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AUTOMATED URANIUM ANALYSIS BY DELAYED-NEUTRON COUNTING

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Abstract. Automated uranium analysis by fission-induced delayed-neutron counting is described. A short description is given of the instrumentation including transfer system, process control, irradiation and counting sites, and computer operations. Characteristic parameters of the facility (sample preparations), background, and standards) are discussed. A sensitivity of 817 ± 22 counts per 10^{-6}g U is found using irradiation, delay, and counting times of 20 s, 5 s, and 10 s, respectively. Presicion is generally less than 1% for normal geological samples. Critical level and detection limits for 7.5 g samples are 8 and 16 ppb, respectively. The importance of some physical and elemental interferences are outlined. Dead-time corrections of measured count rates are necessary and a polynomical expression is used for count rates up to 10^5. The presence of rare earth elements is regarded as the most important elemental interference. A typical application is given and other areas of application are described.

INIS-Descriptors. ACCURACY, AUTOMATION, COUNTING RATES, DELAYED-NEUTRON ANALYSIS, INTERFERING ELEMENTS, NATURAL URANIUM, NEUTRON-ACTIVATION ANALYZERS, QUANTITATIVE CHEMICAL ANALYSIS, SENSITIVITY.

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CONTENT

1. INTRODUCTION

Among routinely used analytical techniques for uranium determinations in geological samples, fission-induced delayed-neutron counting is applied preferably in large geochemical exploration programmes. Uranium is determined by this technique in usually less than 3 minutes, purely instrumentally in 5- to 10-g sample materials. The method first proposed by Echo and Turk in 1957 was investigated in detail by Amiel (1962 and 1964) and by Dyer et al. (1962). Since then a number of delayed-neutron counting facilities were installed at various reactor centres.

Davies and Cole (1964) reported on a facility at the Herald reactor where 30-ml solutions were irradiated in a thermal neutron flux of 2.1×10^{12} n/cm^2·s and delayed neutrons were counted by a ring-like array of six BF_3 counters. The irradiated solution had to be removed from the transfer rabbit before counting. A sensitivity of 7×10^{-9} g ^{235}U/l was found. Gale (1967) described the U and the Th analysis of powdered rocks for geochronological studies at the same reactor and reported lower limits of detection of 5×10^{-8} g/g for uranium and 2×10^{-6} g/g for thorium with a measurement time of about 6 minutes. Three to 6 g of sample material were needed for analysis and the author thoroughly investigated some parameters of influence on the analyses.

Nass et al. (1972) reported on routine U analysis of biological, environmental, and uranium ore samples at the Union Carbide nuclear reactor, Tuxedo, N.Y. (U.S.A.). After 30-s irradiation and 20-s delay the samples were counted by four BF_3 counters for 60 s. A lower limit of detection of 5×10^{-8} g U was predicted.

About 5-g sample material sealed in a polyethylene vial were irradiated in a rabit in a thermal neutron flux of 2.2×10^{13} n/cm^2·s in the delayed-neutron counting facility described by Cumming (1974). Delay and counting times were 25 and 64 s, respectively. Both U and Th were determined.

The instrumentation at Los Alamos, U.S.A., described by Balestrini et al. (1976) uses twenty ^{3}He-detectors for the analysis of water samples in 41-ml containers and twelve counters for 4-ml sediment material. Counters filled with ^{3}He were chosen mainly because of the 2 to 3 times greater counting efficiency of these counters compared to those of BF_3. However, the sensitivity of these detectors is considerably higher than for BF_3 counters. The facility is installed in a laboratory at high altitude (2100 m above sea level), and a relatively high cosmic background occurs.

Recently, Rosenberg et al. (1977) described an automatic device for the analysis of 10-g samples (mainly stream sediments and lake sediments) in a thermal neutron flux of 4×10 n/cm^2·s, the thermal-to-fast flux ratio being about 1. With an estimated detection limit of 0.06 ppm U the sample capacity is stated to be 45 per hour.

Delayed-neutron counting for the analysis of U and Th in mainly geological samples was applied in a manually operated facility at the Risø research reactor DR2 during the years 1972 to 1975 (Løvborg et al., 1976). Ten-g samples were irradiated in rabbits in a thermal neutron flux of 1.1×10^{12} n/cm^2·s, the ratio of thermal-to-fast neutron flux being 6.3. Because of the manual operations involved only about 20 samples per day could be analysed.

A new fully automated delayed-neutron counting facility for U analysis was installed at the research reactor DR3 in 1976. Mostly geological samples are analysed in this facility. With the currently used timing constants (irradiation time of 20 s, delay of 5 s, and measurement of 10 s) a throughput of about 120 samples per 8 hour working day is estimated. Taking into account reactor shut-down periods every third week a total throughput of at least 90 samples per day is a realistic estimate of the capacity of the facility.

In this report we describe this instrumentation and the analytical procedures involved in detail. Special emphasis is given to the parameters that might have an influence on the

analytical result. Characteristic parameters of the analytical facility are evaluated and areas of application outlined.

2. PHYSICAL PRINCIPLES

The physical basis of uranium analysis are delayed-neutron emitting precursors produced during the fission of ^{235}U with thermal neutrons. During partial beta-decay a fission product with atomic number Z and mass A may reach levels lying above the neutron binding energy (Fig. 1), i.e. levels that are neutron-unstable.

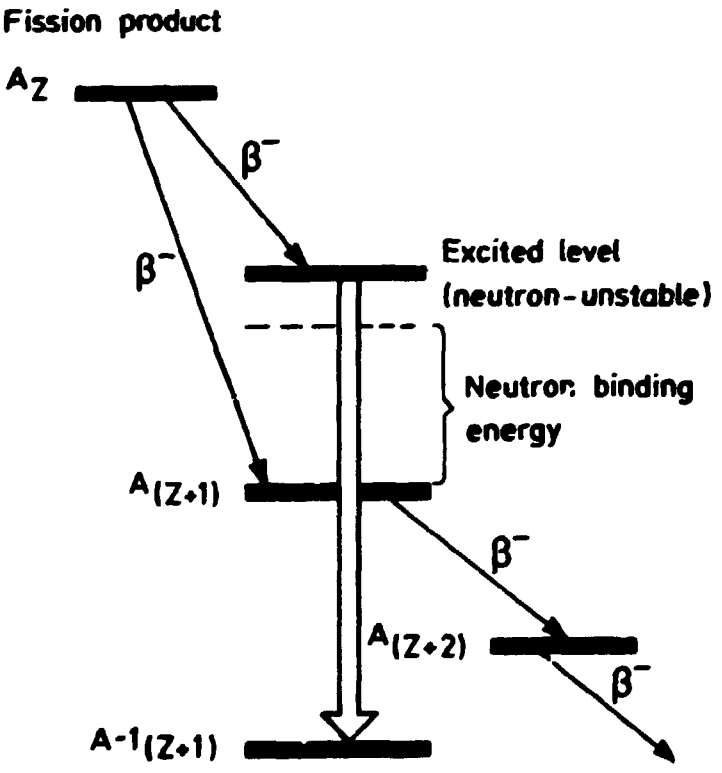

Fig. 1. Schematic presentation of delayed-neutron emission from fission products with β-decay. A and Z are the atomic weight and the atomic number of the decaying isotope, respectively.

The precursors are isotopes of mainly Br, I, Rb, Y, and As and they can be divided into 5 distinct half-life groups, the

precursor with the shortest half-life being ^{97}Rb ($T_{1/2}$ = 0.14 s) and that with the longest half-life ^{87}Br ($T_{1/2}$ = 54.5 s).

The physics of delayed neutrons was thoroughly studied by Keepin (1957 and 1971) and Tomlinson (1970). The identified groups have half-lives in the range of 0.2 to 0.6, and 2, 6, 22, and 55 s. Roughly 157 delayed neutrons are released per 10^4 fission events. About 40% of delayed neutrons are from the precursor group with 2-s half-life and another 40% stems from groups with half-lives of 6 and 22 s.

The energies of the delayed neutrons vary between 250 and 910 keV. Similar physical principles are valid for the fission of ^{232}Th and ^{238}U by fast neutrons, but the fission cross-sections for these reactions are roughly three orders of magnitude lower than that for the fission of ^{235}U with thermal neutrons.

The number of counted delayed neutrons is a direct measure of the amount of ^{235}U being present in a sample. If we suppose the isotopic composition of uranium to be constant in nature, the total uranium concentration in the sample can be estimated from the delayed-neutron count rate. Because 60 s is the longest half-life involved counting a sample for more than 60 s adds only a small amount of additional information to the analytical result. Artificially produced isotopes with high thermal fission cross-sections such as ^{239}Pu and ^{233}U that also may generate delayed neutrons are neglected in the analysis of natural samples.

3. INSTRUMENTATION

The delayed-neutron counting facility installed at the research reactor DR3 is shown schematically in Fig. 2.

After manual loading of a maximum of 24 samples, including 2 standards and 2 blanks, into a transfer tube system, a computer takes over the entire measurement operation.

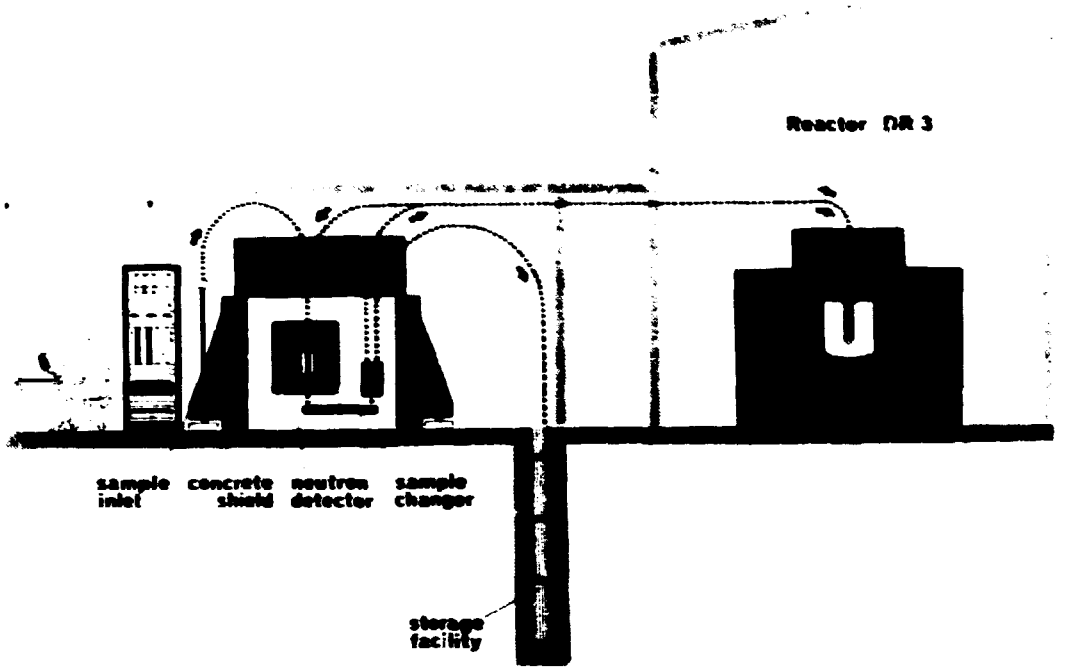

Fig. 2. Schematic arrangement of irradiation and counting at the delayed-neutron counting facility.

At first the samples are transferred pneumatically to a sample changer disc where they occupy sample positions 1 to 24. The sample changer has 48 positions. Irradiation time t_{IR}, delay time t_C and measuring time t_M together with other characteristic data for a sample measurement run are preselected by dialog with the computer. After initiating a measurement series from the computer terminal the first sample arrives at the irradiation position 4V1 of reactor DR3 after about a 2-second travel time in the pneumatic system. The sample is now irradiated for the time t_{IR} and afterwards sent directly (about 2-s travel time) to the counting site. Cooling for t_C seconds is followed by neutron counting for t_M seconds after which the sample is dropped to sample changer position 25 within 1 s. After this operation, sample 2 is sent to the irradiation site. The measurement cycle continues until all samples, standards, and blanks are counted once. The whole cycle is repeated, so that usually a sample load is analysed three times. The following characteristic times of measurement are used:

$t_{IR} = 20$ s $\qquad t_C = 5$ s $\qquad t_M = 10$ s.

Any other timing may be chosen via computer dialog. A brief description of some important units is given below.

3.1. Transfer system and process control

The transfer system for the samples on their way to the irradiation site is made of 2-cm diameter aluminium tubing (Hansen, 1974). The total length of the system from the counting to the irradiation site is about 15 m.

An air pressure supply of about 4 bar is used in the tube transfer system but the different parts of the system work at reduced pressure, e.g. about 3 bar at the sample inlet. At the entrance to the reactor containment region pressure-activated valves are used to control the transfer path to the irradiation site. In case building seal occurs in the reactor these valves are shut within 80 seconds, in due time to finish an irradiation that had been started. To avoid pressure supply stop during operation the supply is provided through a reservoir with a capacity of about 250 l. The air used by the system is sent to an active ventilation subsystem.

During execution of the computer program, microswitches and magnetic valves are activated to control the pathway of the sample. Photo sensors at two positions under the sample changer disc (Fig. 3) keep track of the samples stored at and transferred to the disc. Photo indication is also used at the entrance to the reactor, at the irradiation site and at a site at the place of entry to the shielding box. Light indication on a process control panel on the instrumentation panel in the counting building allows the operator to visually follow each sample during the measurement cycle. By means of the instrumentation panel the operator has also a visual indication of the state of the magnetic valves and can directly interfere by switching the system into the manual-opration mode. The irradiation time is indicated on an alarm panel and a message can then be sent directly to the reactor control building. In the opposite case of a building seal, the message runs from the reactor to the alarm panel

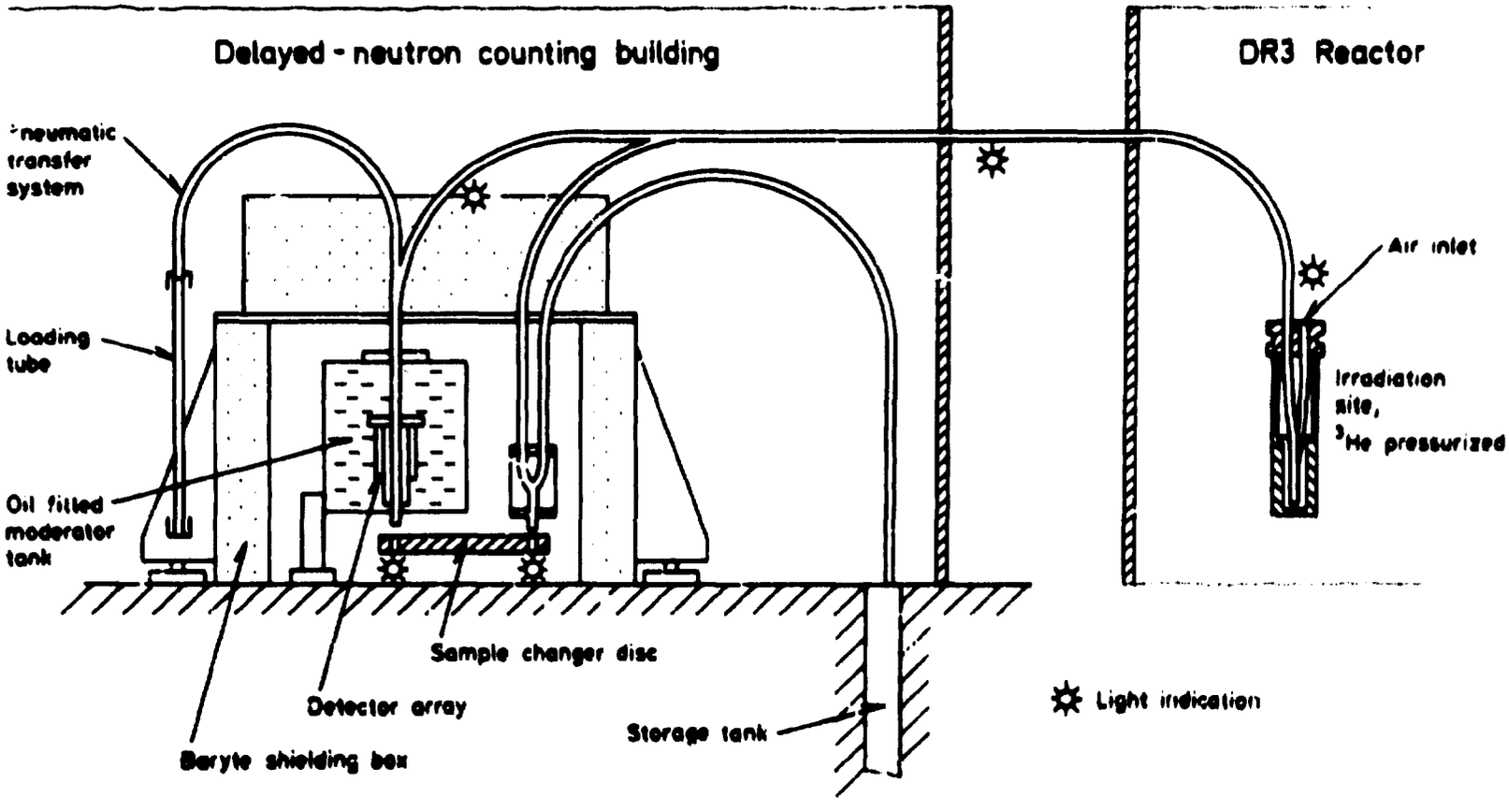

Fig. 3. Main parts and control sites of the delayed-neutron counting facility.

of the analytical facility. Indications exist in the reactor control building in the case where the irradiation time is exceeded for operating magnetic valves and controlling the neutron flux at the irradiation site.

Exact timing of the system is provided by a stable clock generator. Ten-Hz timing pulses are counted by the timers. Delay times between irradiation and counting (cooling) should be greater than about 2.5 s because of the travel time interval of the sample in the tube transfer system mentioned above.

3.2. The irradiation site

The samples are irradiated at a positon about 17 cm apart from the reactor core central plane (site 4V1). At this site the transfer system ends in the thimble of the irradiation site. After irradiation, the sample is transferred by an air stream towards the shielding box. During irradiation, the sample is cooled by an additional air stream of 0.5 l/s to prevent melting. The cooling is necessary because at least 150 mW/g energy are released in the form of heat. A constant temperature of 50°C is aimed at during irradiation. In case of failures during irradiation the sample can be blown out from the irradiation site by the operator at the reactor.

Because of the location of the irradiation site with respect to the reactor the neutron flux exposed to the sample varies along the sample. The measured thermal neutron flux distribution along the sample container is shown in Fig. 4; the measured fast neutron flux distribution is given in Fig. 5. The thermal neutron flux varies about 9% over the entire length of the sample container. Sample and standard should therefore have a similar filling grade if only small amounts of sample material are available. The ratio of thermal-to-fast neutron flux is about 1000.

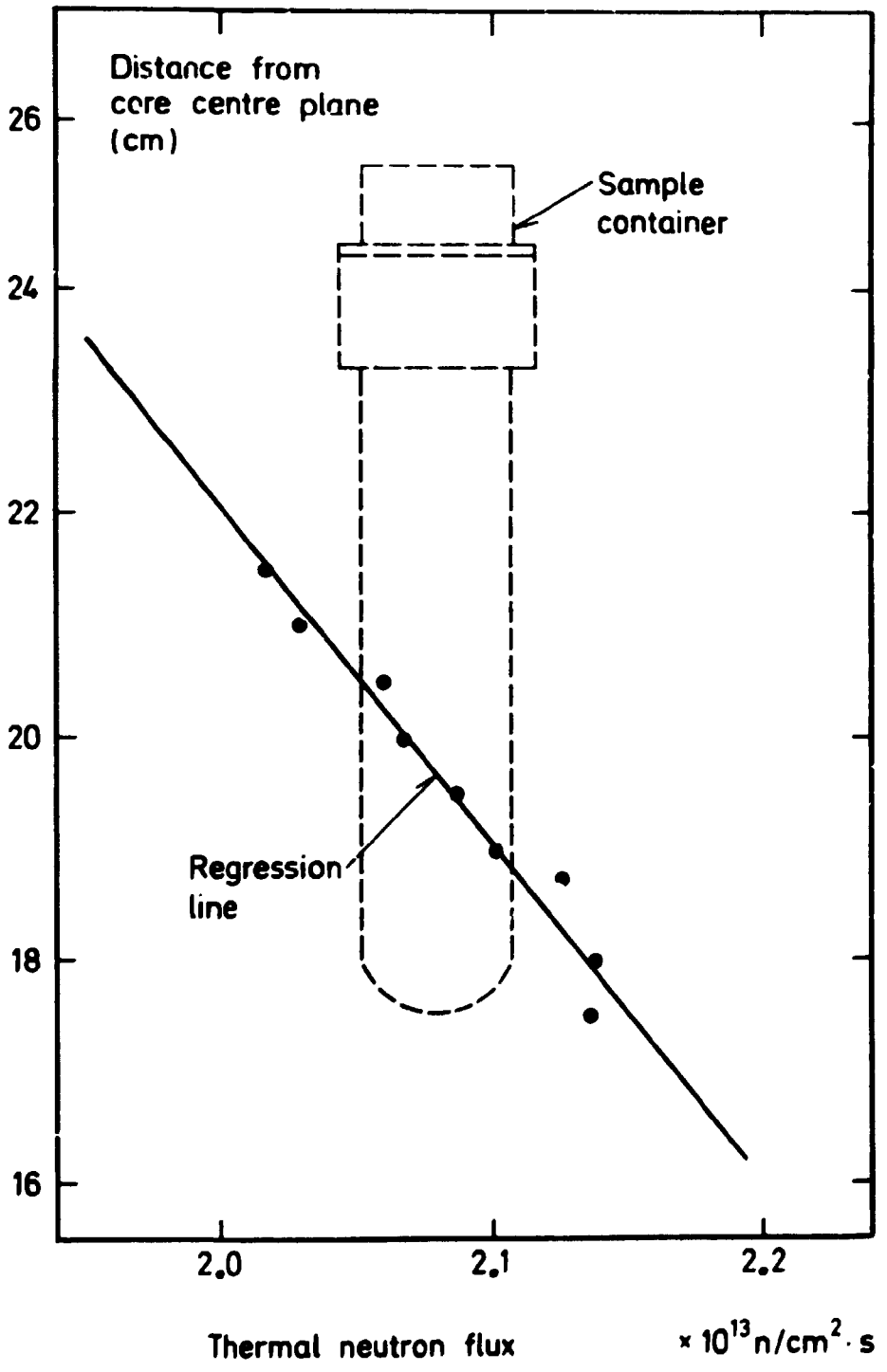

Fig. 4. Measured thermal neutron flux at the DR3 irradiation site 4V1.

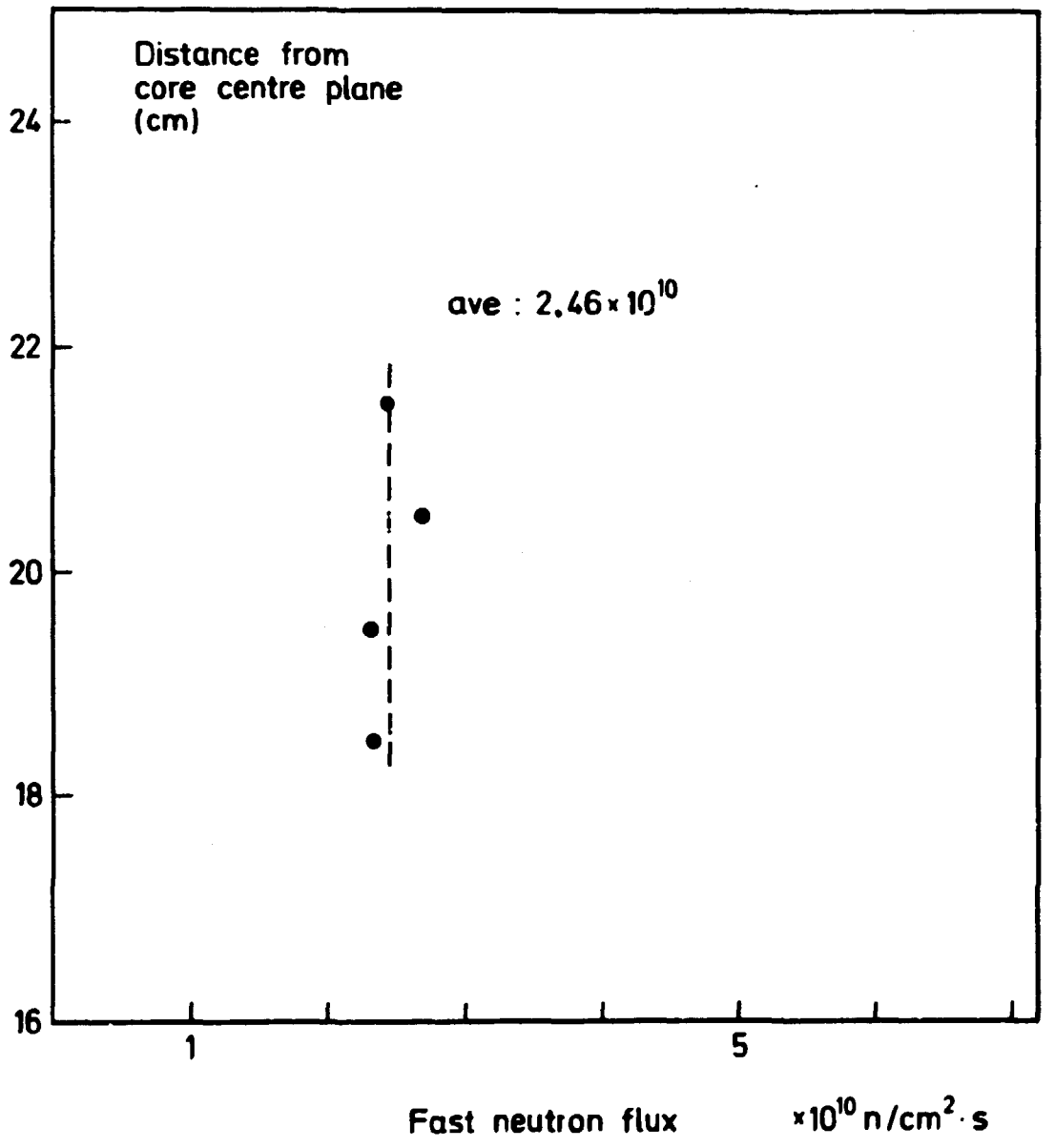

Fig. 5. Fast neutron flux distribution at the DR3 irradiation site 4V1.

3.3. Counting site and sample changer

The counting facility and sample changer are arranged in a concrete shielding box with outer dimensions of 2.135 × 1.83 m. The wall thickness of the shielding box is about 27 cm but on top of the box a layer of 54-cm shielding material is used. Access to the interior of the sheilding box is possible because two of the concrete walls are supported by air floats and therefore can be removed.

Delayed neutrons are counted by a ring-like array of 9 BF_3 counters (supplier: LND, tube type 2035) operated at 2200 V (Fig. 6). The detectors are mounted on a circular disc of 23 cm diameter. The detector array is lowered into a 70-cm diameter cylindrical tank shielded with boron-impregnated polyester. For moderation of the neutrons the tank is filled with about 280 l of water-free oil (type Shell Diala oil D). Water usually

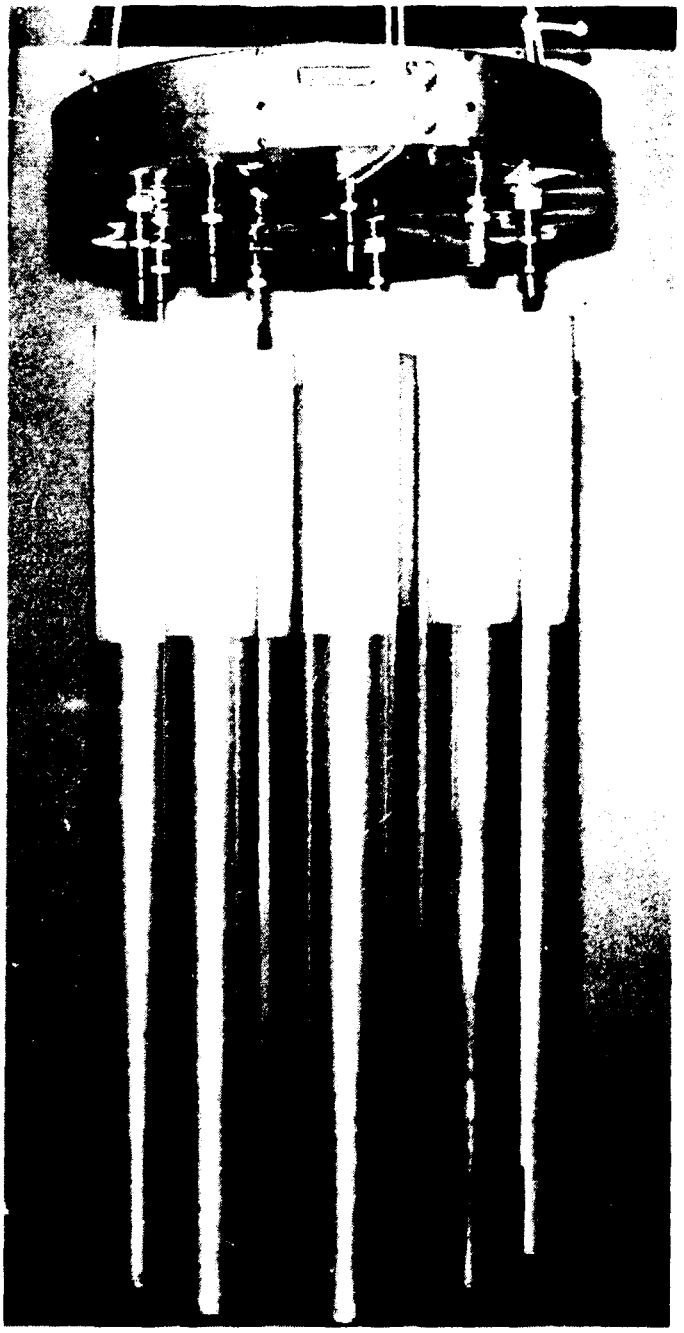

Fig. 6. BF_3 detector array.

applied for thermalisation of fission neutrons is not used here because biological alteration during the time of operation may cause serious problems as found in the previous facility at the reactor DR2. Between the transfer tube with a sample and the detector array a lead shield of 5 cm thickness was installed to suppress the high γ-ray flux from the irradiated sample. This arrangement also enhances the lifetime of the BF_3 counters. Any preselected number of counters of the counter array can be chosen before a measurement run. In case of an unusually high U content in the sample (>100 ppm) only one counter is used to avoid pulse pile-up effects.

The sample changer disc is 78.2 cm in diameter and 8 cm thick. Forty-eight sample positions are arranged on a 70-cm diameter circle. While one-half of the sample positions is used for temporary storage of samples the other half is used for samples to be irradiated.

3.4. Computer operations

The digital instrumentation of the delayed-neutron counting facility is a CAMAC system coupled to a PDP11a computer (Skaarup, 1975). For the automatic control of the analytical process a Fortran IV program was developed (Nielsen and Højbjerg, 1976).

An easily maintainable program and a non-interupt system were envisaged. Briefly, the program carries out the procedures of loading, irradiation and counting (up to 5 times repetition), and storage of irradiated samples. Testing of counters, read-out units and timing scalers are provided through the program. Limited operator participation is necessary and the dialog proceeds through a screen terminal. Typically, the operator has to type characteristic data for the sample measurement series, i. e. sample numbers and sample weights, submit data for irradiation, cooling, and counting times, as well as data regarding numbers of neutron detectors to be used, and of repetition of measurements. The counting data are then stored on a floppy-disc and submitted to the B6700 central computer.

An Algol program treats the counting data from the delayed-neutron counting facility at the central computer. A typical output report from the computer is shown in Table 1. It contains a description of the experimental conditions during analysis

Table 1. Computer-output of a typical delayed-neutron counting measurement run.

DETERMINATION OF NATURAL URANIUM BY DELAYED-NEUTRON COUNTING
FOLLOWING NEUTRON IRRADIATION IN REACTOR DR 3

1. DESCRIPTION OF EXPERIMENTAL CONDITIONS:

SERIAL NUMBER FOR THE JOB	2412
DATE	800506
START TIME	14.35
STOP TIME	15.04
NO. OF NEUTRON COUNTERS USED	9
IRRADIATION TIME (SEC)	20.3
DELAY TIME -	5
COUNTING TIME -	10
BACKGROUND:	
AVERAGE VALUE (COUNTS)	337
STANDARD DEVIATION -	19.2
SENSITIVITY (COUNTS/MICROGRAM)	815

2. RESULTS FOR THE SAMPLES:

SAMPLE NUMBER	SAMPLE WEIGHT (G)	NET SIGNAL (COUNTS)	URANIUM DETECTION	URANIUM CONC. VALUES MIN. (PPM)	MAX. (PPM)	MEAN (PPM)	REL. STAND. DEV. (%)
705/277143/07	5.3700	10300	YES	2.1	2.6	2.35	4
705/277144/07	8.3200	73291	YES	13	16	14.2	4
705/277145/07	5.8100	15075	YES	2.9	3.5	3.18	4
705/277146/07	5.4100	16724	YES	3.5	4.1	3.79	4
705/277147/07	5.0600	48129	YES	9.9	12	10.7	4
705/277148/07	5.5100	40660	YES	8.4	9.7	9.06	4
705/277149/07	5.3100	41641	YES	8.9	11	9.62	4
705/277150/07	5.3200	11794	YES	2.5	3.0	2.72	4
705/277151/07	5.5100	55334	YES	11	14	12.3	4
705/277152/07	5.5200	43296	YES	8.9	11	9.62	4
705/277153/07	4.2700	18126	YES	4.8	5.6	5.21	4
705/277154/07	4.7500	41598	YES	9.9	12	10.7	4
705/277155/07	6.2100	11744	YES	2.1	2.5	2.32	4
705/277156/07	5.6200	96937	YES	19	23	21.2	4
705/277157/07	4.3500	28325	YES	7.4	8.6	7.99	4
705/277158/07	4.7900	24778	YES	5.9	6.8	6.35	4
705/277159/07	4.9100	9376	YES	2.1	2.6	2.34	4
705/277160/07	4.1800	21676	YES	5.9	6.9	6.36	4
705/277161/07	5.0500	5814	YES	1.3	1.6	1.41	4
705/277162/07	5.3400	6042	YES	1.2	1.5	1.39	4

and the analytical results. Sample numbers are given in the form of a user code, number, and index number separated by slashes. Concentration values are calculated using the definitions described by Currie (1968) with two critical levels (min. and max. concentrations) and mean concentration with an appropriate standard deviation. Uranium is undetected if the standard deviation of the mean exceeds 25%. The net signal is always the sum of counts generated by repeated runs. In a series of repeated

runs, statistically untrustworthy measurements are removed by a Dixon-Matthew test. Generally, three runs are carried out on one sample. However, the number of repetitions treated by the computer program is limited to 5. In addition to the summary report, detailed information is given to the operator of the facility on a separate reporting.

4. CHARACTERISTIC PARAMETERS

4.1. Sample preparation

Seven-ml polyethylene vials are used the form and dimensions of which are shown in Fig. 4. Sample material of normally up to typically 7.5 g is poured into the vials, weighed on a digital-reading 0.01-g balance, and sealed by ultrasonic welding. A leak test of the vials is made before irradiation is carried out, especially in the case of liquid samples. The samples are numbered and stored in sample measurement packages including two blank vials and two standards. The sample preparation procedure is shorter than the time of measurement (~50 min. for 20 samples).

Because of varying, unknown U contents in the samples a pre-classification of samples can be made prior to the delayed-neutron counting by counting each measurement series in an automatic γ-ray counting facility. Samples are then classified as high-U and low-U samples and the combination of 1 or 9 BF_3 counters, respectively, can be selected for the different measurement runs. In some cases this check operation is not absolutely necessary because a high-U sample in a measurement run will show up by the delayed-neutron count rate automatically, and the operator may easily arrange for a second measurement run with only 1 BF_3 counter in operation.

4.2. Background

Background counts at the delayed-neutron counting facility are expected from cosmic-radiation-induced neutrons and from neutrons generated during the reactor operation. This part of the background is small and not reduced during reactor shut-down periods; a constant background count rate was estimated by experiment: 0.20 ± 0.04 cps.

The actual background during operation of the facility is much higher, 433 ± 23 cps, deduced from 19 determinations within one week, varying from day to day (Fig. 7). Two background components are important in this respect. Firstly, the polyethylene containers have a certain amount of U, about 0.17 ppm. There is only a slight variation of this value for large numbers of sample containers. Secondly, neutrons are generated during the decay of ^{17}N (half life 4,15 s). This isotope is, however, produced mainly by fast neutron reactions on oxygen isotopes, oxygen being present in both the sample container and the sample (see section on interferences). Relatively low fast neutron flux values and delay times reduce this contribution to negligible values in our facility.

Unfortunately, actual background may vary due to contamination in the transfer system, often progressively increasing between cleaning periods. However, the background variation within one day is usually less than 5%. Because each measurement series implies the measurement of 2 blanks background, usually repeated three times, variations within the time of measurement are properly controlled and the background magnitude is well known for the run.

4.3. Standards

The delayed-neutron count rates from the unknown samples are compared with count rates from standard samples irradiated within the sample measurement run.

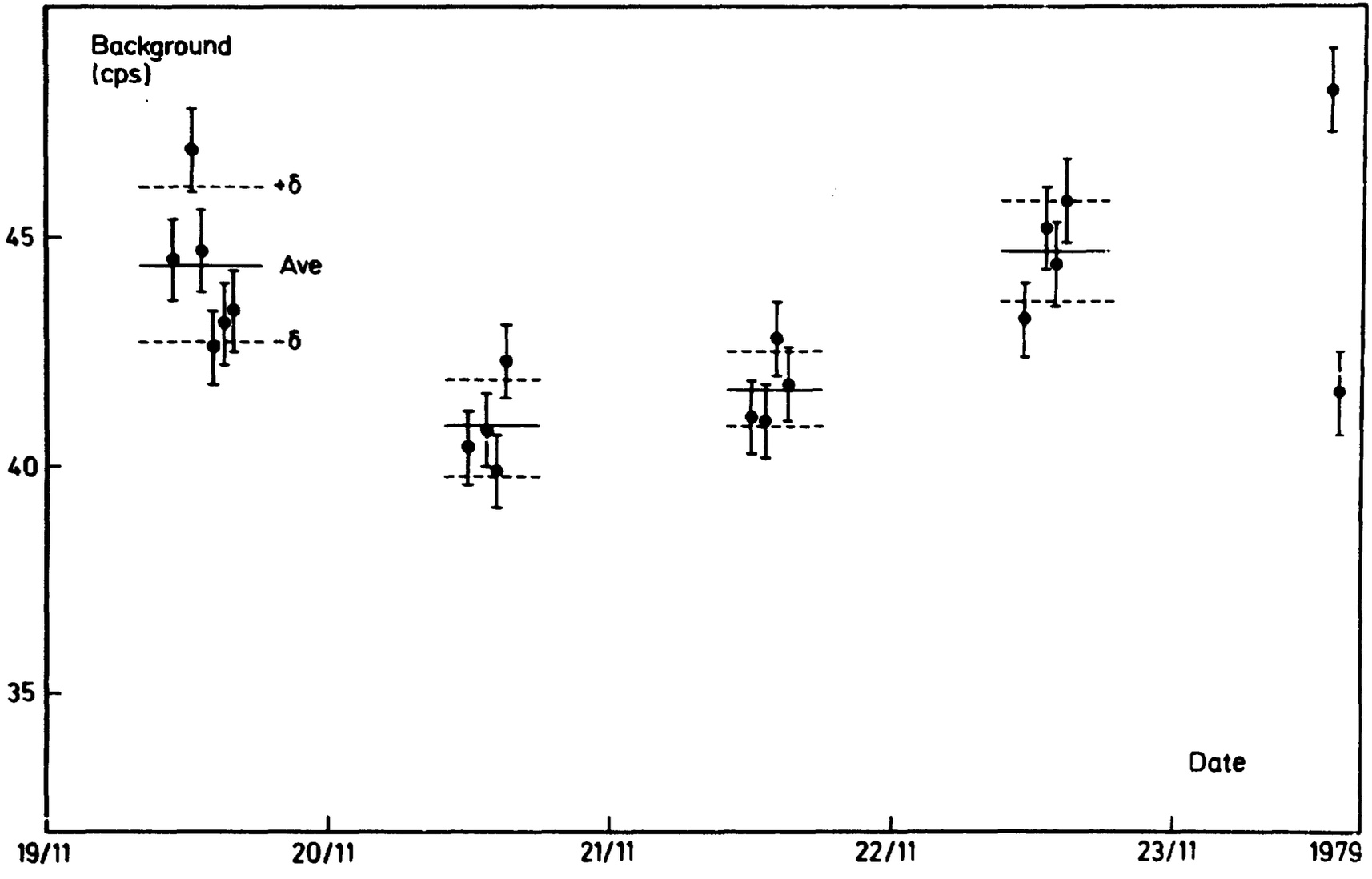

Fig. 7. Weekly background variation of the delayed-neutron counting facility.

Artificial U-standards were prepared from a uranium standard solution, the solution being fixed on silica gel inside the sample container. In this way standards of 120.0 ppm U were prepared (standard 1).

Because of the large sample throughput of the facility, large numbers of standards are necessary. For this purpose, a load of natural potassium feldspar was prepared and carefully analysed for U using standard 1. Large quantities of material are supplied by Norfloat A/S & Co of Norway. The chemical analysis of this material is given in Table 2. The potassium feldspar is crushed to -200 mesh (about 98%). From repeated measurements a value of 2.8 ppm U was evaluated for this reference material (standard 19) and large numbers of samples are prepared from the material.

Table 2. Chemical composition of potassium feldspar used as U counting standard (standard 19). All values in weight-%, U in ppm.

Standard	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	U
19	65.20	19.20	0.07	0.40	12.00	2.80	2.80

For special purposes, a number of natural and mixed ore standards are available through the New Brunswick Laboratory (NBL), U.S.A. These standards are, however, purchased in quantities of less than 500 g only. Table 3 lists the standards used at our laboratory. The U contents of these standards were measured using standards 1 and 19 and varying BF_3 counter configurations (Table 4). Clearly, all U contents of mixed U/Th NBL standards could not be verified by experiment. Therefore, the U values for standards 108 to 110 especially are possibly in error due to mixing gradients and/or splitting problems of monazite in these standards. Also, the Th/U ratio of the monazite used for the preparation of the samples could be erroneous. Some other important conclusion can be drawn from Table 5. Only 1 BF_3 counter should be used in our installation because serious dead-time effects for high count rates are expected for samples with more than

Table 3. Radioelement standards supplied by the New Brunswick Laboratory (NBL), U.S.A.

Sample no	U (ppm)	Th (ppm)	Composition
74A	1040		Pitchblende w. dunite
80A	40	1.005	Monazite w. dunite
101	10000	-	Pitchblende w. quartz
102	1010	-	"
103	470	-	"
104	103	-	"
105	10	-	"
106	350*	10000	Monazite w. quartz
107	35*	1000	"
108	18*	520	"
109	3.7*	104	"
110	0.35*	9.8	"

* U value based on Th/U ratio of monazite.

Table 4. Evaluation of NBL-standard uranium concentrations using potassium feldspar (standard 19) and the artifical standard (standard 1) for different BF_3 counter configurations. ΔU is the deviation from the values given by NBL.

NBL Std	Standard 19				Standard 1			
	9BF_3 counters		1 BF_3 counter		8BF_3 counters		1BF_3 counter	
	U(ppm)	ΔU(%)	U(ppm)	ΔU(%)	U(ppm)	ΔU(%)	U(ppm)	ΔU(%)
74A	772±5	-23.1	896±15	-10.8	854	-17.9	934	-10.1
80A	43.0±0.4	+7.5	44.3±0.7	+9.7	46.5±1.5	+16.3	45.5	+13.8
101	-	-	8060	-19.4	-	-	8540	-14.6
102	823±7	-17.7	973.3±13	-2.7	919	-9.0	1020	+1.0
103	433±2	-13.4	473±6	-5.4	481±4.2	+2.3	498	+6.0
104	99.0±0.3	-1.0	102±1	+2.0	100	-2.9	107	+3.9
105	9.03±0.11	-9.7	9.24±0.33	-7.6	12.8	+28.0	9.72	-2.8
106	342±1	-2.2	369±4	+5.1	371	+6.0	384	+9.7
107	35.9±0.1	+2.6	36.8±0.2	+4.9	40	+14.3	38.6	+10.3
108	20.9±0.2	+15.6	21.4±0.4	+15.9	22.9	+27.2	22.2	+23.3
109	4.29±0.03	+15.9	4.31±0.05	+14.2	4.79	+29.5	4.68	+26.5
110	1.33±0.03	+280	1.32±0.10	+277	1.39	+297	1.47	+320

Table 5. Precision (standard deviation in %) of U measurements for samples with varying U content based on 3 repeated measurements.

Sample no	U (ppm)	Average count rate* (counts/10 s)	Standard deviation (%)
510/01	0.0305	504	4.9
281556	1.62	8725	0.4
281419	5.55	15716	0.9
281418	9.36	27985	0.2
281416	60.1	115391	0.2
280844	108	363812	0.4

* Varying sample weight.

100 ppm U (see chapter 4 on influence parameters). A high-U standard should not be used in connection with samples with relatively low U contents if a measurement error of less than ± 10% is envisaged. Relatively high count rates are measured. A 7.5-g sample with 1 ppm U yields approximately 6000 counts in the 10-s counting period. The counting statistics for this count rate give a relative standard deviation of 1.4%. For concentrations at the background level (about 500 counts) the standard deviation increases to 30%.

4.4. Sensitivity, precision, and detection limit

The sensitivity of the facility is calculated for each measurement run based on the count rates from the standards, i.e. the count rate obtained from an accurately known U quantity. The weekly value for 19 runs is 817 ± 22 counts per 10^{-6} g U using 9 BF_3 counters.

The precision of the analyses based on repeated measurements of samples is generally less than 1%. A typical measurement run of 19 repeated determinations of a potassium feldspar sample yielded 0.9%. Usually the measurement run is repeated three times and the precision of the U determinations can be calculated for each sample. Typical values for different U concentrations are given in Table 5.

According to the definitions introduced by Currie (1968), the critical level L_c for our installation is calculated to be 0.06×10^{-6} g U and the detection limit L_d is 0.12×10^{-6} g U, corresponding to 8 and 16 ppb U, respectively, in a 7.5-g sample. With an unpredictable state of contamination of the transfer tube system these values may be lower or higher at some time depending greatly on the successful cleaning of the system in shut-down periods. The relatively low detection limit is sufficient for the analysis of most geological sample materials of varying composition.

5. PARAMETERS INFLUENCING THE ANALYSIS

The analytical result and its performance is influenced by physical factors and elemental interferences. Whereas a number of experimental physical conditions may vary during measurement the number of elemental interferences is limited. Each influence is treated separately.

5.1. Physical parameter variations

Important physical influence parameters are sample preparation, neutron flux stability, timing controls, and statistical variations, but a number of other experiments were carried out to check the influences of other physical parameters.

Sample preparation is carried out routinely and influences on the analytical result can be expected from weighing errors. In the case of usage of a 0.01-g balance these errors are negligible. More important in this respect is the homogeneity of the sample and therefore only well-homogenized -0.177-mm or less size fractions should be provided for analysis.

Neutron flux variation are generally small during reactor operation. Their influence on the analytical result is estimated to be negligible because a measurement run is completed within one hour.

Timing errors, especially in the delay-time settings, may have, an influence on the delayed-neutron count rates. A very stable clock pulse generator controls the delay time and the counting time, and no influence from these constants is expected. The irradiation time on the other hand is accurate only to within 1 clock pulse (0.1 s, yielding on error in timing of about 1%.

Because of different half-life groups of delayed-neutrons for delay and measuring times, optimal values may be deduced from experiments involving timing variations. An experiment was carried out with a granite sample containing 6.13 ppm U. The results of this experiment are given in Table 6. The deviations from the average result are small for all timing variation experiments, often at the 1% level. But for low irradiation times (<6 s) deviations of up to -3% may occur. For these low irradiation times the production of the neutron emitting ^{17}N, arising from oxygen isotopes may be of importance. Therefore, the experiment outlined in Table 6 confirms the chosen relatively short parameters for routine operation.

Table 6. Deviations (in %) of the analytical result of a granite sample (6.13 ppm U) by varying the timing constants of the delayed-neutron counting facility. Five granite samples were used in the experiments. Timing intervals given in sec.

t_{IR}	t_C	t_M				
		5	10	20	40	60
5	5	-1.0	-3.4	-3.1	-2.8	-1.5
10	5	-0.5	+0.2	-1.5	+0.2	-0.7
20	5	+1.1	-	+0.8	+0.5	+0.7
40	5	+2.6	0	+1.1	0	+0.2
60	5	+1.8	+0.3	0	+0.5	+0.3
20	10		+1.0			+1.6
20	20		+0.3			-1.1

The high neutron count rates mentioned, produced in the facility, may cause serious dead-time effects which cannot be accounted for by the electronics used. To test the influence of dead-time effects on the analytical result, and to evaluated corrections factors for high neutron count rates, a detailed investigation was carried out involving model studies and test measurements (E.M. Christiansen, 1980). Some results of these investigations are given in Table 7. Briefly, with the timing constants used at our facility (20 s, 5 s, and 10 s, respectively) the dead-time correction is about 1.2% at 10^4 counts, increases to about 14% at 10^5 counts, and is 37% at 2×10^5 counts. The dead-time correction function can be approximated by a polynomial expression for count rates up to 10^5. This function is built into the computer program treating the data from the facility. Higher count rates are usually avoided.

Table 7. Dead-time corrections of count rates predicted by model studies and test measurements.
Irradiation time = 20 s, delay time = 5 s, and counting time = 10 s.

Start CR CPS	Start %DT	Aver DT Microsec	Aver %DT	Counts True	Counts Measured	Corr Factor
1682	1.8	11.6	1.2	10119	10000	1.012
3405	3.6	11.6	2.3	20481	20000	1.024
5170	5.4	11.6	3.5	31100	30000	1.037
6981	7.2	11.6	4.7	41989	40000	1.050
8839	9.0	11.5	5.9	53163	50000	1.063
10747	10.9	11.5	7.2	64641	60000	1.077
12709	12.7	11.5	8.4	76443	70000	1.092
14728	14.6	11.5	9.7	88590	80000	1.107
16809	16.5	11.5	11.0	101107	90000	1.123
18956	18.4	11.5	12.3	114019	100000	1.140

In the case of samples with relatively high U concentrations only one BF_3 counter is used. Because each of the 9 counters may be chosen in this case, it is important to know the response to neutrons of each of them. Table 8 outlines the results of an experiment with a granite sample. For counters 6 to 8, significant different analytical results were obtained. Therefore, these detectors should not be used in single-counter experiments.

Table 8. Single BF_3 counter results for 5 granite samples.

Counter no	U (ppm)	Deviation (%)
1	6.16±0.06	+0.5
2	6.14±0.13	+0.2
3	6.23±0.11	+1.6
4	6.13±0.25	0
5	6.07±0.06	-1.0
6	6.00±0.13	-2.1
7	5.83±0.03	-4.9
8	6.31±0.20	+2.9
9	6.14±0.14	+0.2

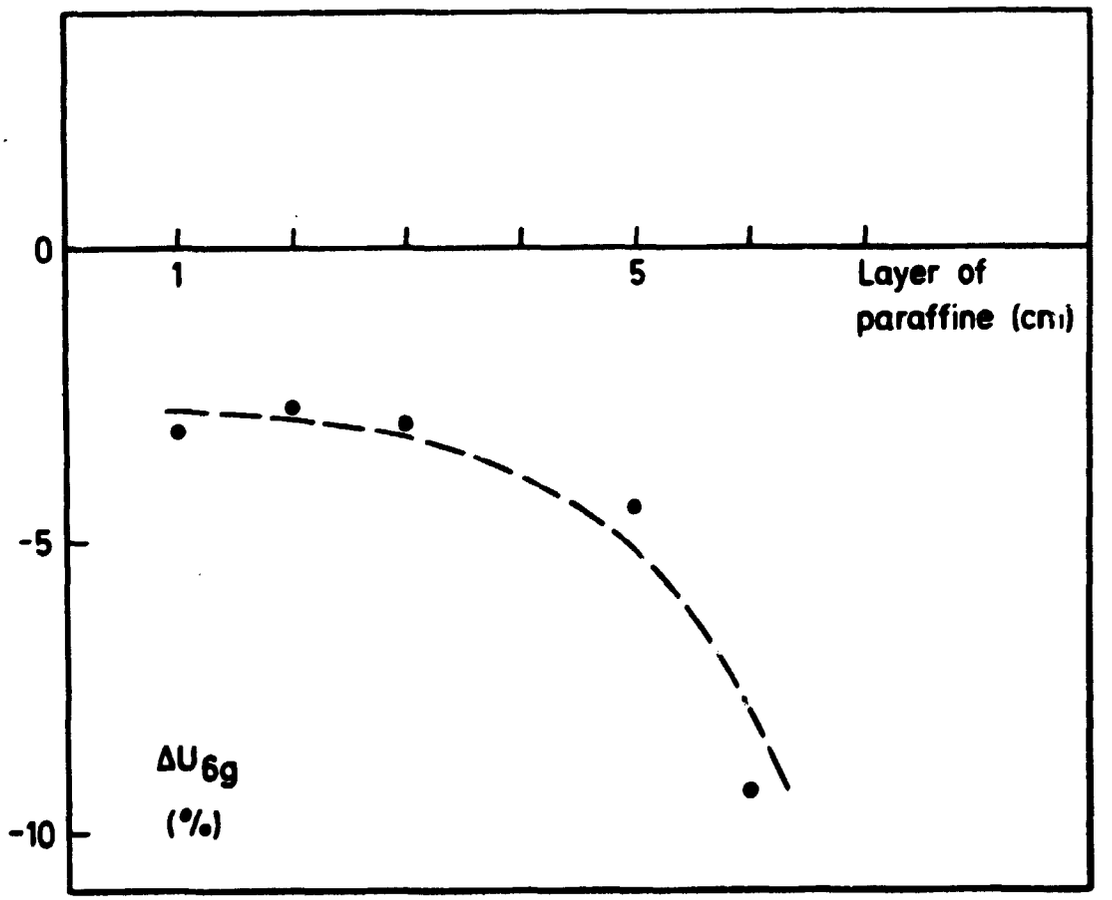

Fig. 8. Influence of paraffin layer in the bottom of the sample vial on the analytical result of 1 g of standard NBL-104 (100 ppm U). The data were compared to the result with a 6-g sample without paraffin layer.

Casted layers of paraffin in the sample container are used for blanks or samples with very small amounts of sample material. This is sometimes necessary to protect the container against vibrations in the pneumatic tube-transfer system. Because of the increase of blank material, however, and the neutron flux variation along the sample container discussed above, errors occur (Fig. 8). Therefore, the use of paraffin layered containers should be limited.

5.2. Elemental interferences

A number of naturally occurring elements are known to contribute to the delayed-neutron count rate either in the form of neutron-emitting or neutron-absorbing isotopes. These elemental interferences may be divided into four groups of reactions as shown in Table 9. To evaluate their importance in the U analysis at the Risø delayed-neutron counting facility, a series of experiments with granitic rock samples containing elements that might give interferences were performed. The results of these measurements are compiled in Table 10, and some of these data are plotted in Fig. 9 and 10. Results of detailed investigations of interelement effects on delayed-neutron counting were given by Kunzendorf and Løvborg (1980).

Enhancement of the delayed-neutron count rates occurs if other delayed-neutron emitters are produced during the irradiation of a sample. This is the case when other fissionable isotopes are present. To naturally occurring fissionable isotopes belongs ^{232}Th which fissions by fast neutrons. This interference is regarded as negligible because the ratio of thermal-to-fast neutrons at our facility is about 1000, i.e. a rather low fast neutron flux is available only. Serious effects are expected from artifical ^{239}Pu with a thermal neutron fission cross-section comparable to ^{235}U. This element is, however, regarded as non-existent in most samples handled at our facility.

Two delayed-neutron-emitting non-fissionable isotopes are important: ^{6}Li with a very short half-life of 0.17 sec and ^{17}N of

Table 9. Interelemental effects in delayed-neutron counting for U analysis.

Kind of interelement effect	Kind of reactions	Elements, mechanisms	
Enhancement	Fissionable neutron-emitting isotopes	Naturally occurring: ^{232}Th, ^{238}U artificially: ^{239}Pu, ^{233}U	
	Other neutron-emitting isotopes	^{9}Li ($T_{1/2}$ 0.17 s) ^{17}N ($T_{1/2}$ 4.14 s)	
	(γ,n) reactions	D(γ,n)p	$E_\gamma \geq$ 2.23 MeV
		Be(γ,2α)n	$E_\gamma >$ 1.67 MeV
Absorption	Neutron capture	^{10}B, ^{113}Cd rare earth elements, especially ^{157}Gd and ^{149}Sm	

Table 10. Evaluation of experiments on elemental interferences in delayed-neutron counting. The data are based on measurements on 5-g samples.

Element	Range of measured variation (ppm)	ΔU, given per 1000 ppm added element (%)
Be	0 - 4000	+ 0.88
Li	0 - 5000	+ 0.13
B	0 - 10000	- 2.68
Cd	0 - 50000	- 0.87
La	0 - 60000	- 0.01
Ce	0 - 70000	+ 0.16
Nd	0 - 50000	- 0.09
Sm	0 - 20000*	- 2.24
Gd	0 - 10000*	-10.19

* Range of experimental data greater; only the linear range of data used.

half-life 4.14 sec. Whereas the former isotope has no effect on delayed-neutron counting if delay times of greater than 2 s (∿10 half-lives of ^{6}Li) are used, ^{17}N, which is produced mainly by fast neutron reactions on oxygen, has a low contribution to the neutron count rate because of the low fast neutron flux at the irradiation site mentioned above. However, if Li is present in a sample, tritons produced by the thermal neutron reaction $^{6}Li(n, \alpha)t$ may generate ^{17}N mainly via the reaction $^{18}O(t, \alpha)^{17}N$. This effect is shown in Fig. 9.

Photo-neutron reactions (γ, n) may occur if a sample is irradiated by high gamma-ray energy-emitting isotopes. Photo-neutrons occur for example, through the reactions $Be(\gamma, 2\alpha)n$ for $E_{\gamma} \geq 1.67$ MeV. Because all geological samples contain large amounts of aluminium, ^{28}Al (half-life 2.' min, E_{γ} = 1.78 MeV) is always produced and if Be is present in a sample the delayed-neutron count rate from U is increased by photo-neutrons from Be (Fig. 9).

Absorption of neutrons occurs within the sample through the physical process of neutron capture leading to self-shielding of the interior of the sample. Serious errors on U analysis may be the result of this kind of reaction. Prominent elements with very

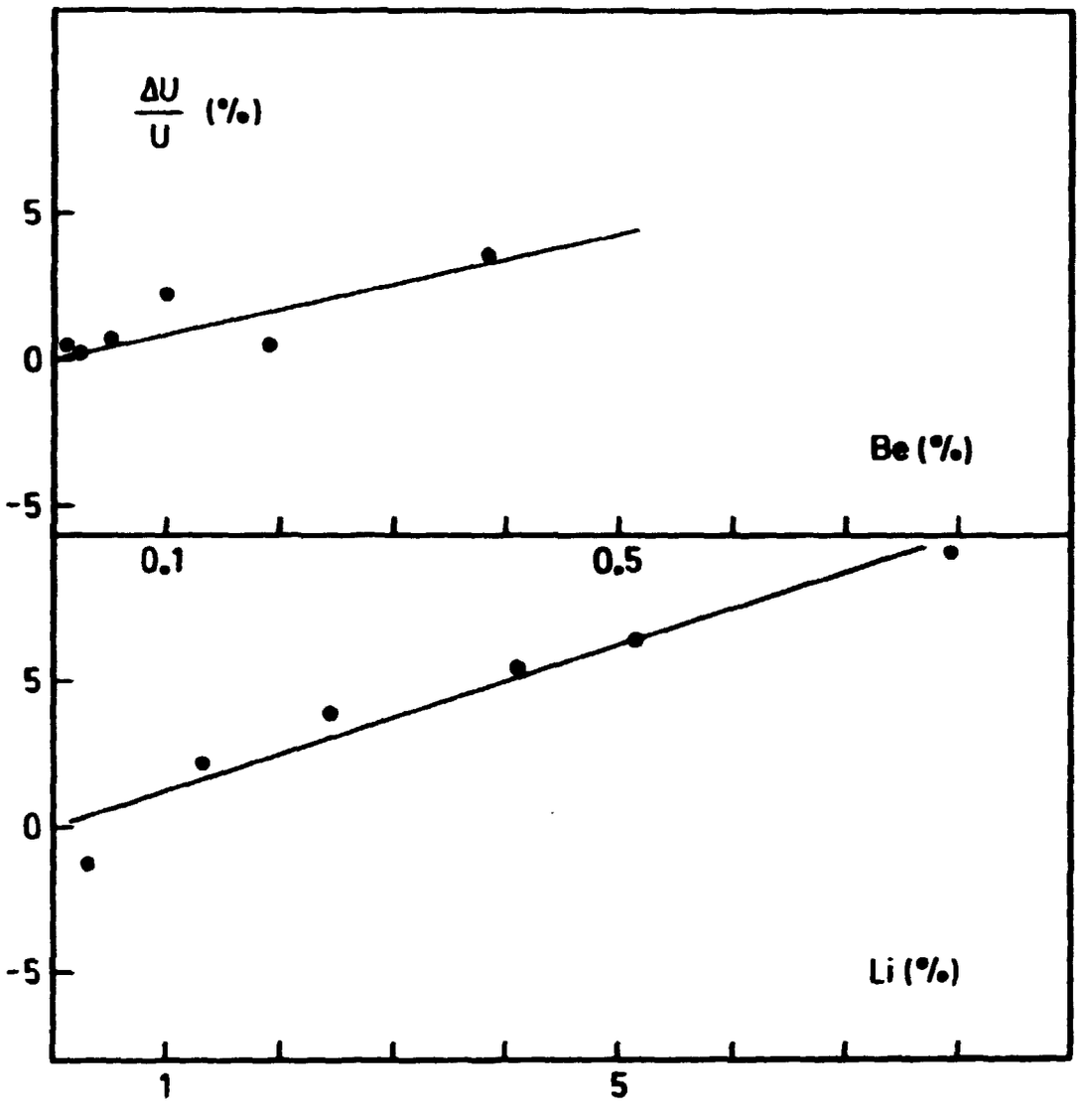

Fig. 9. Variation of the U content of a granite sample by addition of amounts of Be and Li.

high neutron capture cross-sections for thermal neutrons are B, Cd, and the rare earth elements. Important in this respect are the isotopes ^{10}B, ^{113}Cd, ^{149}Sm, and ^{157}Gd. The effect is visualised through Fig. 10 where the influences of Sm and Gd in a granitic sample are plotted.

In general, elemental interferences on U analysis are greatly dependent on the presence of a few elements in the sample. For geological samples, correction of U data is expected if anomalous quantities of Be, B, Cd, and rare earth elements are present. As shown in Table 10, the most serious interference is expected for the rare earth element Gd, which, however, normally is present

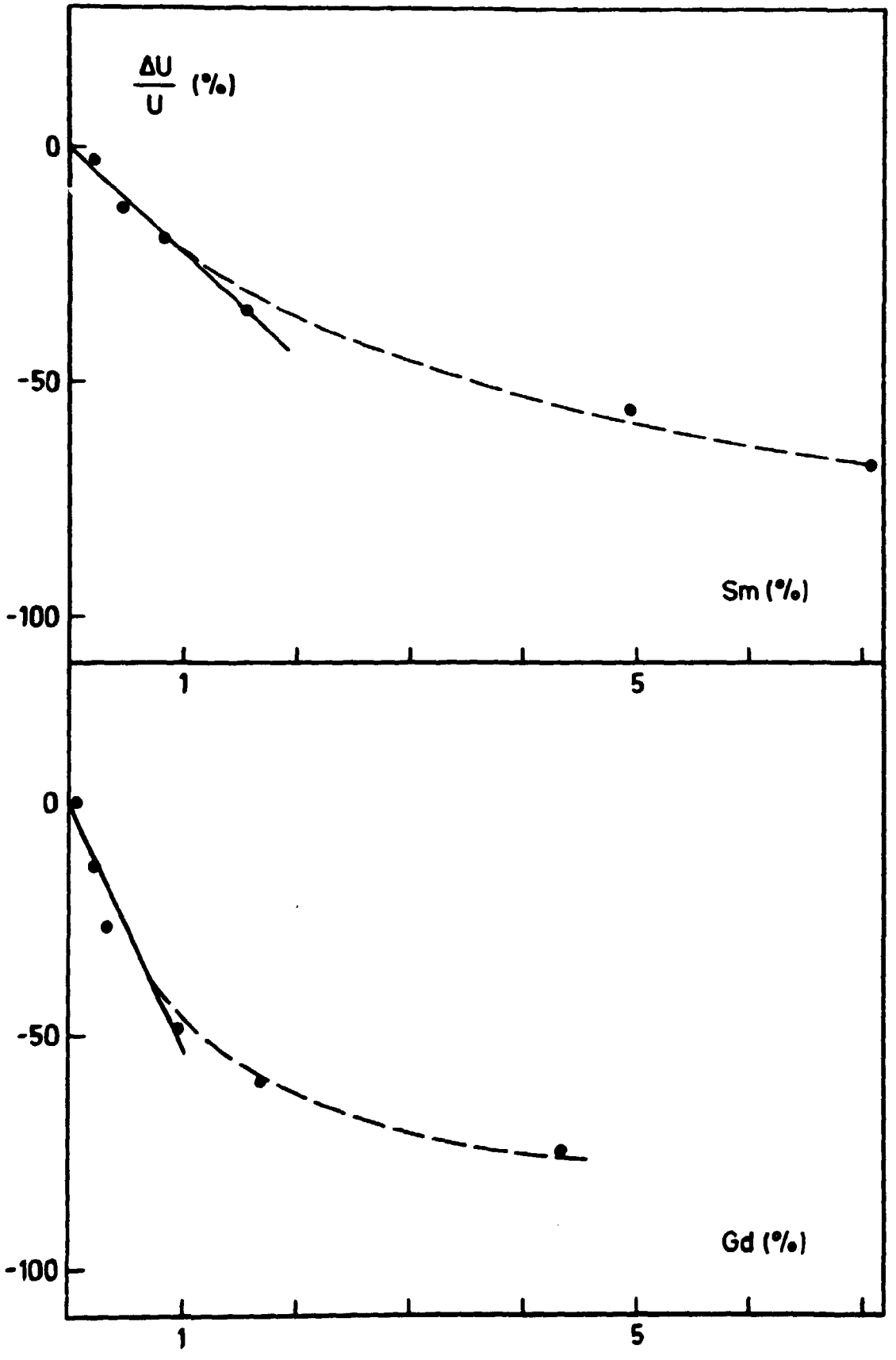

Fig. 10. Variation of the U content of a granite sample by addition of amounts of Sm and Gd.

in quantities of less than 10 ppm in crystal rocks only. It is advisable to check-analyse U values for rocks with economic amounts of Be, Li, Cd, and rare earth elements. U analyses of heavy mineral concentrates should specially use corrections for rare earth elements.

6. APPLICATIONS

Delayed-neutron counting for U can be used on a wide variety of solid and liquid samples. Large quantities of samples can be analysed and the majority of applications lies within the geological and environmental sciences. Delayed-neutron counting is preferrably applied in geochemical exploration for U deposits, in the chemical control of U processing, and in environmental mapping for uranium.

A typical example of U data generated by delayed-neutron counting is given in Fig. 11, where -80 mesh stream sediment samples are plotted from the drainage system of the Kvanefjeld uranium deposit within the Ilímaussaq intrusion, South Greenland. Typical applications of the method were described by Amiel et al. (1967), Dawson and Gale (1970), Henderson et al. (1971), Moxham et al. (1972), Kalsbeek (1974), Kunzendorf and Friedrich (1976), Paul et al. (1977), Steenfelt et al. (1976), Kunzendorf et al. (1978), and Steenfelt and Kunzendorf (1979).

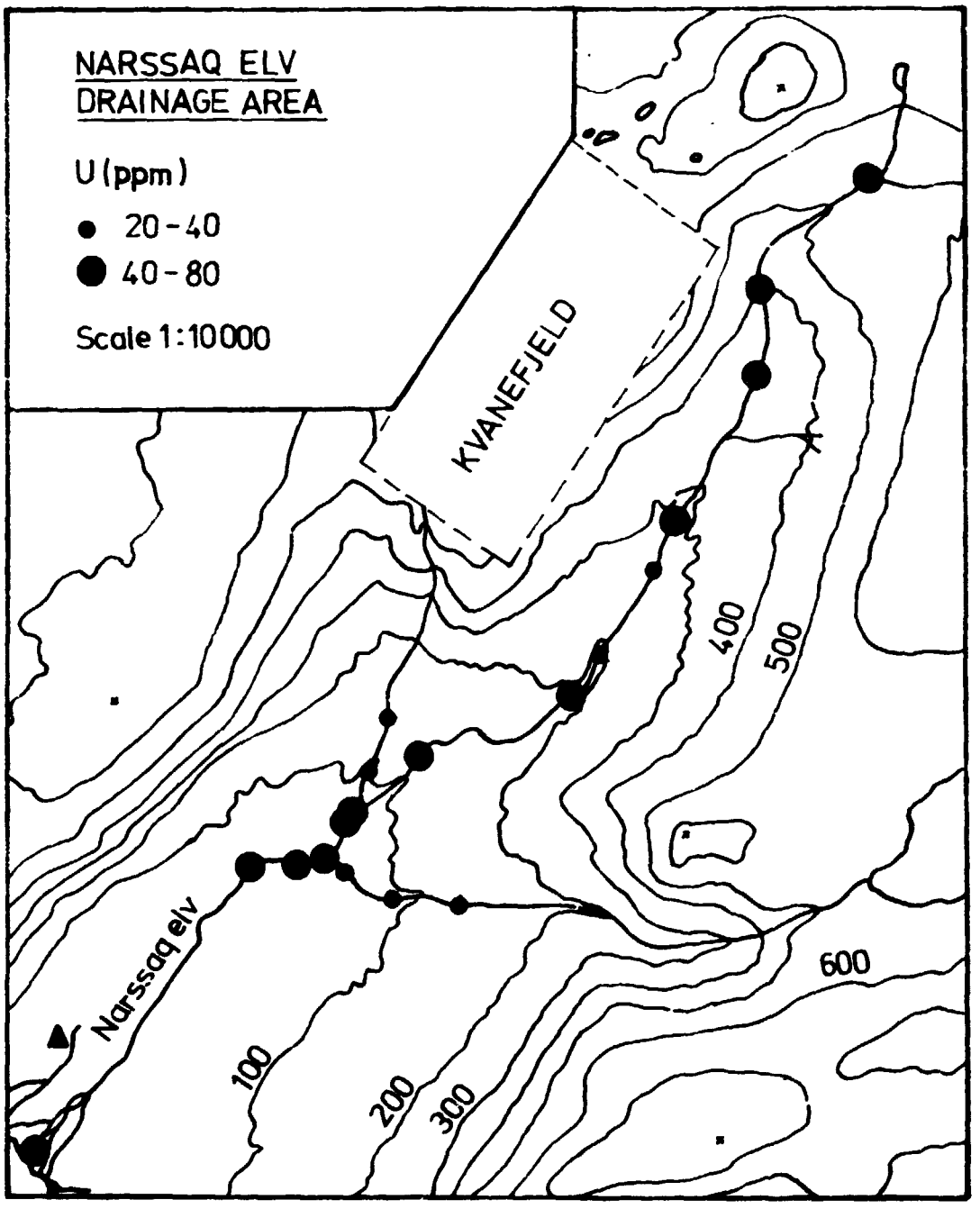

Fig. 11. U results of a stream sediment survey in the drainage area around the Kvanefjeld uranium deposit, obtained by delayed-neutron counting.

CONCLUSIONS

From the detailed investigations of the Risø delayed-neutron counting facility the following can be concluded.

Fission-induced delayed-neutron counting is a fast and reliable non-destructive method of uranium analysis. Large numbers of geological, chemical or environmental samples can be analysed, 90 in our facility during a normal working day, taking into account reactor shut-down periods of usually 1 week per month. This capacity can, however, be increased significantly by the use of less than three irradiations per sample or by increasing the working day during the time of reactor operation. Sample preparation is reduced to filling and weighing of sample containers.

Characteristic data of the Risø delayed-neutron facility are detection limits at the 10-ppb level for geological samples, and precision values well below 5%. The influences of variations of physical parameters on the analytical result is low and greatly controlled during the operation of the facility. Interferences from other elements in the sample are low and negligible for normal geological material.

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