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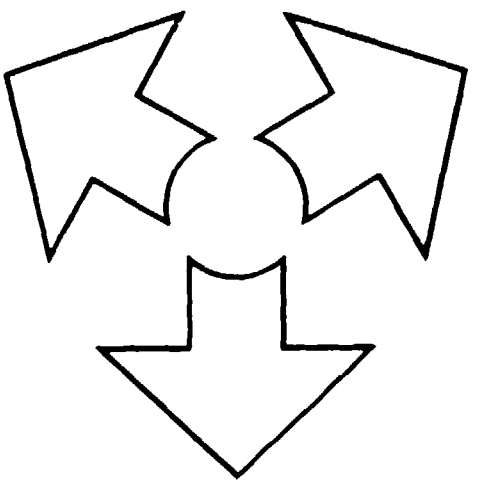

Risø National Laboratory, 4000 Roskilde, Denmark
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Isotope Division November 1978

SOURCES OF VARIABILITY FOR THE SINGLE-COMPARATOR METHOD IN A HEAVY-WATER REACTOR

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SUMMARY

At the end of 1975 our irradiations were transferred to new facilities in the DR 3 reactor at Risø. The well thermalized flux in this heavy-water-moderated reactor prompted us to investigate to what extent a single comparator could be used for multi-element determination instead of our previous multiple comparators.

The reliability of the single-comparator method is limited by the stability of the neutron flux energy spectrum, in particular of the thermal-to-epithermal ratio, and experiments were designed to determine the variations in this ratio throughout a reactor operating period.

The bi-isotopic method using zirconium as monitor was chosen for the determination, because ^{96}Zr and ^{90}Zr exhibit a large difference in their I_0/σ_{th} values, so this isotope pair would permit determination of the flux ratio with a precision sufficient to determine variations.

One of the irradiation facilities comprises a magazine with three channels, each of which can hold five aluminium cans. The rig rotates around the vertical axis to ensure flux homogeneity in cans placed in the same horizontal position. A further facility consists of a pneumatic tube system with a polyethylene rabbit for rapid transfer of samples for measurement of short half-life indicators.

DR 3 operates at 10 MW in periods of 4 weeks including a shut-down period of 4–5 days.

In the rotating rig, the irradiations were carried out in the first and the third weeks of 4 operating periods. Five cans, each holding a polyvial with 1 ml of aqueous zirconium solution, were irradiated simultaneously for half an hour in one channel.

In the pneumatic tube system, the experiments were carried out once a week for 4 periods. Two samples were simultaneously irradiated on top of each other in the rabbit.

All samples were counted on a Ge(Li)-detector for ^{96}Zr and the daughters ^{97m}Nb and ^{97}Nb of ^{97}Zr. The γ-lines used were 724 and 757 keV for ^{96}Zr, 743 keV for ^{97m}Nb, and 658 keV for ^{97}Nb. The thermal-to-epithermal flux ratio was calculated from the induced activity the nuclear data for the two zirconium isotopes and the detector efficiency.

For both facilities, the observations of the flux ratio were subjected to a three-way, mixed factor, analysis of variance. The total variation was separated into a random variation between reactor periods, and systematic differences between the horizontal positions as well as between the weeks in the operating period.

In the rotating rig, the flux ratio increases not only from the lower to the upper position, but also during an operating period. Furthermore, the increase during a period is greater for the upper than for the lower positions. In the pneumatic tube, the flux ratio, being lowest at the bottom of the rabbit, increases during an operating period at the same rate for the two positions.

While the systematic differences are determined with sufficient precision, the random variation is based on 4 reactor periods only. Additional measurements are needed for a better estimate.

If the variations are in statistical control, the error resulting from use of the single-comparator method in multi-element determination can be calculated for any combination of irradiation position and day in the operating period. Both the random and the systematic errors depend on the difference in I_0/σ_{th} values between the comparator and the element to be determined. By suitable choice of irradiation conditions and by selection of an appropriate comparator the overall errors can be reduced.

From our present knowledge of the flux ratio variations, it can be calculated that use of the single-comparator method introduces only small errors in the determination of most elements. This method is therefore expected to be very suitable for use with the irradiation facilities in DR 3.

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INTRODUCTION

Shortly after the 4th Symposium on the Recent Developments in Neutron Activation Analysis at Cambridge in 1975 our Danish reactor DR 2 at Risø, which we had been using for neutron activation analysis, was permanently closed down and it is now being decommissioned.

New irradiation facilities specially designed for neutron activation analysis were installed in the reactor DR 3, which is a heavy water cooled and moderated plant, similar to the PLUTO reactor, but operating at a power level of 10 MW. These facilities are located in the vertical tubes extending into the heavy water as shown in Fig. 1. Their characteristic specifications are summarized in Table 1.

Concurrently with the installation of these new, improved facilities the need for multi-element INAA became acute in connection with the large number of environmental and geological samples from the Narssaq project*.

Instead of using a multi-element comparator, as was the case in earlier work at the DR 2 reactor, we decided to investigate the limits of applicability of the single-comparator method.

The original single-comparator method was described by Girardi [1965], and it is based on the experimental determination of the ratios of specific count-rates of an element and a comparator. These so-called k-factors are valid for the determination of all elements from one comparator standard under conditions of constant

(1) sample type
(2) counting conditions
(3) irradiation conditions.

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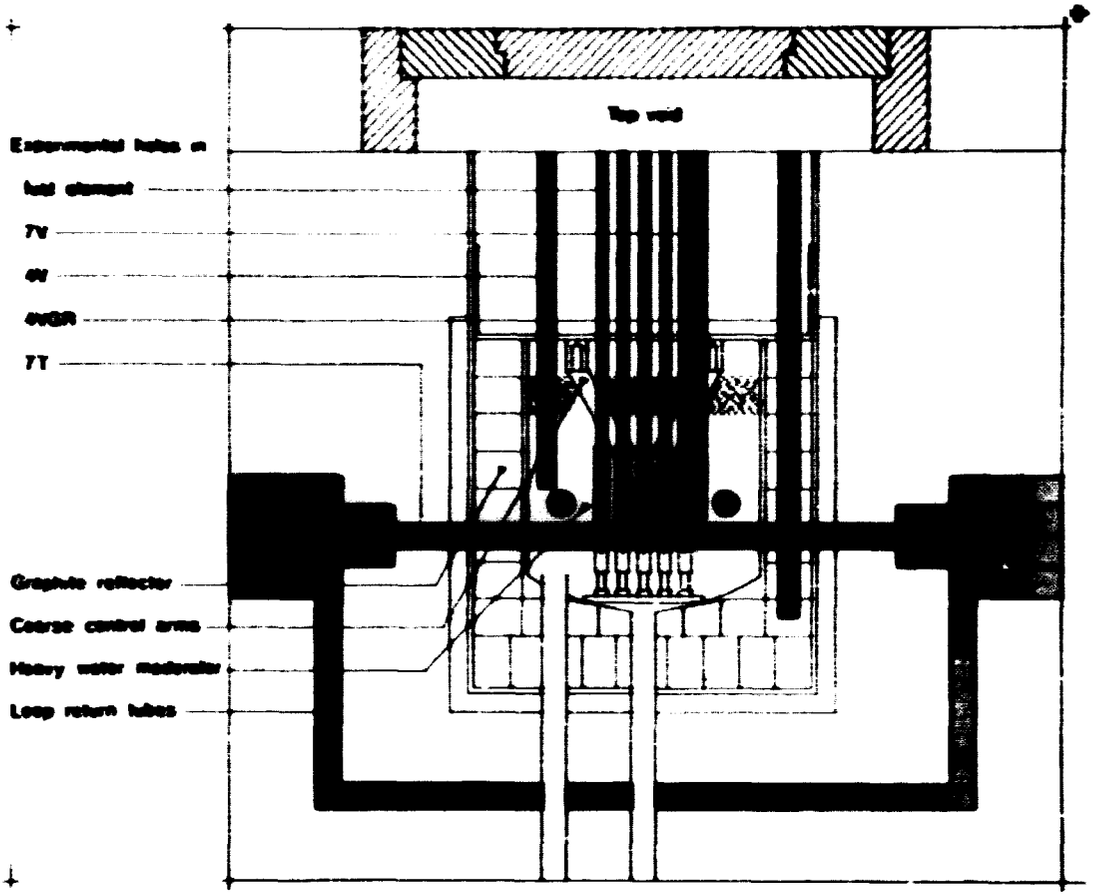
*An environmental geochemical and ecological project carried out in the Narssaq region in Greenland.

Fig. 1. Schematic cross sections



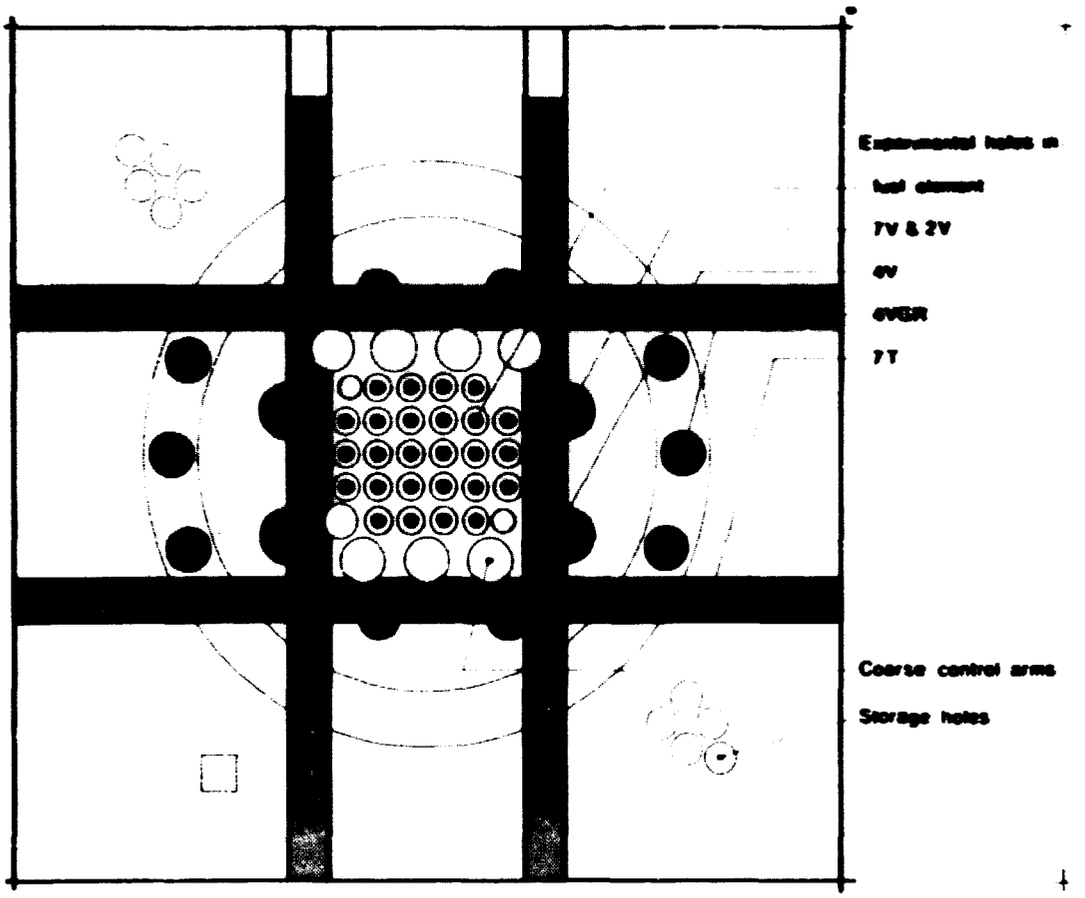
Sample size and composition with respect to moderating power, absorption of thermal and resonance neutrons, as well as differences in γ-ray self-absorption must be taken into account by the analyst [Prouza 1967].

Counting conditions are precisely controlled by the analyst with regard not only to counting time, but also to the choice of detector and counting geometry, etc.

Irradiation conditions are also controlled by the analyst with respect to irradiation time and thermal neutron fluence, whereas changes in neutron flux density distribution are brought about by factors beyond his control.

The stability of the neutron flux spectrum is therefore a limiting factor in the precision and accuracy of results based on the

of the Danish reactor DR 3.



single-comparator method. A study of systematic and random sources of variation and their influence on the k-factor is therefore warranted.

The irradiation facilities used for activation analysis are listed in Table 1 with their normal levels of thermal neutron flux density. Their position in relation to the reactor core can be seen in Fig. 1. Fast neutrons determined by simultaneous irradiation of Co and Ni monitors constitute 0.2% or less of the total number of neutrons, and their influence on the k-factors is therefore negligible.

Epithermal neutrons, however, may contribute significantly to the k-factors of nuclides with high resonance integrals, and actual values of the epithermal fraction and their variability were therefore studied under a variety of experimental conditions.

Table 1

Reactor Irradiation Facilities for Neutron Activation Analysis at Risø

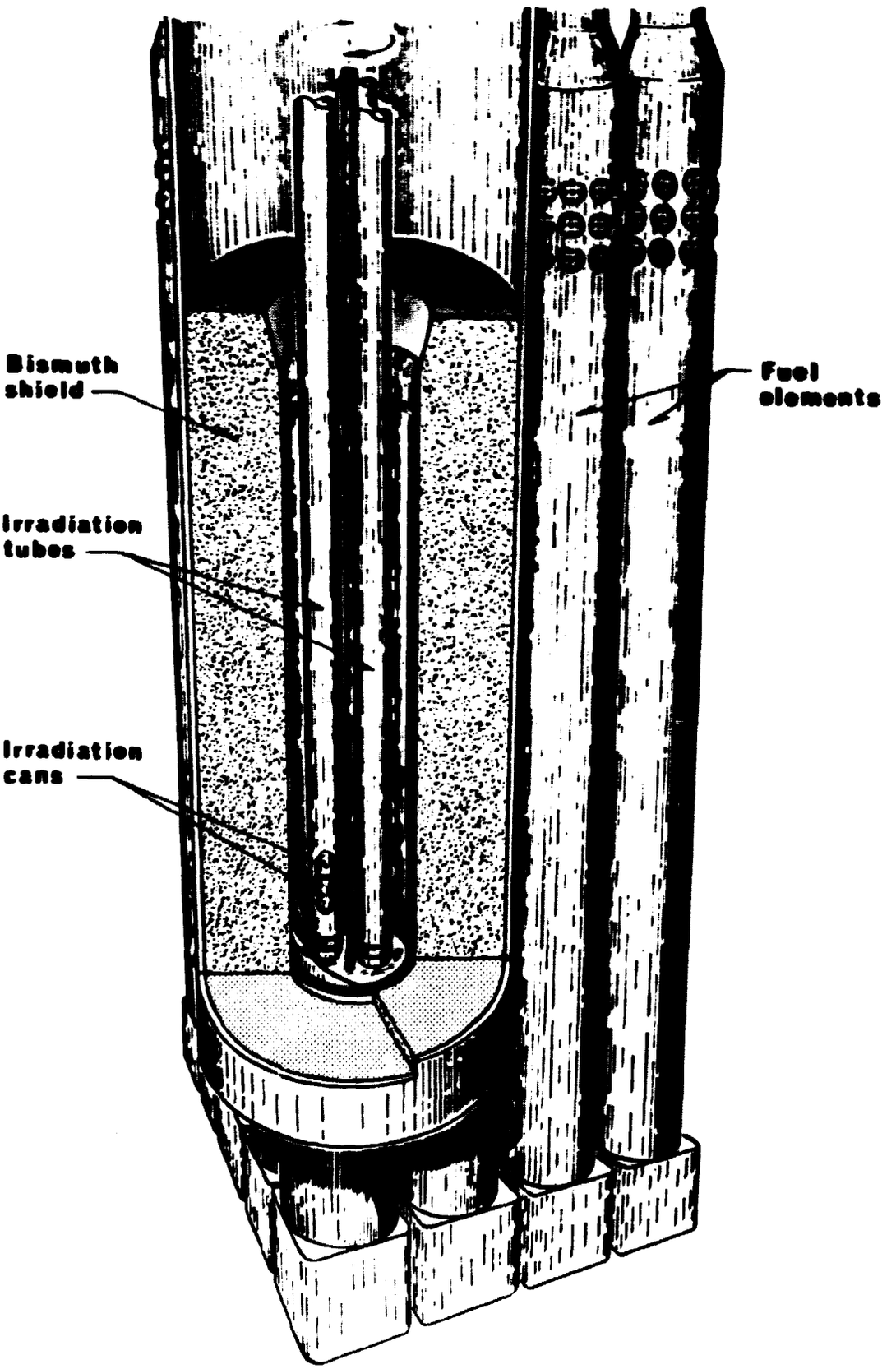
Designation	Position	Thermal neutrons per $cm^2 \cdot s$	Fast neutrons per $cm^2 \cdot s$	Capacity number	Transport time approx.
Rotating Rig	7V2	4.5×10^{13}	10^{11}	5 x 3	30 min.
Pneumatic Tube	4V4	2.5×10^{13}	3×10^{10}	1	30 s
Mach 1 Rabbit	4V3	2×10^{13}	2×10^{10}	1	30 ms

Fig. 2. Cut-away of the rotating rig facility in the DR 3 reactor. The 3 sample tubes in the rotating assembly is surrounded by 50 mm of bismuth in order to reduce the γ-ray exposure. Each tube will accept 5 irradiation cans on top of each other.

Automatic insertion and extraction of 1 can from each tube in succession ensures identical irradiation time for cans in the same horizontal layer.

A flow of gas of CO_2 at the same time maintains an irradiation can temperature <50°C and is used to transport the cans in and out during reactor operation.

IRRADIATION POSITION 7V2 IN DR3 WITH THE ROTATING RIG FACILITY



EXPERIMENTAL

The experimental determination of the epithermal ratio in well-thermalised irradiation positions requires the use of detectors with a high ratio of resonance integral to thermal neutron cross section.

Table 2

Nuclear characteristics of the zirconium isotopes used in the present study

Nuclides	$^{94}Zr\ (n,\gamma)^{95}Zr$	$^{96}Zr\ (n,\gamma)^{97}Zr$
abundance	17.5%	2.8%
σ_{th}	0.052 ± 0.003 b	0.020 ± 0.03 b
I_o	0.30 ± 0.03 b	5.0 ± 0.4 b
$T_{\frac{1}{2}}$	65.5 d	16.8 h
γ keV	724.2 and 756.7	657.9 and 743.4
abundance	44.4 and 54.8%	98.3 and 91.7%

For ^{96}Zr this ratio is approximately 250, and the other stable isotope of zirconium, ^{94}Zr, has a ratio of approximately 5. Other nuclear characteristics are shown in Table 2, and they also favour the use of zirconium as a single-element, combined epithermal and thermal flux monitor [Simonits 1976].

In order to simulate a biological sample, Zr was irradiated as an aqueous solution of $ZrO(NO_3)_2$ containing 13 mg of Zr in a 1 ml sample in a sealed half-dram polyvial.

The irradiation time was 30 min, and the sample was counted after 75 hours decay on a Ge(Li)-detector for 60 min with a dead time of approximately 10%. Both radionuclides, ^{95}Zr and ^{97}Zr, were determined as the mean of the two different photo-peaks given in Table 2, and these peaks contained approx. 50 000 counts.

Table 3

Differences in thermal-to-epithermal flux ratio in the Pneumatic Tube Facility with different reported cross-sections

Pos. 1	Pos. 2	Reference	
173	179	Ricabarra	1970
652	720	*Fulmer	1971
754	843	Van der Linden	1972
538	586	Holden	1972
2365	3356	Santry	1973
383	408	Erdtmann	1976
1131	1336	Walker	1977

*Used in this work

The calculated values for the thermal-to-epithermal flux ratios depend strongly on the actual cross sections used in the calculation, as illustrated in Table 3. The values chosen for the present study are those of Fulmer [1971] included in Table 2.

Table 4

Reactor operation schedule based on a 4 week cycle

1st week	Monday-Friday	Shut-down
	Friday at 9 am	Start up
2nd week		Operation at 10 MW
3rd week		" "
4th week	Sunday at 6 pm	Close down

The DR 3 reactor is regularly operated on a four-week basis as shown in Table 4, and zirconium monitors were irradiated in facilities 7V2 and 4V4 at different times of the operating period. Measurements in 4V3 are not possible, because the activity induced in Zr during a short irradiation is too low. A total of 61 monitors were processed from 4 different operating periods during the course of 5 months.

RESULTS

A total of 39 results for the Rotating Rig gave an overall mean value for the flux ratio of 236 thermal neutrons for every epithermal neutron with a coefficient of variation of 9.7% accounting for all sources of variation, including 5 different vertical positions in the irradiation facility.

An Analysis of Variance showed highly significant influence not only of the vertical position and reactor operating period, but also of the time after start up. No significant interaction between these effects was found, and their magnitudes were determined by multiple, linear regression analysis.

Results are given in Table 5 as the relative contributions from the different sources of variation to the overall variability of measured values, and the influence of the vertical position

Table 5

Sources of variability of 39 thermal-to-epithermal flux ratios of the rotating rig facility

Mean Value	Source of Variation	Residual Variance	σ_{est}
236	all	100 %	9.7 %
	Positions	62 %	7.8 %
	Day of period	36 %	6.0 %
	Period No.	7 %	2.7 %
232	Position 1-4	68 %	8.1 %
	Positions	53 %	7.3 %
	Day of period	31 %	5.7 %
	Period No.	2.5 %	1.7 %
Average	Counting statistics	n.s.	1.5 %

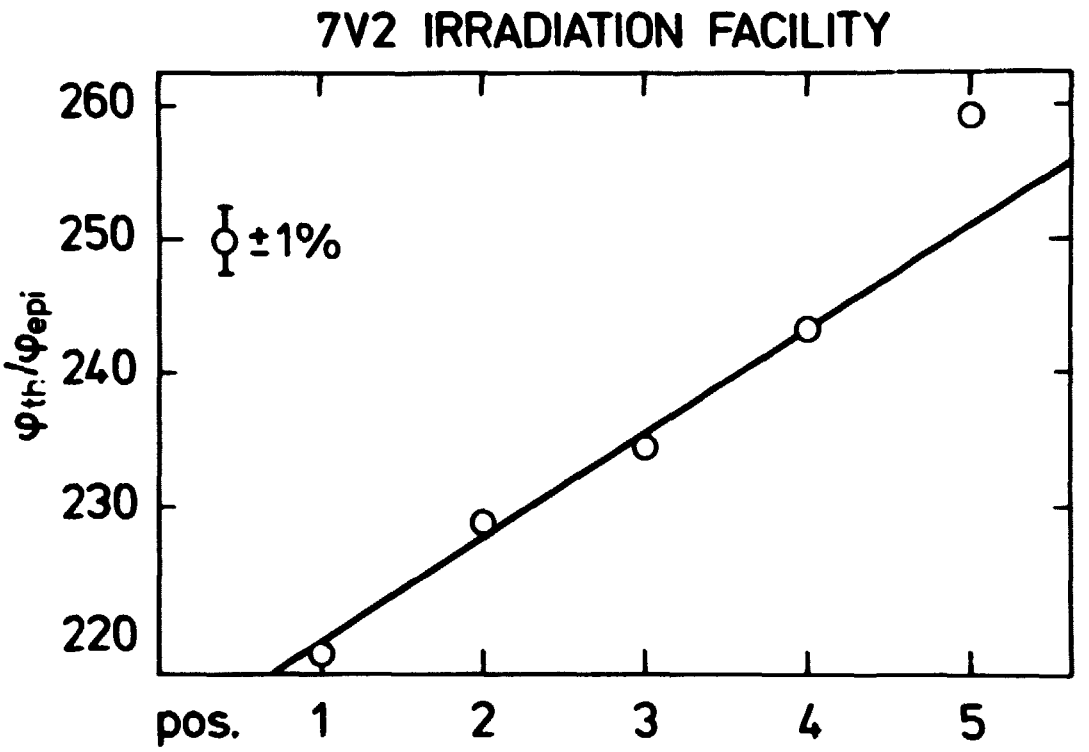


Fig. 3. Thermal-to-epithermal neutron flux ratio in 5 vertical irradiation positions in the rotating rig facility in the DR 3 reactor.

is shown separately in Fig. 3. It is clearly seen that the highest position is out of line with the other positions. Excluding this point, the change in epithermal ratio is a constant 3.4% per unit of vertical displacement - approx. 0.5% per cm.

If the results from position 5 are omitted, a multiple, linear regression analysis on the remaining 31 measured values gives the alternative results shown in Table 5.

By logarithmic differentiation of the expression for calculation of the flux ratio from the recorded number of counts the relative standard deviation can be estimated based on the Poisson statistic. This expression of the counting precision is also included in Tables 5 and 6, and it shows that in this way all sources of variation have been properly accounted for.

Table 6

Sources of variability of 22 thermal-to-epithermal flux ratios of the pneumatic tube facility

Mean Value	Source of Variation	Residual Variance	σ_{est}
715	all	100 %	7.6 %
	Positions	63 %	6.1 %
	Day of Period	33 %	4.6 %
	Period No.	20 %	3.7 %
683	Position 1	59 %	6.1 %
	Day of Period	32 %	4.7 %
	Period No.	8 %	2.6 %
Average	Counting statistics	n.s.	3.2 %

The 22 results for the Pneumatic Tube facility gave an overall mean value of flux ratio of 715 with a coefficient of variation of 7.6%. This includes a systematic difference between top and bottom positions inside the rabbit, corresponding to 8.9% or approx. 3% per cm.

The measured values were treated in exactly the same way as previously, and the results are presented in Table 6 in the same way as in Table 5. The lower epithermal ratio is consistent with the greater distance from the reactor core, and the steeper vertical gradient in the Pneumatic Tube system is caused by its bottom being some distance above the Core Central Plane as can be seen in Fig. 1.

DISCUSSION

The single-comparator method in combination with experimentally determined k-factors [Girardi 1965] may be used without reservation for irradiation conditions with constant epithermal ratio. In actual practice, this ratio varies around a constant mean value, and if this variability is known, the error of assuming a constant k-factor can be estimated.

With a terminology similar to that of Simonits et al. [1976] the variability of the k-factor is determined by the following expression

$$\text{k-factor} \; \alpha \; \frac{1 + D_2/f}{1 + D_1/f}, \quad \text{where} \quad f = \frac{\phi_{th}}{\phi_{epi}};$$

$$D_1 = \frac{I_o}{\sigma_{th}} \; (1) \text{ refers to the single comparator nuclide chosen,}$$

and

$$D_2 = \frac{I_o}{\sigma_{th}} \; (2) \text{ refers to the determinand.}$$

The error propagation function is found by differentiation with respect to f

$$z_k = \left| \frac{\delta \ln k}{\delta f} \right|$$

$$z_k = \frac{|D_1 - D_2|}{(f + D_1)(f + D_2)} \leq \frac{|D_1 - D_2|}{f^2} \leq \frac{D}{f^2}$$

If both comparator and determinand are picked at random, propagation of the relative error of the flux ratio f is limited by the magnitude of the highest value of D,

$$\frac{\Delta k}{k} = z_k \cdot \Delta f \leq \frac{D}{f} \times \frac{\Delta f}{f} .$$

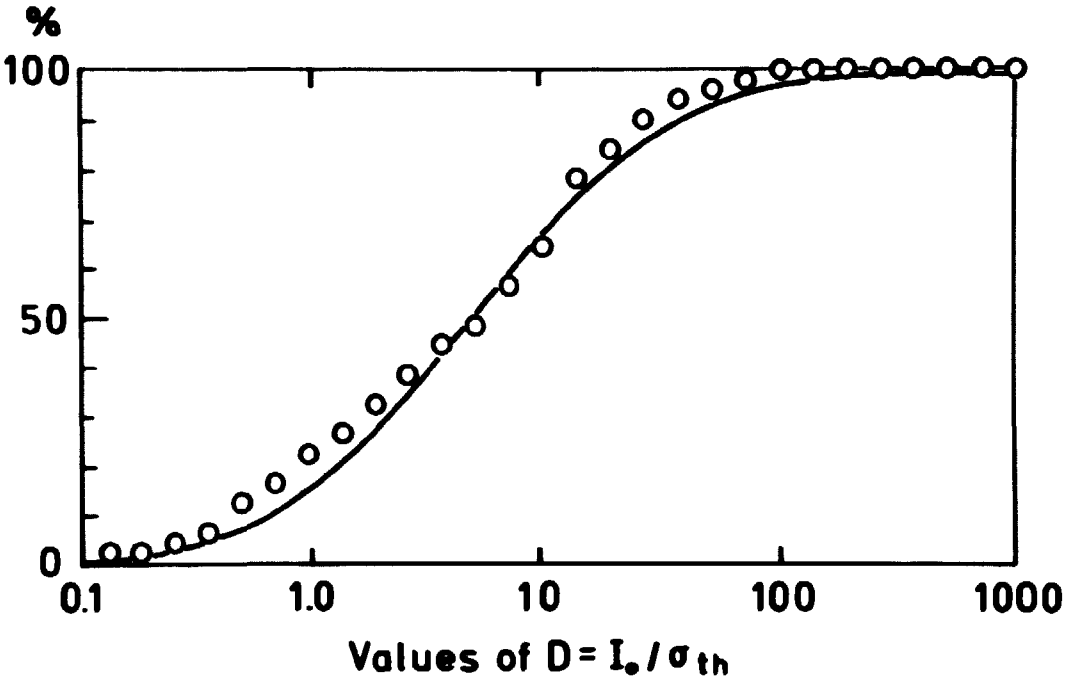


Fig. 4. Cumulative distribution of 138 values of I_o/σ_{th} reported by Van der Linden et al. 1972-1974. The Lilliefors test statistic for normal distribution of the logarithms is 0.0694, which is not significant at the 5 % level.

The distribution of D may be based on the 138 values reported by Van der Linden et al. in the years 1972-1974. The cumulative distribution of the logarithms of $D = I_o/\sigma_{th}$ is plotted in Fig.4 together with the continuous curve for a normal distribution with the same mean value and standard deviation.

It is seen that the distribution of D is very well approximated by a log-normal distribution with a geometric mean of 5.5 and a standard deviation factor of 4.88. In fact no significant deviation was found by subjecting the data to the Lilliefors Test of Normality [Conover 1971].

From this information we can now calculate the cumulative distribution of the maximum error given in eq. (3) for a selected set of conditions, and an example is presented in Fig. 5. Here we have chosen to correct for the systematic influence of vertical position, so that the random variation is reduced to 7.3%, respectively, 6.1% for the two irradiation facilities under consideration.

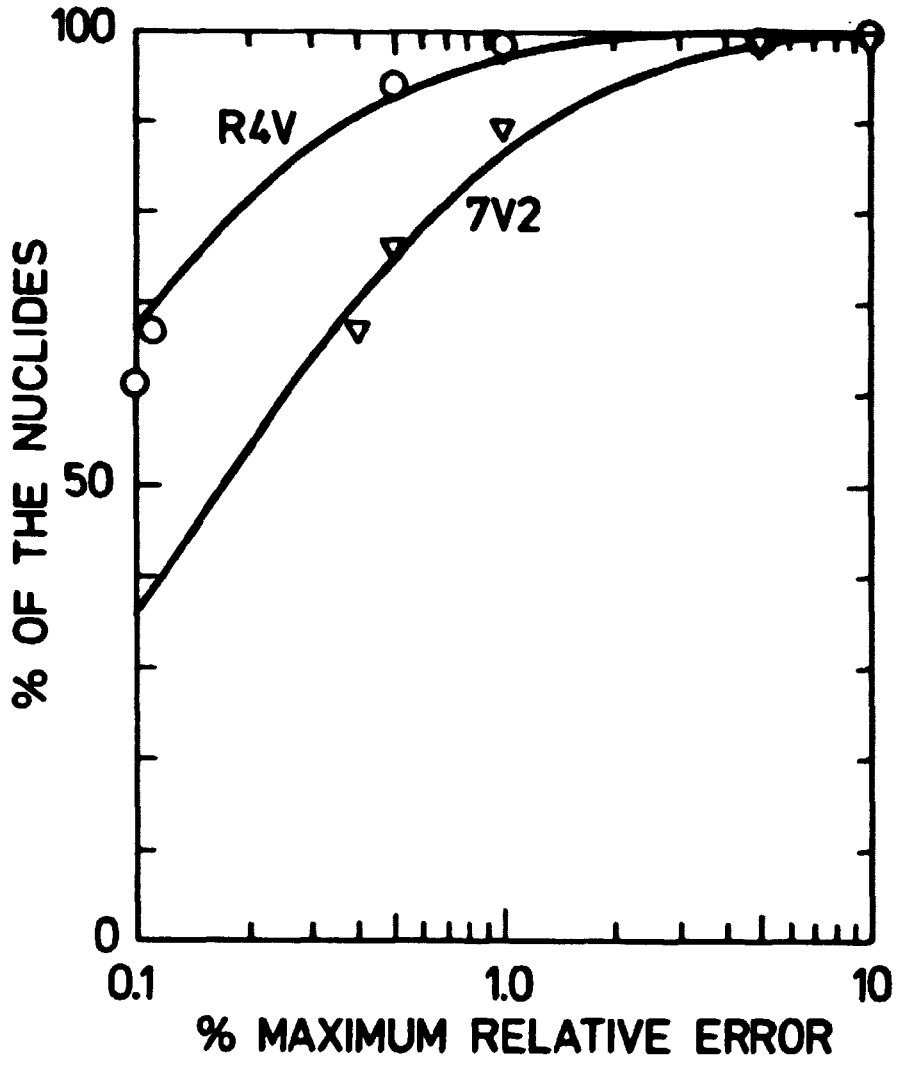


Fig. 5. Cumulative distribution of the maximum uncertainty of results based on the use of a single-comparator at two different locations in a heavy-water nuclear reactor.

Under these circumstances the cumulative distributions show that for 95% of the nuclides involved*, the error will not exceed 2% for the Rotating Rig facility, and 0.5% for the Pneumatic Tube facility.

Within these limitations the original single-comparator method of Girardi [1965] can be used without reservation, and there is no need to determine epithermal ratios on a routine basis.

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*this excludes only 3 elements: Y, Rh, U

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