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EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

ISOTOPIC ANALYSIS OF IRRADIATED FUEL AND TRANSPLUTONIUM ELEMENTS

1. Objectives and Methods

by

M.W. GEERLINGS and L. KOCH

1968

Joint Nuclear Research Center
Karlsruhe Establishment - Germany

European Institute for Transuranium Elements

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KEYWORDS

SPENT FUEL ELEMENTS
TRANSPLUTONIUM ELEMENTS
BURNUP
FERTILE MATERIALS
FISSIONABLE MATERIALS
CHEMICAL ANALYSIS
DETERMINATION
FISSION PRODUCTS
MASS SPECTROMETERS
ALPHA SPECTROMETERS
GAMMA SPECTROMETERS

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ISOTOPIC ANALYSIS OF IRRADIATED FUEL AND TRANSPLUTONIUM ELEMENTS(+)

1. INTRODUCTION

The performance of a nuclear power station is directly linked to the burn up achieved by its fuel load. An overall value of the burn up can be obtained, with a precision of a few per cent, from the heat output of the reactor. For the optimalisation of the reactor however, additional information is needed on the distribution of the burn up and of power ratings over every part of the fuel load. Such a distribution can be calculated, but very often the precision to which effective neutron cross sections are known is insufficient to allow for a reliable estimation of the reactor parameters. More over, a calculation code will only be considered trustworthy if it has been experimentally verified on a well known example.

Isotopic analyses are made at the Institute for Transuranium Elements on irradiated fuel materials and fuel elements. The concentration of the heavy nuclides and of fission neodymium-148 are quantitatively determined by direct methods. The accuracies, at present obtained, for the post-irradiation determination of isotopic concentrations are 0,3 - 3% and of burn up from neodynium-148 about 2%. The results of these analyses can be used for the calculation of the conversion of the fissile and fertile isotopes and of effective neutron cross section ratios, thus permitting improvements to be made in the application of burn up calculation codes.

In addition, radioactive fission products and fission gases are determined. The comparision of the γ-activities of selected fission products in fuel samples with the corresponding burn up data permit an evaluation of the applicability of γ-scanning to the determination of burn up. These analyses are furthermore useful for studies of migration phenomena in fuel during irradiation.

Finally, americium and curium isotopes are determined in order to evaluate the production of transplutonium elements by neutron irradiation. They are created with the operation of nuclear reactors, especially if plutonium is irradiated for prolonged

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periods. Curium isotopes are furthermore purposely produced by the irradiation of plutonium and of americium-241. There still exists a serious lack in the knowledge of neutron cross sections of practically all the transplutonium isotopes. Their successive build up during the course of the irradiation can only be roughly estimated by calculation, and post-irradiation analyses are necessary for an accurate determination of their concentrations.

Methods and procedures have been worked out for the routine execution of the mentioned analyses. In the following paragraphs their usefulness and selection are further discussed and the experimental methods are briefly described. Subsequent reports will deal with specific experimental and numerical procedures - particularly those that were subjects of own development work -, as well as with their application to various programs.

2. THE USEFULNESS OF ISOTOPIC ANALYSES

2.1. Burn up and fission source

1. Burn up is expressed either in megawatt-days per (metric) tonne of initially present fuel, MWD/T, or as per cent of the initially present fuel nuclides that have fissioned, F_T. In both cases, fuel is defined as the sum of all fissile and fertile nuclides. The equivalence of the two expressions is given by :

$$MWD/T = (9,6 \pm 0,3) \cdot 10^3 \cdot F_T \qquad (1)$$

2. Burn up data can be obtained by methods other than isotopic analyses. The burn up of a complete reactor fuel load follows directly (and with a precision of a few per cent) from the integrated heat or electricity output of a power reactor station. This method is used for accounting purposes.

A method that is widely used, because it is non-destructuve and

experimentally relatively simple, is the gamma scanning of complete fuel elements or single fuel rods. The assumption is made, that the gamma activity of selected fission products, measured by high-resolution gamma spectrometry, is proportional to burn up. The reliability of this relation depends on the extent to which the fission products satisfy the conditions for accurate burn up monitors (see par. 3). Absolute determinations of burn up cannot be performed by gamma scanning alone, because geometrical and absorption effects cannot be quantitatively evaluated without calibration by direct analytical methods.

3. The determination of burn up by the quantitative analyses of the heavy nuclides, together with fission neodymium-148 is attractive for several reasons : The determination is absolute, and accurate within 2%, if properly performed. Only microgram quantities of material are needed, which enables a high spatial resolution that is merely limited by the degree of perfection in taking small, reliable samples. This permits the analysis of microsamples, drilled from a fuel rod section at distinct radial and tangential positions, which allows the determination of effects due to self-shielding and neutron anisotropy. The main disadvantage of isotopic analyses is that the experimental procedures are tedious, difficult and expensive.

4. For uranium fuel, irradiated in thermal neutron reactors, total atom per cent fission, F_T, can be expressed as :

$$F_T = F_5 + F_8 + F_9 + F_1$$

where F_5,F_8,F_9 and F_1, represent the contributions from fission of respectively U-235, U-238, Pu-239 and Pu-241 nuclides. F_8 and F_1 together represent generally only a small fraction of F_T. Each term in eq. 2 can only be calculated from the concentrations of the uranium and plutonium isotopes found after irradiation, if the initial fuel isotopic composition and/or the effective ratio of (n, γ) capture to fission cross sections for the fissile isotopes are known.

The amount of U-235 that has fissioned is given by:

$$F_5 = N_8^o \left[R_5^o - R_5 - R_6 + R_6^o\right] \qquad (3)$$

which is to be used at high exposures, where more than 10 per cent of the U-235 is consumed. At low exposures, a more precise result will be obtained by :

$$F_5 = N_8^o \left[R_6 - R_6^o\right] / \alpha_5 \qquad (4)$$

In eq. 3 and 4 :

N_8^o = atom <u>per cent</u> U-238 in the fuel before irradiation,

R_5^o, R_6^o = atom ratio of U-235, resp. U-236 to U-238 in the fuel before irradiation,

R_5, R_6 = idem after irradiation, if necessary corrected for burn out of U-238 and U-236 during irradiation *),

α_5 = effective ratio of U-235 (n, γ) capture to fission cross sections.

From eq. 3 and 4 follows that the accuracy obtained for F_5 is directly dependent on the accuracy to wich the difference in the isotopic composition of the fuel before and after irradiation is known.

The amount of Pu-239 that has fissioned can be calculated from:

$$F_9 = N_8^o \cdot \Sigma R_{>9} / \alpha_9, \text{ where :} \qquad (5)$$

α_9 = effective ratio of Pu-239 (n, γ) capture to fission cross sections,

$\Sigma R_{>9}$ = total amount of Pu-239, relative to U-238, that disappeared by neutron capture. This quantity is obtained from the amounts of Pu-240, - 241 and - 242 found in the irradiated fuel.

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*) The atom ratios R are used, because, by mass spectrometric analyses, the isotopes are determined relative to U-238. Atom ratios R must be corrected for burn-out of U-238 if the latter is more than the (arbitrary) limit of 1 %.

The accuracy obtained for F_9 depends directly on the accuracy to which α_9 is known. The calculation of α_9 is difficult and not precise for reactors with strong spatial spectrum variations, as for example boiling water reactors.

5. The advantage of using fission neodymium-148 as burn up monitor comes from the fact that its concentrations is directly proportional to the amount of heavy nuclides that have fissioned.
Burn up can be expressed as :

$$F_T = \frac{\text{1/2 x amount of fission nuclides present after irradiation x 100\%}}{\text{amount of heavy nuclides present before irradiation}} = \frac{100 \sum K_f(t)}{2 \sum K_h(o)} \qquad (6)$$

Because $\sum K_h(o) = \sum K_h(t) + 1/2 \sum K_f(t)$

and with $K_{148}/Y_{148} = 1/2 \sum K_f(t)$,

where: K_{148} = amount of neodymium-148 found after irradiation

Y_{148} = cumulative fission yield of Nd-148

eq. 6 can be written as :

$$F_T = \frac{100 \cdot K_{148}}{Y_{148} \cdot \sum K_h(t) + K_{148}} ,$$

or, by changing concentrations K into ratios R relative to U-238,

$$F_T = \frac{100 \cdot R_{148}}{Y_{148} \cdot R_h + R_{148}} ,$$

where: R_{148} = atom ratio of Nd-148 to U-238 in the irradiated fuel,

$R_h = 1 + R_5 + R_6 + R_9 + R_0 + R_1 + R_2$,

with: R_5, R_6, etc. = atom ratio to U-238 in the irradiated fuel of respectively U-235 and -236, Pu-239, -240, -241 and -242.

Eq. 7 contains no terms based on pre-irradiation data or on reactor parameters, but only isotope ratios that can be determined directly from an irradiated fuel sample. The constant Y_{148} is known within about 0,6% (1). R_{148} can be determined with an accuracy of I,6%.
The reasons why Nd-148 has been chosen as fission monitor are discussed in par. 3.

6. One of the conditions for a reliable burn up monitor is that the cumulative fission yield Y is identical for the various fission sources. Nd-148 satisfies this condition. On the other hand, if for an otherwise suitable monitor the fission yield depends on the fission source, such a monitor can be used in order to distinguish between fission sources. A practical example is Nd-150, which is determined together with Nd-148 as the ratio $R^{150}/148$. Its thermal fission yield from U-235 is $Y_{150}(25) = 0{,}00637$ and from Pu-239 is $Y_{150}(49) = 0{,}010$ (2). These fission yields are independent of neutron flux and burn up. The ratio of U-235 fission to Pu-239 fission follows from :

$$\frac{F_5}{F_9} = \frac{Y_{150}(49) - Y_{148} \cdot R^{150}/148}{Y_{148} \cdot R^{150}/148 - Y_{150}(25)} ,$$

eventually after using a correction for the contributions F_8 and F_1 to F_T.

2.2. Conversion of isotopes

1. The accuracies obtained for the post-irradiation determination of uranium and plutonium isotope ratios are between 0,3 - 3 % (coefficient of variation for one isolated determination - see par. 4.1.). Apart from the accurate determination of burn up, they permit the calculation of various reactor parameters with an accuracy that is considerably higher than can be achieved on the basis of theoretical data only. The usefulness of the analyses, apart from the data they supply, lies in the fact that they indicate which corrections have to be made in the basic data that are used for reactor calculations. This will be illustrated by the following examples:

2. The reactivity life of a reactor fuel depends on the conversion of fertile into fissile material. Frequently used as criteria are the "effective" conversion ratio :

$$c_e = \frac{R_9 + R_1}{R_5^o - R_5} \qquad (9)$$

and the "total" conversion ratio:

$$c_t = \left[R_9 + \frac{F_9}{N_8^o} (1 + \alpha_9)\right] / (R_5^o - R_5), \qquad (10)$$

where the numerator is a measure for the total amount of Pu-239 nuclides that have been created by neutron capture in U-238. For zero burn up, c_t equals the value of the "initial" conversion ratio. c_e and c_t follow directly from the isotopic post-irradiation analyses and the initial fuel enrichment.

3. The ratios α_5 and α_9 of the effective capture to fission cross sections of U-235 and Pu-239 can be calculated from the isotopic analyses. For U-235 follows from eq. 3 and 4:

$$\alpha_5 = \frac{R_6 - R_6^o}{R_5^o - R_5 - R_6 + R_6^o} \qquad (11)$$

For Pu-239 follows from eq. 5:

$$\alpha_9 = \frac{N_8^o}{F_9} \cdot \Sigma R_{>9}, \qquad (12)$$

where F_9 is obtained from eq. 2 and 7.

The capture to fission cross section ratios are a function of neutron energy. In the near-thermal region a maximum value of 0,25 is found at 0,26 eV for α_5. α_9 has a maximum value of 0,72 at 0,3 eV, which corresponds with the energy for the first Pu-239 absorption resonance. The experimental values of α_5 and α_9 can thus be used as indicators for the thermal spectrum within the fuel, and their spatial variation in radial direction can be determined by the analyses on microsamples, taken from a fuel rod.

4. When uranium and plutonium isotopic concentrations are determined by reactor physical calculations, the values of the various effective neutron cross sections, which are used as basic data, are calculated with respect to approximative neutron spectrum data and estimated self-shielding factors. When the calculations are thouroughly done, multigroup effective neutron fluxes, cross sections and isotope concentrations are recalculated after small irradiation time

increments (3). This leads to a result that is comparable with the experimentally determined isotope ratios, R_5, R_6, R_9, R_0, etc. In this case, the ratios R can be used to correct the basic multi-group neutron flux ratio data used in the calculations.

The general case, however, is that only 2, or maximum 3, neutron energy groups are used for calculations on thermal reactors. The flux ratio of these groups and the effective cross sections of the fissile and fertile isotopes are not corrected for the effects of concentration changes during burn up. Average effective neutron absorption probabilities ($\overline{\sigma\phi}$) in fact are used throughout the burn up calculation. These absorption probabilities can also be calculated from the isotopic analyses.

For example, the reaction rate equations :

$$\frac{dK_5}{dt} = -K_5 (\overline{\sigma\phi})_5 \qquad (13^a)$$

$$\frac{dK_8}{dt} = -K_8 (\overline{\sigma\phi})_8 \quad (K_8 = \text{constant}) \qquad (13^b)$$

$$\frac{dK_9}{dt} = K_8 (\overline{\sigma\phi})_8 - K_9(\overline{\sigma\phi})9 \qquad (13^c)$$

$$\frac{dK_o}{dt} = K_9 (\overline{\sigma_c\phi})_9 - K_o(\overline{\sigma\phi})_o \qquad (13^d)$$

after integration give:

$$(\overline{\sigma\phi})_5 = \frac{1}{t} \ln (R_5^o / R_5) \qquad (14^a)$$

$$(\overline{\sigma\phi})8 = \frac{1}{t} \left[R_9 + F_9 (1 + \alpha_9)/ N_8^o \right] \qquad (14^b)$$

$$R_9 = \frac{(\overline{\sigma\phi})8}{(\overline{\sigma\phi})_9} \left[1 - \exp (- (\overline{\sigma\phi})_9 \cdot t) \right] \qquad (14^c)$$

$$R_o = \frac{\alpha_9 \cdot (\overline{\sigma\phi})8}{(1+\alpha_9).(\overline{\sigma\phi})_o} \left[1 + \frac{(\overline{\sigma\phi})_9}{(\overline{\sigma\phi})_o - (\overline{\sigma\phi})_9} \exp (- (\overline{\sigma\phi})_o.t) - \frac{(\overline{\sigma\phi})_o}{(\overline{\sigma\phi})_o - (\overline{\sigma\phi})_9} \exp (-(\overline{\sigma\phi})_9.t) \right] \qquad (14^d)$$

from which $(\overline{\sigma\phi})_5$, $(\overline{\sigma\phi})_8$, $(\overline{\sigma\phi})_9$ and $(\overline{\sigma\phi})_o$ can be numerically calculated.

$(\overline{\sigma\phi})_5$ and $(\overline{\sigma\phi})_8$ each consist of a thermal and an epithermal contribution, and thus can be used as monitors for the ratio of epithermal to thermal neutron flux. $(\overline{\sigma\phi})_9$ and $(\overline{\sigma\phi})_o$ can be used as spectrum indicators, because σ_9 and σ_o show resonances at respectively 0,3 eV and 1,0 eV. Determination of the absorption probabilities on fuel rod sections will give indications on the variations in the axial direction of neutron fluxes and spectrum. If determined on series of microsamples, they permit the calculation of spatial variations of self shielding effects in radial sense within the fuel.

5. The reaction rate equations for the production of curium by irradiation of plutonium or americium contain additional terms for the effects of radioactive decay of isotopes with short half lives. From the post-irradiation isotopic analyses, together with the integrated reaction rate equations, the average effective neutron absorption probabilities of successive isotopes can be calculated. This allows an estimation of effective neutron cross sections and can lead to an optimalisation of the irradiation procedure.

2.3. Fission products

1. Analyses of the isotopes of fission gases xenon and krypton are of interest, because of their possible use as monitors for various fuel parameters (2).

The abundance ratios of Xe-132/Xe-131 and of Kr-84/Kr-83 are functions of depletion of U-235 and Pu-239 and essentially non-dependent on neutron flux.

The abundance ratio of Xe-136/Xe-134 is essentially non-dependent on depletion, but a specific function of neutron flux level.

The abundance ratio of Xe-134/Kr-86 is an indication of the fission source ratio F_9/F_5 and non-dependent on depletion.

It is worthwhile to investigate the applicability limits of these monitors. A primary requirement to reliability is, that the fission gases do not diffuse noticeably through the fuel during irradiation. Quantitative measurements of fission gas diffusion are therefore made by the systematic determination of isotopic composition of the gases and the amount that is retained in samples that are used for burn up analyses.

2. The comparision of γ-scanning of fuel rods with the destructive isotope analyses is useful, because it permits a verification of the reliability of employing γ-scanning for the determination of the overall burn up pattern. The isotopes used as monitors are generally Ru-106, Ce-144 and Cs-137, but, depending on the irradiation and cooling time of the fuel, other isotopes as Zr-95 and Ba(La)-140 can be taken in addition.

The quantitative analyses of these fission products by y-spectrometry of the dissolved burn up samples is useful in order to determine their value as fission source monitors (4).

3. FISSION PRODUCTS AS BURN UP MONITOR - SELECTION OF Nd-148

A fission product (f), considered for use as a burn up monitor, is the end product of an - isobaric - fission product chain. It is created partly by fission -with fission yield y_f- and partly by the radiactive decay of its predecessors, formed by fission with yields y_{f-1}, y_{f-2},... The predecessors are short-lived β-radioactive nuclides. The cumulative fission yield of the monitor is $Y_f = y_f + y_{f-1} + \ldots$ The fission product chain of mass number 148 is presented in fig. 1.

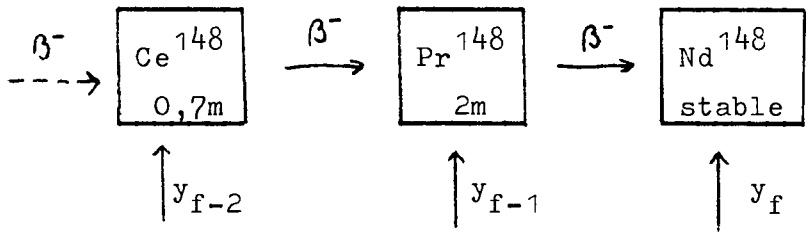

Fig. 1: Formation of fission product Nd-148

In order to make a reliable burn up monitor, the fission product (f) and its chain members must fulfill the following conditions:

1) The cumulative fission yield Y_f must be identical for all the fission sources present in the fuel and independent of neutron energy.

2) The monitor isotope and its chain members must not change location in the fuel by diffusion or other transport mechanisms during irradiation.

3) The monitor should be a stable or a long living isotope, because generally it is impossible to account for neutron flux changes or shut down periods during irradiation. For the same reason, the neutron capture of the chain members must be negligible with respect to their β-decay.

4) The contribution to Y_f should be limited to the fission yields of the monitor chain members. Therefore, the neutron capture of fission products belonging to the lighter, neighbouring chain must be negligible.

5) If the monitor isotope does not have a negligible neutron capture cross section, its neutron capture product (f + 1) must satisfy the monitor conditions and be accounted for in the analysis.

6) The chemical isolation of the monitor isotope and its analysis by isotope dilution mass spectrometry must be possible. Therefore:

- the monitor must have a sufficient stable isotope which does not occur as a major fission product and which is commercially available, in order to use this as a spike,
- if, during the analytical procedure, the sample can become contaminated with the naturally occuring element to which the monitor belongs, there must be a shielded isotope (that is an isotope that does not occur as a fission product) to account for it,
- the chemical separation from isobars of other elements must be well under control.

Neodymium-148 has been selected as burn up monitor, because it fulfills the conditions better than any other fission product. Its fission yield from various sources (1,5,6,7) and the accuracies to which they are known, are given in table 1 :

fission source	U-233		U-235		U-238	U-239		Pu-241
	thermal	fast	thermal	fast	fast	thermal	fast	thermal
	(5)	(6)	(1)	(6)	(6)	(6)	(6)	(7)
Y_{148} in %	1,32± 0,01	1,21	1,70± 0,01	1,81	2,07	1,69	1,71	1,91± 0,1

Table 1: Fission yields of neodymium-148

The determination of Nd-148 is complicated for several reasons. Some contamination by natural neodymium generally occurs during the preparative chemistry work. This, however, can be accounted for via the isotope Nd-142, which occurs in natural noedymium, but not as a fission product. The isotope Nd-150 is to be used as a spike, which requires a sufficient chemical separation from the fission product Sm-150. Because Nd-149 does not occur, this can be verified by the absence of fission product Sm-149 and -152 in the mass spectrum.

In spite of the fact that their reliability depends on the irradiation history, there exists a wide interest for the application of radioactive fission products as burn up monitors (8,9,10). Sometimes even isotopes are selected of which it is known that they are subject to considerable migration within the fuel during irradiation. The attraction lies in the relatively simple, but not the most accurate, determination by γ-spectroscopy. Data concerning their reliability, based on comparisons with Nd-148 determinations have not yet been found.

Other stable fission products have to be rejected as burn up monitors because of various reasons. Technetium-99 must be excluded because no reference isotope is available. The usefulness of Xe, Ce and Ba is limited because of the volatility of their isotopes or their predecessors. Molybdenum and zirconium cannot

be used because they are present in the major cladding materials.

4. SELECTED ANALYTICAL METHODS

4.1. Mass spectrometric analysis

1. Whenever possible, the determination of isotopic abundances is done by mass spectrometry. Single or double filament thermal ionisation sources are used for the actinide elements and neodymium, an electron impact source is used for the fission gases. The equipment consists of two spectrometers type CH-4 of Varian-MAT. The accuracy that is obtained with mass spectrometry is better than with other methods as optical spectroscopy, activation analyses or α - and γ -spectroscopy (4), because no preliminary calibrations are necessary, no particular natural constants enter the calculations and only the ratios of the isotopes of one element are considered. The amount of sample necessary for a determination is of the order of $5 \cdot 10^{-8}$ grams. A mixture of elements can be brought on a filament on order to measure them one after the other if the elements have a sufficiently different ionisation efficiency - practical examples are uranium + plutonium and americium + curium.

The precision obtained was found not to depend on the type of analysis, but to be a sole function of the isotope ratio R which is to be determined (11). This function is plotted in fig. 2 as the coefficient of variation Vc against $R^{-1/2}$ (Vc is defined as the standard deviation over the value of the isotope ratio in per cent $= \frac{\sigma}{R} \times 100\ \%$). The best precision is obtained (Vc $\approx$ 0,3% for one isolated determination)for isotope ratios of 1 : 1. The precision seems to be mainly due to statistical effects in the ion collection and in the reading of the recorded spectra. Efforts are underway to reduce these effects by direct digital counting of the ions. Errors due to cross-contaminations are widely prevented by systematic renewal of filaments after use. The systematic errors due to the mass-discrimination effects, instrumental non-linearities, etc. are negligible with respect to the non-systematic errors.

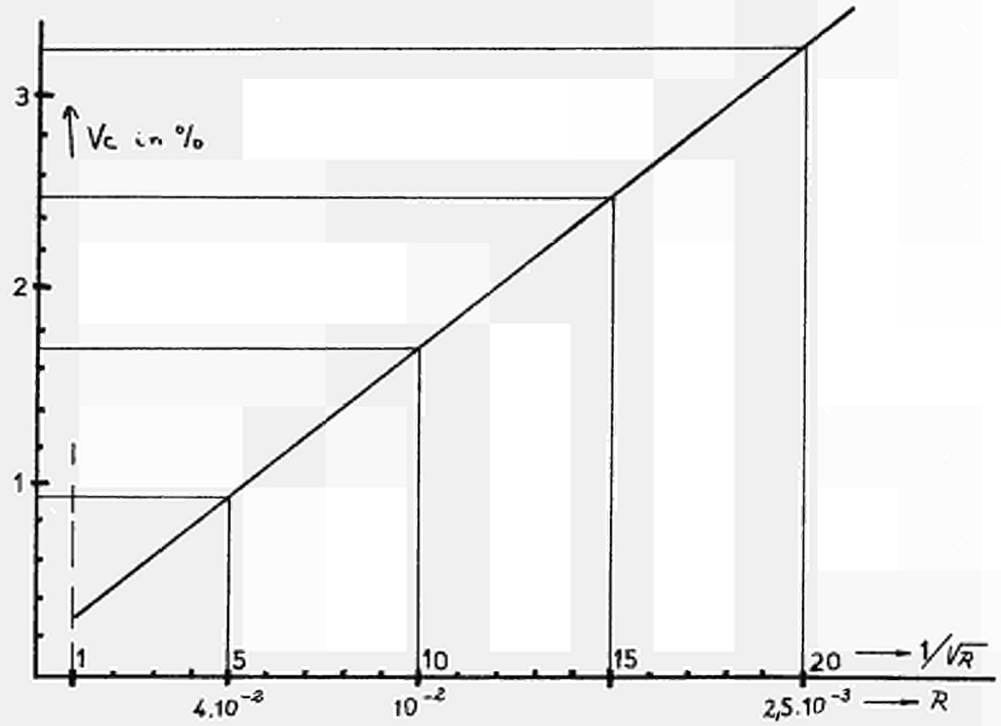

Fig. 2: Relative precision of mass analysis as a function of isotopes ratio

.2. Isotopic concentration are determined by isotope dilution mass spectrometry with suitable reference isotopes (spikes). Calibrated solutions of U-233, Pu-242, Nd-150 and Am-241, and natural Xe are used as spikes for the determination of respectively U-238, Pu-239, Nd-148, Am-243 and fission gas xenon. The concentrations of the spike solutions are calibrated on standards to an accuracy of 0,1%. Because the ratio of the amount of spike to the amount of sample is chosen as close as possible to 1 : 1, the precision of the isotope dilution analyses that can be obtained is about 0,4%.

The concentration $K_s(x)$ of isotope x in the sample solution (as atoms per gram solution) is calculated from the analysis by:

$$K_s(x) = \frac{W_r \cdot K_r(y) \cdot [R_m - R_r]}{W_s \cdot [1 - R_m/R_s]} , \qquad (15)$$

where: $K_r(y)$ = concentration of spike isotope y in the spike solution (at/g. solu.).

W_r = amount of spike solution (g.)

W_s = amount of sample solution (g.)

R_s, R_r, R_m = isotope abundance ratio R(x/y), respectively in the sample, spike and mixed solutions.

4.2. α-Spectrometric analyses

Not every isotope can be determined by mass analysis. An example is plutonium-238, where the interference of U-238 cannot be avoided. Therefore the abundance of Pu-238 in plutonium is determined by α -spectrometry. α -spectrometry is also employed when the ratio of isotopes of different elements in one sample has to be determined, or when for great differences in abundance, the isotope with low abundance has a relatively high specific α -activity. This latter, for example, is the case for the determination of Cm-242 and Cm-244 in irradiated fuel.

α-spectrometry is also used for isotope dilution analysis, for example of Cm-242 with a Cm-244 spike. The method is similar to the one with mass spectrometry.

The precision of the α-spectrometric analyses is about 2% in the majority of cases and depends mainly on the shape of the spectrum. Systematic errors depend mainly on the accuracies to which the half-live values of the isotopes are known.

Specific details concerning sample preparation, measurements and numerical calculations will be reported separately.

4.3. γ-Spectrometric analysis

γ -spectrometry is used for the determination of radioactive fission products Cs-134, Cs-137, Ce-(Pr)-144, Zr(Nb)-95, Am-143, Ru-106 and Sr-90. Quantitative analyses are made on samples - especially microsamples - which are subsequently used for mass spectrometric analysis of burn up. Relative analyses are made in the form of γ-scanning on complete fuel rods.

The equipment consists of Nuclear Diodes type LG4.0-5 and Lgc 2.5 x Li-drifted germanium detectors in combination with Tennelec FET 130 and Tc 200 amplifiers, which permits a resolution of 4,5 keV at an energy of 661 keV. For γ -scanning, 4 single channel amplifiers type 413, connected to ratemeters type 441 of ORTEC are used. γ-spectra are registered with a 4096 channel analyser of LABEN A computer program is in preparation for the calculation of isotope abundances from the registered spectra. The accuracy and precision of the quantitative analyses is still to be determined.

4.4. Microchemical separations

In preparation to the various mass spectrometric analyses, fuel samples are dissolved - usually in nitric acid - and divided into three fractions for each type of analyses. Details concerning the chemical isolation and purification procedures will be given in a following report, but the basic steps that are used for the determination of uranium, plutonium and neodymium are indicated here.

For uranium and plutonium isotope abundance analysis, a fraction containing 1 à 10 μg of Pu is passed over 500 mg Dowex 1x8, 200-400 mesh ion exchanger in 8 M HNO_3, which fixes the U and Pu and passes most of the fission products. Excessive uranium is then washed off with 8 M HNO_3 to permit the simultaneous mass spectrometric analysis of both Pu and U. The sample is then eluted with 0,35 M HNO_3 and the eluate solution prepared for the mass analysis. If the concentrations of U-238 and Pu-239 have to be determined, the weighed sample fraction is first mixed with a weighed amount of a spike solution, containing U-233 and Pu-242 in suitable concentrations. Isotope mixing of plutonium is assured by a reduction-oxydation step using hydroxylamine hydrochloride and sodium nitrite, whereafter the separation on the ion exchanger is done.

For the analysis of neodymium, the sample solution, containing ca. 0,3 μg of Nd, either or not after addition of a weighed amount of Nd-150 solution, is fixed on a column of Dowex-50 x 8, 200 - 400 mesh ion exchanger. Neodymium is separated by chromatographic

elution with 0,25 M α-HIBA of pH = 4,6, monitored with a semi-conductor detector. The neodymium fraction follows immediately the americium α-activity. The fractions are then prepared for mass analysis of both the neodymium and americium isotopes.

4.5. Sampling

For destructive analyses, cylindrical sections are taken from fuel rods at preselected positions. Each of these sections is divided in three cylindrical parts.

The center part, of 2-10 mm length, is dissolved for the analyses listed in par. 5. During dissolution, the fission gases are collected for analysis of their composition by mass spectrometry.

One adjacent part, of about 1 mm length, is dissolved in the same way as the center part, but for the sole purpose of determination of the amount of fission gases by isotope dilution mass pectrometry. The procedure for gas collection and isotope dilution will be described in a spearate report.

The third part, of about 5 mm length, is prepared for microsampling in order to permit analyses as a function of radial and tangential positions. After inbedding in a cylindrical piece of resin and surface polishing, microsamples are taken on preselected positions by two distinct methods :

- Mechanical or ultrasonic microdrilling (12), yielding samples up to 200 μg of about 0,2 mm diameter. These samples are dissolved for fission gas collection and for the analyses listed in par. 5.

- Evaporation of small amounts of material by a laser impulse and collection of this material on a thin glass plate which is placed just above the target. Samples of 10 - 50 μg of about 0,1 mm diameter are collected. They can be used either immediately for α-spectrometry or, after dissolution of the collected material, for mass spectrometric analysis. This sampling method will be described in a separate report.

For the analysis of individually enclosed pellets or small irradiation capsules a special sampling procedure is not generally applied. The complete pellet or capsule is dissolved and the analyses are made on samples of the solution.

5. SUMMARY OF DETERMINATIONS

Depending on the nature of the material to be analysed and the information that is asked, a selection is made from the determinations listed as follows:

On complete fuel rods

a) scanning of the γ-activity of selected isotopes as a function of position in the length direction of the rod,

b) measurement of gamma spectra at selected positions on the rod,

c) determination of pressure, amount and composition of the free gas after puncturing the rod, for example at the position of a gas plenum (13)

On samples and during dissolution

a) measurement of gamma spectrum,

b) on fuel rod sections, determination of the weight of the dissolved sample and of the undissolved cladding,

c) determination of the retained fission gases: either Xe and Kr isotope abundance ratios by mass spectrometry or Xe concentration by isotope dilution mass spectrometry.

On sample solutions

a) determination of the concentrations of the heavy isotopes and of fission neodymium according to the scheme indicated in fig. 3.

b) determination of radioactive fission products by γ-spectrometry.

On laser-produced microsamples

a) determination of the relative activities of Cm-242, Cm 243+244, Pu-239+240 and Pu-238 + Am-241, by α-spectrometry of the sample

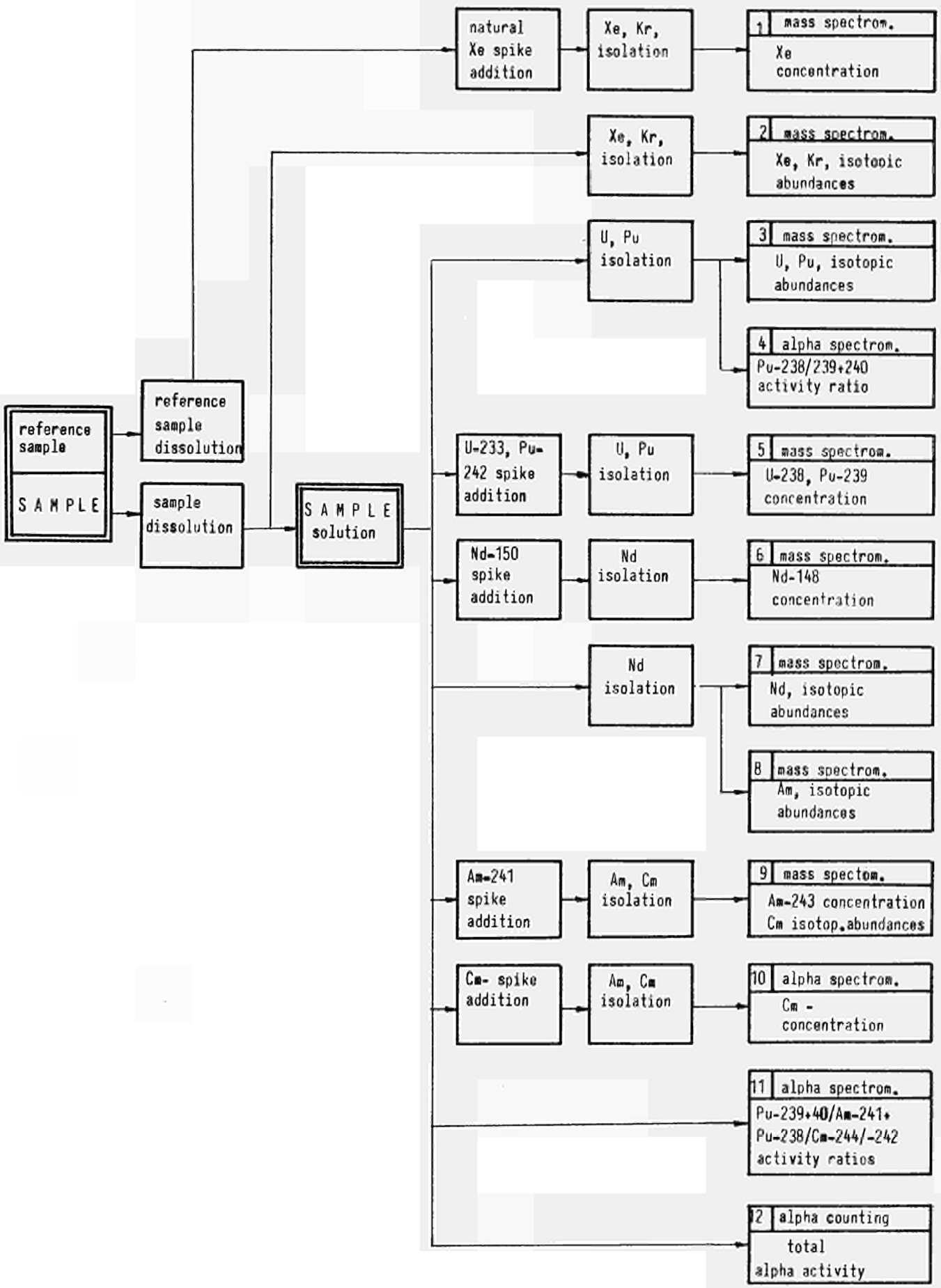

Fig. 3: Schematic summary of procedures for destructive isotopic analyses

collected on the glass plate.

b) For uranium fuel by mass analysis after dissolution of the sample: the abundance ratio of the uranium isotopes. In case sufficient plutonium is present: the abundance ratio of the plutonium isotopes and the Pu/U ratio by isotope dilution mass analysis.

Future reports

Other reports in this series are being prepared on the following subjects:
Various analytical and numerical procedures, quantitative fission gas sampling, microsampling by evaporation with laser light and sample analyses, post-irradiation analyses on a fuel element from the KAHL Boiling Water Reactor, analysis of irradiated americium.

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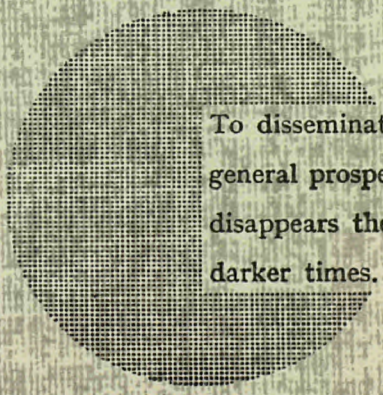

To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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