been described elsewhere (Papadopoulos,N.,1982). The new technique includes a movable sample holder at the counting position in order to approach the irradiated sample to the detector during counting, resulting in count rate decay compensation. Thus the counting period can be prolonged considerably, leading to higher counting statistics and accuracy of the technique. Since the sample holder speed should be relatively low for proper compensation of the count rate decrease from the radioactive decay, an oil driven piston with constant air pressure on the oil in two tanks is used. A low frequency motor is envisaged to be used for higher repeatability, reliability and accuracy.

In addition, cyclic activation with intermediate sample storage is used to further improve the counting statistics and accuracy, with optimum count rates in order to avoid dead-time losses and pulse pile-up effects.

The new technique has been tested for uranium analysis by delayed neutron counting of short-lived fission products. Some preliminary measurements give promising results. The U concentration and the measured counts C of two standards S_1, S_2, as well as the measurements and results of an unknown-test sample X are given in Table 1. Further improvements of the experimental device are necessary for more reliable results.

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

Table 2. Measurements and concentrations of standard and test samples.

	C	U
S_1	3673	68.306
S_2	4633	86.786
X	4643	86.947

Another advantage of the technique is the possibility to automate the analytical procedure. Thus a programmable logic controller is being installed for the automatic operation of the short-time analytical system and computer software programs are being developed for automatic data evaluation.

For long-lived nuclide neutron activation analysis, after sample irradiation in a rotating device at the reactor core, the measurement is performed with a conventional gamma spectrometer system and the data processing by proper software (Papadopoulos,N.N. and Synetos,S.,1988).

CONCLUSIONS

The continuous improvement of the analytical system for neutron activation analysis and its adjustment to specific analytical needs, such as for geological research, is expected to broaden the analytical capability and the application range.

ACKNOWLEDGEMENTS

The authors would like to thank G. Sideris, G. Lefkopoulos, G. Hatzakis and the reactor and machine shop staff for their contribution to the work.

REFERENCES

Hoffman,E.L. and Ernst,P.C., (1982). Analytical geochemistry advanced by neutron activation, J. Radioanal. Chem., 71, 447-462.

Vobecký,M., Randa,Z., Benada,J. and Kuncir,J., (1970, 1972, 1979). Nondestructive neutron activation analysis of mineral materials I, II, III, Czechoslovak Atomic Energy Commission, Nuclear Information Centre, Prague.

Frost,J.K., Koszykowski,R.F. and Klemm,R.C., (1982). Chemical characterization of gas- and oil-bearing shales by instrumental neutron activation analysis, J. Radioanal. Chem.,

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

71, 199-214.
Rosenberg,R.J., Kaistila,M. and Zilliacus,R., (1982). Instrumental epithermal neutron activation analysis of solid geochemical samples, J. Radioanal. Chem. 71, 419-428.
Parry,S.J., (1982). Epithermal neutron activation analysis of short-lived nuclides in geological material, J. Radioanal. Nucl. Chem., 72, 195-207.
Papadopoulos, N.N., (1987). Development of activation techniques for extensive requirements in uranium and multi-element analysis, J. Radioanal. Nucl. Chem., Articles, 113, 351-356.
Papadopoulos,N.N. and Tsagas,N.F., (1993). Multiparameter neutron activation analysis, J. Radioanal. Nucl. Chem., Articles, 167, 103-110.
Papadopoulos,N.N., (1982). Uranium and short-lived nuclide activation analysis by delayed neutron and gamma-spectrum measurements with a new versatile sample transfer system, J. Radioanal. Chem., 72, 463-477.
Papadopoulos,N.N. and Synetos,S., (1988). Adjustment of nuclear analytical techniques to special applications, Isotopenpraxis, 24, 288-290.

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.