

# Highly Sensitive Chromatography Mass Spectrometry Determination of Impurities in High-Purity Monogermane Using Adsorption Capillary Column with Carbon Sorbent

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**Abstract**—It is shown that the employment of a quartz capillary column with carbon adsorbent provides an effective separation of impurities of permanent gases, carbon dioxide, nitrous oxide, C<sub>1</sub>–C<sub>2</sub> hydrocarbons, and carbon dioxide in monogermane. The effect of the injected volume of monogermane specimen on the determination of ethane and carbon dioxide is studied. Chromatography mass spectrometry detection limits of impurities are  $(1–10) \times 10^{-6}$  mol %. The detection limit of the limiting impurity represented by ethane is decreased by the factor of seven as compared to the published data.

**Keywords:** high-purity monogermane, adsorption capillary column, impurities, detection limit, accuracy, chromatography mass spectrometry

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High-purity monogermane (GeH<sub>4</sub>) is in high demand for various modern technologies from the fabrication of detectors of IR and gamma radiation and glasses based on GeO<sub>2</sub> to the preparation of germanium isotopes. Therefore, the development of the procedures for the determination of microimpurities in germanium hydride is quite relevant. The main method for the deep purification of monogermane is low-temperature rectification. Ethane ( $T_b = -88.7^\circ\text{C}$ ) is an impurity that is the most difficult to separate from monogermane ( $T_b = -88.5^\circ\text{C}$ ) [1]. There were numerous attempts to develop procedures of highly sensitive gas chromatographic determination of this impurity in germane [2–8]. The main problem of the determination of ethane is the difficulty of its separation from germane. Packed and capillary columns with various adsorbents and stationary liquid phases were used. In neither case was a desirable separation achieved. In a single work [9], the detection limit of ethane of  $2 \times 10^{-5}$  mol % was obtained during its determination using reaction chromatography with chemical separation of monogermane. The number of possible analyses is determined by the capacity of the reaction column and is less than 12–15. The possible solution to the problem of separation of ethane and germane is the employment of a capillary column with carbon adsorbent. According to the principles of chro-

matographic retention on carbon sorbents [10], ethane should be eluted earlier and its peak does not overlap with the tail of the peak of monogermane. This would prevent using chemical binding of the main component and reduce the detection limit of ethane.

These requirements can be fulfilled by a CarbonPLOT adsorption column with carbon sorbent.

The aim of this work was to study its application for the detection of impurities in high-purity monogermane.

Specimens were analyzed using an Agilent 6890/MSD 5973N chromatograph mass spectrometer equipped with a CarbonPLOT capillary column  $25 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ }\mu\text{m}$  with carbon sorbent. Chromatographic analysis was carried out in the isothermal mode at the temperature of the column of  $30^\circ\text{C}$ . As a carrier gas, helium of 7.0 brand was used (TU 0271-0001-45905715-02). The linear velocity of the carrier gas was 36 cm/s. The equipment for sampling and operating conditions of the mass spectrometer are described in detail in [5, 11].

Impurities were identified by comparing of their mass spectra with those of the NIST database. Measurement was carried out at selected ion monitoring (SIM). To avoid blowout of the cathode during the output of the main component, the supply of the detector was switched off and ethane was not deter-

**Table 1.** Retention times of impurities, their content in monogermene, and detection limits ( $C_{\min}$ , mol %)

Impurity	Retention time, min	$m/z$	Content, mol %	$C_{\min}$ , mol %	
				our data	reference data
N <sub>2</sub>	0.84	28	$(1.8 \pm 0.2) \times 10^{-4}$	$5 \times 10^{-6}$	$1 \times 10^{-5}$ [12]
O <sub>2</sub>	0.85	32	$(1.6 \pm 0.2) \times 10^{-5}$	$5 \times 10^{-6}$	$2 \times 10^{-6}$ [12]
Ar	0.85	40	$(6.1 \pm 0.6) \times 10^{-5}$	$1 \times 10^{-6}$	$6 \times 10^{-6}$ [12]
CH <sub>4</sub>	0.93	15	$(3 \pm 1) \times 10^{-5}$	$1 \times 10^{-5}$	$2 \times 10^{-6}$ [6]
CO <sub>2</sub>	1.26	44	$(5.1 \pm 0.5) \times 10^{-5}$	$1 \times 10^{-6}$	$2 \times 10^{-5}$ [13]
N <sub>2</sub> O	1.49	44	$(4 \pm 1) \times 10^{-6}$	$1 \times 10^{-6}$	—
C <sub>2</sub> H <sub>2</sub>	2.30	26	$(1.6 \pm 0.2) \times 10^{-5}$	$2 \times 10^{-6}$	—
C <sub>2</sub> H <sub>4</sub>	2.44	27	$(5 \pm 1) \times 10^{-6}$	$2 \times 10^{-6}$	$2 \times 10^{-5}$ [9]
SiH <sub>4</sub>	2.52	30	$(4.7 \pm 0.5) \times 10^{-5}$	$5 \times 10^{-6}$	$9.2 \times 10^{-5}$ [7]
C <sub>2</sub> H <sub>6</sub>	3.03	27	$(3.7 \pm 0.4) \times 10^{-5}$	$3 \times 10^{-6}$	$2 \times 10^{-5}$ [9]

mined under this pressure. The concentrations of impurities were determined by absolute calibration according to peak areas. Calibration mixtures were prepared on a gas-mixing setup in calibrated ampoules from molybdenum glass and in the balloons made from stainless steel of 12Kh18N10T brand (volume is 200–300 cm<sup>3</sup>) using the volume-manometric method. As a dilution gas, monogermene purified by rectification with the impurity content of 10<sup>-5</sup> mol % was used. As initial substances, the following were used: O<sub>2</sub> (GOST 5583-78), N<sub>2</sub> (GOST 923-74), Ar (TU 6-21-12-79), CO<sub>2</sub> (GOST 8050-85), N<sub>2</sub>O (TU 2114-051-00203772-2006), a series of hydrocarbons C<sub>1</sub>–C<sub>2</sub> (TU 6-09-2454-85), and SiH<sub>4</sub> (from the Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences).

The partial pressure of the component of the mixture  $P_i$  was calculated using the following equation:

$$P_i = \frac{p_{\text{mix}} C_i}{100\%}$$

The pressure was measured using a VTI manometer of the 0.6 accuracy class. Calibration mixtures were prepared in the partial pressure range of 10<sup>-7</sup>–10<sup>-3</sup> atm (10<sup>-5</sup>–10<sup>-1</sup> mol %). The error of their preparation was less than 7%.

Impurities were determined by recording their ions, which are intrinsic to the maximum signal-to-

noise ratio, with the  $m/z$  values, which are given in Table 1.

The content of impurities in monogermene specimens  $C_i$  were determined as follows:

$$C_i = \frac{P_i}{p_{\text{GeH}_4}} \times 100\%,$$

where  $p_{\text{GeH}_4}$  is the pressure of the monogermene specimen.

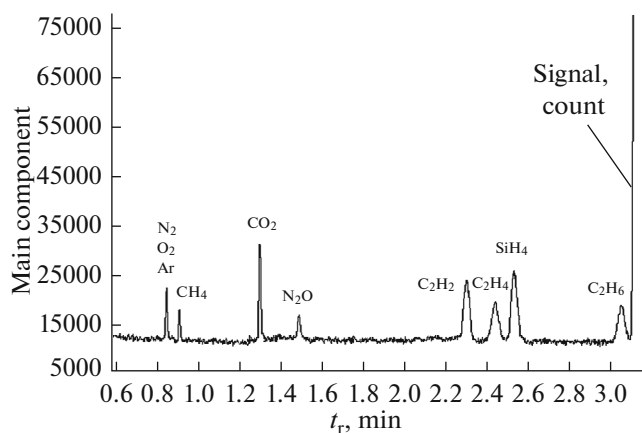
The detection limits of impurities according to partial pressure  $p_{\min}$  were calculated for the SIM mode as a triple standard deviation of the signal of the reference experiment:

$$p_{\min} = 3S/A,$$

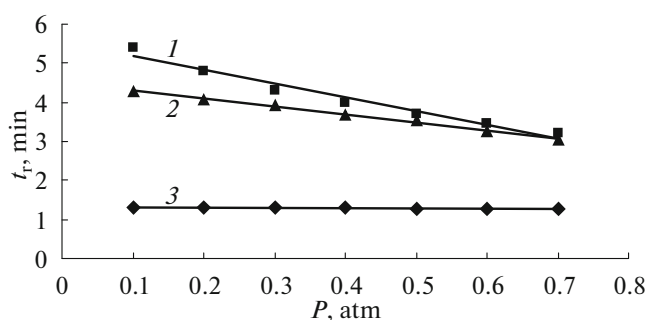
where  $S$  (count) is the standard deviation of the analytical signal of the reference experiment and  $A$  (count/atm) is the sensitivity coefficient of the detector to the test substance (determined by calibration plots). The detection limits of impurities by the concentration  $C_{\min}$  were calculated from the correlation of  $p_{\min}$  and maximum pressure of monogermene in the injection system  $p_{\max} = 0.7$  atm:

$$C_{\min} = \frac{p_{\min}}{p_{\max}} \times 100\%.$$

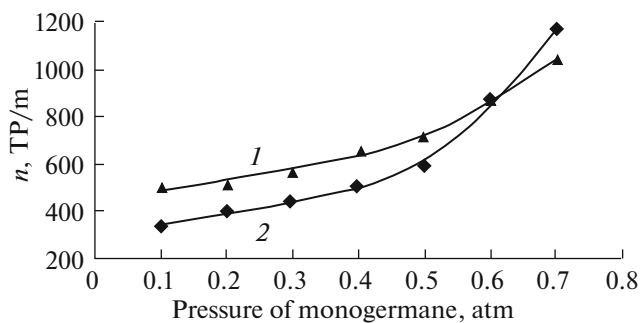
The standard deviation of the signal of the reference experiment was calculated according to the oscil-



**Fig. 1.** Chromatogram of the monogermene specimen obtained in the mode of full ionic current monitoring.



**Fig. 2.** Dependence of the retention time of impurities of (2)  $C_2H_6$  and (3)  $CO_2$  and (1) the shift of the front of the peak of monogermene on the pressure of the shot.



**Fig. 3.** Dependence of the CarbonPLOT column performance on the pressure of the shot of monogermene for (1)  $C_2H_2$  and (2)  $C_2H_6$ .

lations of the area of the peak, which is related to the output time of the test impurity:

$$S = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (B_i - \bar{B})^2},$$

where  $B_i$  (count) is the unit value of the area of the peak of the impurity,  $\bar{B}$  (count) is the mean value of

the area of the peak of the impurity, and  $n$  is the number of measurements.

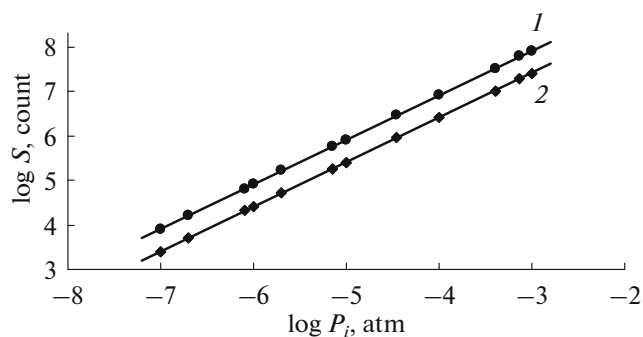
Figure 1 gives the chromatogram of the monogermene specimen obtained using the CarbonPLOT column in the full ionic current monitoring mode. It is clear that the impurities of permanent gases, carbon dioxide, nitrous oxide, acetylene, ethylene, silane, and ethane were separated and identified. The impurities of nitrous oxide and acetylene were identified in monogermene for the first time. As follows from the chromatogram, the peaks of most components are resolved sufficiently for measurement. Impurities of Ar,  $N_2$ , and  $O_2$  are not resolved; however, this does not interfere in their individual determination because of the difference of mass spectra. Impurities of carbon dioxide, acetylene, ethylene, and ethane are eluted up to the main component, which is important for their determination by nonselective detectors (helium, thermal-conductivity detector).

The effect of the amount of the main substance on separation and determination of impurities in monogermene was investigated. In Fig. 2, the dependences of the shift of the front of the monogermene band and retention times of the impurities of  $C_2H_6$  and  $CO_2$  on the pressure of the injected shot are given. It is clear that, with an increase in the pressure of the specimen from 0.1 to 0.7 atm, the front of the peak of monogermene shifts from 5.4 to 3.2 min. An increase in the pressure of monogermene above 0.7 atm leads to the overlap of the front of its peak with the peak of ethane.

An increase in the amount of the main substance also leads to the exclusion of impurities. It manifests itself to the highest extent for impurity components whose peaks are close to the front of the peak of monogermene ( $C_2H_6$ ,  $SiH_4$ ,  $C_2H_4$ ,  $C_2H_2$ ). As an example, with the change in the pressure of injected monogermene from 0.1 to 0.7 atm, the retention time of  $C_2H_6$  decreases by 1.3 min. In the case of "light" substances represented by  $N_2O$ ,  $CO_2$ , Ar,  $O_2$ , and  $N_2$ , the retention time hardly changes.

Exclusion of impurities is accompanied by the narrowing of their chromatographic peaks and an increase in the column performance. The largest change in the column performance is also intrinsic to the substances whose peaks are located on the chromatogram near the monogermene peak. As follows from Fig. 3, the column performance in the case of acetylene increases by the factor of 2.1 (curve 1), while that for ethane grows by the factor of 3.5 (curve 2).

Examples of calibration plots for the determination of the impurities of ethane and carbon dioxide in monogermene are given in Fig. 4. It follows that, in the pressure range of  $10^{-3}$ – $10^{-7}$  atm, they are linear [ $\log S = 1.011 \log P_i + 10.912$ ,  $R^2 = 0.998$  ( $CO_2$ );  $\log S = 1.016 \log P_i + 10.408$ ,  $R^2 = 0.996$  ( $C_2H_6$ )]. The detection limits of impurities are given in Table 1. The detection limits of acetylene and nitrous oxide in



**Fig. 4.** Dependence of the logarithm of the area of the chromatographic peak on the partial pressures of (1)  $\text{CO}_2$  and (2)  $\text{C}_2\text{H}_6$ .

monogermane were calculated for the first time. In the case of ethane and carbon dioxide, they are less by a factor of 7–20 as compared to previously published data [9, 12].

The results of analysis of the purest specimen of monogermane are given in Table 1. It is seen that the content of impurities is at the level of  $10^{-4}$ – $10^{-6}$  mol %. Convergence of the determination of impurities in this range is characterized by the relative standard deviation of 0.08–0.2.

Correctness of the results was confirmed by varying the specimen volume and its comparison with the results of gas chromatography analysis. For this purpose, the absolute value of the difference of mean val-

ues of the results  $|\bar{C}_1 - \bar{C}_2|$  was compared with the maximum error of this difference  $\varepsilon$ , which was calculated using the following relationship:

$$\varepsilon = t_{p,f} S_{\text{weighted}} \sqrt{\frac{1}{n_1} + \frac{1}{n_2}},$$

where  $t_{p,f}$  is the Student coefficient with the confidence interval of  $P = 0.95$  and the number of degrees of freedom of  $f = n_1 + n_2 - 2$ .

The weighted mean of standard deviations  $S_{\text{weighted}}$  was calculated as follows:

$$S_{\text{weighted}} = \sqrt{\frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2}}.$$

The results of the verification of correctness by example of the determination of impurities of  $\text{CO}_2$ ,  $\text{C}_2\text{H}_6$ , and  $\text{CH}_4$  are given in Tables 2 and 3. It is clear that the difference of the results of determination with the change in the inlet pressure of monogermane by the factor of three and using an independent method of analysis is statistically insignificant.

Thus, in the case of the gas chromatographic determination of impurities in germanium hydride, a quartz capillary column with carbon adsorbent was employed for the first time, which provides the determination of the impurities of permanent gases, carbon dioxide, nitrous oxide,  $\text{C}_1$ – $\text{C}_2$  hydrocarbons, and silane. The chromatography mass spectrometry detection limit of ethane in monogermane is  $3 \times 10^{-6}$  mol %, while that

**Table 2.** Results of verification of the correctness of analysis of monogermane by varying the specimen volume ( $n_1 = n_2 = 5$ ;  $P = 0.95$ )

Impurity	$P = 1.0, \text{ atm}$		$P = 0.3 \text{ atm}$		$S_{\text{weighted}},$ % mol	$ \bar{C}_1 - \bar{C}_2 ,$ % mol	$\varepsilon, \text{ \% mol}$
	$\bar{C}_1, \text{ \% mol}$	$S_1, \text{ \% mol}$	$\bar{C}_2, \text{ \% mol}$	$S_2, \text{ \% mol}$			
$\text{CO}_2$	$1.1 \times 10^{-5}$	$0.2 \times 10^{-5}$	$1.2 \times 10^{-5}$	$0.2 \times 10^{-5}$	$0.2 \times 10^{-5}$	$0.1 \times 10^{-5}$	$4.5 \times 10^{-6}$
$\text{C}_2\text{H}_6$	$6.2 \times 10^{-5}$	$0.5 \times 10^{-5}$	$5.7 \times 10^{-5}$	$0.4 \times 10^{-5}$	$0.4 \times 10^{-5}$	$0.5 \times 10^{-5}$	$9.1 \times 10^{-6}$

**Table 3.** Results of chromatography mass spectrometry (CMS) and gas chromatography (GC) determination of impurities in monogermane ( $n_1 = n_2 = 3$ ;  $P = 0.95$ )

Impurity	CMS		GC		$S_{\text{weighted}},$ % mol	$ \bar{C}_1 - \bar{C}_2 ,$ % mol	$\varepsilon, \text{ \% mol}$
	$\bar{C}_1, \text{ \% mol}$	$S_1, \text{ \% mol}$	$\bar{C}_2, \text{ \% mol}$	$S_2, \text{ \% mol}$			
$\text{CH}_4$	$1.1 \times 10^{-4}$	$0.2 \times 10^{-4}$	$1.2 \times 10^{-4}$	$0.2 \times 10^{-4}$	$0.2 \times 10^{-4}$	$0.1 \times 10^{-4}$	$4.5 \times 10^{-5}$
$\text{C}_2\text{H}_6$	$2.2 \times 10^{-4}$	$0.2 \times 10^{-4}$	$2.0 \times 10^{-4}$	$0.2 \times 10^{-4}$	$0.2 \times 10^{-4}$	$0.2 \times 10^{-4}$	$4.5 \times 10^{-5}$

of other impurities is  $1-10 \times 10^{-6}$  mol %, which is less by factors of 7–20 than those previously achieved.

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