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Destructive and Nondestructive Methods for Controlling Nuclear
Materials for the Purpose of Safeguards in the ČSSR

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Abstract

Central Control Laboratory (CCL) of the Nuclear Research Institute, charged with the control of nuclear materials in ČSSR, has been directed by the Department of Nuclear Safety and Safeguards of the CSAEC according to a long-term plan. The CCL has mainly been performing independent, rapid, accurate and reliable analyses of nuclear materials using destructive as well as nondestructive methods.

The experience is given, obtained at the CCL during a routine use of the methods for sampling, sample treatment before the analysis, highly precise determination of U, Pu and Th content, and mass-spectrometric determination of isotopic composition of U and Pu.

The burnup determinations and some nondestructive methods for controlling nuclear materials are discussed [1].

The Agreement for safeguards application between the IAEA and the ČSSR came into operation on March 5, 1972. In the same year, the Central Control Laboratory was established by a decision of the CSAEC and located into the area of the Nuclear Research Institute at Řež. Its functional independence of all MBAs in the ČSSR was established by statute. All research and control activities of the CCL are directed by the Department of Nuclear Safety and Safeguards of the CSAEC in compliance with a long-term plan for the control of nuclear material in the ČSSR and also with respect to the fact that the CCL should assert itself also in the international safeguards system.

The main task of the CCL is to perform independent, highly accurate and reliable analyses of nuclear materials including the balance and arbitration analyses of fissile materials in the Czechoslovak territory. Also problems related to the burnup determination are solved.

The sampling of nuclear materials has been carried out by the Department on Nuclear Safety and Safeguards of the CSAEC. The CCL participates in taking perfectly homogeneous and representative samples. To avoid any physical or chemical changes, the samples are transported and stored in airproof plastic containers, which are sometimes sealed. The oxide fuels are homogenized by a special grinding process in a N_2 atmosphere. By storing in air, the composition of UO_2 samples changes gradually by the oxidation to U_3O_8 [2].

The CCL is supplied with samples of uranium, thorium and plutonium materials of a technological or research character, taken within the framework of Czechoslovak safeguards system or obtained during the development of fuels. Concerning the uranium materials, mostly metal U, U alloys (Zr-U), ammonium diuranate, UO_2 (powder and pellets) carbides and nitrides have been analysed. The thorium samples involved metal Th and ThO_2 whereas the Pu samples were of metal Pu and low-fired PuO_2 .

To determine U, Th and Pu in microgramme concentrations, spectrophotometric methods, radiometry and mass-spectrometric method of isotopic dilution have been applied whereas for mg amounts of these elements titration methods have been used.

Dissolution of U, Th and Pu samples

For dissolving samples of metal uranium fuels mostly conc. nitric acid or a mixture (20 + 0,5) of $\text{HNO}_3 + \text{H}_2\text{SO}_4$ are used with heating; similarly, the samples of diuranate as well as oxide fuels are dissolved. Using a reduction-oxidation titration method for determining U in oxide fuels, the dissolution in 2M HNO_3 and cond. H_3PO_4 is convenient. An annealing of samples to U_3O_8 before the dissolution proved to be useful for analysing carbides. Some samples for Safeguards (scraps etc.) require to be refluxed for a long time. For the case of an insoluble residue, the completeness of the U dissolution is checked gamma-spectrometrically and/or by the method of activation analysis.

The Th fuels are dissolved with a mixture of 3M $\text{HNO}_3 + 0,01\text{M}$ HF; sometimes a longterm reflux is necessary for a complete dissolution. Metal Pu samples are dissolved in 2-3M HCl without heating whereas PuO_2 is dissolved in a mixture of 7M $\text{HNO}_3 + 0,05\text{M}$ HF with heating.

Determination of U in uranium fuels

Various methods were studied [3] and a reduction-oxidation titration method based on those of Davies, Gray [4] and Eberle et al. [5] was chosen for a precise determination of U contents and modified for a routine analyses. A Radiometer titration set, consisting of a titrator, automatic burette, and a recorder, was used for the titration. The equivalence was indicated potentiometrically, using the Pt/Rh - SCE electrodes. The method was standardised using a NBS-U 960 standard; the solution of the standard displayed more reproducible results than the standard

in the form of solid aliquots. Parallel analyses of 4 aliquots were performed for each sample.

The method has been used as:

- a) an automatic volumetric titration (the burette volume was calibrated by weighing) for 250 mg U; the relative standard deviation was 0,02-0,05 %,
- b) an automatic volumetric titration for about 25 mg U with the relative standard deviation 0,1-0,12 %,
- c) weight-volumetric titration for 2-3 g U; the main part of the reagent was weight as solid $K_2Cr_2O_7$ (NBS-136c) and the reagent remainder was added volumetrically. The rel. standard deviation was only 0,008 %.

Determination of Th in thorium materials

From the solution of a Th fuel, the aliquots were taken and F⁻ were removed by evaporation. The Th were titrated in the medium of a monochloroacetate buffer with 0,01M Complexon III, using xylenol. orange as an indicator. The equivalence is indicated visually or photometrically. A Radiometer titration set adapted for performing photometric titrations was used for the photometric indication. The amount of 20-2 mg Th was determined with 0,15-0,2 % RSD.

Analysis of Pu fuels

An indirect determination based on a reduction of Pu(VI) [6,7] was used. Pu is oxidized to Pu(VI) with AgO surplus of which was decomposed by NH_2SO_3H . Pu(VI) was reduced by an excess of Mohr's salt and the Fe^{2+} surplus titrated with $Ce(SO_4)$. The effect of F⁻ was eliminated by evaporation or by an addition of H_3BO_3 [8]. The contents of Pu in the aliquots analysed were 10 - 15 mg, RSD 0,10-0,15 %. The NBS-Pu-949e was used for the standardization of the method. The experimental device was

similar as for determining U. Pu in irradiated uranium fuel (ug Pu/mg U) was determined ordinarily by radiometry or by the method of isotopic dilution. Besides the analyses for the USSR safeguards system, also plutonium and mixed (Pu, U) fuels were analysed in the co-operation with IAEA, in the framework of Pafex-1.

Determination of impurities

To evaluate the purity of uranium used for a manufacturing fuel elements, a carrier distillation method was applied, Ga_2O_3 being used as the carrier; nineteen elements within the concentration range of 0,04-300 ppm were determined. During routine analyses the concentrations of the elements were evaluated with a computer. The relative standard deviation was between 8-25 %. In some special cases the spectrophotometric method was used.

Determination of U and Pu by the method of isotopic dilution

The mass-spectrophotometric method of isotopic dilution was applied preferentially to the determination of U, Pu and Nd in irradiated fuels, using ^{233}U , ^{242}Pu and $^{150}Nd/^{142}Nd$ as spikes [9,10,11]. The spike concentration was estimated by the method of isotopic dilution by a comparison with NBS-U 960 and NBS-Pu 949 standards as well as Nd_2O_3 of a known purity (Koch-Light). The measurement technology of isotopic composition and the preparation of samples for the analysis is concisely described in the following chapter. The precision of the U(Pu) concentration determination in burnt fuel samples, expressed as RSD for the weight-based dilution, is < 0,2 and 0,3 % for U and Pu, respectively.

Determination of isotopic composition

At the CCL, the methods for determining isotopic composition of U, Pu and Nd, isolated from irradiated and nonirradiated

fuel materials, were established [12]. The isotopic composition was measured with a TH-5 Varian Mat mass spectrometer. Its basic equipment was completed with a 10 channel mass selector and a SS 006 spectroscopy system which makes it possible to record spectra in a punched tape. The data were treated with a computer using a generally constructed program, involving the corrections for the samples burnup from the filament, mass discrimination, non-linearity of the detector system, and elimination of randomwise deviated points according to the 2σ criterion.

The mass spectrometer was calibrated and its function checked by measuring standards with a known isotopic abundance (NBS-U 500, U 010, U 020, U 100, U 200, U 930). To obtain a solution in $9M$ HNO_3 of the element to be analysed free of impurities of both cationic and anionic types, the sample is always chemically treated before the mass spectrometric measurement; the impurities could affect thermochemical process in the ionic source, ionization effectiveness, sample vaporization, etc. For ordinary uranium materials (metal U, oxides), the extraction with diethyl ether, little time consuming and giving a product of a satisfactory purity was the most convenient. For the analyses of small sample amounts of alloys (U-Al, U-Zr) and oxides $(Th,U)O_x$ as well as burnt fuels, uranium was separated on a column with a Dowex 1x8 anion exchange resin, using HCl or a HCl-HF mixture as a elution reagents.

For isolating Pu, an extraction with $0,5M$ TTA solution in xylene in the medium of $1M$ HNO_3 - $HClO_4$ mixture or a separation on Dowex 1x4 in HNO_3 with heating were used. The decontamination factor (for fission product and U), during the isolation of Pu from a sample of burnt fuel by a two step extraction with TTA was $10^6 - 10^9$.

From the solution of isolated U, ≈ 5 ugU was loaded on the Re filament. After degassing the sample, adjusting the working temperature of ionization filament to $2010 \pm 10^\circ$ C, and focusing

the ionic beam, the ionic currents of U isotopes were recorded by means of a Faraday collector; the ionic currents of low-abundant isotopes (^{234}U , ^{235}U , ^{236}U) were detected with an electron multiplier. The gain was $\approx 5 \cdot 10^5$. Two groups of spectra, containing 5 mass spectra (scans), were recorded for each analysis, the focusing of the ionic beam being controlled between the group records.

Similarly, the isotopic composition of Pu was measured, with loading 0,1 ug Pu on the filament and using an electron multiplier for detection.

The precision of the isotopic ratio determination, calculated from 10 parallel analyses with repeating the measurements in series expressed as RSD for 1 determination was 0,1 - 0,5 % within the range of isotopic ratios $0,007 < R < 1$ and for low-abundant ^{234}U and ^{236}U masses $0,003 < R < 0,01$, respectively. The determination accuracy, with respect to NBS uranium standard expressed as a reliability interval for 95 % confidence level, was 0,17 % within the range of $0,007 < R < 1$. The accuracy of the Pu isotopic ratio determination, with respect to the NBS-Pu 947 standard, was $< 0,25$ % for the isotopic ratios of $0,01 < R < 0,4$.

The mass-spectrometric measurements were completed with alpha-spectrometry. A Si detector with the resolving power of 25 keV with a Plurimat 20 analyser was applied to the ^{238}Pu determination. Pu was extracted by TTA and loaded onto a stainless disc by evaporation or electrolytically.

For the control of isotopic composition and contents of U and Pu, the gamma spectrometric method served as an additional method. The laboratory equipment consists of two 1000-channel and one 4096-channel Plurimat 20 analyser with a Multi-8 computer. The semiconductor Ge(Li) and Si(Li) detectors were used. The resolving powers of a 77 cm^3 Ge(Li) and a small Si(Li) detector were 2,5 keV and 560eV for 1332,4 and 59.6 keV, respectively.

For the determination of the $^{235}\text{U}/^{238}\text{U}$ ratio, also the method of measuring delayed neutrons as well as the activation analysis method have been tested and modified at the CCL [13]. These methods are less accurate as compared with mass-spectrometry but they are simple and fast.

Burnup determination

The burnup values are important as an information revealing the effectiveness of utilization of the reactor fuel; further they supply us with data necessary for improving the reactor construction and development and controlling the reactor operation. Within the framework of Safeguards, the burnup data can be used for calculating the U and Pu concentrations in an irradiated fuel as well as their isotopic composition.

At the CCL, the following destructive methods have been developed:

- a) measurement of the change in U and Pu isotopic composition during the irradiation
- b) measurement of the radioactivity of radioactive fission products (^{137}Cs , ^{106}Ru , ^{144}Ce , ^{95}Zr) in the fuel
- c) measurement of concentration of stable Nd isotopes in the fuel

The first method displays reliable results for high burnup values; the ^{235}U burnup was determined with an error of $\pm 4\%$ for the total burnup of 7.2000 MWd/t [14]. The burnup values obtained mass-spectrometrically for ^{239}Pu had an considerably higher error. The gamma-spectrometric method b/ using radioactive burnup monitors, showed an error of 5% - 10%. The most precise results were obtained by measuring the conc. of stable Nd isotopes (2 - 5 %) [15,16].

Nondestructive methods

A gamma spectrometric method in 2 modifications was estab-

lished for a nondestructive determination of the content of ^{235}U in nuclear materials.

- 1) a method based on the comparison of a ^{235}U spectrum with that of $^{234\text{m}}\text{Pa}$, which is a product of ^{238}U was applied to the determination of ^{235}U in materials of different chemical composition and geometry [17]. No reference sample is necessary but the method displays an average relative error of 5%.
- 2) from the point of view of the requirements for precision of accountancy and inventory, a method with more precise results had to be chosen for determining ^{235}U in fuel elements. A method of passive gamma-spectrometry [18] was therefore selected for controlling the IRTM fuel elements with 80 % abundance; an element with a known ^{235}U content (determined mass-spectrometrically) was the standard. The ^{235}U concentration was evaluated from the 185,72 keV peak areas of ^{235}U . The result displayed a relative error of 0,3 % owing to a good measurement statistics ($\approx 3,5 \cdot 10^6$ pulses in the peak).

The results of both methods were evaluated using a 4096-channel an alyser Plurimate 20 with a memory of 24 Kbit with a Ge(Li) coaxial detector.

A possible application of CdTe detectors manufactured in the ČSSR, to the control of nuclear fuels [19] is a perspective work involving gamma-spectrometry. CCL collaborates with the Department of semiconductor in the field of use these detectors for the nondestructive control of fuel materials under both the laboratory and field conditions.

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