

## Thin Layer Method for LA-ICP-MS Analysis of Trace Elements Concentrates of Germanium Dioxide

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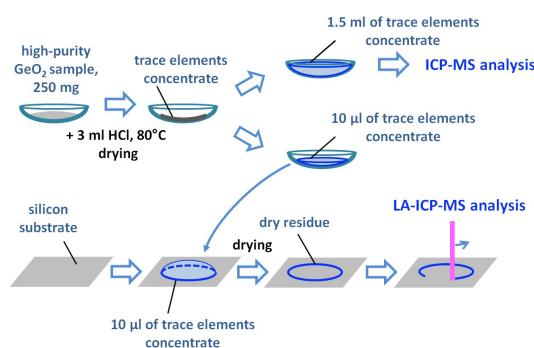
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**ABSTRACT:** A combination of trace elements preconcentration and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is proposed for the analysis of high purity substances. The analytical figures of merit of this combination were evaluated using high purity germanium dioxide as an example. Trace elements were preconcentrated by germanium volatilization in the form of germanium tetrachloride from sample solutions. The trace elements concentrate was evaporated to dryness on the surface of a high-purity silicon substrate and analyzed by LA-ICP-MS. Indium was used as an internal standard to obtain quantitative data. Limits of detection (LODs) for 47 trace elements are in the range from 0.3 to 300 ppt wt (0.3 to 300 pg g<sup>-1</sup>). The obtained LODs are 10-100 times lower compared to ICP-MS analysis of germanium with preconcentration of trace elements. The accuracy of results was confirmed by comparing with results obtained by the traditional ICP-MS analysis of the trace elements concentrates and by the “spike” experiments.



## INTRODUCTION

Nowadays, inductively plasma mass-spectrometry (ICP-MS) is a widespread method of quantitative chemical analysis of high purity substances. The advantages of ICP-MS are the ability to determine a large number of trace elements with low detection limits (LODs) and wide dynamic range. The preliminary concentration of trace elements is an effective way to significantly improve their LODs.<sup>1-6</sup> Matrix distillation off is suitable approach of trace elements preconcentration for high-purity substances analysis. The standard sample introduction technique in ICP-MS is pneumatic nebulization of solutions.<sup>7-9</sup> Main limitation of this technique for trace analysis of concentrates is their significant dilution. Usually, the concentrates after sample matrix distillation off are the dry residues weighting about 10-20 μg or solutions with volume ~ 10 μL. For ICP-MS analysis with pneumatic nebulization the solution of about 2 mL is required. So, the trace

elements concentrates have to be diluted to ~ 100 times or more. This leads to reduction the analytical signal, increases a probability of sample contamination and increases LODs.

Laser ablation (LA) is an alternative method of the sample introduction into the ICP.<sup>10-11</sup> Usually LA is used for analysis of solid geological and biological samples, ceramics, metals *etc.*<sup>12-16</sup> At the same time there are a number of works describing LA-ICP-MS analysis of liquids evaporated on solid substrates.<sup>17-20</sup>

Previously, the so-called “thin layer technique” was proposed for the analysis of concentrates of traces using a spark source mass-spectrometry (SMS).<sup>21-23</sup> This technique allows avoid the dilution of the concentrates and helps reduce significantly the analytes LODs. SMS thin layer technique has been applied for the analysis of ultra-high purity water, acids (nitric, hydrochloric, hydrofluoric) and cadmium, tellurium, mercury, germanium and its oxide. It provided the ability to control contents of up to 60

analytes with LODs from ppt to ppb wt ( $\text{pg g}^{-1}$  to  $\text{ng g}^{-1}$ ) range. Recently thin layer technique combined with LA-ICP-MS has been successfully applied for ultra-trace analysis of high-purity nitric acid with preliminary concentration of analytes. The achieved LODs of ~60 analytes were from  $0.3 \text{ pg g}^{-1}$  to  $0.4 \text{ ng g}^{-1}$ .<sup>24</sup> Thus, it was found that thin layer technique combined with LA-ICP-MS is very promising for trace analysis of high-purity substances. In present paper we evaluate the efficiency of this technique to the analysis of high-purity germanium dioxide ( $\text{GeO}_2$ ) with preconcentration of analytes by the sample matrix distillation off.

## EXPERIMENTAL

**Instrumentation.** An iCAP Qc quadrupole spectrometer (Thermo Scientific, USA) was used for ICP-MS measurements. LA-ICP-MS measurements were performed using NWR-213 laser ablation system (ESI, USA). The main instrumental parameters of the LA-ICP-MS analysis are presented in Table 1. An iCAP 6500 Duo (Thermo Scientific, USA) optical emission spectrometer with ICP (ICP-OES) was used to determine the germanium content in trace element concentrates.

**Reagents and materials.** High-purity water ( $18.2 \text{ M}\Omega \text{ cm}$ ) was obtained by Direct-Q 3 water purification system (Millipore, USA). High-purity nitric acid and high-purity hydrochloric acid were additionally purified by double distillation without boiling using DuoPUR system (Milestone, USA). The calibration solutions were prepared using multielement standard solutions (MES, Skat, Russia). The MES 1 contains next analytes: Al, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, P, Zn – at  $50 \text{ mg L}^{-1}$  and Li – at  $10 \text{ mg L}^{-1}$ . MES 2: B, Bi, Co, Cu, Ga, In, Ni, Si, Ti, V – at  $50 \text{ mg L}^{-1}$ ; MES 3: As, Pb, Rb, Sb, Se, Sn, Te – at  $50 \text{ mg L}^{-1}$ ; Ba, Sr – at  $20 \text{ mg L}^{-1}$ ; Ag, Au, Be – at  $10 \text{ mg L}^{-1}$  and Hg – at  $5 \text{ mg L}^{-1}$ . MES 4: Hf, Mo, Nb, Re, Ta, W, Zr – at  $50 \text{ mg L}^{-1}$ . MES REE: Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y –  $50 \text{ mg L}^{-1}$  and Yb – at  $25 \text{ mg L}^{-1}$ . The standard solution of indium (GSO 11123-2018) with concentration  $1.0 \text{ g L}^{-1}$  was used as internal standard. The samples of electronic purity germanium dioxide (99.9999 % wt., “GP Germanium”, Russia) was used for testing the accuracy of proposed method.

**Preliminary concentration of trace elements.** Germanium oxides samples ( $250 \text{ mg}$ ) were placed in PTFE cups with lids. Then  $3 \text{ mL}$  of additional purified hydrochloric acid was added. The PTFE cups were placed in a thermostat and heated at  $80 \text{ }^\circ\text{C}$  for  $8 \text{ h}$ . The duration of dissolution was ~ $8 \text{ h}$ . The resulting solutions were transferred to PTFE bowls and evaporated to dryness at ~ $80^\circ\text{C}$  under an IR lamp. Evaporation was carried out in a clean box connected to exhaust ventilation with air purification. Germanium volatilized in the form of germanium

**Table 1.** Instrumental parameters of LA-ICP-MS and ICP-MS analysis

Parameter	Setting
	<b>ICP-MS</b>
ICP power, W	1550
External argon flow rate, $\text{L min}^{-1}$	14
Auxiliary argon flow rate, $\text{L min}^{-1}$	0.8
Nebulizing argon flow rate, $\text{L min}^{-1}$	1.2
Dwell time (for each mass), s	0.1 for ICP-MS, 001 for LA-ICP-MS
	<b>Laser ablation (LA)</b>
Carrier helium flow rate, $\text{L min}^{-1}$	0.5
Diluting argon flow rate, $\text{L min}^{-1}$	0.8
Repetition rate, Hz	20
Fluence, $\text{J cm}^{-2}$	0.005-1.0
Scan speed, $\mu\text{m s}^{-1}$	10-1000
Beam diameter, $\mu\text{m}$	100

tetrachloride ( $\text{Tbp} = 86.55 \text{ }^\circ\text{C}$ ). After evaporation, the dry residue of the concentrate was transferred into solution by adding  $100 \mu\text{L}$  of high purity nitric acid (Concentrate 1).

**ICP-MS analysis of concentrates.** For ICP-MS analysis the solution of Concentrate 1 ( $100 \mu\text{L}$ ) was diluted to  $1.4 \text{ mL}$  of  $0.5 \text{ M}$  nitric acid solution. For calibration, solutions prepared from MES were used with element concentrations of  $0, 1, 5,$  and  $25 \mu\text{g L}^{-1}$ . Then conventional ICP-MS analysis was performed. The dilution factor of the germanium oxide samples was ~6.

**LA-ICP-MS analysis of concentrates by thin layer method.** A silicon wafer of the semiconducting purity (99.9999%) was used as a substrate. The substrate surface was firstly etched by hydrofluoric acid and then triple cleaned by distilled water before each sample was applied.

Concentrate 1 was transferred into Teflon cups with a hemispherical bottom and placed under an IR lamp to evaporate to dryness. Indium was added to the analyzed solutions from standard solution as an internal standard to improve the accuracy of the results. Dry residue was transferred into solution by adding the  $10 \mu\text{L}$  of a  $0.5 \text{ M}$  nitric acid solution with internal standard: indium ( $100 \mu\text{g L}^{-1}$ ) – Concentrate 2. Then Concentrate 2 was placed on the prepared substrate and again evaporated in a clean box under an IR lamp at ~ $80^\circ\text{C}$ . The dry residues of the sample on the substrate were analyzed by LA-ICP-MS under the optimized conditions of laser radiation. To confirm the absence of losses during drying of Concentrate 2 on the substrate, recovery experiments were carried out. The experiments were performed as follows: analytes were added to germanium oxide at the stage of its dissolution in hydrochloric acid, preconcentration of trace elements and sample preparation procedures were performed, and LA-ICP-MS analysis was performed. The recovery experiments confirm the absence of losses of analytes during evaporation of the trace elements concentrates. A blank experiment was performed to evaluate the background substrate and solvent signal. The solution of  $0.5 \text{ M}$  nitric acid (same concentration as in the sample solutions)

was passed through the all steps of preliminary concentration of analytes. Sample preparation procedure as for germanium oxide and LA-ICP-MS analysis was performed. The background signal was subtracted from the sample signal.

**Determination the germanium in the trace elements concentrates.** To optimize the parameters of LA and obtain low LODs of analytes, it was necessary to evaluate the germanium concentration after matrix volatilization. The germanium concentration was determined by the ICP-OES analysis using standard instrumental settings. It was found that concentration of germanium in the 10  $\mu\text{l}$  of trace elements concentrate solution was not exceed 300  $\text{mg L}^{-1}$ . So, optimization of the LA parameters was performed using germanium solutions with concentration of 300  $\text{mg L}^{-1}$ .

**Optimizations the parameters of LA for trace analysis by thin layer method.** Optimization of LA parameters was carried out to ensure efficient sampling of analyzed materials from the substrate surface. In this case, the contribution of the substrate material should be minimal. Moreover, high analytical signals must be achieved that will provide low LODs. The energy density of LA is one of the most important parameters affecting the sampling of analyzed material. To choose the optimal energy density of LA, we used a multielement solution prepared from standard MES solutions with analytes concentrations 50  $\mu\text{g L}^{-1}$  and germanium concentration 300  $\text{mg L}^{-1}$ . The multi-element solution was evaporated from the substrate surface as described above. Analytes and blank signals were measured at the following energy densities: 0.005; 0.01; 0.025; 0.05; 0.1; 0.25; 0.5; 0.75 and 1  $\text{J cm}^{-2}$ . Second sampling from the same area of the surface was carried with an energy density 1  $\text{J cm}^{-2}$  to evaluate the efficiency of sampling of the trace elements concentrate. The efficiency of sampling for each element was calculated using the formula:

$$Es = \frac{ASav1}{ASav1+ASav2} \times 100\% \quad (1)$$

where ASav1 is the average analytical signal value of analyte, obtained as a result of sampling the dry sample residue, ASav2 is the average analytical signal value of analyte, obtained as a result of repeated sampling of the same section of the dry sample residue. After that the proportion of the sample material taken during the first period of LA was calculated.

The maximum values of the signal of analytes were achieved at a LA energy density from 0.05 to 0.5  $\text{J cm}^{-2}$  (Fig. 1). For convenience, the figure shows signals normalized to the maximum reached signal ( $I/I_{\text{max}} \cdot 100\%$ ). The signal of the substrate material (silicon) does not exceed 4% of the maximal signal for LA energy density up to 0.1  $\text{J cm}^{-2}$  and dramatically increases for energy density values higher than 0.1  $\text{J cm}^{-2}$ . During LA energy densities from 0.1 to 0.5  $\text{J cm}^{-2}$  the signal of analytes does not change

**Fig. 1** Effect of the LA energy density on the signal of analytes, signal of the substrate material (silicon) and efficiency of sampling.

**Fig. 2** Effect of the LA energy density on the LODs of Ag, Be, Co and Pb.

**Fig. 3** Influence of scan speed on the signal of analytes, signal of the substrate material (silicon) and efficiency of sampling.

**Fig. 4** Influence of scan speed on the LODs of Ag, Be, Co and Pb.

significantly or slightly decrease but at the same time, the signal of the substrate material begins to increase. Further increasing of the LA energy density (more than 0.5 J cm<sup>-2</sup>) leads to deterioration of the signals and LODs of analytes, which may be due to an increase in the amount of substrate material entering the ICP. The efficiency of sampling is at least 97% for energy density from 0.1 to 1 J cm<sup>-2</sup> (Fig. 1). Also, the lowest LODs of analytes are achieved when LA energy density is 0.1 J cm<sup>-2</sup> (examples for Ag, Be, Co and Pb are presented in Fig. 2). For lower LA energy densities values the efficiency of sampling decreased and signals and LODs of analytes are worsen. Based on the data obtained, the value of 0.1 J cm<sup>-2</sup> was used for further measurements.

Another parameter that affects the sampling efficiency, analytical signals and trace elements LODs is scanning speed of the sample surface. The scan speed was varied from 10 to 1000 μm s<sup>-1</sup> to select the optimal value. Sampling was carried out at the energy density equals 0.1 J cm<sup>-2</sup>. As can be seen from Fig. 3, the analytical signals increased rapidly as the scan speed increased from 50 to 200 μm s<sup>-1</sup> (the dependence is close to linear). With a further increase in scanning speed to 400 μm s<sup>-1</sup>, the analyte signals do not change significantly. With scan speed higher 400 μm s<sup>-1</sup> the signal of analytes and efficiency of sampling are decreased. The efficiency of sampling is close to 100% when the scan speed ranges from 10 to 600 μm s<sup>-1</sup>.

Thus, it was found that a scan speed of 400 μm s<sup>-1</sup> provides maximum analytical signals and lowest LODs of analytes

(examples for Ag, Be, Co, and Pb are presented in Fig. 4).

## RESULTS AND DISCUSSION

The advantage of the thin layer method is a significant reduction of the LODs of analytes compared to the traditional ICP MS method. To confirm this, we used high-purity germanium dioxide. The results obtained using the thin layer method were compared with the results obtained by the traditional ICP-MS method with preliminary concentration of trace elements. Solutions with a germanium concentration of 300 mg L<sup>-1</sup> corresponding to trace elements concentrates were prepared to evaluate the analytes LODs by LA-ICP-MS analyses with the thin layer method. 10 μL aliquots of germanium solution and calibration solutions were placed to the surface of a silicon substrate and sample preparation was performed. After this the dry residue of the samples were analyzed by LA-ICP-MS and LODs of analytes were evaluated using 3s-criteria, n=8.

It was found that concentration of germanium in solutions of trace elements concentrates for ICP-MS analysis after their dilution does not exceed 2 mg L<sup>-1</sup> (paragraph ICP-MS analysis of concentrates). So, to estimate the LODs of analytes during ICP-MS analysis of germanium dioxide with preconcentration of analytes, the solutions of 0.5 M nitric acid with a germanium concentration 2 mg L<sup>-1</sup> were prepared. The resulting solutions were analyzed by

**Table 2.** LODs of analytes for analysis of germanium dioxide with preliminary concentration of trace elements provided by the thin layer method in combination with LA-ICP-MS (n=8) and by ICP-MS\*

Analyte	LOD of LA-ICP-MS, pg g <sup>-1</sup>	LOD of ICP-MS, pg g <sup>-1</sup>	(2)/(1)	Analyte	LOD of LA-ICP-MS, pg g <sup>-1</sup>	LOD of ICP-MS, pg g <sup>-1</sup>	(2)/(1)
	(1)	(2)			(1)	(2)	
<sup>7</sup> Li	200	9000	45	<sup>121</sup> Sb	20	100	5
<sup>9</sup> Be	1	80	80	<sup>137</sup> Ba	100	600	6
<sup>24</sup> Mg	100	2000	20	<sup>139</sup> La	4	30	8
<sup>27</sup> Al	300	3000	10	<sup>140</sup> Ce	3	20	7
<sup>45</sup> Sc	5	100	20	<sup>141</sup> Pr	1	30	30
<sup>47</sup> Ti	20	500	25	<sup>146</sup> Nd	1	40	40
<sup>51</sup> V	1	800	800	<sup>147</sup> Sm	3	40	13
<sup>53</sup> Cr	20	400	20	<sup>153</sup> Eu	2	30	15
<sup>55</sup> Mn	30	300	10	<sup>157</sup> Gd	2	20	10
<sup>59</sup> Co	1	20	20	<sup>159</sup> Tb	2	20	10
<sup>60</sup> Ni	20	300	15	<sup>163</sup> Dy	2	20	10
<sup>63</sup> Cu	30	200	7	<sup>165</sup> Ho	1	30	30
<sup>66</sup> Zn	70	3000	43	<sup>166</sup> Er	2	20	10
<sup>71</sup> Ga	2	400	200	<sup>169</sup> Tm	2	30	15
<sup>75</sup> As	9	3000	333	<sup>172</sup> Yb	2	30	15
<sup>85</sup> Rb	3	100	33	<sup>175</sup> Lu	2	20	10
<sup>88</sup> Sr	8	200	25	<sup>178</sup> Hf	0.5	10	20
<sup>89</sup> Y	2	200	100	<sup>181</sup> Ta	0.3	10	33
<sup>90</sup> Zr	8	200	25	<sup>182</sup> W	10	100	10
<sup>93</sup> Nb	2	90	45	<sup>185</sup> Re	0.4	50	125
<sup>95</sup> Mo	20	300	15	<sup>197</sup> Au	0.6	30	50
<sup>107</sup> Ag	0.7	60	86	<sup>208</sup> Pb	2	200	100
<sup>111</sup> Cd	20	90	5	<sup>209</sup> Bi	10	100	10
<sup>118</sup> Sn	10	200	20				

\* LA-ICP-MS concentration factor=25; ICP-MS concentration factor= 167

**Table 3.** Results of high-purity germanium dioxide sample analysis with preliminary concentration of trace elements (n = 4, P = 0.95)

Analyte	LA-ICP-MS, ng g <sup>-1</sup>	ICP-MS, ng g <sup>-1</sup>
<sup>24</sup> Mg	24±6	19±5
<sup>27</sup> Al	14±3	10±2
<sup>47</sup> Ti	5±1	4.5±0.4
<sup>51</sup> V	0.10±0.03	0.15±0.03
<sup>53</sup> Cr	7±1	9±1
<sup>55</sup> Mn	0.9±0.1	0.8±0.1
<sup>60</sup> Ni	7±1	6±1
<sup>63</sup> Cu	2.1±0.5	2.8±0.5
<sup>66</sup> Zn	27±5	33±4
<sup>75</sup> As	0.6±0.2	0.8±0.2
<sup>95</sup> Mo	3.5±0.3	2.8±0.8
<sup>111</sup> Cd	0.6±0.1	0.6±0.2
<sup>118</sup> Sn	2.3±0.5	3.0±0.3
<sup>121</sup> Sb	12±2	8±2
<sup>182</sup> W	2.7±0.5	3.0±0.6
<sup>208</sup> Pb	2.9±0.6	3.4±0.5

**Table 4.** Results of the spike experiment for LA-ICP-MS with thin layer technique (n = 6, P = 0.95)

Analyte	Added, pg g <sup>-1</sup>	Found, pg g <sup>-1</sup>	Recovery, %
<sup>7</sup> Li	2000	2100±300	105
<sup>9</sup> Be	60	70±10	117
<sup>45</sup> Sc	300	230±30	77
<sup>59</sup> Co	300	270±30	90
<sup>71</sup> Ga	300	250±50	83
<sup>77</sup> Se	300	300±90	100
<sup>85</sup> Rb	300	250±50	83
<sup>88</sup> Sr	120	100±30	83
<sup>89</sup> Y	300	250±30	83
<sup>90</sup> Zr	300	390±90	127
<sup>93</sup> Nb	300	280±40	93
<sup>107</sup> Ag	60	70±20	117
<sup>137</sup> Ba	120	150±50	125
<sup>139</sup> La	300	310±30	103
<sup>140</sup> Ce	300	300±20	100
<sup>141</sup> Pr	300	260±30	87
<sup>146</sup> Nd	300	260±60	87
<sup>147</sup> Sm	300	250±60	83
<sup>153</sup> Eu	300	240±40	80
<sup>157</sup> Gd	300	220±50	73
<sup>159</sup> Tb	300	320±80	107
<sup>163</sup> Dy	300	250±30	83
<sup>165</sup> Ho	300	260±40	87
<sup>166</sup> Er	300	240±50	80
<sup>169</sup> Tm	300	240±40	80
<sup>172</sup> Yb	300	280±40	93
<sup>175</sup> Lu	300	280±30	93
<sup>178</sup> Hf	300	250±20	83
<sup>181</sup> Ta	300	320±40	107
<sup>185</sup> Re	300	330±50	110
<sup>197</sup> Au	60	70±20	117
<sup>209</sup> Bi	300	300±80	100

ICP-MS. The LODs of analytes were evaluated using 3s-criteria, n=10. The results of evaluation of the LODs are shown in Table 2. During calibration, the approximation coefficient by a linear dependence was no less than 0.995.

The analytes LODs for germanium dioxide analysis by LA-

ICP-MS the thin layer method and pre-concentration of trace elements are in the range from 0.3 to 300 pg g<sup>-1</sup>. ICP-MS analysis with preliminary concentration of trace elements provides LODs of analytes from 10 to 9000 pg g<sup>-1</sup>. Using of the internal standard during LA-ICP-MS measurements allows taking into account the possible differences of the sample distribution. Due to the lower dilution and efficient using of trace elements concentrates LA-ICP-MS analysis with the thin layer technique allows to significantly reduce the LODs of the number of analytes an average of 10-100 times. So, the possibility of control of the concentration of studied analytes in germanium dioxide up to 99.9999998 % wt purity is provided (total content of 47 trace elements from 0.0000002 % wt. While standard ICP-MS analysis with preliminary concentration of trace elements allows controlling the concentration of studied analytes in germanium dioxide up to 99.999998 % wt purity.

The accuracy of the proposed LA-ICP-MS the thin layer method was confirmed by analysis of a real electronic purity germanium dioxide G2-22 sample and analyte recovery («spike») experiments. Also, sample G2-22 was analyzed by the traditional ICP-MS method with pre-concentration of trace elements. Table 3 shows the analysis results obtained by both methods. Trace elements such Al, As, Cd, Cr, Cu, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Ti, V, Zn, and W were found in the sample. Concentration of trace elements varied from 0.1 to 27 ng g<sup>-1</sup>. As can be seen, good agreement is achieved between the LA-ICP-MS thin layer method and ICP MS. This confirms accuracy of the developed LA-ICP-MS thin layer method.

For the analytes not found in the high purity germanium dioxide sample the accuracy of the proposed method was confirmed by analyte recovery experiment. The analytes were added to the germanium oxide at the stage of its dissolution in hydrochloric acid. After this the all procedures of the preliminary concentration of traces were performed. The trace elements concentrates were analyzed by LA-ICP-MS with thin layer technique. The experimental results are presented in Table 4. The recovery values are varied from 73 % to 127 %. It confirms the accuracy of the proposed LA-ICP-MS method. Also, the recovery experiment confirms the absence of losses of analytes during volatilization of the trace elements concentrates. Thus, the proposed method allows us perform accurate analysis of germanium oxide samples.

Note that there are some limitations of the thin layer technique with LA-ICP-MS. The first limitation is the complication and increasing of the duration of sample preparation. Specifically, trace elements concentrates are evaporated from a volume 100 µl to 10 µl, an internal standard is added and dried on substrate surface. The internal standard must be used to account for possible heterogeneity of sample distribution on the substrate and heterogeneity in sampling to carry out quantitative measurements. It is worth noting the need to use additional equipment to introduce

samples into the ICP, a laser ablation device. However, the undoubted advantage of the thin layer method is ultra-low analytes LODs ( $\text{pg g}^{-1}$ ) when analyzing high-purity substances.

## CONCLUSION

The analytical capabilities for the analysis of high-purity substances were improved using preliminary concentration of trace elements and LA-ICP-MS by thin layer technique. The concentrate of trace elements was evaporated on the surface of silicon substrate and then LA-ICP-MS analysis of the dry residue was performed. High sampling efficiency and analytes signal were achieved for LA energy density  $0.1 \text{ J cm}^{-2}$  and scan speed  $400 \mu\text{m s}^{-1}$ . Due to the low dilution and efficient using of the trace elements concentrates the LODs of 47 trace elements in germanium oxide were reduced by an order of magnitude compare to the common ICP-MS analysis with preliminary concentration. It is shown that thin layer technique in combination with LA-ICP-MS for trace analysis of high-purity germanium dioxide provides LODs of 47 analytes ranges from 0.3 to  $300 \text{ pg g}^{-1}$ . The accuracy of proposed method was evaluated by “spike” experiment. Recovery analyte concentrations ranged from 73 to 127 %. Good agreement between results of analysis of the germanium oxide samples by thin layer LA-ICP-MS technique and the common ICP-MS analysis is confirms the accuracy pf proposed method.

## AUTHOR INFORMATION



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### Notes

The authors declare no competing financial interest.

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## REFERENCES

1. C. Agatemor and D. Beauchemin, *Anal. Chim. Acta*, 2011, **706**, 66–83. <https://doi.org/10.1016/j.aca.2011.08.027>
2. W. Nischkauer, M. A. Neouze, and F. Vanhaecke, *Microchim. Acta*, 2015, **182**, 2369–2376. <https://doi.org/10.1007/s00604-015-1643-0>
3. J. Sondergaard, G. Asmund, and M. Larsen, *MethodsX*, 2015, **2**, 323–330. <https://doi.org/10.1016/j.mex.2015.06.003>
4. S. L. Jackson, J. Spence, D. J. Janssen, A. R. S. Ross, and J. T. Cullen, *J. Anal. At. Spectrom.*, 2018, **33**, 304–313. <https://doi.org/10.1039/C7JA00237H>
5. F. A. Aydin and M. Soylak, *J. Hazard. Mater.*, 2010, **173**, 669–674. <https://doi.org/10.1016/j.jhazmat.2009.08.137>
6. M. Niemela, H. Kola, and P. Peramaki, *Anal. Sci.*, 2014, **30**, 735–738. <https://doi.org/10.2116/analsci.30.735>
7. R. S. Houk, V. A. Fassel, G. D. Flesch, H. J. Svec, A. L. Gray, and C. E. Taylor, *Anal. Chem.* 1980, **52**, 2283–2289. <https://doi.org/10.1021/ac50064a012>
8. A. L. Gray and A. R. Date, *Analyst*, 1983, **108**, 1033–1050. <https://doi.org/10.1039/AN9830801033>
9. N. H. Bings, J. O. Orlandini von Niessen, and J. N. Schaper, *Spectrochim. Acta B*, 2014, **100**, 14–37. <https://doi.org/10.1016/j.sab.2014.08.011>
10. A. L. Gray, *Analyst*, 1985, **110**, 551–556. <https://doi.org/10.1039/AN9851000551>
11. M. Thompson, S. Chenery, and L. Brett, *J. Anal. At. Spectrom.*, 1989, **4**, 11–16. <https://doi.org/10.1039/JA9890400011>
12. J. Koch and D. Günther, *Appl. Spectrosc.*, 2011, **65**, 155–162. <https://doi.org/10.1366/11-06255>
13. K. P. Jochum, B. Stoll, U. Weis, D.E. Jacob, R. Mertz-Kraus, and M. O. Andreae, *Geostand. Geoanal. Res.*, 2014, **38**, 265–292. <https://doi.org/10.1111/j.1751-908X.2014.12028.x>
14. M. Wang, L. Zheng, and B. Wang, *Anal. Chem.*, 2014, **86**, 10252–10256. <https://doi.org/10.1021/ac502438n>
15. Q. Li, Y. Fang, and J. Liu, *Atom. Spectrosc.*, 2021, **42**, 154–159. <https://doi.org/10.46770/AS.2021.019>
16. W. Zhang, Z. Wang, Z. Hu, Q. He, Y. Li, Y. Feng, H. Liu, and X. Zhang, *Atom. Spectrosc.*, 2022, **43**, 60–69. <https://doi.org/10.46770/AS.2022.007>
17. H. J. Stark and R. Wennrich, *Anal. Bioanal. Chem.*, 2011, **399**, 2211–2217. <https://doi.org/10.1007/s00216-010-4413-1>
18. A. Villasenor, C. Greati, M. Boccongellic, and J. L. Todoli, *J. Anal. At. Spectrom.*, 2017, **32**, 587–596. <https://doi.org/10.1039/C6JA00343E>
19. M. A. G. Nunes, M. Voss, G. Corazza, E. M. M. Flores, and V. L. Dressler, *Anal. Chim. Acta*, 2016, **905**, 51–57. <https://doi.org/10.1016/j.aca.2015.11.049>

20. M. Aramendía, L. Rello, S. Berail, A. Donnard, C. Pecheyrand, and M. Resano, *J. Anal. At. Spectrom.*, 2015, **30**, 296–309. <https://doi.org/10.1039/C4JA00313F>
  21. I. R. Shelpakova, A. I. Saprykin, T. A. Chanysheva, and I. G. Yudelevich, *J. Anal. Chem.*, 1983, **38**, 581.
  22. T. A. Chanysheva, I. R. Shelpakova, A. I. Saprykin, L. M. Yankovskaya, and I. G. Yudelevich, *J. Anal. Chem.*, 1983, **38**, 979.
  23. I. R. Shelpakova, A. I. Saprykin, and I. G. Yudelevich, *Problems of Analytical Chemistry*, 1983, **7**, 143.
  24. N. S. Medvedev, V. D. Kurbatova, and A. I. Saprykin, *J. Anal. Chem.*, 2023, **78**, 208–215. <https://doi.org/10.1134/S1061934823030097>
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