

Determination of Impurity Elements in High-Purity Solid Precursors Based on Tantalum Pentoxide by Inductively Coupled Plasma Mass Spectrometry

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Received April 11, 2013; in final form, November 13, 2013

Abstract—Conditions for the inductively coupled plasma mass-spectrometric (ICP MS) analysis of high-purity tantalum pentoxide and tantalum pentoxide doped with rare-earth elements without the separation of a sample matrix from analytes (Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo, Sn, W, Gd, Dy, Er, and Pb) were determined. The metrological parameters of ICP MS analysis (accuracy, precision, and detection limits) were calculated. It was established that, in the analysis of test sample solutions with tantalum concentrations higher than 30 mg/L, a matrix effect appeared: the intensity of the measured ion current of analytes decreased against the background of a high concentration of sample matrix (tantalum) ions. This caused a proportional underestimation of the results of analysis. It was shown that it is reasonable to plot calibration functions against the background of a solution containing no more than 30 mg/L of tantalum ions. The results of the ICP MS analysis were compared with X-ray fluorescence (XRF) and optical emission spectrometry (OES) analysis data and calculation data on the amounts of admixtures introduced into tantalum pentoxide at the stage of the extraction preparation of a precursor.

Keywords: high-purity tantalum pentoxide, tantalum pentoxide doped with rare-earth elements, inductively coupled plasma mass-spectrometric analysis, analytical signal intensity drift, standard and certified samples, metrological parameters

DOI: 10.1134/S1061934814060069

The relationship between the impurity content and the properties of pure tantalum pentoxide is qualitatively and quantitatively ambiguous. Some of these relations can be predicted theoretically; however, as a rule, a relationship between the composition and property of a substance is established experimentally without extrapolation from high to low concentrations of admixtures. In the current production of semiconductor materials and substances for the manufacture of optical fibers and microelectronic elements, admixtures with concentrations to $10^{-5}\%$ or lower should be controlled.

Radiochemical [1], mass-spectrometric, and atomic spectrometry methods with the preconcentration of admixtures or their separation from a matrix are used for the analysis of tantalum metal and tantalum oxides. As a rule, the preconcentration is performed using extraction methods from fluoride solutions [2–4]. Sorption methods for the separation of a matrix from analytes also found use.

Impurities in high-purity tantalum and niobium were determined by inductively coupled plasma atomic emission spectrometry after the sorption separation of tantalum and niobium ions on a Poliorgs VII

sorbent [5]. The limits of detection (LODs) of the impurities varied from 1×10^{-5} to $10^{-3}\%$. According to published data [6–11], the LODs after the separation of impurity elements varied from 1×10^{-6} to $10^{-3}\%$. In the analysis of Nb and Nb₂O₅, the LODs of 1–10 ng/g were obtained for a number of elements, including Ca and Fe [11]. It is likely that these LODs were reached as a result of the preliminary separation of analytes from a matrix on an anion exchanger with the use of an SPQ 9000 quadrupole mass spectrometer. Under standard conditions, the LODs of 0.2 and 0.3 ng/L for Ca and Fe, respectively, can be reached in the analysis of high-purity solutions. These data were reported by SchelTec (the authorized distributor of Perkin Elmer) in accompanying documentation to an ELAN 9000 DRC-e mass spectrometer.

Impurities in high-purity tantalum with the limits of detection at a level of $1 \times 10^{-5}\%$ were determined by ICP MS analysis [12]. The liquid–liquid extraction of sample matrix ions from aqueous solutions containing HF and HCl with methyl isobutyl ketone was used. The ions of Nb, V, Zr, Hf, and W remained in the aqueous phase, and tantalum passed to the organic phase.

In the determination of isotopes in tantalum neutron-producing targets, ICP MS analysis with the preliminary liquid–liquid extraction of tantalum was used [13, 14]. Rare-earth elements whose isotope ratios were strongly different from natural ones were detected in the targets. In connection with this, the analysis was complicated by an isobaric effect. The isotopes of rare-earth elements were separated by ion chromatography.

The matrix effect created by the ions of the main component of a test sample can substantially influence the analytical signal intensity. Elizarova and Ryzhukhina [15] observed this phenomenon in the ICP MS analysis of high-purity niobium pentoxide. They observed a decrease in the intensity of signals due to Ca, Fe, Ti, Mg, and Si in the analysis of solutions with an increase in the niobium content to more than 15 mg/L; in this case, the element : niobium ratio was 1 : 50 or higher. A considerable decrease in the analytical signal intensity of admixtures (signal drift) was observed on the prolonged continuous passing of a sample through the solution injection system into the measuring system of a mass spectrometer. The occurrence of a matrix effect of niobium ions (50–1000 mg/L) on the results of the determination of impurities in Nb₂O₅ was noted by Novikov [16]. The plasma-chemical formation of niobium oxides and their deposition as a glassy layer around skimmer and sampler openings, which can considerably change the results of sample analysis, were referred to as a hypothesized cause.

Shengging et al. [17] considered ICP MS analysis after the electrothermal evaporation of niobium pentoxide powders in a graphite cell with fluorinating agent additives. They also described possible polyatomic effects. Shengging et al. [17] indicated the occurrence of a matrix effect at a niobium concentration of 140 mg/L in the test solution. The absolute limit of detection of 0.026–1.1 pg was reached in the determination of Ti, Ta, W, Cr, Ni, Cu, and Mn.

In a recent survey publication, Karandashev et al. [18] summarized data on the analysis of high-purity substances with the use of ICP MS, in particular, on quadrupole mass spectrometers. They considered the matrix effect on the determination of impurity elements and noted in general recommendations that, in the direct analysis of solutions, the test samples should be diluted to a matrix component concentration of 100 mg/L. However, in this case, the instrument sensitivity can be decreased by a factor of 1.5 even in the analysis of three or four samples. The analysis of test samples with a W matrix and Cr, Ti, and Mn in the solutions of gallium was given as an example. It was noted that the development of methods for the direct analysis of the solutions of solid samples without pre-concentration as a simpler version for introducing this method into the routine practice of laboratories is of considerable current interest. Evans and Giglio [19] described in detail the interferences of ions and the

influence of this phenomenon on the results of the determinations of impurities in high-purity compounds and also reported data on the matrix effect.

Thus, almost all of the above studies were dedicated to the determination of analysis conditions with the preliminary separation of impurities from the sample matrix because of the matrix effect of tantalum and niobium. The safe level of a matrix concentration of tantalum in solutions for the direct ICP MS determination of impurity concentrations remains an open question.

The aim of this work was to study the application of inductively coupled plasma mass spectrometry and to optimize conditions for the determination of Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo, Sn, W, Gd, Dy, Er, and Pb in solid precursors based on high-purity and specifically doped tantalum pentoxide.

EXPERIMENTAL

Instrumentation and equipment. A ViBRA AF-R220CE Shinko Denshi laboratory balance (special accuracy rating according to GOST [State Standard] 24104-01), an electronically operated Varta TP 703 muffle furnace with temperature controlled to within $\pm 2^\circ\text{C}$, Digi Tubes (the United States) or Handy-Pak (Canada) polypropylene test tubes, platinum crucibles, Eppendorf (10, 50, and 100 μL) or BIOHIT (10–50, 50, and 100 μL) pipettes with relative error of no higher than 2%, and disposable Eppendorf or BIOHIT tips were used.

The measurement of mass spectra and quantitative elemental analysis were carried out on an ELAN-9000 DRC-e instrument (Perkin Elmer, the United States), which combines the effective characteristics of the excitation of ions with the aid of inductively coupled plasma and the low LODs. The instrument has a liquid sample injection system resistant to HF: a riton transverse-flow spray chamber with a demountable HF-resistant torch. A distinctive special feature of the mass spectrometer is the special geometry of a plasma torch formation zone, sample injection system units, and torch cooling, which are responsible for the absence of noticeable interactions between the torch quartz tube and the test sample aerosol.

The quadrupole of the mass spectrometer has a mass transmission range from 2 to 270 amu. The ELAN software developed by Perkin Elmer makes it possible to automatically consider and correct a number of influences and to determine silicon, calcium, and iron based on the ²⁸Si, ⁴⁴Ca, ⁴³Ca, ⁵⁴Fe, and ⁵⁷Fe isotopes. In the course of measurements performed with the use of the program files of a method, the operator can introduce correction equations, which take into account the effects of ions, and the coefficients of these equations are calculated based on the natural abundance of the isotope.

Standard substances, reagents, and calibration solutions. High-purity gaseous argon according to GOST 10157-79 was used; it was supplied to the mass spectrometer as the following three flows: (1) a cooling and plasma-forming flow, (2) a flow regulating the position of a plasma torch relative to the burner, and (3) a sample aerosol carrier.

High-purity concentrated HF and HNO₃ (GOSTs 10484-78 and 11125-84, respectively) preliminarily distilled with the aid of a BERGHOF infrared distillation system were used as reagents for the acid decomposition of test samples. Potassium hydrofluoride of high-purity grade, which was recrystallized and dried, was used in decomposition by melting and pharmaceutical H₂O₂ was used for complex formation. The Milli-Q A10 five-step water purification system with electrical resistance control (18.0–18.4 MΩ) made it possible to obtain deionized water that meets the requirements of GOST R 52501-2005.

The following standard solutions were used: Tune Solution Std ELAN & DRS-e no. 1 from Perkin Elmer based on 5% HNO₃ containing Be, Ce, Co, Bi, Ni, Pb, In, Mg, and U at an initial concentration of 10 mg/L and diluted to 10 μg/L for the adjustment and optimization of the mass spectrometer and Tune Solution Std ELAN & DRS-e nos. 2, 3, and 5 based on 5% HNO₃ containing Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo, Sn, W, Gd, Dy, Er, and Pb (10 mg/L each) for the preparation of calibration solutions. The Tune Solution Std ELAN & DRS-e no. 5 contained 1% HF.

The following reference solutions prepared with the use of the standard samples (1.0 g/L with 1% error in certified values) of ions were used for the operational control and the quality of the analysis of calibration characteristics: GSO 7190 (Mg), GSO 7854 (Al), GSO 8212 (Si), GSO 8065 (Ca), GSO 7205 (Ti), GSO 7774 (the V), GSO 8035 (Cr), GSO 8056 (Mn), GSO 8032 (Fe), GSO 8089 (Co), GSO 8001 (Ni), GSO 7998 (Cu), GSO 8858 (Zr), TA Perkin Elmer Pure Atomic Spectroscopy Standard (Ta), OF GSO 8086 (Mo), GSO 7238 (Sn), 15-189 NB Perkin Of Elmer Pure Atomic Spectroscopy Standard (Nb), OF GSO 9117 (W), (GSO 8390 (Gd), GSO 7012 (Pb), and high-purity trivalent Dy and Er oxides.

The stock solutions of decomposed samples were diluted before analysis to a tantalum concentration of no higher than 30 mg/L. The background concentration of tantalum ions in reference and calibration solutions was created by the addition of a TA Perkin Elmer Pure Atomic Spectroscopy Standard (Ta) solution so that it would be the same as in the solutions of the test samples.

Tantalum pentoxides prepared at the Solikamsk Magnesium Plant (SMZ) and certified by the metrologists of this plant with a confidence probability of 0.95% were used as O.S.-1, O.S.-2, and O.S.-7 reference samples; a certified sample of Ta₂O₅ according to

TU [Technical Specifications] 48-4-408-78 (TAO-1) was also used. Table 1 summarizes the composition of these samples.

Calibration was carried out using an external standard by plotting a function that passed through the origin of the Cartesian coordinates. The calibration functions were taken as acceptable at an approximation coefficient of no lower than 0.999. The accuracy of the plotting of calibration functions was checked by a comparison between certified and experimental concentrations in the analysis of reference solutions prepared with the use of the GSO standard solutions of test ions. The relative standard deviation of all parallel measurements did not exceed 0.04. The uncertainty δ_0 in the preparation of calibration solutions did not exceed 2%.

Sample preparation. The ICP MS determination of admixtures in tantalum pentoxide was conducted immediately after the decomposition of the samples. Tantalum pentoxides obtained upon the extraction processing of rare-metal raw materials at the Tananaev Institute of Rare Element and Mineral Chemistry and Technology, Kola Research Center, Russian Academy of Sciences and certified and standard Ta₂O₅ samples from SMZ were analyzed. The complete decomposition of undoped high-purity tantalum pentoxides was performed by acid digestion with the use of distilled HF (5 mL) and HNO₃ (15 mL); in this case, the formation of insoluble fluorides was not observed.

In the closed acid digestion, the weighed portions of samples (70–100 mg) were placed in Digi Tubes (the United States) or Handy-Pak (Canada) 50-mL polypropylene test tubes and HF was initially added. The test tubes were tightly closed with screw stoppers and kept in a water bath at 90–100°C for 1–2 h; then, HNO₃ was added until the complete dissolution of Ta₂O₅; the solution was cooled to room temperature, and 5–10 drops of pharmaceutical H₂O₂ were added for the stabilization of ions in the highest degree of oxidation as the constituents of oxygen-containing complexes to prevent disproportionation and hydrolysis. The freshly precipitated niobium and tantalum hydroxides (in the form of acids) are dissolved in an excess of mineral acids and H₂O₂ with the formation of complex compounds, and the water solubility of the hydrated complex compounds [NbOF₃]²⁻ is higher than the solubility of [TaF₇]²⁻ by a factor of 10–12 [20]; this is responsible for the stability of solution upon the complete dissolution of a sample. The stability of the dissolved samples was confirmed by the automatic calculation of $s_r \leq 0.04$ in the computer-assisted quantitative analysis.

The stock solutions of samples after acid decomposition with a volume of 50 mL contained 5 mL of distilled HF. Before the supply to the injection system of the mass spectrometer, they were diluted in a ratio of 1 : 40–1 : 60 depending on the weight of a sample. Thus, the concentration of HF in analyzed solutions

Table 1. Results of the mass-spectrometric analysis of the O.S.-1, O.S.-2, and O.S.-7 standard samples of Ta₂O₅ produced at SMZ (%)

| Element | O.S.-1 | | | O.S.-2 | | | O.S.-7 | | | LOD ^{***} , µg/L |
|---------|---------------------|---------------------|-----------------------------|-------------------|-------------------|-----------------------------|-------------|-------------------|-----------------------------|------------------------------|
| | certified | found* | error ^{**} δ, % | certified | found* | error ^{**} δ, % | certified | found* | error ^{**} δ, % | |
| Mg | 0.00021 ± 0.00005 | 0.00019 ± 0.00005 | 9.5 | 0.00039 ± 0.00006 | 0.00035 ± 0.00007 | 10.3 | 0.10 ± 0.02 | 0.094 ± 0.018 | 6.0 | 0.0150 |
| Al | 0.00024 ± 0.00005 | 0.00027 ± 0.00006 | 12.5 | 0.00053 ± 0.00003 | 0.00060 ± 0.00003 | 14.0 | 0.10 ± 0.02 | 0.101 ± 0.021 | 0.7 | 0.0383 |
| Si | 0.00027 ± 0.00005 | 0.00026 ± 0.00005 | 3.7 | 0.00067 ± 0.00012 | 0.00072 ± 0.00013 | 7.5 | 0.10 ± 0.02 | 0.091 ± 0.017 | 9.0 | 0.0420 |
| Ca | — | 0.00040 ± 0.00006 | — | — | 0.0025 ± 0.0004 | — | 0.10 ± 0.02 | 0.092 ± 0.018 | 8.0 | 0.0270 |
| Ti | 0.00069 ± 0.00006 | 0.00056 ± 0.00007 | 8.1 | 0.00089 ± 0.00004 | 0.00072 ± 0.00006 | 19.1 | 0.10 ± 0.02 | 0.098 ± 0.014 | 2.0 | 0.0105 |
| V | 0.00010 ± 0.00002 | 0.00082 ± 0.00012 | 18.0 | 0.00030 ± 0.00005 | 0.00033 ± 0.00005 | 10.0 | 0.10 ± 0.02 | 0.092 ± 0.016 | 8.0 | 0.0233 |
| Cr | 0.00010 ± 0.00003 | 0.00085 ± 0.00017 | 15.0 | 0.00030 ± 0.00007 | 0.00027 ± 0.00006 | 10.0 | 0.10 ± 0.02 | 0.101 ± 0.015 | 1.1 | 0.0133 |
| Mn | 0.00010 ± 0.00002 | 0.00098 ± 0.000016 | 2.0 | 0.00030 ± 0.00007 | 0.00028 ± 0.00006 | 6.7 | 0.10 ± 0.02 | 0.101 ± 0.013 | 1.0 | 0.0088 |
| Fe | 0.000156 ± 0.000025 | 0.000166 ± 0.000022 | 6.4 | 0.00032 ± 0.00005 | 0.00036 ± 0.00004 | 12.5 | 0.10 ± 0.01 | 0.0999 ± 0.0051 | 0.1 | 0.0250 |
| Co | 0.00010 ± 0.00001 | 0.00011 ± 0.00002 | 10.0 | 0.00030 ± 0.00003 | 0.00031 ± 0.00004 | 3.3 | 0.10 ± 0.02 | 0.089 ± 0.012 | 11.0 | 0.0200 |
| Ni | 0.00010 ± 0.00002 | 0.00012 ± 0.00003 | 20.0 | 0.00030 ± 0.00005 | 0.00027 ± 0.00004 | 10.0 | 0.10 ± 0.02 | 0.097 ± 0.017 | 3.0 | 0.0101 |
| Cu | — | 0.00040 ± 0.00005 | — | — | 0.00051 ± 0.00009 | — | 0.10 ± 0.01 | 0.096 ± 0.011 | 4.0 | 0.0106 |
| Zr | — | 0.00015 ± 0.00002 | — | — | 0.00058 ± 0.00008 | — | — | 0.091 ± 0.011 | — | 0.0107 |
| Nb | — | 0.0025 ± 0.0003 | — | — | 0.0050 ± 0.0006 | — | — | 0.0064 ± 0.0007 | — | 0.0200 |
| Mo | — | 0.00010 ± 0.00003 | — | — | 0.00030 ± 0.00004 | — | — | 0.00032 ± 0.00005 | — | 0.0138 |
| Sn | 0.00010 ± 0.00003 | 0.00013 ± 0.00004 | 30.0 | 0.00030 ± 0.00007 | 0.00027 ± 0.00005 | 10.0 | 0.10 ± 0.01 | 0.088 ± 0.006 | 12.0 | 0.0391 |
| W | — | 0.00060 ± 0.00005 | — | — | 0.00070 ± 0.00006 | — | — | 0.00081 ± 0.00008 | — | 0.0231 |
| Pb | 0.00010 ± 0.00001 | 0.00011 ± 0.00002 | 10.0 | 0.00030 ± 0.00004 | 0.00031 ± 0.00004 | 3.3 | 0.10 ± 0.02 | 0.094 ± 0.017 | 6.0 | 0.0116 |

* Determined based on three parallel samples in three series of analysis.

** The value certified in the O.S. standard samples was taken as a reference value.

*** Determined in a solution containing 30 mg/L of tantalum.

was lower than 0.08%; this did not lead to noticeable interaction of an aerosol with the quartz burner. In this case, the LOD of silicon was 0.0420 $\mu\text{g/L}$.

Silicon was determined 1 h after the digestion of samples in a Speedwave BERGHOF MWS-3+ microwave digestion system (Germany) with a set of fluoroplastic autoclaves with built-in contactless temperature and pressure sensors. The airtight conditions of autoclave digestion at a temperature to 230°C and a pressure to $\sim 10^4$ kPa (100 atm) made it possible to rapidly transfer test samples into solution with a mixture of HF–HNO₃ (1 : 3) without the noticeable losses of silicon as volatile tetrafluoride.

We failed to completely transfer tantalum pentoxides doped with rare-earth elements into solution in the polypropylene test tubes in a water bath because of the strengthening of an oxide lattice after alloying and heat treatment at a temperature higher than 1000°C. A portion of the sample remained in the form of insoluble sediment. The sediment was decomposed by melting with potassium hydrofluoride in platinum crucibles at 700°C. The melts were leached with deionized water with the addition of high-purity H₂SO₄ and transferred into the polypropylene test tubes, and 6–10 drops of pharmaceutical H₂O₂ were added. The sample solutions were diluted to 50 mL by the addition of 2% HNO₃ immediately before the analysis.

Conditions for analysis. The inductively coupled plasma discharge was maintained at atmospheric pressure and a temperature of about 6000°C; in this case, the plasma power was 1100–1350 W, the spraying gas flow rate was 0.80–1.2 L/min, and the ion lens voltage was 6–11 V.

The main working units of the mass spectrometer were adjusted and optimized immediately before the analysis in order to maintain a maximum analytical signal intensity at a minimum intensity of oxide (no more than 1.5%) and divalent ions (no more than 3%). The limits of detection of Si, Ca, and Fe were calculated in the automatic mode with the use of the ELAN software and the dynamic reaction cell (DRC) system with the inflow of high-purity methane from Aldrich (99.998%). The optimization of DRC operation made it possible to determine operating conditions for providing the minimum limits of detection of Si, Ca, and Fe: nebulizer gas flow rate, 0.86 L/min; cell gas flow rate, 0.1 mL/min (for Si, Ca, and Fe); DRC mode cell path voltage, –15 V; DRC mode quadrupole rod offset, –6.5 V; and rejection parameters q of 0.10, 0.55, and 0.40 V for Si, Ca, and Fe, respectively.

The analysis was carried out under the conditions of clean room facilities. The clean room was separated from laboratory rooms by a lobby, and it had two accommodations for performing ICP MS analysis and sample preparation, respectively. The walls and ceilings of the accommodations were plastic-coated, and the floor was covered with antistatic linoleum, under which a copper grounding mat was arranged. An

increased atmospheric pressure was maintained in the accommodation for dust control. The ventilation system was equipped with two types of filters: a rough filter as filtering cloth fixed on a profile and a FyaS 13s36.P fine filter (class 1; effectiveness, 99.95%; maximum flow, 0.56 m³/s; and maximum depression, 250 Pa). The temperature conditions of 20–23°C were provided with a self-contained heater. Wet cleaning with the use of distilled water was carried out in the accommodations before analysis on a daily basis. Operators used working clothes, disposable shoe covers, headgear, and talc-free gloves only for operations in the clean room. The above measures ensured the necessary level of analytical cleanliness.

RESULTS AND DISCUSSION

The controlled impurities at all of the stages of the extraction preparation of high-purity tantalum pentoxide and tantalum pentoxide doped with different elements were chosen based on the requirements of TU 48-4-408-78. The results of analysis were checked by the Perkin Elmer standard addition method and with the use of reference solutions based on the GSO samples of the test analyte ions as external standards.

In the analysis of solutions with high tantalum contents, the matrix effect, which manifests itself in the suppression of the analytical signal of an analyte, can be an important factor affecting error in the determination of analytes. According to published data, the main reasons for the matrix effect can be the following: the influence of matrix ions on the scattering of analyte ions on their transport into the high-vacuum part of the mass spectrometer, a change in the physicochemical parameters of the migration of a solution or aerosol in the sample injection system, the influence of the physicochemical nature of a matrix component, the state of the working surfaces of cones and other parts of the interface, and difference in the mass numbers of test and matrix ions [18]. In this context, it is important to choose a limiting salt solution concentration on the dilution of test samples.

We studied the effect of a change in the concentration of tantalum ions on the analytical signal of impurities to be determined. For this purpose, we consecutively analyzed model solutions containing from 1 to 60 mg/L of tantalum and 10 $\mu\text{g/L}$ of an analyte. Each particular measurement was accompanied by the preliminary and subsequent washing of the sample injection system of the mass spectrometer with a control 2% solution of the digestion acid mixture.

The analytical signal intensity remained stable for all elements up to a Ta concentration of 30 mg/L; in this case, the concentrations of the controlled impurities differed from a specified value of 10 $\mu\text{g/L}$ by no more than 5%. As the concentration of tantalum was increased from 30 to 60 mg/L, the determined concentration of impurities considerably decreased (Table 2). At a tantalum concentration of 60 mg/L,

Table 2. Deviations of the results of the determination of elements from a reference analyte concentration of 10 µg/L with changes in the tantalum content of solution (%)

| Concentration of Ta, mg/L | Mg | Al | Si | Ca | Ti | V | Cr | Mn | Fe |
|---------------------------|-------|------|-------|-------|------|------|------|------|------|
| 30 | 2.5 | 2.2 | 3.4 | 3.3 | 2.9 | 2.8 | 2.1 | 2.4 | 4.1 |
| 40 | 9.14 | 5.95 | 14.99 | 7.25 | 5.21 | 5.53 | 6.57 | 6.45 | 6.75 |
| 50 | 12.79 | 9.69 | 16.09 | 10.14 | 7.55 | 9.84 | 6.75 | 8.02 | 6.33 |
| 60 | 29.3 | 19.7 | 23.7 | 18.1 | 16.2 | 17.1 | 15.2 | 15.7 | 14.9 |
| Concentration of Ta, mg/L | Co | Ni | Cu | Zr | Nb | Mo | Sn | W | Pb |
| 30 | 2.0 | 2.1 | 2.0 | 1.8 | 1.8 | 1.6 | 2.0 | 1.9 | 3.0 |
| 40 | 6.22 | 6.05 | 5.21 | 5.87 | 7.57 | 5.68 | 6.07 | 8.35 | 11.5 |
| 50 | 9.70 | 9.50 | 7.38 | 9.74 | 9.84 | 8.62 | 8.14 | 12.0 | 16.3 |
| 60 | 15.8 | 15.1 | 12.5 | 13.7 | 18.0 | 13.7 | 15.4 | 13.0 | 29.4 |

the result of analysis for lead was almost 30% lower than the specified concentration. It is evident that the matrix effect is significant for not only lead but also light analytes, for example, magnesium and silicon. For this reason, the degree of dilution of solutions in the routine analysis of test samples was chosen in such a way that the final concentration of tantalum was no higher than 30 mg/L.

We tested the stability of the ion current of test elements at a tantalum ion concentration of 30 mg/L. Figure 1 shows the results. The measurements were performed on a real-time basis with the continuous supply of a sample solution to the instrument for 1 h 40 min. Tune Solution Std ELAN & DRS-e nos. 2, 3, and 5 based on 5% HNO₃ containing Pb, Mn, Ni, Cr, Co, Cu, Al, Mg, Fe, Si, Zr, Sn, Ca, Nb, V, Mo, Ti, Gd, Dy, and Er (7.5 µg/L each) in the presence of 30 mg/L of tantalum were used. This analyte : tantalum ratio in the determination of an impurity in a solid precursor corresponds to an impurity concentration level of 10⁻²% in tantalum pentoxide.

We found that a considerable drift of the analytical signal was characteristic of only niobium; its signal intensity decreased in accordance with nearly exponential dependence, whereas the ion current measured with the detector was stable for the other analytes. It is believed that the deposition of sample components at the orifices of cones did not occur at the matrix component (tantalum) concentrations to 30 mg/L in the analyzed solution. The drift of the analytical signal of niobium in the first 100 s from the passage of a test sample into the mass spectrometer was insignificant, and it did not exceed 5%, which is sufficient for performing quantitative analysis.

In the determination of the concentration of niobium in tantalum pentoxide by calibration graph and standard addition methods, the repeatability of the results was 95% at a 15- to 25-s duration of the preliminary passage of a test solution through the measuring

system before the determination of the analyte. Repeated measurements were performed with alternating them with the washing of the injection system with a control digestion solution for 1–2 min. For determining all of the other analytes, the condition of supplying a solution into the instrument were not so strictly limited.

The effect of the concentration of tantalum ions in solution on the determination of rare-earth elements was studied in a range of 1–30 mg/L of tantalum, that is, in the absence of a matrix effect, as demonstrated in Fig. 2. It is evident that, in this range, tantalum ions do not exert a matrix effect on the determination of rare-earth elements. At a tantalum concentration of 30 mg/L, an error in the results of the determination of 10 µg/L of test rare-earth elements did not exceed 5%.

Analysis of high-purity tantalum pentoxide. The O.S.-1, O.S.-2, and O.S.-7 reference samples of tantalum pentoxide produced and certified at SMZ were analyzed for evaluating the accuracy of analysis under intermediate precision conditions (time and operator were variable factors). With the use of the standard addition method, the additives of standard multielement solutions with a concentration of 0.015–0.075 mg/L were introduced into a diluted (1 : 50) solution of the digested tantalum pentoxide sample (70–90 mg in 50 mL of solution) with a tantalum concentration of 23–30 mg/L to obtain linear functions like $y = ax + b$, where y is the analytical signal of the test sample component, and x is its concentration. The ratio of the absolute term of the linear function to its slope made it possible to calculate the desired analyte concentration in the pentoxide. Table 1 summarizes the results. It was demonstrated that the results of measurements were consistent with the certified concentrations. The error δ (%), which was calculated as the degree of proximity of the obtained result of analysis to the reference values (certified concentrations in

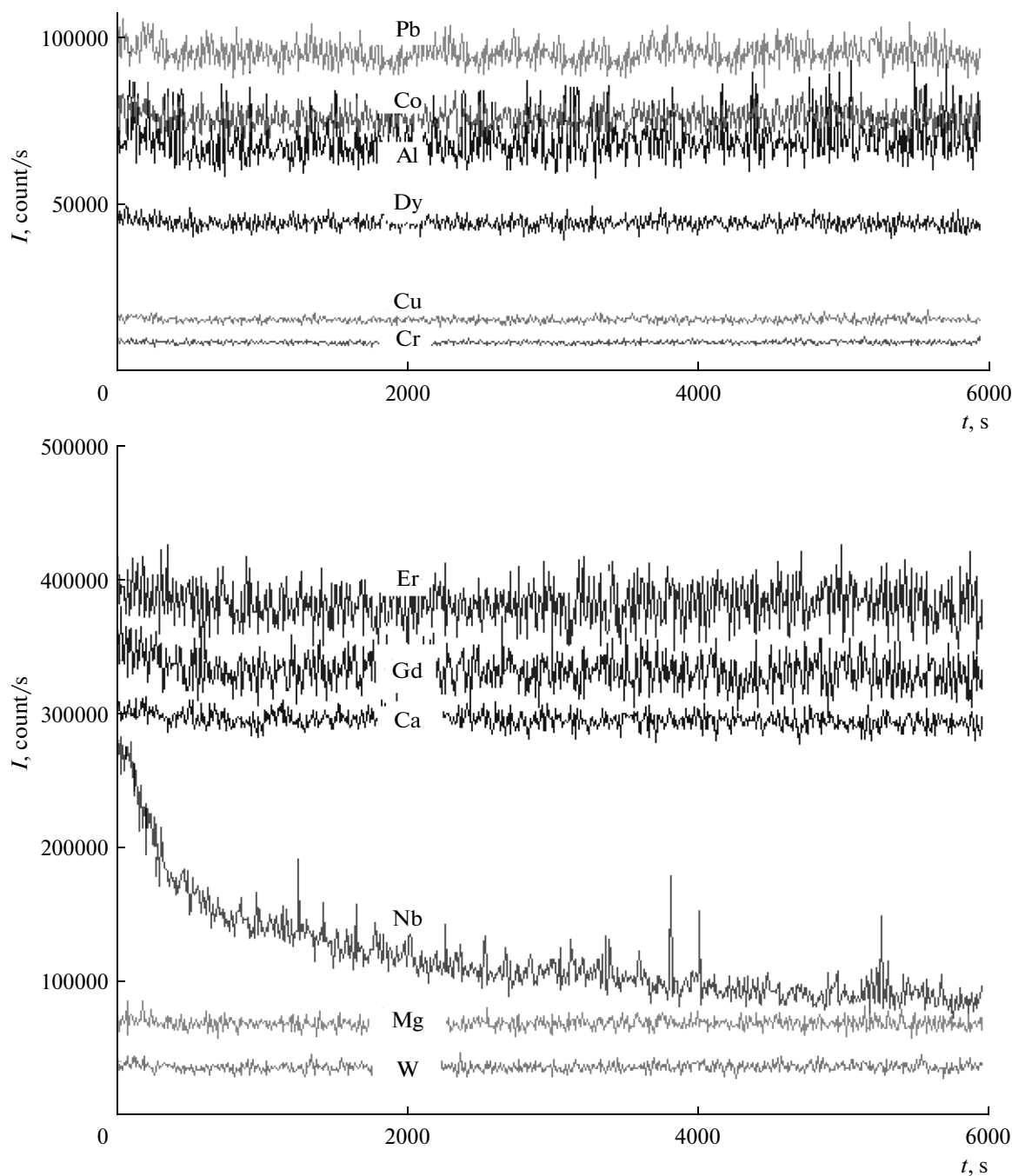


Fig. 1. Intensity of analyte signals (7.5 $\mu\text{g/L}$) in the real-time mode with the continuous supply of test solution containing 30 mg/L of Ta into the mass spectrometer.

standard tantalum pentoxide), was used for evaluation tests.

The LODs of controlled impurities (Tables 1 and 3) were determined based on a $3s$ value using a control sample of a calibration solution—2% HNO_3 with the addition of 30 mg/L of tantalum ions (15-81TA Perkin Elmer Pure Atomic Spectroscopy Standard)—and a control sample of the acid digestion of tantalum pentoxide with the same additive of tantalum ions. The

sample dilution factors were as high as 20000–33000; they were taken into account for the calculation of LODs in solid test samples. For rare-earth elements, the LODs were 1.51, 1.87, and 1.31 ng/L for Gd, Er, and Dy, respectively.

The reproducibility of the results of parallel measurements was evaluated according to data on $s_r \leq 0.04$. The automatic statistical processing of the results of three replicate measurements in the regime of peak

jump analysis (three measurements at each peak) was used; the peaks were scanned three times in each replicate measurement. Thus, in the detection, one measurement result was obtained based on the data of 27 analytical signal measurements. The samples were digested using three parallel weighed portions; three dilutions were made for each solution. The result of analysis was determined as the arithmetic mean value of three measurements. Three series of such measurements were performed.

After the evaluation of the accuracy of ICP MS data based on the accuracy of analysis of standard samples and tantalum pentoxide produced at SMZ, we analyzed the samples of high-purity tantalum pentoxide prepared by an extraction technology at the Tananaev Institute of Rare Element and Mineral Chemistry and Technology, Kola Research Center, Russian Academy of Sciences [21]. Table 3 indicates that the results obtained using ICP MS analysis and optical emission spectrometry with an arc atomization source on a DFS-13 instrument in accordance with a procedure developed at the Tananaev Institute of Rare Element and Mineral Chemistry and Technology are consistent. A discrepancy was observed only in the determination of calcium. This can be due to the absence of data on calcium concentrations in the standard samples of high-purity tantalum pentoxide. The OES determinations were performed with the use of a

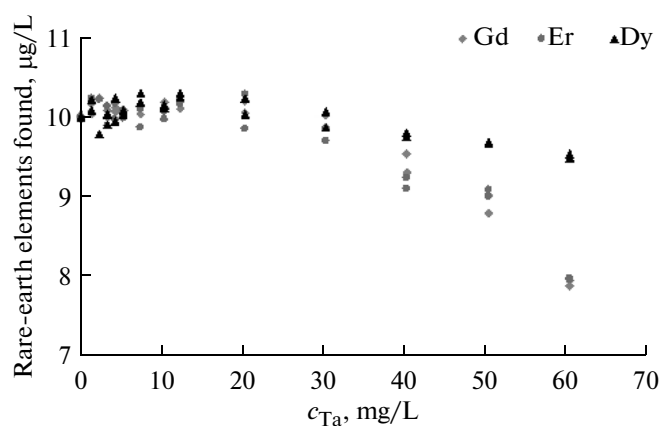


Fig. 2. Effect of the tantalum content of the test solution on the determination of rare-earth elements (dopants); 10 μg/L of rare-earth elements were added to a sample.

reference mixture of high-purity Ta₂O₅ with an additive of high-purity CaO.

Analysis of specifically doped tantalum pentoxide. The doped solid precursors Ta₂O₅ : Gd, Ta₂O₅ : Dy, and Ta₂O₅ : Er were obtained based on an extraction technology in the laboratory of electronic materials at the Tananaev Institute of Rare Element and Mineral Chemistry and Technology in accordance with meth-

Table 3. Results (wt %) of the ICP MS and OES analysis of high-purity Ta₂O₅ (TO-1) according to TU 48-4-408-78

| Element | LOD*, μg/L | TU 48-4-408-78 (TaO-1), no more than | ICP MS** | OES |
|---------|------------|---|----------|---------|
| Mg | 0.0308 | — | 0.00022 | 0.0002 |
| Al | 0.0381 | 0.0005 | 0.00017 | <0.0005 |
| Si | 0.0531 | 0.001 | 0.00087 | <0.001 |
| Ca | 0.103 | — | 0.0004 | 0.0025 |
| Ti | 0.0281 | 0.0001 | 0.00018 | <0.0003 |
| V | 0.0019 | 0.00001 | 0.000008 | <0.0005 |
| Cr | 0.0101 | 0.00005 | 0.000044 | <0.0002 |
| Mn | 0.0027 | 0.00001 | 0.000010 | <0.0002 |
| Fe | 0.0852 | 0.0005 | 0.0006 | <0.0007 |
| Co | 0.0019 | 0.00001 | 0.000009 | <0.0005 |
| Ni | 0.0153 | 0.00002 | 0.000015 | <0.0005 |
| Cu | 0.0027 | 0.00001 | 0.00001 | <0.0005 |
| Zr | 0.0202 | — | 0.000081 | <0.0005 |
| Nb | 0.0318 | 0.02 | 0.0021 | 0.002 |
| Mo | 0.0007 | 0.00005 | 0.000013 | <0.0005 |
| Sn | 0.0020 | — | 0.00015 | <0.0005 |
| W | 0.0195 | 0.0001 | 0.00010 | — |
| Pb | 0.0086 | 0.00001 | 0.00009 | <0.0005 |

* Determined in the sample acid digestion solution of high-purity Ta₂O₅.

** Determined based on three parallel samples in three series of analysis.

Table 4. Comparison between the results of XRF and ICP MS analysis of the solid precursors of Ta₂O₅ doped with gadolinium

| Concentration of Gd in Ta ₂ O ₅ , wt % | | | Consistency with calculation data, % | | Consistency between XRF and ICP MS analysis data, % |
|--|--------------|-----------------|--------------------------------------|-----------------|---|
| calculation data | XRF analysis | ICP MS analysis | XRF analysis | ICP MS analysis | |
| 0.11 | 0.110 | 0.102 | 100.00 | 92.73 | 92.73 |
| 0.24 | 0.256 | 0.239 | 93.33 | 99.58 | 93.36 |
| 0.53 | 0.592 | 0.522 | 88.30 | 98.49 | 88.18 |
| 0.87 | 0.943 | 0.989 | 91.61 | 86.32 | 95.12 |
| 1.39 | 1.43 | 1.27 | 96.91 | 91.15 | 88.42 |
| 1.73 | 1.69 | 1.88 | 97.69 | 91.21 | 88.64 |
| 2.60 | 2.38 | 2.57 | 91.62 | 98.77 | 92.19 |
| 3.71 | 3.68 | 3.81 | 99.22 | 97.30 | 96.50 |

Table 5. Comparison between the results of the ICP MS analysis of the solid precursors of Ta₂O₅ doped with dysprosium and erbium and calculation data

| Concentration of rare-earth elements in Ta ₂ O ₅ , wt % | | | Consistency with calculation data, % | |
|---|-------|------|--------------------------------------|-------|
| calculation data | Dy | Er | Dy | Er |
| 0.1 | 0.101 | 0.12 | 99.00 | 80.00 |
| 0.5 | 0.52 | 0.51 | 96.00 | 98.00 |
| 1.0 | 1.05 | 0.87 | 95.00 | 87.00 |
| 1.5 | 1.53 | 1.35 | 98.00 | 90.00 |
| 2.0 | 1.97 | 1.84 | 98.50 | 92.00 |
| 3.0 | 2.90 | 2.88 | 96.67 | 96.00 |

ods described previously [22, 23]. These precursors are used as components in the synthesis of the homogeneously doped charge of lithium tantalate and the growth of single crystals of high optical quality from it.

Tables 4 and 5 summarize the results of the mass-spectrometric determination of gadolinium, dysprosium, and erbium in Ta₂O₅, which are consistent with the calculated values based on the weighed portions of dopants introduced at the stage of the preparation of Ta₂O₅ precursors. The repeatability was 80.00–99.58%. The correspondence of the results of analysis to calculated values simultaneously reflects both the quality of analysis and the quality of the precursor preparation procedure. The consistency of the results of XRF and ICP MS analysis of Ta₂O₅ doped with erbium with a calculated concentration of 0.5% was 91.07%; for the samples doped with gadolinium, it varied from 88.18 to 96.50% over the entire range of doping.

ACKNOWLEDGMENTS

We are grateful to T.E. Shchur and O.V. Rybalkina, staff members of the analytical department of the Tananaev Institute of Rare Element and Mineral

Chemistry and Technology, Kola Research Center, Russian Academy of Sciences. This work was supported by a grant for leading scientific schools (project no. NSH 1937.2012.3).

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Translated by V. Makhlyarchuk