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Improvement of Precision Spectrophotometric Method with Internal Reference and Its Application to Analysis of Plutonium Solutions

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Abstract—A spectrophotometric precision method with internal reference [1, 2] was applied to analysis of straight Pu solutions for certifying Pu reference materials and for studying the PuO_2 solubility in the framework of developing methods for accounting and control of nuclear materials. In the context of the activities mainly concerned with certification of reference materials, a two-channel spectrophotomer and the corresponding technique were further improved in order to decrease the error of the method. This allowed the random component of the relative error of the method to be decreased from 0.1 to 0.04% at the confidence level $p = 0.95$ and the number of degrees of freedom $f = 25$. The fixed component of the error of the method was studied in relation to impurities of U, Np and corrosion products of structural materials. Also, the extent of Pu oxidation during sample preparation was studied as influenced by the fluoride ion. The revealed lack of such influence within the limits of the study indicates that the method is suitable for analysis of Pu in mixed solutions.

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Enhancement of the precision of methods for determination of U and Pu in various nuclear materials remains urgent in view of the need in their accounting and control. This implies improving precision methods for determination of U and Pu in certification of the corresponding reference materials (RMs).

Development of RMs of Pu certified to both the isotope composition and mass fraction of Pu in the material is under way now in Russia, and Radium Institute is actively engaged in this work. These materials will be distributed among Pu-handling enterprises in Russia to ensure consistent measurements of the isotope composition and total mass of Pu. Clearly, such RMs should be certified to the highest possible precision. In this connection, Radium Institute undertakes improvement of the existing methods and instruments, in particular, the spectrophotometric procedure with internal reference (IRSP) [1, 2].

This method consists in measuring the light absorption of the test solution when illuminated with nonfiltered (white) light simultaneously in two sections of the spectrum. One of these sections incorporates the analytical absorption band of the element to be determined, and the other (reference band) is a transparent spectral window acting as internal reference. The analytical signal in this case is the ratio of the intensities R in the transparent window and in the absorption band, rather than the absolute value of the intensity of the light that passed through the solution at the absorption band.

The internal referencing principle was implemented with a two-channel spectrophotometric analyzer designed at the Radium Institute [1]. In this instrument, the light sent by an incandescent lamp passes through a cell containing the test solution, whereupon it is split into two monochromatic beams: The absorption band is cut with an MDR-23 monochromator, and the reference band, with a narrow-band interference filter having a transmission band width of ~5 nm.

Two light guides send the light to a measurement channel switching unit. This is a rotating disk with two slitlike slots (one slot for each measurement

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† Deceased.

channel), sharing the case with the measurement system consisting of a photomultiplier, one-electron pulse amplifier, and signal formation and synchronization units. The electric background of the instrument is measured at the disk position when both light guides are shielded. The measurements are carried out in a cyclic (each cycle lasts 2.2 s) mode under preset control. The measurement in one cycle yields the ratio of the light intensities R, corrected for the dead time of the instrument.

The variability of the intensities in both spectral sections can be due to instability of the light source, drift of the amplification coefficient of the amplification tract, poor reproducibility of the geometric position of the cell, variability of the temperature of the solution, etc. To achieve as rigorous correlation between the signals as possible, the measurements are carried out virtually simultaneously, using the same amplification tract, and the measurement cycles are many times replicated. To ensure identical conditions of the photomultiplier operation when recording the light intensities at the analytical and reference bands, the ratio R should be close to unity; this is achieved by setting neutral light filters in the reference channel.

In view of the fact that all the instrumental errors are mutually correlated, the relative random error of measuring the ratio of the light intensities R at close intensities can be determined by the expression [3]

$$\delta_R^2 = 2\delta^2(1 - r), \tag{1}$$

where δ is the relative rms deviation (RRMSD) of the results of direct intensity measurements; δ_R, RRMSD of the intensity ratios R; and r, correlation coefficient.

Expression (1) shows that RRMSD can decrease at the correlation coefficient $r > 0.5$ only. Previously [1], we estimated the correlation coefficient at 0.97.

The number of the measurement cycles n can be preset at 1–250, which allows decreasing the random error by a factor of $n^{1/2}$. The measurement results are summed up, averaged, and computer-processed. Further increase in the number of cycles has no sense, as this significantly increases the measurement time, which can be responsible for nonidentical conditions of the photometric measurement for the calibration and test solutions. The concentration of the element in solution, measured by the two-reference method, is calculated by the formula

$$C_x = C_1 + \frac{(C_1 - C_2)(\log R_x - \log R_1)}{\log R_1 - \log R_2}, \tag{2}$$

where R_x, R_1, and R_2 are the light intensity ratios at the absorption and reference bands for the test and two reference (calibration) solutions; C_x, Pu concentration in the test solution; and C_1 and C_2, Pu concentrations in the two reference (calibration) solutions, chosen so that $C_1 < C_x < C_2$.

The three (two calibration and one test) solutions are subjected to photometeric measurements in the same 1-cm cell (after washing) within the total time of ~20 s. During one working day, 2 unknown solutions can be analyzed with 5–6 observations for each of them (the instrument achieves the working regime 1.5 h after turning on).

We utilized the internal referencing principle in our previous studies on precision determination of Pu, U, Rh, and Nd [1, 2] based on their intrinsic absorption, as well as for development of a method of precision determination of Th and Pu in Arsenazo III solutions [4]. The RRMSD of the results of determining the concentrations of these elements with these techniques lies within 0.1–0.3%.

Determination of Pu(VI) in a nitric acid solution [1] utilizes a very intense band at 830.2 nm (hereinafter, 830 nm for brevity) with the molar absorption coefficient ≥500 $\mathrm{l\,mol^{-1}\,cm^{-1}}$, and a transparent segment at 700–800 nm (in this study, 720 nm) served as the reference band.

Along with the random error of measuring the light intensities, the method is characterized by the fixed error. It has the following sources: certification of the reference material; weighing in the sample preparation; nonlinear response of the recording system to the change in the analytical parameter, Pu concentration (this nonlinearity is mainly due to inaccurate determination of the coefficient taking into account the dead time of the recording system and the intensity of the input signals); temperature instability of solutions during photometric measurements; and influence of chemical impurities.

Solving the problems involved in application of the IRSP method to determination of Pu in mixed solution, reducing the fixed and random errors of the method, and widening the scope of its application called for further improvement of the analytical instrumentation and technique.

IMPROVEMENT OF INSTRUMENTATION AND SOFTWARE

To decrease the random component of the error of the method, we undertook improvement of the detection system and its software. This improved the time

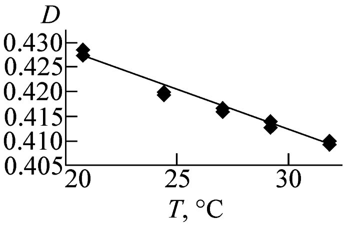

Fig. 1. Temperature dependence of the optical density of the Pu(VI) solution at 830 nm.

resolution of the system in recording one-electron pulses and made the operation of the instrument more stable via decreasing the interferences.

We created a new signal amplifier with a photomultiplier, which decreased the dead time from 380 to 80 ns and increased the signal/noise ratio from 150 to 1000. We chose the optimal discrimination threshold of the comparator and ensured its additional stabilization. To decrease the electric and other interferences, we chose an appropriate connection point for the "analog ground" and the instrument case. We revealed an additional source of error, magnetic interferences from electric motor rotating the channel switching disk. In this design, setting a magnetic shield is troublesome. Therefore, we modified the software of the instrument, namely, chose the observation time strictly divisible by the interference period. The resistance to interferences was enhanced via changing the scheme of formation of signals from the sensors of the position of the rotating disk for channel switching. We developed a microcontroller-based scheme for controlling the instrument operation, collecting the data obtained, and sending them to a PC. We developed an appropriate controlling program for the microcontroller. Also, a computer program was developed that allows the operator to control the instrument in the Windows environment, acquire information and carry out its statistical processing, print the results, and store them in a database.

Requirements to the spectral width of the monochromator slit. The measured half-width of the Pu absorption band is 3.38 nm at the Pu concentration of 0.94×10^{-3} M. The optimal spectral width of the monochromator slit at $R \to 1$ was estimated at 1.7 nm.

Role of temperature. A study of the temperature dependence of the optical density of the Pu(VI) solution at 830 nm within 20–30°C showed (Fig. 1) that the temperature coefficient of the optical density is 0.4% $\deg^{-1}$. The experiments with a Nd solution showed that, for Nd(III), the temperature coefficient for the band at 794 nm is even greater, namely, 0.8% $\deg^{-1}$. Evidently, such a temperature dependence is due not only to physical expansion of aqueous solutions, whose coefficient is only 0.03% $\deg^{-1}$, but also to a decrease in the population of the ground f levels involved in the corresponding electronic transitions of Pu and Nd.

In view of a substantial contribution of the temperature to the fixed error of the method, we had to take fairly hard measures to stabilize the temperature conditions of measurement of the Pu concentration. In the room where the two-channel spectrophotometer is located, an automatic conditioner was set to maintain a constant air temperature. Also, the optical cell holder is designed in such a way that the temperature of the cell can be maintained constant using a water ultrathermostat. These measures, combined with a brief time taken by one measurement series (~20 min), allowed decreasing the temperature component of the relative fixed error to 0.04%.

EXPERIMENTAL

Sample preparation. The initial sample of Pu with a concentration close to 10 mg g^{-1} was prepared by dissolving a reference material of metallic Pu [OSO (Branch Reference Material) 95.086–89] in hydrochloric acid which was further removed by adding HNO_3 and heating the solution on a water bath. The solutions for photometric measurements with a Pu concentration of 200–220 μg g^{-1} in 1 M HNO_3 were prepared from the initial solution of Pu by two-stage dilution by weight.

For quantitative oxidation of Pu(IV) to Pu(VI) by the reaction

$$\mathrm{Pu(IV)} + 2\mathrm{Ce(IV)} \rightleftarrows \mathrm{Pu(VI)} + 2\mathrm{Ce(III)} \qquad (3)$$

we used a 0.05 M solution of Ce(IV) in 1 M HNO_3, prepared from analytically pure grade $(NH_4)_2 \cdot Ce(NO_{3)6}$.

Nitric acid solutions of U were prepared from a U_3O_8 [GSO (State Reference Material) 2396-83P] reference material.

A reference material of the Np solution composition [SOP (Reference Material of Enterprise) RI 007-83P] with the Np concentration (corrected for evaporation) of 1.05 mg g^{-1} served as the working Np solution.

Solutions simulating corrosive impurities were prepared by the following procedures: Cr(VI) solution, from pure-grade CrO_3; Cr(III) solution, by reducing

Cr(VI) with hydrazine; Fe(III) solution, by dissolving Fe (pure grade) metallic powder in 4 M HNO_3; and Ni(II) solution, from chemically pure grade $Ni(NO_3)_2 \cdot 6H_2O$. The working solutions of the metals had the following concentrations, mg ml^{-1}: Fe 2.64, Cr(III) 2.7, Cr(VI) 2.15, and Ni 2.41.

The solution of Al(III) was prepared by dissolving 8.75 g of ultrapure-grade $Al(NO_3)_3 \cdot 9H_2O$ in 50 ml of distilled water; 1-day settling yielded a transparent solution.

INFLUENCE OF IMPURITIES

Determination of Pu in mixed solutions with U and Np. Considering that the instruments used for implementation of the IRSP method are fairly simple and inexpensive and that their use, especially with Pu-containing materials, allows the mass of Pu in the samples analyzed to be reduced by approximately an order of magnitude (compared to electrochemical methods under comparable precision of the analysis), it seems promising to extend the application field of the method from pure Pu solutions to mixed solutions containing, along with Pu, above all, U.

The U to Pu concentration ratio in these solutions was close to that in MOX fuel.

In determination of Pu in mixed nitric acid solutions, Pu was not treated to remove U. In preparation of such solution to analysis, we adjusted the HNO_3 concentration to 1 M, and the concentration of the oxidant, Ce(IV), was maintained at 0.05 M.

As calibration solutions (references) we used Pu solutions free form U. The mass fraction of Pu in the test and calibration solutions was 200–250 μg g^{-1}; the references differ in the Pu concentration by under 5%. In view of the difference in the densities of the calibration and test solutions, due to the presence in the latter of U, the mass fraction of Pu, calculated by formula (2), was multiplied by the d_0/d_x ratio, where d_0 and d_x are the densities of the calibration and test solutions, respectively. Given below are the data for Pu in mixed uranium–plutonium solutions.

Pu/U ratio, %	Number of observations	RRMSD of C_x, %	$[(C_x - C_0)/C_0]$ deviation, %
11	9	0.2	+0.14
5	9	0.23	–0.06
2.5	9	0.2	–0.02

It is seen that, in all the experiments, the ratio of the introduced, C_0, and found, C_x, Pu concentrations does not differ substantially from unity; the deviation is smaller than RRMSD.

The influence of Np was elucidated at the mass fraction of Pu in solution of ~210 μg g^{-1} and the Np/Pu ratio of 2%. Given below are the Pu concentrations calculated by Eq. (2).

Pu/U ratio, %	Number of observations	RRMSD of C_x, %	$[(C_x - C_0)/C_0]$ deviation, %
2	3	0.095	–0.11

The deviation of the average found from the taken Pu concentration was –0.11%, which is comparable to RRMSD. This suggests that, when in amount of ≤2% relative to Pu, the Np impurity does not significantly interfere with its determination.

Influence of corrosion products. To a weighed portion of Pu containing ~2.5 mg of Pu, aliquots of four solutions [of Cr(VI), Cr(III), Fe, and Ni] were added simultaneously in amounts such that the concentration of each of the impurities was 2% relative to Pu and all the concentrations made 8% in total. The solution of Pu with the mixture of corrosion products was kept for 1 day. Simultaneously with preparation of the test solution, we prepared (by weight) two calibration solutions of Pu, free form impurities. The mass fraction of Pu in the test solution was ~220 μg g^{-1}. Five observations yielded the following results: C_x RRMSD 0.24, and $[(C_x - C_0)/C_0]$ deviation, –0.12%.

When in amount of 8%, the sum of the Ni, Fe, and Cr impurities does not affect substantially the fixed error in determination of Pu by the IRSP method. In real products from the plutonium cycle, the content of the corrosion products is significantly lower.

Influence of aluminum and HF. The reference materials of the mass fraction of Pu, certified in the framework of the Program for Development of Russian Reference Materials, for Accounting and Control of Nuclear Materials are represented by PuO_2, whose stability in time is ensured through calcinations at a high temperature (close to 1200°C). However, such treatment severely complicates the subsequent dissolution of PuO_2. Obviously, when reference materials of the mass fraction are used in destructive methods, they should be dissolved quantitatively. We used the IRSP method for studying the degree of dissolution of high-calcined PuO_2 intended for certification of the RMs.

Most techniques for transferring high-calcined PuO_2 to a nitric acid solution imply addition of minor

Results of determination of the mass fraction of Pu in a solution of high-calcined PuO_2

Aliquot no.	Number of replicate measurements	RRMSD, %	Average mass fraction of Pu, %	Preparation of aliquots for analysis
1	5	0.1	87.97	Without preliminary treatment
	3	0.2	88.04	Evaporation of F^- with 3 M HNO_3 on a water bath
	4	0.1	88.12	Evaporation and introduction of 0.25 ml of 1 M $Al(NO_3)_3$ per 10 ml of the measured solution in 1 M HNO_3
2	3	0.1	88.12	Introduction of 0.25 ml of 1 M $Al(NO_3)_3$ per 10 ml of the measured solution
3	7	0.1	88.05	Introduction of 1 ml of 1 M $Al(NO_3)_3$ to 30 ml of the intermediate solution

amounts of HF. Even after removal of excess HF the solution can contain the fluoride ion interfering with the spectrophotometric determination of Pu via hindering its conversion to the hexavalent state because of formation of complexes with Pu(IV) and Ce(IV).

The logarithms of the stability constants of PuF^{3+} and PuF_2^{2+} in the perchlorate medium were estimated at $\log K_1 = 7.87$ and $\log K_2 = 6.67$, respectively [5]. The fluoride complexes of Ce(IV) are comparable in stability with the Pu(IV) complexes. However, considering that in the analytical technique the Ce concentration is 50 times that of Pu, we can expect predominant complexing with the F^- for Ce(IV) rather than for Pu(IV). However, formation of the CeF^{3+} complex decreases the ionic potential of Ce^{4+}, thereby decreasing the redox potential of the CeF^{3+}/Ce^{3+} couple relative to the Ce^{4+}/Ce^{3+} couple, which is responsible for a shift of equilibrium (3) to the left.

For binding free fluoride ions by the reaction $Al^{3+} + 6F^- \rightarrow AlF_6^{3-}$, we introduced a 10–30-fold excess of Al into aliquots of the solutions with the Pu concentration of ca. 0.001 M before photometric measurements. Since prolonged storage of Pu solutions in 4.5 M HNO_3 can involve accumulation of the HNO_3 decomposition products (in particular, of HNO_2), we evaporated the weighed portions of the solution on a water bath before introducing Al. The table presents the mass fractions of Pu in PuO_2, calculated from the measured results.

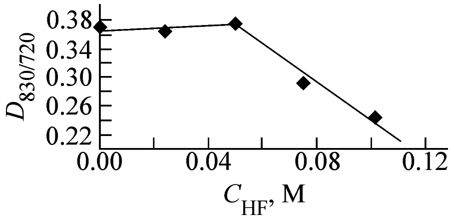

Fig. 2. Optical density of Pu solution at 830 nm, measured with respect to the transmission band (720 nm), as a function of the HF concentration in solution of the composition, M: 0.8×10^{-3} Pu(VI)–0.05 Ce(IV)–1 HNO_3.

To estimate how the sample preparation affects the results of determination of Pu by the IRSP method, we carried out one-factor analysis of the variance of the tabulated data. Additional operations of binding of free F^- ions or their removal from the solution by evaporation proved to affect the spectrophotometric results insignificantly. The lack of influence of the sample preparation allows us to consider all the tabulated data as uniform and belonging to the same population.

Next, we studied in detail how HF in concentrations of up to 0.1 M affects reaction (3) at the concentrations, M, of Pu of 0.8×10^{-3}, Ce, of 5×10^{-2}, and HNO_3, of 1.

We took weighed portions of Pu and introduced the required volume of solution of 0.48 M HF, whereupon the resulting solutions were kept for 3–15 h. Next, a Ce(IV) solution was added, the volume was brought to 10 ml, the solutions were weighed, and the molar concentration of Pu was calculated. The solutions were subjected to photometric measurements both immediately after their preparation and in regular intervals; in further calculations by formula (4) we used the average values $\bar{R}$

$$D_{830/720} = \log(\bar{R}/\bar{R}_0) = \varepsilon Cl, \qquad (4)$$

where $\bar{R}_0$ is the average ratio of the light intensities for air, equal to 0.341; $\bar{R}$, average ratio of the light intensities for the solution; l, cell length; and ε, molar extinction coefficient.

Figure 2 presents the optical density of the solution at 830 nm, measured with respect to the transmission band (720 nm), as a function of the HF concentration. A clear inflection is observed at $C_{HF}/C_{Ce} = 1$, which suggests complete binding of Ce into CeF^{3+}. As C_{HF} in solution further increases, a precipitate appears in the solution, and the latter loses color; at $C_{HF} = 0.24$ M, CeF_4 precipitates completely.

Thus, our studies showed that the presence of HF in the solution with the composition of interest (see above) does not prevent oxidation of Pu and its determination up to $C_{HF} = 0.05$ M.

Also, we examined the molar extinction coefficient of Pu(VI) as dependent on the time of keeping of the solution of Pu with $C_{HF} = 0.024$ M. Within 2 h, the molar extinction coefficient remained unchanged, 488.0 ± 0.6 $1\,mol^{-1}\,cm^{-1}$ (RRMSD 0.11%).

APPLICATION OF THE IRSP METHOD TO CERTIFICATION OF THE REFERENCE MATERIALS

Earlier, we more than once applied the IRSP method to measuring the mass fraction of Pu in solutions free from impurities. The reference materials certified to the mass fraction of Pu using the IRSP method are as follows: Pu metal composition, GSO 8567–2004; RM of the composition of solution: $^{239}Pu/^{240}Pu$, OSO 95.836–2002; ^{242}Pu, GSO 8568–2004; and the isotope labels $^{235}U/^{238}U/^{240}Pu$ and ^{240}Pu prepared by the Radium Institute for the Analytical Laboratory for Guarantees, IAEA, [6] and Institute of Reference Materials and Measurements (IRMM) [7].

Given below are the results of the certification analysis of the ^{242}Pu solution for the mass fraction of the total Pu, illustrating the application of the IRSP method.

For calibration we used solutions of the reference material of the composition of Pu metal GSO 8567–2004 with the relative error of the mass fraction of Pu of 0.05%.

Method	IRSP	IDMS
($C_{Pu} \pm \Delta$), mg g^{-1}	0.9155 ± 0.0006	0.9157 ± 0.0019
Number of determinations	48	4
Relative total error, %	0.06	0.21

For certification measurements, we took three ampules with the ^{242}Pu solution. A total of 48 measurements were carried out; the relative random error of the result was 0.04% for the confidence level $p = 0.95$.

For control measurement of the mass fraction of the total Pu in the ^{242}Pu solution, we applied isotope dilution mass spectrometry (IDMS) with OSO 95.836–2002, characterized by a certified value of the mass fraction of ^{239}Pu in solution, as the label.

The results obtained by two different analytical methods are totally consistent.

Thus, we improved the instrumentation and technique for spectrophotometry with internal reference. The IRSP method was also applied to certification of the reference Pu materials in studies of the solubility of high-calcined PuO_2. The relative random error achieved was 0.04%. The relative fixed error is determined by the error for the reference materials used. Comparison of the results obtained by IRSP and IDMS revealed no bias.

The influence of U, Np, Fe, Ni, Cr, and Al impurities and the fluoride anions on the fixed and random errors of the method was studied. The suitability of the precision IRSP method was demonstrated, and its application limits (with RRMSD of 0.1–0.2%) for analysis of mixed Pu solutions were established.

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[1] This ^{240}Pu solution was further certified by the Institute for Reference Materials and Measurements (Geel, Belgium) as Spike Isotopic Reference Material IRMM-083.