



## Application of bromine trifluoride for pre-concentration and determination of rare-earth elements in fuel uranium dioxide

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### ABSTRACT

Radioactive indicator's ( $^{152}\text{Eu}$ ) method was used to study the behavior of rare-earth element (REE) micro-impurities at fluorination of fuel  $\text{UO}_2$  with bromine trifluoride. The proposed process is very simple and carried out under a blanket layer of Freon-113 in the glassy carbon (vitreous) crucibles.

It was shown that uranium matrix completely removes from reaction sphere in the form of  $\text{UF}_6$  and REE contaminations quantitatively remain in crucible owing to practical non-volatility of their fluorides. High purity of fuel  $\text{UO}_2$  causes small amount of the non-volatile rest (0.3–2 wt.% from initial weight) that considerably facilitates a problem of confident diagnostics of the strictly limited REE content in this material. Removal of uranium and concentration of REE from analyzed test samples via fluorination is several hundred times more rapid scheme of pre-sampling to atomic emission spectral determination of REE micro-quantities in  $\text{UO}_2$  than traditionally used extraction and ion-exchange ways of the preliminary concentration of contaminations and removal of uranium.

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### 1. Introduction

Natural uranium is present mainly in two isotopic forms: 99.28% of  $^{238}\text{U}$  (fertile) and 0.71% of  $^{235}\text{U}$  (fissile). Only  $^{235}\text{U}$  can be used in majority of nuclear plants to give rise to energy by fission. Such nuclear plants consume uranium which constitutes 3–5% of  $^{235}\text{U}$ . Therefore, a uranium enrichment process is carried out from  $\text{UF}_6$  (only volatile compound of uranium) not only because of its relative chemical stability and its low sublimation temperature but also because of the fact that fluorine has only a single stable naturally occurring isotope ( $^{19}\text{F}$ ) [1]. Consequently, isotopomers of  $\text{UF}_6$  differ in their molecular weight only because of uranium. After the enrichment step,  $\text{UF}_6$  is converted by chemical reduction to uranium oxide ( $\text{UO}_2$ ), which are packaged as small pellets of a ten of sintered at high temperature. Then, the pellets are introduced in long zirconium-based alloys hermetically closed tubes and are introduced in the hole of the reactor. Modern equipments are required to evaluate the quality of uranium dioxide tablets ( $\text{UO}_2$ ), including the accurate determination of rare-earth elements (denoted REE henceforth) at a concentration level of 0.1 ppm ( $10^{-5}$  wt.%). The most common method of REE determination in fuel  $\text{UO}_2$  is atomic emission spectral analysis (AESA). Nevertheless, the exact determination of REE contents

from the analysis of the spectral lines relative to the uranium matrix are strongly under-evaluated. Consequently, before carrying out AESA, it is necessary to collect REE impurities simultaneously onto graphite powder and to complete the removal of uranium as much as possible.

The separation of uranium matrix from the analyzed samples is now recommended to be done by the dissolution of  $\text{UO}_2$  tablets in nitric acid solution with subsequent extraction [2–4] or ion-exchanged concentration of REE in analyzed sample [5–7]. Extraction processing of pre-sampling is included in the dissolution of  $\text{UO}_2$  fuel tablets with the preparation of U(VI) nitrate solution. Then, several stages of uranium extraction by tributylphosphate solution in benzene or sintone from nitrate solution are followed [2–4], separation of organic extract with the subsequent introduction of the obtained organic extract into graphite powder for final AESA tools. Parameters of extraction process are strictly controlled in order to prevent any significant loss of micro-impurities that is the subject of analyses. It is commonly considered that losses of REE do not occur during careful extraction procedure.

The pre-concentration of REE from uranium solutions by extraction is well studied and now commonly applicable in analytical laboratories within the limits of the national standards for nuclear fuel producers. The typical AESA method usually concerns analyzed samples of graphite powder (200 mg) with collected impurities, and the common detection level of REE micro-impurities is within the range of 0.1 ppm. Therefore, a larger

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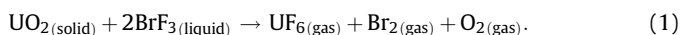
amount of  $\text{UO}_2$  (5–10 g) is required for pre-sampling processing. As a consequence, it requires the use of a significant amount of high purity extractant and also increases the duration of the extraction process. It is obvious that the extraction pre-sampling is a rather long and inconvenient process for REE determination by AESA.

Ion-exchange method [5] can be considered as an alternative to the extraction schemes [2–4] described above. This method consists in the recovery of U(VI) from a muriatic solutions by strong-based anion exchange resins [5–7] with the separation of some impurities such as REE into eluate, which is introduced into the graphite powder. Then, the excess of liquid phase from the obtained suspension is evaporated for the preparation of dried powder and further for the determination of REE using AESA tool. However, this method needs the conversion of a nitrate solution into a chloride form. It induces a significant increase of the duration of the pre-sampling process. In addition, a very careful ion-exchange technique [5] is necessary for guarantying the full removal of uranium from a large starting amount of  $\text{UO}_2$ . The latter, in turn, demands the presence of columns of greater sizes (25–50 ml). It implies to obtain to have a larger eluate volume with the subsequent evaporation to the minimal volumes before their introduction into graphite powder. As a consequence, the efficiency and productivity of processes are low (no more than 2 columns in a day for one operator).

It is obvious that despite abundance of various techniques for REE determinations [2–7], it is better to develop new, simple and high-efficiency laboratory techniques of pre-sampling processes; providing full and fast removal of uranium matrix and a higher concentration degree of REE impurity into the rest for a better determination by AESA.

In this way, investigations for expressing one-stage concentration of REE impurity from greater  $\text{UO}_2$  samples are starting using oxidizing fluorination processes: in that case, uranium matrix can be quantitatively removed by the formation of volatile  $\text{UF}_6$ . The most appropriate fluoroxidant for gasification of uranium in laboratory conditions could be liquid bromine trifluoride. In addition, experiences with  $\text{BrF}_3$  do not require complicated and expensive equipments and can be carried out at atmospheric pressure in the open systems.

As it has already been shown by Emeleus et al. [8], the fluorination of  $\text{UO}_2$  and other uranium compounds with liquid  $\text{BrF}_3$  proceeds at atmospheric pressure and temperatures less than  $126^\circ\text{C}$  (b.p. of  $\text{BrF}_3$ ). In such soft conditions, this fluorination reaction leads to the formation of volatile uranium hexafluoride according to reaction (1), whereas the impurities of Tl, Pb, Th, Ac and Pa initially present in uranium do not form volatile fluorides [8].



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It is quite obvious that the fluorination using liquid bromine trifluoride do not concern only the fuel uranium dioxide but also

the existing contamination REE oxides which should be transformed into their non-volatile fluorides. Therefore, the gasification of U using  $\text{BrF}_3$  to form  $\text{UF}_6$  according to reaction (1) could allow the careful analysis of fuel tablets by massive extraction of a lot of impurities from  $\text{UO}_2$ , in particular REE.

The purpose of the present work was to demonstrate the feasibility to use  $\text{BrF}_3$  at laboratory scale for the separation and extraction of REE impurities from larger amounts of the uranium matrix than those commonly used. In that frame, we will evaluate the characteristics of the fluorination parameters vs the extraction and an optimized ion-exchange technique of pre-sampling for AESA determination of REE.

## 2. Results and discussion

Averaged results of  $\gamma$ -spectra measurements of all experimental samples (residuals) are presented on Figs. 2 and 3 and shown in Table 1.

Our experiments made on various samples of  $\text{UO}_2$  tablets (5–10 g) have shown that complete removal of uranium after fluorination is achieved at weight ratio  $\text{BrF}_3/\text{UO}_2$  not less than 2.8:1. The most typical weight ratio  $\text{BrF}_3/\text{UO}_2$  was established as 3:1.

Firstly, it is necessary to note a small excess of the found  $\gamma$ -activity for almost all the  $^{152}\text{Eu}$   $\gamma$ -peaks vs initially entered activity in the case of the fluorination procedure, whereas the same peak activity (less than initial activity) is observed in all  $^{152}\text{Eu}$   $\gamma$ -peaks after ion-exchange processing. In the later case, an averaged value of  $97.2 \pm 3.7\%$  from the analytical  $\gamma$ -peaks at 344, 964 and 1408 keV was found. For more accurate calculations, we used for  $^{152}\text{Eu}$  determination just the analytical  $\gamma$ -peak at 1408 keV. Indeed, this peak presents a much better resolution, and the influence of background on it is minimal.

The noted feature of small increase of analytical  $\gamma$ -peaks at 112, 344, 964, 1086 and 1112 keV (except the peak at 1408 keV) for fluorination products is not too unusual and could really be explained by a certain geometry difference of the measured initial and final samples (visual distinctions in the thickness of samples and in the varieties of  $\gamma$ -rays absorbance for some heavy elements at different parts of spectra). Nevertheless, the mentioned exceed value (ca. 0.5%) keeps within frameworks of typical error of the radioactive indicator's method.

It is therefore possible from the exploitation of data given in Table 1 to conclude that REE microcontents were not lost during fluorination procedure.

Comparison of the  $\gamma$ -spectra presented in Figs. 2 and 3 shows that uranium was completely eliminated after fluorination with  $\text{BrF}_3$  and only radioactive products of its self-disintegration ( $^{231}\text{Th}$ ,  $^{234}\text{Th}$  and  $^{234\text{m}}\text{Pa}$  isotopes) were left in the crucible. The residual radioactivity of the crucible in  $^{235}\text{U}$  corresponds to the limits of measurement accuracy of the spectral line of a background. It is

**Table 1**  
Comparison of results in recovery of radionuclide  $^{152}\text{Eu}$  ( $n = 5$ ;  $1 - \alpha = 0.68$ , time of each measurement 30 min) via fluorination method and ion-exchange method

Analytical peaks of $^{152}\text{Eu}$ (keV)	Method of fluorination $\gamma$ -activity $^{152}\text{Eu}$ (impulses)		Ion-exchange method $\gamma$ -activity $^{152}\text{Eu}$ (impulses)		
	Introduced $^{152}\text{Eu}$ till fluorination	Find $^{152}\text{Eu}$ after fluorination	$I_0$ , Introduced $^{152}\text{Eu}$	$I_f$ , Find $^{152}\text{Eu}$	$I_0/I_f$ $^{152}\text{Eu}$ , %rel.
121	10047 $\pm$ 71	10100 $\pm$ 103			
344	4899 $\pm$ 47	4998 $\pm$ 58	4880 $\pm$ 89	4862 $\pm$ 94	99.6 $\pm$ 1.8
964	895 $\pm$ 22	919 $\pm$ 25	990 $\pm$ 42	986 $\pm$ 44	99.6 $\pm$ 4.4
1086	681 $\pm$ 19	722 $\pm$ 22			
1112	764 $\pm$ 20	794 $\pm$ 21			
1408	935 $\pm$ 18	934 $\pm$ 19	997 $\pm$ 33	921 $\pm$ 45	92.4 $\pm$ 4.9
	Recovery of $^{152}\text{Eu}$ , estimation through analytical peak at 1408 keV – 99.9%		Averaged recovery of $^{152}\text{Eu}$ , analytical peaks 344, 964, 1408 keV – 97.2 $\pm$ 3.7%		

also possible to note the presence of  $^{212}\text{Pb}$  peak which can come from micro-impurity of  $^{232}\text{Th}$  in fuel  $\text{UO}_2$ . Indeed,  $^{212}\text{Pb}$  is one of nucleus in the self-disintegration chain of  $^{232}\text{Th}$ .

Our experiments made on various samples of  $\text{UO}_2$  tablets (5–10 g) have shown that full removal of uranium is achieved at weight ratio  $\text{BrF}_3/\text{UO}_2$  not less than 2.8:1. Thus, as shown from data extracted from Fig. 3 the residual radio-activity of  $^{235}\text{U}$  in crucible lays within the limits of measurement accuracy of  $\gamma$ -spectral line of a background. Practically, it means that 99.9% of uranium is removed and shows that basic fluorination process can be considered as a convenient and effective method for uranium removal. Amounts of dry residual powders in crucibles after fluorination of 10 g fuel  $\text{UO}_2$  samples, taken from various industrial sets, make usually 30–50 mg. It means that weight's concentration of all contaminations after  $\text{BrF}_3$  processing is equal  $\sim 200\text{--}300:1$ . It is obviously provided with a deep concentration of all non-volatile contaminated fluorides, including REE and creates a convenient condition for the pre-sampling to AESA determination of REE in small residue, because the following stage of preparation of tests to AESA tools includes introduction of obtained residuals into portion of spectral pure graphite 200 mg. After mixing the residue with graphite, the achieved degree of concentration reaches 50:1, and it is quite enough for REE contents determination at a level  $\sim 0.01$  ppm in tablets of fuel  $\text{UO}_2$ .

For further direct demonstration and confirmation of the fluorination method's efficiency, an additional experiment for the determination of REE in a random test fuel  $\text{UO}_2$  sample has been conducted. The tablet for experiment has been chosen from an industrial series of fuel  $\text{UO}_2$  tablets. Usually, contents of REE in all industrial fuel tablets of uranium dioxide do not exceed the standard established level 0.05–0.1 ppm. These REE amounts are determined by the standard AESA tools [2], having a common level of detection  $<0.2$  mkg REE (Eu, Sm, etc.) per 1 g U within the framework of applied extraction technique of pre-sampling.

For these experiments, 1 ml of 4 M  $\text{HNO}_3$  containing 0.8 mkg Gd was put into a crucible. Then, the solution was evaporated. Further, the randomly chosen  $\text{UO}_2$  fuel tablet (weight of uranium – 4.2 g) was placed into a crucible and the fluorination process as described above was developed. At the end of the reaction, the walls of the crucible were washed by several drops of concentrated  $\text{H}_2\text{SO}_4$ . Then, acid evaporated and the crucible was processed by hot 4 M  $\text{HNO}_3$ . The final obtained solution was dispersed into 200 mg of high purity spectral graphite powder (GOST 23463–79). Further, a pulp of graphite containing the solution was collected and dried. Finally, the dried powder was analyzed by AESA method using the direct current arch with spectrograph DFS-13 and technical equipment of the computer registration MAES.

The analysis had shown the presence of  $0.8 \pm 0.2$  mkg Gd in test. The contents of Eu and Sm in test remained the same that is below the level of analytical detection, i.e. less than 0.2 mkg per 1 g U (0.2 ppm). The conclusion of this experiment is an additional confirmation of the absence of REE lost during the fluorination processing.

Comparison of the developed pre-sampling method of uranium matrix removal by fluorination with liquid  $\text{BrF}_3$  and further REE analyses shows that the new technique is more rapid than extraction or ion-exchange method [2–7]. It consists of three short stages – fluorination with  $\text{BrF}_3$ , processing by small amount of hot 4 M  $\text{HNO}_3$  and introduction of a nitrate solution in graphite powder with evaporation and final drying. The process of full pre-sampling to AESA of 4 tablets of fuel  $\text{UO}_2$  (10 g each tablet) under the new fluorination scheme demands no more than 3.5–4 h, and uranium leaves quantitatively. One operator can execute within one working day full pre-sampling at least 8 separate  $\text{UO}_2$  tablets daily. Conventional ion-exchange or extraction techniques require at least 4 times more time.

It is also necessary to note that quantities of a dumped uranium matrix (up to 10 g) within the limits of an offered fluorination technique at 40–50 times more than the experimental amounts of uranium compounds, described in [8].

### 3. Conclusions

In the present article, a new scheme of the fuel  $\text{UO}_2$  pre-sampling for concentration of the REE micro-impurities is presented. This new technique is rather universal – many fluorides of contained elements, and not just REE, at rather low temperatures of fluorination and small time of reactions should not disappear significantly because of non-volatility of their fluorides (e.g. Pb, Bi, Th, Fe, Ni, Co, Cd, Ba, etc.). The hardware scheme of performance of such a liquid phase fluorination is represented to be very simple and quite safe in practice for any factory laboratory.

Process of pre-sampling is combined well with the standard instrumental tools. The method of fluorination with liquid  $\text{BrF}_3$  can be hardly considered as an alternative if compounds of uranium, which practically are not decomposed with traditional “wet” methods, are subjected to the analysis. In summary, it is necessary to note that the way of pre-sampling with application of liquid  $\text{BrF}_3$  can be applied not only for the analysis of micro-impurities in uranium compounds but also for the analysis of other elements, easily forming volatile fluorides, e.g. W, Mo, Se, Te, etc.

### 4. Experimental

#### 4.1. Chemicals

The chemical products used in this study, including acids, organic extractants and solvents, resin, etc. were of commercial analytical grade products: extra pure  $\text{HNO}_3$  (GOST 11125-78), chemical pure  $\text{H}_2\text{SO}_4$  (GOST 4204-77), chemical pure HCl (GOST 3118-77).

Bromine trifluoride was prepared for laboratory use by direct reaction of fluorine gas or gaseous chlorine trifluoride with purified liquid bromine in the temperature range 20–45 °C. The reaction took place in a quartz vertical reaction tube using the procedure described by Mitkin and Zemskov [9] and by Nikolaev et al. [10]. Before this step, reactive grade liquid bromine was purified by extraction with concentrated  $\text{H}_2\text{SO}_4$  and distilled twice. The typical contaminants in liquid  $\text{BrF}_3$  are HF and  $\text{BrF}_5$ , and their contents estimated from  $^1\text{H}$  and  $^{19}\text{F}$  NMR studies [11,12] did not usually exceed 1 wt.%. It is important to note that these impurities present in the liquid  $\text{BrF}_3$  did not have any incidence on the gasification of uranium and the completed fluorination of REE micro-tracers.

As we will discuss later in this manuscript, a “heat carrier” was used to enhance the safety related to the use of liquid bromine trifluoride [11,12]. In the present case, Freon-113 (F-113,  $\text{CCl}_2\text{F}-\text{CClF}_2$ , b.p. 47.6 °C) has been selected. Before using, Freon-113 was thoroughly dried using calcinated silica-hell and then filtered. The presence of micro-impurities such as  $\text{H}_2\text{O}$ ,  $\text{CCl}_3-\text{CCl}_3$ ,  $\text{CHCl}-\text{CCl}_2$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , hydrocarbon greases tracers in F-113 has to be fully excluded to avoid any possible exothermic reaction of these contaminants with liquid bromine trifluoride [10]. To succeed, test was performed by introducing 1 ml  $\text{BrF}_3$  into a quartz glass vessel containing 50 ml F-113. If after  $\text{BrF}_3$  addition no boiling and no occurrence of brown color are observed, the F-113 was suitable to be used as heat-carrier media (blanket) for the fluorination of uranium dioxide.

Finally, note that before further applications, bromine trifluoride and Freon-113 were tested to check the absence of REE traces by carrying out control tests.

## 4.2. Equipment and laboratory facilities for uranium fluorination by bromine trifluoride

### 4.2.1. Reaction vessels for $UO_2$ fluorination

Open conical crucibles (40–150 ml in volume) made of Russian glassy carbon of the type SU-1500 (vitreous carbon) have been used as reaction vessels for fluorination of  $UO_2$  by liquid  $BrF_3$ . The dimensions of the glassy carbon crucibles were: 60–80 mm height, 1–1.2 mm wall thickness and about 65–75 mm maximal external diameter. These crucibles were very convenient for the rapid fluorination of large amount of  $UO_2$  tablets (5–10 g) with  $BrF_3$ .

### 4.2.2. Minibox for fluorination in vitreous carbon

Safe conditions for the fluorination of  $UO_2$  in open systems (glassy carbon crucibles) by  $BrF_3$  are required via the trapping and the adsorption of the volatile products resulting from reaction (1). To solve this problem, a special ventilated stainless steel minibox was used, supplied with a trap for the sorption of  $UF_6$ ,  $Br_2$  and  $BrF$ . The scheme of the fluorination minibox is presented in Fig. 1.

The process was carried out simultaneously in 3–4 crucibles on a standard electrical hot plate (regulated power ~200–1000 W) located into this fluorination minibox.

### 4.2.3. Pipettes for dosing and dispensing of liquid $BrF_3$

Pipettes for dispensing liquid bromine trifluoride must be manufactured from the fluoro-resistant transparent or semi-transparent material such as special fluoropolymers. We used pre-calibrated pipettes made from Russian Ftoroplast F4-MB with a typical volume of 5–10 ml [12]. These are similar to pipettes available in the West and made from transparent PFA, FEP or semi-transparent PTFE fluorine-resistant polymers. Glass pipettes are not applicable for liquid  $BrF_3$  due to the high rate of corrosion. Quartz pipettes are usable, but their application as dispensers was not very useful due to the necessity of good flexibility when fitting a connector as the dosing aid. All high-flexibility fluoropolymers contain various organic additives unstable in contact with  $BrF_3$ . For this reason, the most convenient and rigid

construction for dispensing was achieved by using an auto-pipette fitted with teflon tips. All moving parts of this auto-dispenser (5–10 ml) were covered by a thin film of a perfluororganic liquid (from the perfluoroalkane family or perfluorodecaline) with the boiling point of not less than 140 °C (e.g., perfluorocerosine). The best results were obtained using fluoro-liquids of the type KS-4 or KSP (so called manometric and barometric liquids), which are available in Russia.

### 4.2.4. Safety of experiences with bromine trifluoride and uranium

For safety reasons, fluorination reactions were carried out in standard laboratory fume cupboards with a high face velocity (1.0–1.5  $m s^{-1}$ ). Higher standard of safety can be achieved by conducting all fluorination decompositions in stainless steel ventilation box (type 3SH-NZH) using protective clothing for eyes and skin (polyethylene, polyvinyl chloride or surgical gloves and plastic safety glasses). All organic compounds and water must be completely excluded from contact with fluoroxidants during their storage and handling.

The enhancement of the safety related to the use of fluoroxidant reagents can be achieved by using a “heat carrier” as we described in references [9,11,12]. It was designed to prevent spontaneous ignition on first contact with  $BrF_3$  during the oxidative fluorination of reactive samples. Freon-113 ( $CCl_2F-CClF_2$  denoted as F-113 henceforth) was used as a “heat-carrier”. It has a low boiling point liquid, a dried commercial Freon has a boiling point of 47.6 °C. Moreover, one may notice that other perfluorinated liquids with low boiling points (50–80 °C) such as  $C_6F_{14}$ ,  $C_7F_{16}$ ,  $C_8F_{18}$ , etc. [12] can be used for the same purpose.

All procedures involving an oxidative fluorination with  $BrF_3$  were carried out with complete safety under a 40–50 mm protective layer of F-113 [11,12].

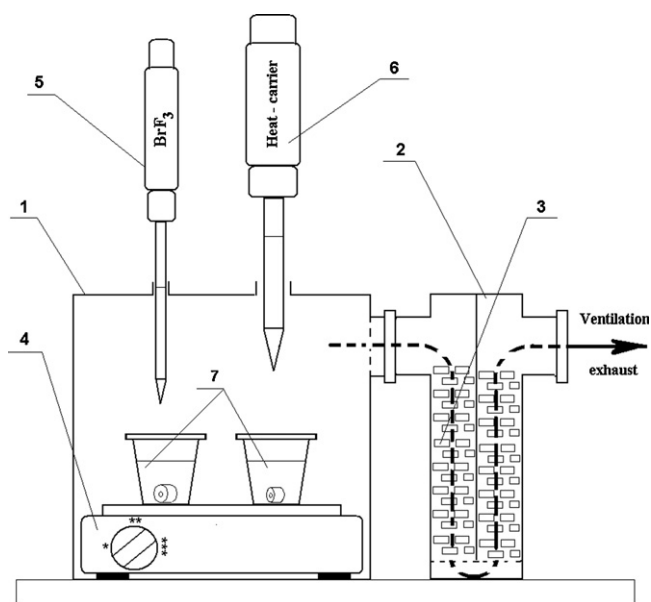
## 4.3. Measurements of radionuclide concentration

Study of REE behavior was carried out by radioactive indicator's method by using  $^{152}Eu$ . The behavior of uranium and the  $\gamma$ -nuclides present at fuel uranium was traced as on scale-radiation of peak  $^{235}U$  at 185 keV, and visually, on change of solution color. For  $\gamma$ -activity measurements, Ge-Li gamma-detector DGDK-04 and  $\gamma$ -spectrometer “Nokia-4096” were used. Calculations of  $\gamma$ -nuclei concentration spent on the areas of peaks with use of standards.

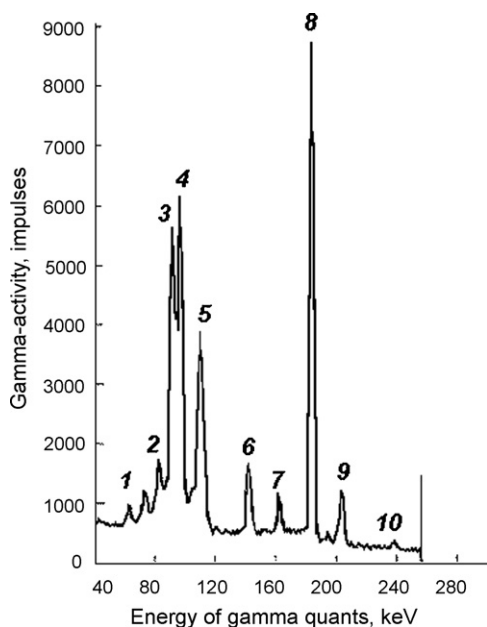
Averaged results of  $\gamma$ -spectra measurements of all experimental samples (residuals) are presented on Figs. 2 and 3 and shown in Table 1.

## 4.4. Fluorination process of $UO_2$ tablets with $BrF_3$

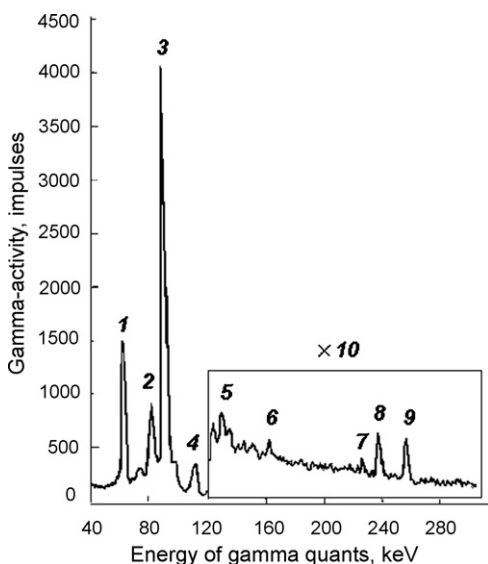
Weighted portion  $UO_2$  in the form of pressed tablets with diameter and height of about 1 cm were placed at the bottom of glassy carbon crucibles (Russian trademarks SU-1500, i.e. vitreous carbon) and filled with a cover layer of 40–50 mm of the F-113 heat-carrier which is solvent for  $BrF_3$ ,  $BrF$  and  $Br_2$  allocated at reaction (1). Then, the calculated amount of liquid  $BrF_3$  was slowly added (drop by drop) using an autopipette (i.e. during 1–2 min). Carrying out the process under a blanket protective layer of F-113 allowed to avoid any highly exothermic process relative to the decomposition of test sample. Efficiency of the  $UO_2$  decomposition reaction by addition of  $BrF_3$  is easily regulated by quiet slow boiling of the covered layer of F-113. The process is completely safe and losses of determined substances are fully prevented [10,11]. One skilled laboratorore assistant is confidently able to supervise the  $UO_2$  decomposition process simultaneously in 3–4 crucibles.



**Fig. 1.** Scheme of simple experimental equipment for liquid phase fluorination. 1, stainless minibox 350 mm × 350 mm × 400 mm; 2, sorption trap; 3, sorbent-mixture of  $NaF + CaCO_3$ ; 4, electroplate with regulated power (200–1000 W); 5, dispenser pipette for  $BrF_3$ ; 6, pipette for F-113; 7, carbon glassy (vitreous carbon) crucible.



**Fig. 2.** Gamma-spectrum of  $\text{UO}_2$  tablet in energy region of  $^{235}\text{U}$  before fluorination: 1,  $^{234}\text{Th}$ ; 2,  $^{231}\text{Th}$ ; 3, ( $^{234}\text{Th} + ^{235}\text{U}$ ); 4 and 5, edge of soft  $\gamma$ -region for U/Pa family; 6–9,  $^{235}\text{U}$ ; 10,  $^{212}\text{Pb}$ .



**Fig. 3.** Gamma-spectrum of residual in energy region of  $^{235}\text{U}$  after fluorination: 1,  $^{234}\text{Th}$ ; 2,  $^{231}\text{Th}$ ; 3,  $^{234}\text{Th}$ ; 4–7 and 9, ( $^{234} + ^{234\text{m}}\text{Pa}$ ); 8,  $^{212}\text{Pb}$ .

Initial rate of  $\text{UO}_2$  reaction with  $\text{BrF}_3$  is quite insignificant and the small starting heating is usually required (position 4 in Fig. 1). Then, the  $\text{UF}_6$  formation proceeds more quickly and its course needs to be adjusted to avoid any warming up: introduction of additional F-113 was done, i.e. cooling of a liquid phase. 25–30 min were usually required for slow decomposition of 5–10 g of  $\text{UO}_2$  and for quantitative removal of uranium as  $\text{UF}_6$  gas. After complete decomposition, a thin light powdered cover has been observed at the bottom part of the crucible. The weight of this residual varied from 0.5 up to 2% from initial  $\text{UO}_2$  sample.

After a preliminary investigation to find the optimum mode of fluorination, the occurrence of the REE impurity losses has been checked.  $\text{HNO}_3$  solution with a known (measured) amount of

introduced radionuclide  $^{152}\text{Eu}$  was added in the glassy carbon crucible. Then the solution evaporated and the intensity of  $\gamma$ -peaks of  $^{152}\text{Eu}$  was measured by gamma-radiometry method using a Ge–Li detector. Then, the weighted tablet of  $\text{UO}_2$  was placed in a crucible and spent fluorination as it is stated above. After completing fluorination, the walls of the crucible were washed by small amount of  $\text{H}_2\text{SO}_4$ . The collected solution was evaporated and the radio-activity of  $^{152}\text{Eu}$  and of other radioactive nuclei existing in the fuel table were measured.

It was shown that the subsequent triple washing of the crucible walls with hot portions of 4 M  $\text{HNO}_3$  (15 ml) provided a complete deletion all radio-activity of europium and thorium from the crucible. The resulting solutions are transparent. It means that REE micro-impurities are quantitatively taken *via* pre-sampling into graphite powder.

#### 4.5. Ion-exchange technique of REE concentration

Separation of uranium from REE was spent by a technique described in reference [6] based on the use of a strong-basis resin AV 17-8-CHS in the Cl-form. The column for elution has been made from a standard chemical cylinder tube (internal diameter: 11 mm) with the calibrated volume (50 ml). It is practically the limiting size of a laboratory column for practical work of an operator. Resin was kept on inserted web-net filter sieve, made from fibber glass tissue. The height of a resin layer was 40 cm. In the present case, the sieve was composed of Teflon F4. The layer of resin was covered with a similar sieve. Thus, the equipped column provided the quantitative separation of 1 g uranium from impurity cations. As eluent we used two portions of 25 ml of 7 M HCl, passed through column equipped with resin (speed of about 2 ml/min). The operation was repeated twice. Received volumes (25 ml) were measured by gamma-radiometry method and then the contents of natural uranium row nuclei and radionuclide  $^{152}\text{Eu}$  were determined using the standards.

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#### References

- [1] H. Groult, F. Lantelme, M. Salanne, C. Simon, C. Belhomme, B. Morel, F. Nicolas, J. Fluorine Chem. 128 (2007) 285–295.
- [2] J.C. Warf, J. Am. Chem. Soc. 71 (1949) 3257–3258; see also A.T. Eberle, Anal. Chem. 29 (1957) 1134–1139.
- [3] V.B. Shevchenko, V.S. Smelov, A.G. Kozlov, E.Ya. Smetanin, V.V. Chubukov, V.I. Anisimov, Radiochemistry 18 (5) (1976) 784–789 (in Russian).
- [4] J.O. Liljenzin, J. Ridberg, G. Skarnemark, Sep. Sci. Technol. 15 (1980) 799–824.
- [5] K.A. Kraus, F. Nelson, J.E. Moore, J. Am. Chem. Soc. 78 (12) (1956) 2692–2694.
- [6] F. Nelson, K.A. Kraus, J. Am. Chem. Soc. 77 (17) (1955) 4508–4509.
- [7] B.M. Shavinsky, V.N. Mitkin, A.I. Kamelin, Ind. Lab. 66 (9) (2000) 24–26 (in Russian).
- [8] H.J. Emeleus, A.G. Maddock, G.L. Miles, A.G. Sharpe, J. Chem. Soc. 11 (1948) 1991.
- [9] V.N. Mitkin, S.V. Zemskov, Zh. Prikl. Khim. 10 (1981) 2180–2186 (in Russian).
- [10] N.S. Nikolaev, V.F. Sukhoverchov, Yu.D. Shishkov, I.F. Alenichikova, Chemistry of Haloid Fluorine Compounds (Khimiya Galoidnykh Soedinenij Ftora – in Russian), Nauka Publishers, Moscow, 1968, p. 348.
- [11] S.V. Zemskov, V.N. Mitkin, V.G. Torgov, A.N. Glinskaya, J. Anal. Chem. 38 (1) (1983) 38–41 (in Russian).
- [12] V.N. Mitkin, Spectrochim. Acta Part B 56 (2001) 135–175.