Determination of Uranium by Neutron Activation Analysis and Delayed Neutron Counting

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Quantitative determination of uranium at low levels has many ap-
plications, *e.g.*, in the environmental field, screening of soils, stream
sediments, various water supplies, mining organisations in search of
new sites, monitoring of run off from existing mines, personnel monitor-
ing for those working with uranium from its raw ores to the purified
element and assoicated compounds. In this work two analytical methods
of uranium determination were used to analyze the same set of clay
samples from various places from Al-Washime district. Both neutron
activation analysis and delayed neutron counting have been examined.
The comparison was carried out to show the agreement and degree of
accuracy between the two methods used.

INTRODUCTION

Delayed Neutron counting (DNC)

^{235}U has a certian affinity for capturing a thermal neutron. This capture, measured by a parameter called the croos-section, results in a new isotope, ^{236}U, being formed in a highly existed state. In the majority of such cases, the excited ^{236}U uncleus undergoes fission and the whole process may be written:

$$^{235}U + n \longrightarrow {}^{236}U^* \longrightarrow fp + c(n) \tag{1}$$
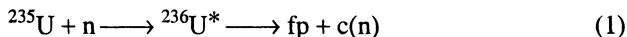
where ^{236}U* on excited state, fp is the fission product, and c is the whole number of prompt neutrons (n). The average c value is approximately 2.5.

Bombardment of ^{235}U by thermal neutrons induces fission, and some delayed neutrons will consequently be emitted. A vast number of neutrons exist in nuclear reactors. Indeed, neutrons may be considered as the working fluid of reactors, so irradiation of uranium bearing samples in reactor will induce fission and, hence, the subsequent delayed neutron emissions. This is the basis of the DNC method for uranium analysis: irradiation of a sample in the neutron flux of a reactor, followed by detection and counting of delayed neutrons emitted. Since the half-lives involved are short, the delay between irradiation and counting should be minimal. Likewise, both irradiation and counting times need only be of the order of seconds, since the saturation activity is approached rapidly.

There are many examples of delayed neutron counting procedures in the literature[1-4] and in general the process consists of a 60s irradiation, 25s decay period and a 60s counting period using proportional BF_3 or ^{3}He detectors.

Neutron Activation Analysis (NAA)

A useful, accurate and sensitive method for determination of uranium is neutron activation analysis. It can be carried out with any source of thermalized neutrons, but usually requires access to a reactor, since other sources do not produce an adequate neutron flux. When an atom of ^{238}U captures a neturon, it is convered into ^{239}U which, in turn, decays by β emission, with a half-life of 23.5 minutes, to ^{239}Np:

$$^{238}U(n, \gamma)\ ^{239}U(\beta, 23.5\ \text{minutes})\ ^{239}Np \qquad (2)$$
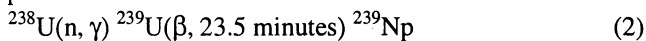
^{239}U with half-life 23.5 minutes and γ-ray at 75 KeV or ^{239}Np with half-life 2.35 day and γ-ray at 298 KeV can be used to determine the quantity of uranium in the sample. This quantity can be calculated from the activation formula, but is more often evaluated by simultaneous activation and subsequent measurement of a suitable uranium reference sample[1].

EXPERIMENTAL

Clay samples were collected from Al-Washime district 200 Km northwest of Riyadh, Saudi Arabia. The clay source in that site is used for the production of bricks. The sampels were dired at 120°C for overnight and then sieved up to 200 mesh. Neturon activation analysis and delayed neutron counting methods were used for determination of uranium.

Delayed neutron counting (DNC):   A known mass of sample approximately 1 g is double contained in a polyethylene "rabbit" tube. The irradiation were carried out at the Imperial College Research Reactor Centre (ICRC) Ascot, UK. The sample is blown into the irradiation site with compressed nitrogen gas and irradiated for 60 seconds and left to decay 25 seconds and counted for 60 seconds.

The irradiation tube is made of aluminum, has an internal diameter of 38.1 mm, and is situated on the edge of the reactor core. The irradiation position is at the center line of the core and the thermal neutron flux is 10^{12} cm^{-2} s^{-1}. There is an epithermal neutron component of about 10^{10} cm^{-2} s^{-1}.

The neutron detection rig consist of eighteen pressurized boron trifluoride (BF_3) proportional detectors 25.4 mm diameter and 60.98 cm long, arranged in the configuration of two concentric rigns of nine detectors surrounding the sample which is delivered to the center of the rig. Polyethylene beads with an average diameter of 3 mm are used as the neutron moderator between and sorrounding the sample and detectors.

To ensure a low neutron background the deterction rig is covered in cadmium sheet (1 mm), paraffin wax (45 mm), a further sheet of cadmium and the whole surrounded by concrete blocks 0.230 m thick. The cadmium is present to absorb thermal neutrons from external sources and concrete and paraffin wax to thermalise fast neutrons for capture by the cadmium.

Constant blank counts and system sensitivity are essential for quantitative uranium determination. Five blanks were measured before the analysis to ensure no variation. The system sensitivity was monitored during the analysis by measurement of a uranium standard, IAEA Soil-7 reference material, after every 10 samples.

Neutron Activation Analysis (NAA):   Approximately 0.2 g of the samples were weighed into cylindrical polyethylene tubes. The individual sample capsules were located within a larger polyethylene container from which they were removed after irradiation. The irradiation were carried out at the Imperial College Reactor Center (ICRC) Ascot, UK. A fast rabbit system was used for irradiation. Nitrogen gas propelled the sample in and out of the reactor. Standards were irradiated at regular intervals. The irradiation time was 90 seconds at 100 kW and the thermal neutron flux is 10^{12} cm^{-2} s^{-1}. The sample was allowed to cool for twenty minutes to ensure the ^{28}Al had decayed sufficiently to eliminate the chance of it swamping the spectrum. The sample was counted about 10 cm above the Ge(Li) detector for five munutes. The system was energy calibrated using ^{152}Eu. The "FIDDLE" program was used for analysis; FIDDLE is the 1992 PC version by Dr. Nicholas Bryan based on the original LSI-11 version by Dr. Graham Blower[5].

The standard used in this study was Podmore Red clay. The sample and the standard were irradiated together and counted in an identical fashion. A direct comparison method was used to calculate the uranium concentration on the samples.

RESULTS AND DISCUSSION

In order to evaluate the accuracy of the analysis two methods were used. The data consist of two points (NAA and DNC) (x_i, y_i) the results are given in Table 1. If we consider the quantity to be the dependent variable, that the data should correspond to a straight line of the form:

$$y = a + bx \qquad (3)$$

If there is no correlation between the quantities x and y, then there will be no tendency for the values of y to increase or decrease with increasing x, and, therefore, the least-squares fit must yield a horizontal straight line with a slope $b = 0$. However, since in both methods it is the absolute concentration, the expected value of b is one and of a is zero.

Since we are discussing the interrelationship between the variables x and y, we can equally well consider x as a function of y and ask if the data correspond to a striaght line of the form:

$$x = a^* + b^*y \qquad (4)$$

The value of the coefficients a^* and b^* will be different from the values of the coefficients a and b in equation (3), but they are related where the variables x and y are correlated.

If there is complete correlation between x and y, then there exists a relationship between the coefficients a and b of equation (3) and between a^* and b^* of equation (4). To see what this relation, we rewrite equation (3).

$$Y = -a^*/b^* + 1/b^*x = a + bx$$

and equate coefficients

$$a = -a^*/b^*$$

$$b = 1/b^* \qquad (5)$$

If there is complete correlation, we see from equation (5) that $bb^* = 1$. We therefore define the experimental linear correlation coefficient $r = (bb^*)^{1/2}$ as a measure of the degree of linear correlation.

$$r = \frac{n\Sigma x_i y_i - \Sigma x_i \Sigma y_i}{\sqrt{n\Sigma x_i^2 - (\Sigma x_i)^2} \times \sqrt{n\Sigma y_i^2 - (\Sigma y_i)^2}} \tag{6}$$

where n is the number of samples, x_i is the NAA data and y_i is the DNC data.

The value of r ranges from 0, when there is no correlation to ± 1, when there is complete correlation. The sign of r is the same as that of b (and b*), but only the absolute magnitude is important[6].

When using the values of n, x_i and y_i from Table (1) in equation (6) the correlation is 0.99 which mean a good correlation between the NAA and DNC methods.

TABLE-1

URANIUM CONCENTRATION IN PPM OBTAINED BY NAA AND DNC

Sample No.	NAA			DNC		
	Mean	σ	%σ	Mean	σ	%σ
1	3.95	0.10	2.50	3.48	0.31	8.91
2	3.03	0.06	1.98	2.97	0.06	2.02
3	5.36	0.53	9.89	5.75	0.58	10.09
4	2.65	0.03	1.13	2.61	0.03	1.15
5	4.13	0.10	2.42	4.12	0.12	2.91
6	3.93	0.10	2.54	4.02	0.15	3.73
7	2.29	0.01	0.44	2.27	0.01	0.44
8	4.11	0.04	0.97	4.05	0.07	1.73
9	4.12	0.07	1.70	4.06	0.07	1.72
10	3.14	0.04	1.27	3.07	0.06	1.95
11	2.28	0.08	3.51	2.15	0.06	2.79
12	3.25	0.04	1.23	3.19	0.07	2.19

Conclusions

Samples from various places from Al-Washime district have been analyzed by NAA and DNC. Multiple analyses, five replicates, of each sample were performed. Each analysis is performed in exactly the same manner as any other. Therefore, any difference in the uranium concentrations obtained will be due to the experimental errors inherent in our analysis. The important conclusions of this work are summarized below:

1. The agreement between the NAA and DNC techniques is satisfactory. The correlation between the two methods is 0.99.
2. For determination of uranium both NAA and DNC are accurate and fast methods.
3. The NAA was performed on smaller samples than DNC, 0.2 g of the sample is required for the NAA but 1 g is required for the DNC.

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