Deep Tellurium Purification for the Production of Electronic and Photonic Materials

M. B. Grishechkin[a], E. N. Mozhevitina[a], A. V. Khomyakov[a], M. P. Zykova[a],
R. I. Avetisov[b], *, and I. Kh. Avetissov[a]

[a] Mendeleev University of Chemical Technology of Russia, Moscow, 125047 Russia
[b] OOO Armoled, Moscow, 125047 Russia
*e-mail: igor_avetisov@mail.ru
Received @@, @

Abstract—To carry out the process of obtaining high-purity tellurium by the vacuum distillation method, a reactor design consisting of high-purity quartz glass and graphite is proposed. During the process, the tellurium melt evaporates; and the vapor is transferred from the hot part of the system to the colder one and condenses in the form of a solid phase (distillate) without the formation of a liquid. Regularities in the redistribution of impurities between the distillate and the cube stillage residue, as well as the spatial distribution of impurities in the distillate during the purification of metallic tellurium, are studied. It is established that some impurities, for example, s-metals, Zn, Ni, and V, and rare metals, are distributed uniformly along the length (20 cm) of the distillate. At the same time, Se tends to concentrate in the far (from the still) part of the distillate with a difference of more than one order of magnitude than in the near part.

INTRODUCTION

Currently, high-purity tellurium (6N or better) is widely used in the semiconductor industry and IR optics [1−5]. In [6−8], the description of the preparation of high-purity tellurium by the so-called "wet" methods is given, including the steps of transferring the initial tellurium to the solution in an oxidized form, followed by selective reduction by sulfur (IV) compounds or by electric current. However, such methods have low productivity, they are associated with high labor costs and consumption of high purity acids and reagents, and also with the formation of significant quantities of liquid waste that require utilization. ~~However, such methods have low productivity levels and are associated with high labor costs, the consumption of high purity acids and reagents, and also with the formation of significant quantities of liquid waste that require recycling.~~ The most common methods for obtaining high-purity tellurium are vacuum distillation and zone melting [9, 10]. The theory of these processes is described clearly in [11]. The production of significant amounts of tellurium with a purity above 6N remains an urgent problem. One of the main impurities in the commercially available technical tellurium is selenium [11, 12]. It is known that the vapor phase above the alloys in the Se−Te system has a complex composition at temperatures of ~800 K, when the vacuum distillation of tellurium is

usually carried out [11, 13]. At low concentrations of selenium in the tellurium melt, the vapor consists predominantly of Te_2, $Se_{(2-8)}$, and $TeSe_{(1-6)}$ molecules [15, 16]. As the temperature rises, the fraction of complex molecules decreases. The main components of the vapor are Te_2, Se_2, and Se_4 molecules and complex $Se_{(1-4)}Te$ molecules. The higher partial pressure of molecules containing selenium makes it possible in principle to purify tellurium from selenium by vacuum distillation.

When developing the technology ~~for obtaining~~ high-purity tellurium, the primary attention is paid to reducing the number of operations and increasing the yield of purified tellurium [1, 17]. The ~~aim~~ of this work is to study the process of vacuum distillation of tellurium, which represents the evaporation of tellurium from the melt, the transfer of the vapor to the colder part of the system, and vapor condensation in the form of a solid phase (distillate), bypassing the liquid. The whole process was carried out in a dynamic vacuum, which ensured an ~~effective~~ mass transfer of the vapor phase.

METHODOLOGY

Impurity analysis. The concentration of impurities in the initial tellurium, ~~cube stillage~~, and distillate was determined by inductively coupled plasma mass spec-
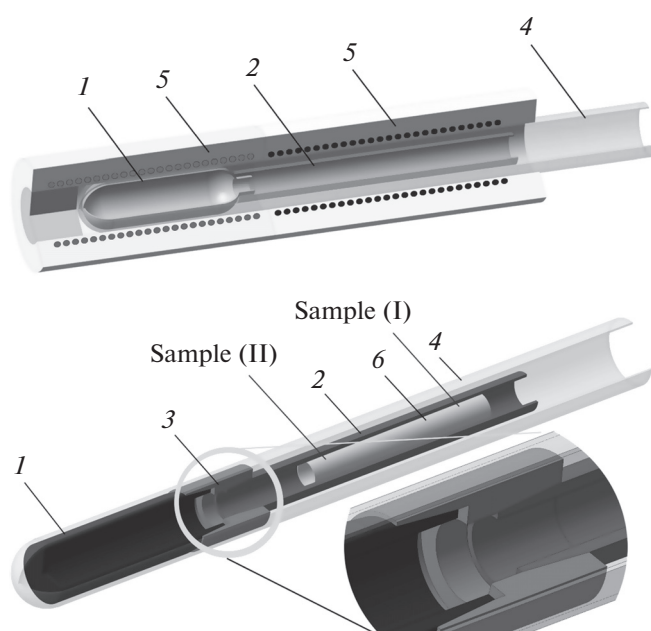
Fig. 1. Scheme of plant for tellurium purification by vacuum distillation using quartz reactor (a) and quartz reactor with graphite parts (b): *1*—still; *2*—receiver; *3*—diffuser; *4*—reactor housing made of quartz glass; *5*—two-zone resistive furnace; *6*—tellurium distillate.

trometry. The measurements were performed using a NexION 300D mass-spectrometer (Perkin Elmer, United States) in the collision mode (KED) [18]. The measurement conditions are given below:

Nebulazer type	Concentric (Meinhard), PFA
Nebulazing chamber	Two-pass Scott chamber, PFA
Argon flows, l/min:	
- through nebulizer	0.96
- plasma forming	15
- auxiliary	1.2
Generator power, W	1450
Gas collision flow (He), l/min	4.6
Scanning cycle number	10

The impurity concentration in Te was determined by the method of PerkinElmer Total Quant [19]. This method allows us to determine the concentration of 68 chemical elements in one measurement and it is suitable for the semiquantitative comparative analysis of the samples. When using Total Quant, the relative error in determining the concentrations of impurity elements was 25% and increased to 100% in concentrations close to the detection limit [19].

To dissolve the Te samples (~200 mg), 5 mL of nitric acid (HNO_3) obtained by surface distillation

(BSB-929-IR, Berghof, Germany) corresponding to an acid brand of high purity (GOST (State Standard) 11125-84) was used with a purity of 99.9999 wt % (68 elements). The resulting solution was diluted by a factor of 10 with deionized water. The electrical resistance of the deionized water used (H_2O, Aqua-MAX-Ultra 370 Series, Young Lin Instruments, South Korea) was 18.2 MΩ cm, and the purity relative to the 68 elements was 99.99999 wt %. Indium was used as the internal standard in the analysis.

Method of distillation. Distillation was carried out in a reactor under a dynamic vacuum of not less than 10^{-5} mm Hg (Fig. 1a). The internal diameter of the reactor was 40 mm with a total length of 700 mm. A still with the initial material and a receiver for the distillate were placed inside the reactor. Three types of reactors were used. Reactor (I) and all the internal elements were made of fused quartz glass of the Kg1dA brand (according to State Standard 15130-86). All parts of the reactor were alternately etched with concentrated nitric acid and 10% hydrofluoric acid and repeatedly washed with deionized water.

Reactor (II) was also made of quartz glass of the Kg1dA brand; however, in contrast to reactor (I), a pyrolytic coating was deposited onto all its internal parts, obtained by the pyrolysis of high-purity acetone TU 6-09-3513-86 (5N relative to inorganic impurities). After pyrolysis, the parts of the reactor were repeatedly washed with high-purity acetone.

The reactor body (III) was fabricated of quartz glass of the Kr1dA brand (Fig. 1b). The internal parts included a distillation cube, a receiver, and a diffuser. The diffuser is designed to regulate the flow of the vapor from the distillation cube to the receiver. All the internal parts were made of extremely pure graphite (MG-1, OOO PKP VIAL, Russia).

Before carrying out the process of tellurium purification, reactors of all types were annealed at temperature $T = 1200$ K for 6 hours under a dynamic vacuum of 10^{-5} mm Hg.

The loaded reactor was placed inside a two-zone resistive furnace, evacuated to 10^{-5} mm Hg, and heated to the set temperature with an accuracy of ±1 K under the conditions of a dynamic vacuum. After the distillation process was completed, the reactor was cooled to room temperature, the distillate was extracted, and the samples were taken from its various parts.

RESULTS AND DISCUSSION

The original material for purification was tellurium 3N8 of the TA-1 brand (manufactured by the Mining and Metallurgical Company Norilsk Nickel). During the distillation in the quartz glass reactor (I), the distillate adhered to the walls of the receiver. At the same time, difficulties arose in extracting the distillate, and, as a consequence, the product, the purity of which was
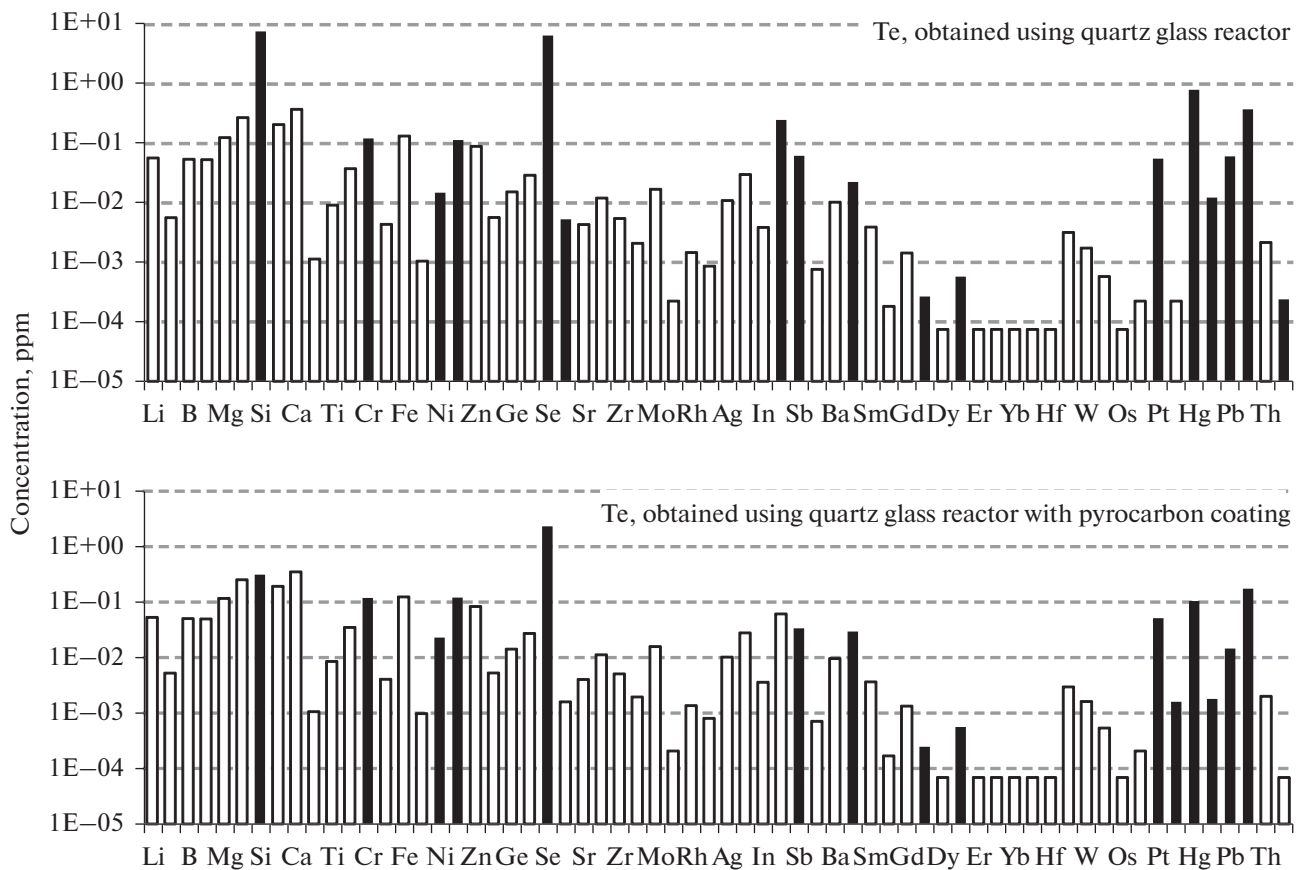
Fig. 2. Distribution of impurity concentrations in tellurium after distillation in quartz reactor (a) and in pyrocarbon-coated reactor (b). Hereinafter, *1*—measured impurity concentrations; *2*—limits of detection of impurity elements.

4N8 (Fig. 2a, Table), was additionally contaminated. An attempt to reduce the adhesion of tellurium to the quartz walls by applying pyrolytic coating on them [20] (reactor (II)) did not lead to a significant improvement in the distillate purity, 5N5 (see Fig. 2b). A detailed analysis showed that the pyrolytic coating had micropunctures, which were formed due to defects in the quartz glass.

In the next design, all the internal elements of the reactor were made of high-purity graphite instead of quartz glass. The adhesion of tellurium to bulk graphite is much lower than to the thin pyro-carbon coating.

Table 1. Content of main substance in samples of tellurium obtained under various conditions with and without allowance for detection limit (DL) wt %

Specimen / process description	Substance content, % (wt)	
	with DL	without DL
Original TA-1	99.988	99.989
Distillation in quartz glass reactor	99.9982	99.9984
Distillation in reactor with pyrocarbon	99.9995	99.9997
Distillation in reactor with graphite rigging:		
Residue in distillation cube	99.9910	99.9913
Distillate	99.99931	99.99952
Specimen (I)*	99.99936	99.99958
Specimen (II)*	99.99967	99.99992

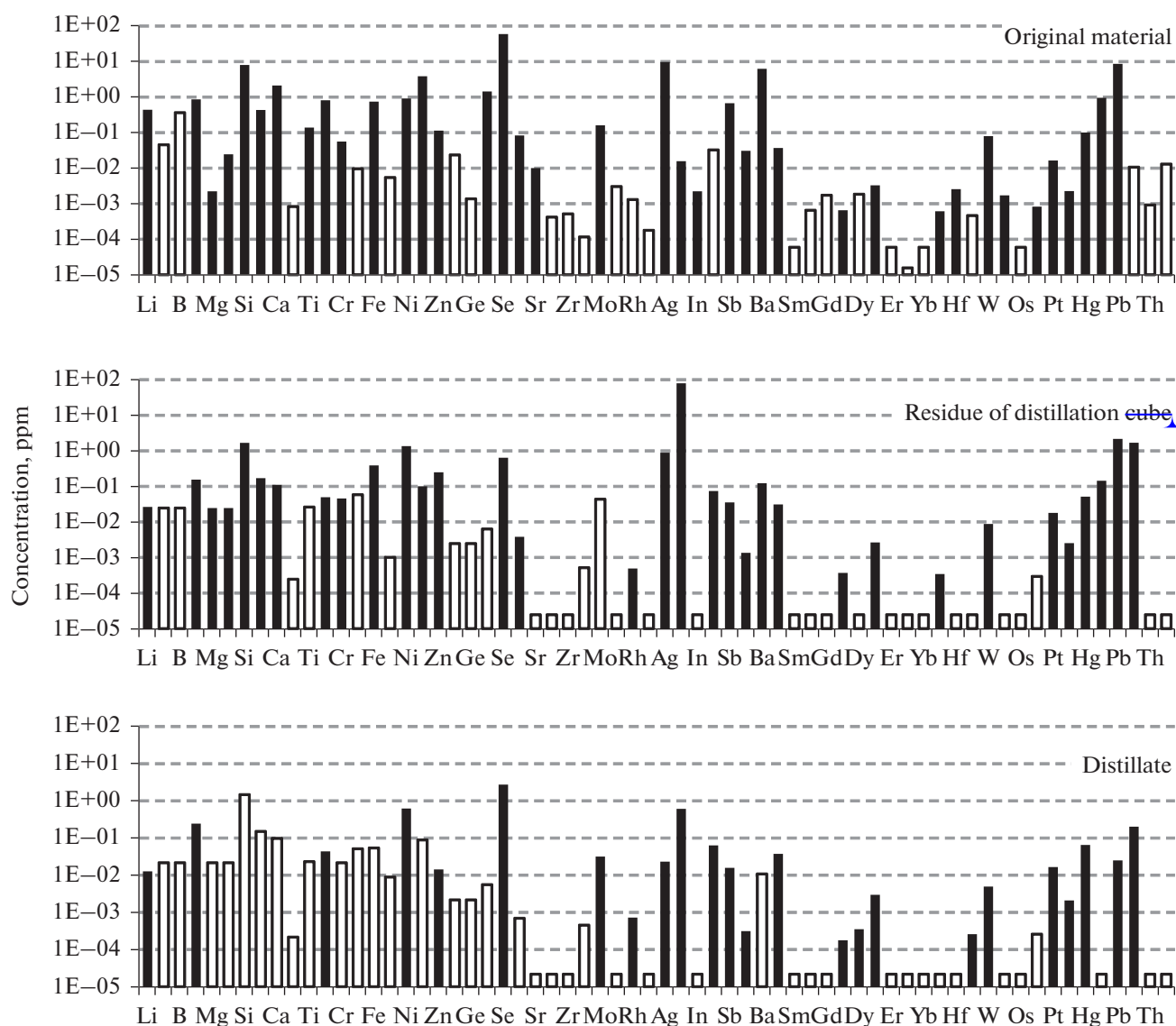* Sampling site is shown in Fig. 1b.

Fig. 3. Distribution of impurity concentration in tellurium samples before (a) and after (b, c) distillation process in reactor equipped with high-purity graphite: (a) original material; (b) bottom residue of distillation cube; (c) distillate.

Therefore, the use of bulk graphite made it possible to overcome the problem of the distillate sticking and reduce the contamination associated with unloading the product, which in turn made it possible to obtain a preparation with purity 5N5 (Fig. 3).

The patterns of the distribution of impurities between the distillate and the bottom residue of the distillation cube, as well as the distribution of impurities along the length of the distillate (20 cm), were studied. According to [13], at the temperature of the distillation process, the vapor pressure of selenium exceeds the vapor pressure of tellurium by approximately two orders of magnitude. Theoretically, the distillation process is promising for the quantitative removal of selenium impurities from tellurium. However, in practice, a single distillation leads to a decrease

in the concentration of selenium by one order of value (see Fig. 3).

In addition, it was established that some impurities, such as alkali metals, Zn, Ni, and V, and rare earth metals, are distributed uniformly along the length of the distillate. Selenium, in contrast, demonstrates a pronounced distribution: in the far part of the distillate (off the distillation cube, Fig. 4a), the Se concentration exceeds the concentration of Se in the near part by an order of magnitude (Fig. 4b). This can be explained by the spatial separation of the $Se_{(1-8)}$, $TeSe_{(1-7)}$, and Te_2 molecules in the vapor phase at a distillation temperature of ~800 K due to the difference in the partial pressures [15]. Among the listed molecules, Te_2 will have the smallest partial pressure. Therefore, the samples of tellurium condensing in the
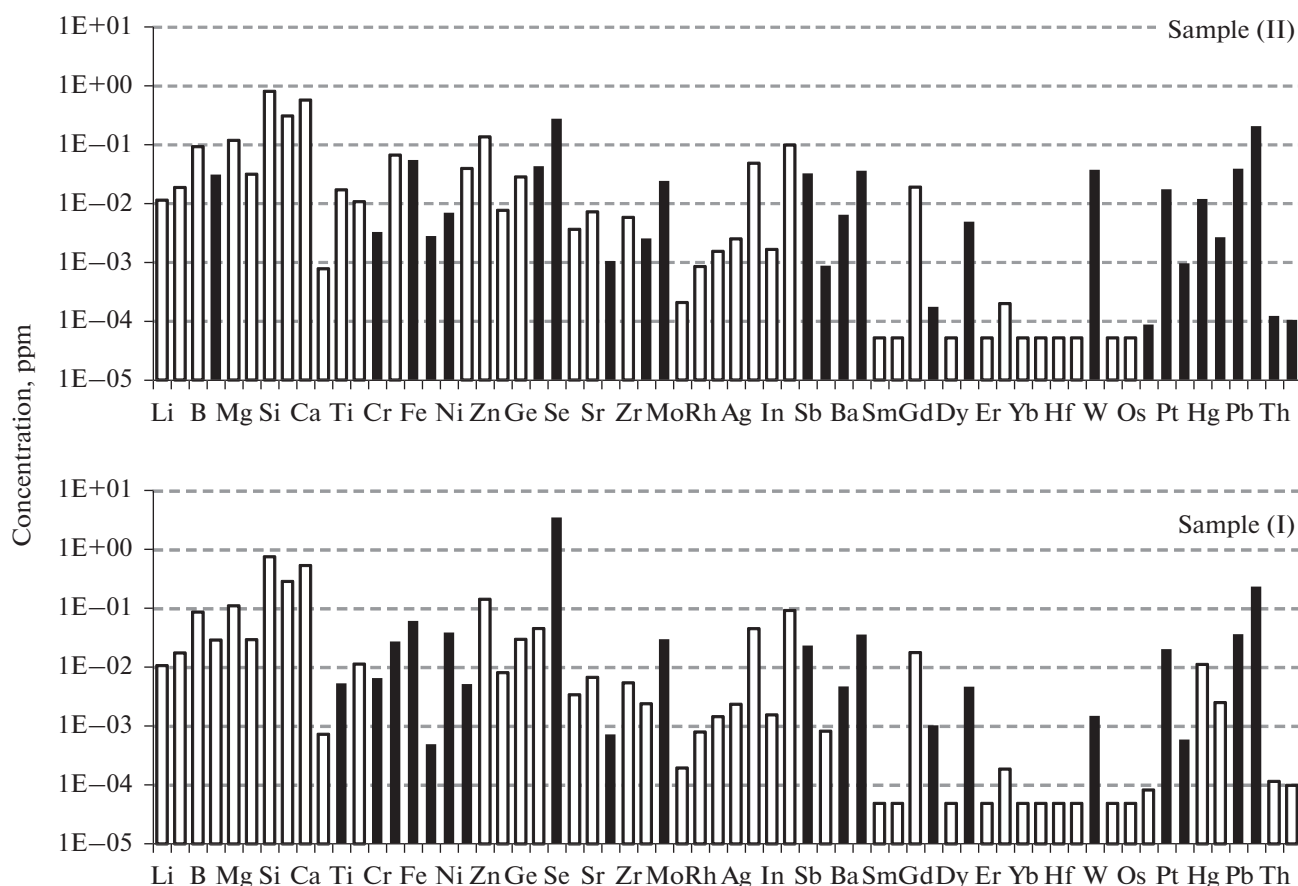
Fig. 4. Distribution of impurity concentration in tellurium distillate along length of graphite receiver: (a) sample (II); (b) sample (I).

far part of the distillation ~~cube~~ of the receiver contained more selenium than the samples taken closer to the ~~cube~~. The final yield of the product with a purity of at least 99.9999 wt % was 20%.

CONCLUSIONS

The developed method of vacuum distillation allows us to reduce the concentration of most impurities to a level of 10^{-5} to 10^{-6} wt %. However, the average residual concentration of Se in the distillate remains at the ppm level. Meanwhile, part of the distillate located closer to the distillation ~~cube~~ has a purity level of 99.99992 wt % at a selenium concentration of 0.27 ppm with a yield of ~20%.

ACKNOWLEDGMENTS

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