A Precision Spectrophotometric Method for Determining U, Pu, Nd, and Rh, Based on the Internal Standardization Principle

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Abstract—The principle of spectrophotometric determination of the concentrations of elements based on internal standardization of the sample analyzed is presented. As the function of the parameter to be determined, namely, the concentration of element in solution, we suggest the ratio of two signals, one of which is the light intensity at the wavelength of an absorption band of an element being analyzed and the other is the reference signal of a sample, namely, the light intensity at a wavelength at which the solution of the element being analyzed is virtually transparent. The analysis is performed with a specially designed two-channel spectrophotometer in which fairly strict correlation between the signals is provided by measuring their intensities virtually simultaneously, with the same detector and amplification system. The signals are isolated by a monochromator and interference light filters. The spectrophotometer operation control and data processing are effected by a PC. The metrological characteristics of the method proposed were experimentally determined. The relative root-mean-square deviation of the uranium, plutonium, neodymium, and rhodium concentrations in pure solutions of their salts was within 0.1–0.25%.

Increase in the precision of analytical procedures for determining uranium and plutonium in various nuclear materials is still urgent in view of the necessity of their strict accounting both at concentrating facilities and spent fuel processing enterprises. Also, high-precision methods are required for certification of the corresponding reference samples.

The precision of certain modern methods for determining uranium and plutonium that are widely practiced now in inspections as part of national and international systems of guarantee measures for nuclear nonproliferation can be estimated using the so-called “target indices,” that is, relative root-mean-square deviations which, for the most of the utilized methods, lie within 0.1–0.3 % [1]. The commonly used high-precision methods of determining uranium and plutonium in nuclear materials are potentiometric titration [2, 3], gravimetry [4], isotope dilution mass spectrometry [5], and coulometry [6].

It is believed that spectrophotometric methods are of little use for the precision analysis of uranium and plutonium because of their substantially lower accuracy. However, McLaren and MacDonald showed fairly recently [7] that under sufficiently stabilized conditions of photometric measurements and repeated scanning of the absorption spectrum, hexavalent plutonium can be determined with a relative error of about 0.1%.

As an alternative, the precision of spectrometric measurements can be increased by utilizing the internal standardization principle. It involves simultaneous measurement of the light absorption of the solution analyzed when illuminated with unfiltered (“white”) light in two spectral ranges, one of which contains the analytical band of the element to be determined, and the other is a transparent window, for which the transmission of the solution is taken as 100%. As the analytical signal we suggest the intensity ratio for the analytical band and the transparent window, rather than the absolute intensity of the light that passed through the solution at the absorption wavelength. In view of the fact that the variations of the intensities in both spectral ranges, which originate from the light source instability, drift of the amplification coefficient of the amplification system, poor reproducibility of the geometric position of the cell, etc., are largely correlated, the relative inaccuracy of determining the intensity ratio should be lower than in the direct measurements. If the root-mean-square deviations of the directly measured light intensities in both spectral ranges are approximately the same, the relative random error of measuring the intensity ratio can be determined as [8]

\[ \delta^2_R = 2s^2(1 - r). \]  

† Deceased.
Here, $\delta$ is the relative root-mean-square deviation of the directly measured intensities, $\delta_R$ is the relative root-mean-square deviation of the intensity ratio, and $r$ is the correlation coefficient.

Equation (1) shows that the relative root-mean-square error in measuring the analytical signal, i.e., the intensity ratio, can decrease only at the correlation coefficient $r > 0.5$.

The above-mentioned method of internal standardization can be realized to a fairly full extent for nitric acid solutions of uranyl. The absorption spectrum of uranyl ions in perchlorate and nitrate solutions consists of three major overlapping bands at 404, 416, and 428 nm and two very weak bands at 470 and 490 nm [9]. At wavelengths above 500 nm uranyl solutions in dilute HNO₃ virtually do not absorb light (are transparent).

Internal standardization can be applied in the case of hexavalent plutonium. In nitric acid solutions it exhibits a very intense absorption band at 830 nm with the molar extinction coefficient over 400 l mol⁻¹ cm⁻¹ and has ranges of virtually no absorption in the interval 700–800 nm.

The absorption spectra of Nd(III) and Rh(III) solutions also contain transparent ranges at wavelengths of 650 and 700 nm, respectively.

The aim of this work was to design equipment for realizing the internal standardization principle, to work out the corresponding procedures for determining uranium and plutonium, as well as neodymium and rhodium, and to obtain the metrological characteristics of these procedures.

**EXPERIMENTAL**

**Equipment.** For measuring the concentrations of uranium, plutonium, and other elements using the internal reference, we designed a two-channel spectrophotometric analyzer (Fig. 1).

In this instrument, non-filtered (“white”) light from the incandescent lamp (stabilized power supply) is passed through the cell containing the solution analyzed, whereupon it is split into two beams. Then, the intensities at the analytical absorption band, reference band, corresponding to ca. 100% transmission of the solution analyzed, and the background of the recording system are determined using the same detector and amplification system. This provides a fairly good correlation between the signals. The analytical band is isolated with a monochromator, and the reference band (transparent “window”), with narrow-band interference filters with the transmission band width of 4–5 nm; the background is measured when the light source is fully screened. Channels are switched by a switching unit designed as a rotating disk with slit-like holes at different distances from the center.

These measurements are carried out in cycles, with the program controlled by the one-photon pulse counting method. Each measurement cycle takes 1.8 s (i.e., 0.6 s per channel) and yields the ratio $R$ of the light intensities corrected for the dead time of the instrument. This ratio can be calculated by the following equation, valid at small $k$:

$$R = \frac{(J_t - J_b) + k(J_t - J_a) + k^2(J_t - J_a)}{(J_a - J_b)}$$

$$\approx \frac{(J_t - J_b)}{(J_a - J_b)} + \frac{k}{(1 - k)} \frac{(J_t - J_a)}{(J_a - J_b)},$$

where $J_a$ is the light intensity at the analytical band, $J_t$ is the light intensity at the reference band, $s^{-1}$; $J_b$ is the background intensity, $s^{-1}$; and $k$ is the ratio of the molar extinction coefficients of the element analyzed at the reference and analytical bands.

The number of measurement cycles can be varied from 1 to 250.

The results of the corresponding measurements are summed up and averaged.

The optical density of the solution of the element analyzed $D$ can be calculated by the formula

$$D = \log(\frac{R}{R_0}).$$