Chapter Z

Uranium and thorium by delayed neutron counting

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Contents

Tables

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Principle

Delayed neutron counting (DN) is a nuclear activation analysis method that is used to measure uranium and thorium in complex geologic sample matrices without chemical processing. Neutron irradiation of thorium and uranium induces nuclear fission reactions yielding fission products that subsequently decay by delayed neutron emission. Most other naturally occurring elements undergo neutron capture reactions yielding radioisotopes which subsequently undergo beta/gamma decay. Delayed neutrons from an irradiated sample can be selectively and quantitatively counted with practically no interference from beta/gamma emitters.

This procedure for the simultaneous determination of uranium and thorium employs two equivalent, sequential irradiation-counting cycles for each sample consisting of individual uranium, thorium, and oxygen standards, and sample aliquots. A custom-built, automated DN facility integrates the irradiation termini, transfer systems, and neutron counters with a computer that provides on-line experiment control and data handling. First a Cd-shield epithermal neutron irradiation cycle is performed to maximize the thorium fission contribution relative to uranium. A thermal neutron irradiation cycle is then performed which yields predominately uranium fission. Using the sensitivity data for each elemental standard measured individually for each irradiation-counting condition, an iterative algorithm is applied to the gross neutron-counting data for a composite sample to resolve individual contributions and compute the concentrations of uranium and thorium. A detailed description of the DN principles, facilities, and procedure has been published by McKown and Millard (1987).

Interferences

There are three types of potential interferences: nonfission delayed neutron emitters, uranium and thorium interelement interference, and anomalous levels of certain elements which affect the standard/sample sensitivity equivalency.

The only direct source of nonfission delayed neutron interference arises from the activation of O-17 and Be-9. These interferences are insignificant in the analyses of most geologic materials because oxygen is accounted for by standardization, and Be is low in abundance and its activation product is very short-lived. Another neutron-counting interference, indistinguishable from the DN signal, may arise from γ (gamma), n (neutron) reactions during the counting cycle caused by extreme levels of very high energy gamma rays emitted from a sample. This interference is insignificant except for samples with highly anomalous concentrations of beryllium and fluorine. Such samples are considered unsuitable for DN analysis.

Even under optimum conditions, thorium and uranium represent a mutual interference to each other. The iterative data reduction algorithm used in this procedure adequately resolves and corrects this interference for all geologic materials that exhibit a thorium-to-uranium ratio greater than three.

Highly anomalous levels of Li, B, Cd, and Gd in a sample can seriously affect the accuracy of DN results because of neutron shielding (flux depression) within the sample. Samples of this type are not suitable for DN analysis. Similarly, the analysis of highly carbonaceous materials, such as coal, and ammonium compounds, may yield erroneously high thorium values due to neutron thermalization within the sample. To minimize this error, samples must be designated as carbonaceous and run with standards of equivalent matrix.

Scope

The method is generally applicable to a wide variety of geologic materials, including most common silicate rocks, soils, and sediments that exhibit a thorium-to-uranium ratio greater than three. Most moderately mineralized materials, except those highly anomalous in F, Be, Li, B, Cd, or Gd, are also generally suitable for DN. The analysis of uranium and thorium ores may exhibit decreased sensitivity and confidence for thorium if the thorium-to-uranium ratio is less than three, and similarly, for uranium if the ratio is greater than 50. Coal matrix samples are suitable for DN analysis if designated as such.

The reporting range of concentrations for the analysis of suitable 10 g sample is about 0.1-300 ppm for uranium and 1-900 ppm for thorium.

Apparatus

Custom-built delayed neutron facility (USGS-TRIGA Reactor)

Vial heat-sealer
2-dram polyvials
Pneumatic-transfer capsules

Reagents

None

Safety precautions

This procedure requires on-line access to the USGS TRIGA reactor and thus entails potential radiological hazards. All analysts (DN operators) must be trained and receive authorization as experimenters (DN operators) under the provisions of a valid Reactor Utilization Permit, and Operation Reference Manual (ORM), Section IV (1991).

Procedure

Additional details of the procedure are in the on-site ORM. This manual is regularly updated and used for training. No analyst is allowed to operate the system without this training.

1. Load 2-dram polyvial full (~10 g silicate)
2. Group into experimental run sets consisting of 20 samples, U, Th, O standards, and QC monitor (ORM, Sect. I).
3. Prepare computer sample files corresponding to the run sets using the computer program SFPREP (ORM, Sect. II. A. 1-4).

4. Tare the computer-interfaced Mettler balance using an empty 2-dram polyvial, and weigh each sample using the program SFWGT (ORM, Sect. II. A. 5) to automatically enter sample weights into corresponding sample files.
5. Trim, seal, and place polyvials into pneumatic "rabbits", and stack into DN system magazines.
6. For a group of sample sets (sample files) to be included in a DN analysis run, create and zero corresponding data files on a DN-nn Run Disk using the programs DNOPEN and DNPREP (ORM, Sect. II. B).
7. Prepare for a DN analysis run session by scheduling reactor time and health physics coverage, and check that the DN system electronics are turned on (ORM, Sect. III).
8. Place a blank test rabbit in each DN system changer and initiate a test run using the automatic system control program DN (ORM, Sect. IV., A,B). Confirm that all parts of the DN analysis system are functioning properly.
9. Place a sample set magazine on the DN system changer and initiate the sample set run using the automatic system control program DN (ORM, Sect. IV. D). Repeat for each sample set magazine corresponding to the DN run data disk.
10. After a DN run session is completed, reduce the raw counting data to U and Th concentration values and generate an analysis report using the program DNCALC or DNAUTO, an auto-sequencing version of DNCALC (ORM, Sect. VI).

Standardization of Instrument

Operating conditions:

Instrument Power	ON (Ref. ORM, Sect. III)
Initial Test Run	OK (Ref. ORM, Sect. IV, B)

Calibration is performed automatically during data reduction using the instrument response obtained for U, Th, and O standards run with each experiment set of 20 samples.

Standards:
Uranium standards are prepared by homogeneously doping a low-uranium rock powder (dunite DTS-1, which contains 3 ppb U and 10 ppb Th) with uranium standard solutions prepared from isotopically normal uranium oxide (National Bureau of Standards SRM 950a). Thorium-doped standards are prepared in a similar fashion using solutions prepared from reagent grade thorium nitrate. The undoped DTS-1 (USGS reference material) is used as an oxygen standard. Weighed aliquots of these materials, sealed in 2-dram polyvials, constitute a set of reusable working standards for the DN analysis procedure. The calibration value for each working standard is verified by replicate analyses of a set of at least five reference material samples for which reliable literature values are available (McKown and Millard, 1987).

Calculation

Raw data deconvolution and comparison to standard sensitivities using computer programs DNCALC or DNAUTO (ORM, Sect. VI).

Assignment of uncertainty

From McKown and Millard (1987) and Millard and Keaten (1982), the DN method is inherently more sensitive to the measurement of uranium than to the measurement of thorium. Comparing the 3σ uncertainty of the counter background with the uranium sensitivity yields an absolute detection limit of 1 μg uranium, which corresponds to 0.1 ppm (μg/g) uranium in a 10-g sample. For thorium, the minimum detectable count rate depends on counter background plus uncertainties in correcting the gross counts for oxygen and uranium contributions. For samples having a thorium to uranium ratio greater than three, the 3σ detection limit for thorium is about 10 μg thorium, or 1 μg/g for a 10-g sample. The detection limit for thorium is correspondingly higher if the thorium to uranium ratio is less than three. Thorium is not measured reliably, even at high levels, if the thorium to uranium ratio is less than one.

The data reduction program DNCALC (ORM, Sect. VI) automatically generates and reports an analytical uncertainty estimate (coefficient of variation) for each uranium and thorium value based on appropriate propagation of the counting statistics (measurement uncertainty) associated with each individual sample and standard counting interval.

Table 1 is the analytical results of uranium and thorium for selected reference materials, duplicate samples, and method blank. Please note: duplicate samples of submitted materials are not run routinely due to time and cost constraints.

Table 1.—Analytical performance summary for U and Th (ppm) by DN

[A=National Bureau of Standards, 1981; B=Knight, 1990; remaining *pv* from Potts and others, 1992]. See page ix of the introduction to this Methods Manual for an explanation of the abbreviations used in the analytical performance summary tables.

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Thorium, Th							
SRM 688	basalt	10	<2	--	**0.33** A *cv*	--	--
W-2	diabase	5	2.7	0.3	2.2	11	123
BCR-1	basalt	6	5.3	0.8	**5.98**	15	89
AGV-1	andesite	9	7	1	**6.50**	14	107
GXR-2	soil	21	9.6	0.8	8.8	8	109
SRM 1646	estuarine sediment	10	10	1	*10*	10	100
G-2	granite	6	24	1	**24.6**	4	98
PPG	granite	37	31	2	29.2 B	6	106
Uranium, U							
SRM 688	basalt	9	0.45	0.06	0.37 A	13	122
W-2	diabase	10	0.53	0.05	0.53	9	100
BCR-1	basalt	6	1.81	0.06	**1.75**	3	103
AGV-1	andesite	10	2.1	0.1	1.89	5	110
G-2	granite	6	2.15	0.07	2.07	3	104
GXR-2	soil	21	3.12	0.09	**2.90**	3	108
SRM 1646	estuarine sediment	10	3.2	0.1	**2.99**	3	107
TMB	andesite	62	4.3	0.1	4.10 B	2	105
PPG	granite	37	5.8	0.2	5.40 B	3	107

Table 1.—Continued—Duplicate samples results

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
Thorium	18	2	13.9	0.6	5	6.84 to 24.4	1	0
Uranium	19	2	4.17	0.04	1	2.37 to 8.4	0	0

Table 1.–Continued--Method blank results 3s values are considered the lower limit of detection (LOD), and 5s values are considered the lower limit of determination (LLD)

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Counter background					
Thorium	33*	0.8	0.1	0.4	0.6
Uranium	33*	0.21	0.03	0.09	0.1

*same day replicates.

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