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Development of Super-Pure ($7N^+$) Liquid Gallium Analytical Sample Preparation for GDMS Analysis

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The application of the membrane nanotechnology for obtaining super-pure (up to $8N$) non-crystalizing over-cooled big mass (>30 g) gallium melt by refinement of commercially available $5N\div 6N$ purity gallium, give us opportunity to obtain unique samples in order to develop a new methodology of analytical sample preparation for GDMS analysis, which excludes artifacts tied to impurity atoms segregation on the analytical Ga sample surfaces. Using comparison of results of GDMS analysis of samples prepared by the existed method and by the new method from the essays of initial $6N$ commercial gallium and super-pure ($7N^+$) gallium obtained by the membrane purification from the initial gallium, we have determined the most reliable analytic procedure for the final check on the production and certification of super-pure (up to $8N$) gallium.

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1. Introduction

Achievements in the field of obtaining super-pure ($\geq 7N^+$) substances and their application in practice are directly related to the development of experimental methods of analysis of impurity concentration in them. Therefore, the reliability problem of the impurity concentration analysis in simple substances having more than $6N$ purity level remains urgent and requires great effort for individual specific cases, which is conditioned by the absence of super-pure (up to $8N$) standards of substances (etalons).

Spark source mass spectrography [1] and glow discharge mass spectrometry (GDMS) [2] are the most common of the modern analysis methods of content level determination of impurities in the case of high-purity gallium. Methodology of optical spectrum analysis [1, 3, 4] enables one to determine separate impurity concentration in gallium with an accuracy of 10 ppb, which is sufficient to define gallium purity level up to $6N$ (but not higher) with satisfactory reliability; whilst, using GDMS analysis, in the case of gallium, most of the impurities (with a few exceptions) can be determined with an accuracy of 1 ppb and accordingly gallium sample purity level can be specified up to $8N$.

However, distorting artifacts of analysis results appear during the process of determination of gallium purity level by the GDMS method, which are linked to the solid analytical sample preparation from liquid gallium assay [1–3]. In particular, a significant segregation of some impurities (especially Sn) in the surface layer of solidified sample occurs during solidification of gallium melt assay using liquid nitrogen (a necessary procedure

for analytical sample preparation). This can lead to obtaining of overestimated impurity concentration by two (and more) orders of magnitude, expressed in ppb units, in GDMS analyses results.

Therefore, manufacturers of commercial $5N\div 6N$ purity gallium are not indicating Sn content in the product certificate while using GDMS analysis method or are certifying gallium having $6N$ (or less) purity via optical-spectral methods, for which assay preparation methodology does not encounter the problem of surface impurity segregation. However the detection limits of these methods restrict gallium purity level at $6N$.

Consequently, GDMS analysis remains one of the main ways (if not the only one) for certification of gallium having higher purity than $6N$ (up to $8N$) at the present time because of its high detection limit (~ 1 ppb). However, realization of the unique opportunities of the analysis in the case of super-pure gallium requires an improvement of the existing method of solid analytical sample preparation from Ga melt. The new method should maximally exclude artifacts induced by surface impurity segregation before loading the sample into the GDMS analyzer chamber (cryocooled discharge cell). This represents the goal of the present work.

2. Materials and methods

Super-pure gallium ($7N^+$ and even higher purity) obtained by the membrane nanotechnology of refinement (purification) [5, 6] of commercially available $5N\div 6N$ purity gallium is the subject of a great interest not only because it reveals fascinating properties [7, 8] and a big potential of possible application in several scientific [9, 10] and industrial fields [11], but also due to the fact that it represents a unique object for development of analytical sample preparation method for GDMS certification of super-pure gallium with purity level very close to $8N$.

To solve this problem, we have conducted GDMS analysis of assays of commercial $6N$ purity gallium, produced

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and certificated by the MaTecK GmbH manufacturer company (Germany), and analysis of assays refined by membrane technology of purification of liquid gallium up to 8N (expected level of purity). All measurements were carried out using the VG-9000 (Fisons, UK) magnetic sector glow discharge mass spectrometer with a cryocooled discharge cell requiring a pin-shaped cylindrical analytical sample.

The experiment was conducted in the following sequence: 1) Initial 6N purity commercial gallium of ~ 40 g was melted in the Teflon cell under $\sim 50^\circ\text{C}$. Then, a L-Ga assay of ~ 2 g was taken from the volume of the melt using a syringe and placed into a Teflon tube. After applying the existing method (standard steps) of solid analytical sample preparation [1, 2] to the assay, the obtained sample was inserted into the chamber of a mass spectrometer. 2) The remaining melt (~ 38 g) was encapsulated in a membrane skin to obtain a “melt-membrane-air” type module for additional purification from impurities up to 8N [5, 6]. After this refinement, a super-pure L-Ga assay was taken from the volume of the encapsulated melt in the same way as mentioned above. Then, an analytical solid sample was prepared from the assay using a new method with additional steps, with the intention of pre-removal of impurity segregation layers from the sample surface (particularly enriched with Sn, In and other elements strongly inclined toward segregation on a solidified gallium surface) and inserted into the chamber.

We have studied also the morphology and composition of a solid sample surface obtained after the solidification of gallium melt in liquid nitrogen using the scanning electron microscope (SEM) DSM-960 (Opton, Germany) with EDX analyzer.

3. Results and discussion

Data from the certificate of a commercial 6N purity gallium, taken as an initial material for our experiments, which was provided by the MaTecK GmbH manufacturer company (Germany), is shown in Table I. As seen, in the certificate with defined 16 impurity elements the concentration of Sn is not given.

Therefore, we have conducted sample preparation from the gallium melt assay by the existing (standard) method for GDMS analysis. Realization steps of the preparation are schematically shown in Fig. 1a. The steps are described below. Liquid assay (~ 2 g) was collected by suction, using a syringe, from gallium melt (~ 40 g) into a thin-walled Teflon tube with 2.5 mm inner diameter and ~ 5 cm length and placed into a Teflon Petri dish (I step). After detachment from the syringe, the tube was placed horizontally in a liquid nitrogen bath for full solidification of L-Ga assay (II step). After taking out the tube from the bath, the solid cylindrical assay is partly pushed out from one side of the Teflon tube by pushing with tantalum rod and an analytical sample of required length (1.5 cm) was cut by tantalum scissors. Then, the obtained sample was mounted into a pin sample holder of mass-spectrometer for insertion into a cryocooled discharge cell (III step).

TABLE I
Data from the certificate of a commercial 6N purity gallium sample with defined 16 impurity elements.

N	Element	Concentration ppb [mass%]
1	Mg	50
2	Al	50
3	Si	100
4	Fe	50
5	Cu	50
6	Ag	50
7	Hg	100
8	Cd	10
9	Zn	10
10	Ge	50
11	As	10
12	Sb	10
13	In	100
14	Tl	100
15	Pb	50
16	Bi	50
17	Sn	–
18	Cr	–
19	Mn	–
20	Ni	–
Σ_{20}		840

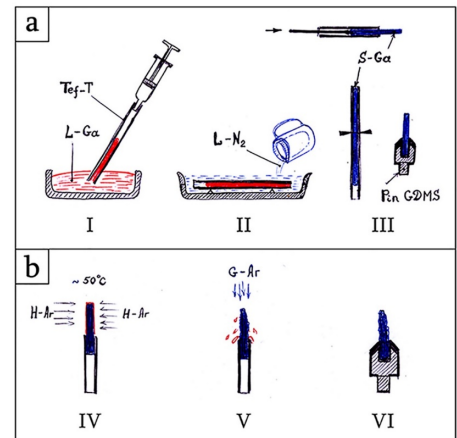


Fig. 1. Taking of an assay from gallium melt and analytical sample preparation for GDMS analysis: (a) steps of the existing (standard) method; (b) additional steps of the method developed by us.

The result of GDMS analysis of an initial commercial gallium sample prepared by the described protocol for 20 impurity elements (including Sn) is given in Table II. Evidently a significantly increased amount (700 ppbw) of Sn concentration was revealed, which reduces the sample purity level defined by a total concentration of the 20 elements to 5N^+ instead of 6N, given by the certificate.

TABLE II

Content of 20 (limiting) impurity elements in the analytical sample prepared from the assay of initial commercial 6N purity gallium melt using the existing (standard) method.

N	Element	Concentration ppb [mass%]
1	Mg	2
2	Al	10
3	Si	80
4	Tl	1
5	Cr	6
6	Mn	1
7	Fe	20
8	Ni	25
9	Cu	40
10	Zn	50
11	Ge	<30
12	Mo	6
13	In	60
14	Sn	700
15	Sb	100
16	Te	20
17	Pt	10
18	Hg	60
19	Pb	150
20	Bi	7
Σ_{20}		1378

The detection of such high level of Sn concentration is related to the extraction of Sn atoms (and some other impurities of gallium) from the melt volume into the surface of the solidified sample and their segregation with a significant amount during cooling of gallium melt assay in liquid nitrogen.

Therefore, the mentioned large concentration of Sn is observed as a result of secondary ionization of sputtered atoms in a GDMS analyzer during the analysis of such a sample, which is obviously an artefactual result. Indeed, after cutting the solidified analytical sample for GDMS analysis, surface SEM observation of the second half of the assay, remaining in the Teflon tube, has revealed an existence of segregated insular precipitates on the entire surface, which is demonstrated in the SEM image given in Fig. 2a.

The secondary X-ray spectra taken locally from a separate insular precipitate have shown that the observed precipitates represent practically pure Sn segregations (see Fig. 2b).

Considering that melting point of gallium is very low, "precleaning" of the surface of analytical sample by plasma inside the analyzer chamber, before running GDMS analysis, is severely restricted.

Thus for certification of super-pure (7N and higher purity level) gallium samples by GDMS method it is necessary to avoid the cause of the above mentioned arti-

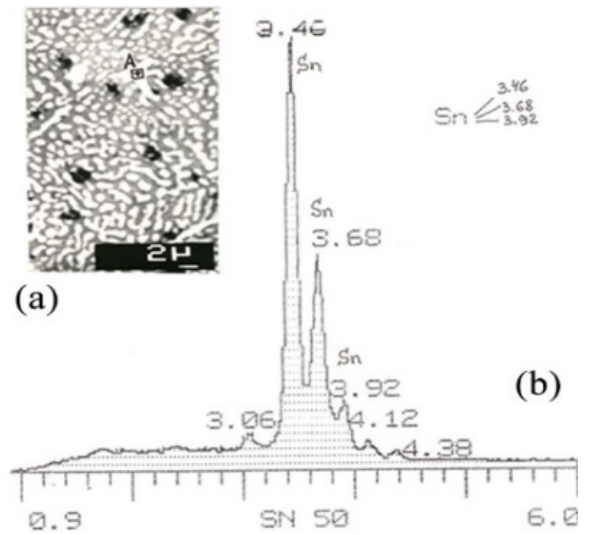


Fig. 2. (a) SEM image of the Ga sample surface obtained after cooling of 6N purity L-Ga assay by liquid nitrogen for GDMS analysis; (b) secondary X-ray spectra of the precipitate area, marked by letter A in image (a), taken locally from the surface of $1 \times 1 \mu\text{m}^2$.

facts (so-called "surface impurity cementation" and most of them induced by Sn) using analytical sample precleaning before their insertion into a cryocooled discharge cell of a mass-spectrometer.

To solve the mentioned problem, a new protocol of analytical sample preparation was developed by us for certification of super-pure gallium by GDMS method, which includes two additional new steps (step IV and V) shown in Fig. 1b. The steps of the existing (standard) method are shown in Fig. 1a.

In particular, after the cylindrical rod ($\varnothing = 2.5 \text{ mm}$) of solidified gallium assay with the required length ($\sim 15 \text{ mm}$) is pushed out from the Teflon tube, the expelled part was blown on by argon flow, heated up to $\sim 50^\circ\text{C}$, thus melting $\sim 100 \mu\text{m}$ thick surface layer (step IV). The melted surface layer was instantly shaken off along the longitudinal direction using argon high pressure jet pulse (step V).

Then, after cutting off the expelled part, the prepared analytical sample was mounted into the pin sample holder and inserted into the analyzer chamber. It should be also noted that after the surface melting (step IV) implementation of step V is possible by extrusion of Ga cylindrical sample with 2.5 mm diameter into a hole (filler) with 2.3 mm diameter made in a thin tantalum plate ($0.2 \div 0.3 \text{ mm}$ in thickness), which completely removes the melted "cemented" surface layer ($\sim 100 \mu\text{m}$) from the surface of the analytical sample.

In accordance with the described new protocol we have carried out a preparation of the analytical sample from noncrystallizing super-pure Ga melt assay obtained by membrane purification of commercial 6N purity gallium melt using the acting laboratory model (industrial mod-

TABLE III

Content of 20 (limiting) impurity elements in the analytical sample prepared from non-crystallizing super-pure Ga melt assay using the new protocol.

N	Element	Concentration ppb [mass%]	Detection limit of GDMS analysis ppb [mass%]
1	B	0.5	0.2
2	Na	<0.5	0.2
3	Mg	<0.2	0.2
4	Al	0.3	0.3
5	Si	3	0.4
6	Tl	0.5	0.08
7	Cr	1.3	0.3
8	Fe	5	0.3
9	Ni	0.7	0.3
10	Cu	1	0.8
11	Zn	0.8	1.2
12	Se	ND	10
13	In	1.3	0.8
14	Sn	5	5
15	Sb	ND	2
16	Te	0.5	1.5
17	Pt	0.6	0.8
18	Hg	3	5
19	Pb	0.6	0.9
20	Bi	0.4	1.3
Σ_{20}		25.2	

ND – not detectable, below detection limit

ule prototype) of membrane purification of liquid gallium up to 7N⁺ and its GDMS multicomponent analysis according to 20 limiting impurity elements.

The result of the analysis is given in Table III. It clearly shows and confirms the following three facts: first, the artifacts caused by the so-called “surface impurity cementation” effect (the problem of a gallium sample) are completely removed as a result of the analytical sample preparation using the new protocol. Specifically, the concentrations of Sn and some other concomitant impurity elements (In, Pb, Sb, Hg, etc.) of the gallium sample purified by the membrane purification are registered at the level very close to the detection limits of GDMS; second, the membrane refinement (purification) [5, 6] of commercial 6N gallium melt provides an increase of initial 6N purity level up to 8N; and third, the developed new protocol of solid analytical sample preparation from gallium melt ensures the full (effective) realization of the highest sensitivity (1 ppb) of GDMS of impurity elements of gallium and allows to obtain a reliable (authentic) certificate of a product having 6N⁺, 7N or 8N purity.

4. Conclusions

- The new protocol of solid analytical sample preparation from gallium melt has been developed, which

ensures the full (effective) realization of the highest sensitivity (1 ppb) of GDMS of impurity elements of gallium and allows to receive a reliable (authentic) certificate of a product having 6N⁺, 7N or 8N purity. In particular, the developed method gives opportunity to exclude artifacts induced by “well-known Sn problem” (and by other impurities of gallium) during super-pure (~8N) Ga certification.

- The high efficiency of the developed new methodology of gallium analytical sample preparation for GDMS analysis was confirmed experimentally based on the comparative study of results of the GDMS analysis of samples prepared by existing (standard) method and the new method from the essays of initial 6N commercial gallium and super-pure 7N⁺ gallium obtained by membrane purification from the initial gallium melt.

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