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1964

SovietRxiv

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Abstract

Full Text

CHEMISTRY

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CHROMATOGRAPHIC ANALYSIS OF MIXTURES OF SOME VOLATILE INORGANIC HYDRIDES

(Presented by Academician N. M. Zhavoronkov, 30 XII 1963)

The methods currently used for the analysis of mixtures of volatile inorganic hydrides are based mainly on their decomposition into the element and hydrogen, followed by analysis of the precipitated solid (^{1}). Mass-spectrometric (^{2}) and spectral (^{3,4}) methods are used less often. A number of works are also known that are devoted to the chromatographic analysis of mixtures of volatile hydrides ($^{5-11}$). Papers ($^{5-8}$) describe the analysis of borohydrides and chloroboranes. There is brief information on the analysis of a mixture of silanes,

Fig. 1. Diagram of the chromatographic apparatus. **1**—nitrogen cylinder, **2, 8**—gas reducers, **3, 4, 5, 6**—columns with granulated copper, silica gel, granulated alumina, and molecular sieves, respectively; **7**—trap with a sodium-potassium eutectic mixture, **9**—manometer, **10, 11**—valves for precise regulation of the nitrogen flow rate, **12, 13**—separating tube, **16**—thermostating jacket, **17**—furnace for thermal decomposition of hydrides, **18**—catharometer, **19**—electrometric part of the catharometer, **20**—current amplifier of type F-116/2, **21**—self-recording potentiometer EPP-09, **22**—thermostat, **23**—cylinder with the mixture to be analyzed, **24**—mercury manometer.

as well as germanes ($^{9-11}$). There are no reports in the literature devoted to the chromatographic analysis of mixtures of volatile inorganic hydrides of various elements. The present work describes a chromatographic method developed by us for the quantitative analysis of a mixture of volatile inorganic hydrides of a number of elements of the fourth to sixth groups of the periodic system of D. I. Mendeleev. Inorganic hydrides of elements of groups IV–VI are unstable with respect to oxygen and moisture; therefore, high demands are placed on the sealing of the chromatographic apparatus and on the purity of the carrier gas. The scheme of the chromatographic apparatus used by us is shown in Fig. 1.

Fig. 2. Chromatogram of a mixture of hydrides of silicon, germanium, phosphorus, arsenic, sulfur, and hydrogen

Figure 2: Fig. 2. Chromatogram of a mixture of hydrides of silicon, germanium, phosphorus, arsenic, sulfur, and hydrogen

Fig. 3. Chromatogram of arsine with microimpurities of phosphine, germane, and silane

Figure 3: Fig. 3. Chromatogram of arsine with microimpurities of phosphine, germane, and silane

The separating tube

was filled with diatomaceous brick with a grain size of 0.25–0.5 mm, wetted with solvent in an amount of 25% of the weight of the solid support. The sample to be analyzed was introduced into the column by means of a 1-ml inlet system. The components emerging from the chromatographic column were recorded, relative to hydrogen, by means of a katharometer with tungsten filaments made in the form of spirals. The volume of the katharometer chambers was approximately 0.6 ml. Hydrogen was obtained by thermal decomposition of the hydrides in a capillary furnace made of quartz glass, 1.5–2 mm in diameter and 100–150 mm long, placed between the column and the katharometer. With this procedure, the formation of a film of the hydride-forming element on the surface of the hot katharometer filament was prevented. The appearance of such a film ultimately disables the katharometer. At the same time, the sensitivity of the analysis was increased. This is due to an increase in the concentration of molecules in the stream of carrier gas, since more than one molecule of hydrogen is formed from a hydride molecule, and also to the fact that the difference in thermal conductivity between hydrogen and nitrogen is greater than that between the hydride and nitrogen.

Fig. 2. Chromatogram of a mixture of hydrides of silicon, germanium, phosphorus, arsenic, sulfur, and hydrogen

Fig. 3. Chromatogram of arsine with microimpurities of phosphine, germane, and silane

Table 1

Temperatures of parts of the nitrogen-purification system during regeneration in the course of gas purification

Column packing	Temperature during nitrogen purification, °C	Temperature during regeneration, °C
Granulated copper	200	180–190
KSK silica gel	Room temperature	300

Column packing	Temperature during nitrogen purification, °C	Temperature during regeneration, °C
Active granulated aluminum oxide	Room temperature	300
Molecular sieves	Room temperature	350
Eutectic mixture of sodium and potassium	Room temperature	Mixture is replaced

The furnace temperature for decomposition of the hydrides was maintained close to 1000°. From preliminary experiments it was established that the ratio of the peak area to the hydride charge at a furnace temperature above 950° does not change. This same ratio also does not depend on the furnace length if it is greater than 20 mm. Nitrogen purified from moisture and oxygen was used as the eluting gas. The purification system consisted of successively arranged columns with granulated copper, KSK-grade silica gel, active granulated aluminum oxide, molecular sieves of the 5 Å type, and a trap with a liquid eutectic mixture of sodium and potassium. The copper was obtained by reduction of copper oxide with hydrogen. Silica gel, aluminum oxide and molecular sieves were regenerated by evacuation to a residual pressure of 10^{-1} –10^{-2} mm Hg with simultaneous heating. The temperatures of the parts of the system during regeneration and in the process of nitrogen purification are indicated in Table 1.

When passed through the purification system, nitrogen was freed from moisture to $7–8 \cdot 10^{-5}$%, and from oxygen to below $1 \cdot 10^{-3}$%; purification from moisture was monitored by the dew point, and from oxygen by the Mugdan method ([28]).

Table 2

Retained volumes in column volumes and ratios of retained volumes

Component	Didecyl phthalate V_R	Didecyl phthalate V_R/V_{R1}	Silicone oil 702 V_R	Silicone oil 702 V_R/V_{R1}	Silicone oil VKZh-94B V_R	Silicone oil VKZh-94B V_R/V_{R1}	Silicone oil PFMS-4 V_R	Silicone oil PFMS-4 V_R/V_{R1}	Ethyl Cellosolve V_R	Ethyl Cellosolve V_R/V_{R1}	Paraffin oil V_R	Paraffin oil V_R/V_{R1}
SiH_4	1.25	1.00	1.34	1.00	1.33	1.00	1.39	1.00	1.09	1.00	1.25	1.00
GeH_4	1.58	1.26	1.58	1.18	1.58	1.19	1.72	1.23	1.50	1.38	1.42	1.13
AsH_3	2.2	1.76	2.17	1.62	2.17	1.63	3.34	2.40	2.08	1.91	2.00	1.60
PH_3	1.8	1.43	1.75	1.31	1.58	1.19	2.52	1.81	1.63	1.49	1.71	1.37
H_2	–	–	–	–	–	–	3.54	2.54	–	–	–	–

Qualitative analysis. In developing the chromatographic analysis, individual hydrides purified on a rectification column were used. As solvents, didecyl phthalate, ethyl Cellosolve, silicone oil 702 D, polymethylphenylsiloxane liquid PFMS-4, polyethylsiloxane liquid VKZh-94 B, and paraffin oil were used. Table 2 gives the retained volumes V_R in units of column volume and the relative values of the retained volumes. From the data of Table 2 it is evident that silicone oil PFMS-4 exhibits the best selective properties with respect to the hydrides. The optimum conditions for separation of the components when using this solvent were as follows: temperature 30° and carrier-gas flow rate 17 ml/min. A chromatogram of a six-component mixture obtained on an 8 m long column is shown in Fig. 2.

Quantitative analysis. For quantitative analysis the method of absolute calibration was used. For this purpose, plots of peak area versus the amount of component introduced were recorded. The sensitivity of the analysis was evaluated for each hydride. The sensitivity values are given in Table 3.

Table 3

Sensitivity of chromatographic analysis for hydrides and hydrogen

Component	Sensitivity, mg/ml	Sensitivity, vol. %
SiH_4	$2.9 \cdot 10^{-6}$	$2.0 \cdot 10^{-4}$
GeH_4	$9.0 \cdot 10^{-5}$	$2.6 \cdot 10^{-3}$
PH_3	$2.0 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$
AsH_3	$4.2 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$
H_2S	$9.4 \cdot 10^{-4}$	$6.6 \cdot 10^{-2}$
H_2	$3.5 \cdot 10^{-6}$	$3.9 \cdot 10^{-3}$

The reproducibility of the analyses was checked on individual substances and on their mixtures at different introduced amounts. The reproducibility at contents

Table 4

Results of analysis of a standard mixture

Component	Taken, mole fractions	Introduced amount 0.24 ml: found, mole fractions	Introduced amount 0.24 ml: relative error, %	Introduced amount 0.49 ml: found, mole fractions	Introduced amount 0.49 ml: relative error, %	Introduced amount 0.53 ml: found, mole fractions	Introduced amount 0.53 ml: relative error, %
SiH_4	$2.39 \cdot 10^{-4}$	$2.40 \cdot 10^{-4}$	0.41	$2.37 \cdot 10^{-4}$	0.83	$2.33 \cdot 10^{-4}$	2.51
GeH_4	$2.51 \cdot 10^{-4}$	$4.60 \cdot 10^{-4}$	1.99	$4.48 \cdot 10^{-4}$	0.66	$4.54 \cdot 10^{-4}$	0.66

Component	Taken, mole fractions	Introduced amount 0.24 ml: found, mole fractions	Introduced amount 0.24 ml: relative error, %	Introduced amount 0.49 ml: found, mole fractions	Introduced amount 0.49 ml: relative error, %	Introduced amount 0.53 ml: found, mole fractions	Introduced amount 0.53 ml: relative error, %
PH_3	$2.31 \cdot 10^{-3}$	$2.26 \cdot 10^{-3}$	2.16	$2.31 \cdot 10^{-3}$	0.00	$2.28 \cdot 10^{-3}$	1.29
AsH_3	0.99700	0.99704	0.004	0.997005	0.0005	0.997053	0.005

of hydrides in the mixture from $1 \cdot 10^{-1}$% to $1 \cdot 10^{-3}$ vol.% is 2–3 rel.%. Figure 3 presents a chromatogram of arsine with a silane content of $4.3 \cdot 10^{-2}$, germane $4.4 \cdot 10^{-2}$, and phosphine $8.8 \cdot 10^{-2}$% on a 4 m column. The analysis time is 7 min.

Table 4 gives the results of analysis of a four-component mixture at different sample loadings.

From the data in Table 4 it is evident that the greatest deviation between the content of the components in the initial mixture and the chromatographic-analysis data does not exceed 2.5%. At higher concentrations of impurities, the error is smaller.

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Received
30 XII 1963

CITED LITERATURE

1. G. G. Devyatykh, *Tr. po khim. i khim. tekhnol.*, Gorky, issue 2, 221 (1962).
2. I. L. Agafonov, N. V. Larin, G. G. Devyatykh, *Tr. po khim. i khim. tekhnol.*, Gorky, issue 2, 327 (1962).
3. H. G. Nadeau, D. M. Oaks, *Anal. Chem.*, **32**, No. 11, 1418 (1960).
4. M. E. Grenoble, P. J. Launer, *Appl. Spectroscopy*, **14**, No. 4, 85 (1960).
5. J. J. Kaufman, J. E. Todd, W. S. Koski, *Anal. Chem.*, **29**, No. 7, 1032 (1957).

6. H. W. Myers, R. F. Putnam, *Anal. Chem.*, **34**, No. 6, 664 (1962).
7. R. F. Putnam, H. W. Myers, *Anal. Chem.*, **34**, No. 4, 486 (1962).
8. N. M. Turkel' taub, S. A. Ainshtein, S. V. Savilov, *Zav. lab.*, **28**, No. 2, 141 (1962).
9. K. Borer, C. Phillips, *Proc. Chem. Soc.*, 1959, 189.
10. J. E. Drake, W. L. Jolly, *Proc. Chem. Soc.*, 1961, 379.
11. L. R. Harper, S. Joller, H. C. Miller, *J. Inorg. and Nucl. Chem.*, **21**, 294 (1962).
12. M. Mugdan, *Angew. Chem.*, **46**, No. 5, 90 (1935).

Note: Figure translations are in progress. See original paper for figures.