

COMPARISON OF HYDRIDE GENERATOR/GAS-LIQUID PHASE SEPARATOR SYSTEMS FOR CONTINUOUS HYDRIDE GENERATION IN ATOMIC ABSORPTION SPECTROMETRY

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A comparison of five kinds of hydride generator/gas-liquid phase separator systems used in the hydride generation in AAS is made. These systems are also compared with a newly designed type of separator. Optimum working conditions were tested and basic characteristics were measured for all the types of systems. The basic criteria for comparison of the systems were the measuring sensitivity, reproducibility and detection limit for the given system. Additional comparison criteria were the analysis frequency achieved, applicability of the given separator for flow-injection measurements and economic criteria.

Key words: Gas-liquid phase separator; Hydride generator; Atomic absorption.

To overcome difficulties in the determination of As and Se and later on also Ge, Sn, Pb, Te and Bi by AAS, the technique of generation of volatile hydrides was developed at the late 60's and early 70's for the determination of these elements. The main characteristic of this technique is the formation of the gaseous hydride of the given element, its separation from the sample matrix and thus achieving a higher concentration of the given analyte in the absorption environment when compared with the flame AAS technique.

The hydride generation technique can be divided into three phases. In the first phase, the acidified sample solution reacts with the reducing agent to form a covalent volatile hydride of the element contained in the analyte. In the second phase, this hydride is separated from the reaction mixture and transported by the carrier gas to the atomizer. In the last phase, the hydride is decomposed to the gaseous metal atoms^{1,2}.

In the technique of generation of volatile hydrides, the greatest attention is paid to the mechanism of hydride formation, the atomizing process³⁻⁵, study of interferences both in the liquid phase (affecting the rate or efficiency of formation and release of the hydride from solution) and in the gas phase (transport and atomizing interference), and also to the process of thorough separation of the gas phase formed.

The means of hydride generation and the principle of separation of the gas phase from the liquid in the continuous generation technique may be different. In the former

case, the hydride is formed in the reaction coil and continuous separation of the liquid phase from the gas phase occurs in the phase separator. In the latter case, the generation process and hydride separation occur simultaneously in a generator-separator joint apparatus.

The hydride is separated from the reaction mixture either by expulsion by an excess of generated hydrogen and carrier gas⁶ (HG apparatus working with high acid concentrations) or by a carrier gas flowing into the joint generator-separator through a porous frit^{7,8} (systems working with low acid concentrations). Another method separates the gas phase on the basis of diffusion of the hydrides through the wall of a silicone tube (membrane) or PTFE microporous membrane^{9,10}.

In general, it can be concluded that the following conditions must be fulfilled for the most efficient functioning of the system for continuous hydride generation:

- a) most efficient hydride generation,
- b) complete separation of the gaseous hydride from the reaction mixture, and
- c) continuous transport of the separated gas phase into the atomizer and continuous drainage of the waste liquid from the system.

A number of authors have described the principle, construction changes and optimization of working conditions for their hydride generator/gas-liquid phase separator systems; however, they rarely make a comparison with other types of systems or with conventional systems.

This work deals with the comparison of five selected systems used in the hydride generation technique in AAS and comparison of these apparatuses with a newly designed gas-liquid phase separator.

EXPERIMENTAL

Apparatus

The measurements were carried out using a Varian SpectrAA 300A spectrometer equipped with a deuterium background correction system. The radiation source was an EDL lamp for As (charging power 7 W). The measurements were carried out at 193.7 nm using a spectral interval of 0.5 nm.

Continuous generation of hydrides was achieved using the specially designed apparatus depicted in Fig. 1.

An eight-channel peristaltic pump (Cole-Parmer Masterflex, Cat. No. 07550-62), eight-roller pump head (Cole-Parmer Masterflex, Cat. No. 07623-10) with tygon tubing with inner diameters of 2.06 mm, 1.42 mm and 0.89 mm (Cole-Parmer) was used for the reagent feed; polypropylene connectors were used for connection. The carrier gas (nitrogen) flow rate was measured using a Cole-Parmer (Cat. No. 03216-45) flow-meter. The reaction coil was a PTFE tube with an inner diameter of 1 mm. The appropriate reaction coil lengths are shown in Table I.

The hydrides were atomized using an absorption cell (conventional quartz T-tube with a length of 170 mm and i.d. 12 mm, narrowed in the centre to an i.d. 4 mm, with 70-mm side arm of i.d. 1.5 mm) located along the optical axis of the AA spectrometer. The quartz atomizer was heated electrically to a temperature of 950 °C (Varian Electrothermal Temperature Controller ETC-50).

TABLE I
Working conditions of all tested systems

Parameter	System ^a					
	A	B	C	D	E	F
$w(\text{NaBH}_4)$, % ^b	1.0	1.7	1.7	1.0	1.5	1.0
$q_v(\text{NaBH}_4)$, ml/min ^b	1.8	1.8	1.8	1.8	1.0	1.8
$c(\text{HCl})$, mol/l ^c	6.0	0.5	5.0	5.0	7.0	7.0
$q_v(\text{HCl})$, ml/min ^b	1.8	1.8	1.8	1.8	1.0	1.8
$q_v(\text{sample})$, ml/min ^b	7.0	7.0	7.0	7.0	4.0	7.0
$q_v(\text{carrier gas})$, ml/min ^b	40	138	138	25	0	40
l , mm ^b	3 000	—	—	—	2 000	2 000
T , °C ^b	45	—	—	—	25	45

^a w mass fraction, q_v volume flow rate, l reaction coil length, T temperature of reaction coil;
^{b,c} sample 10 µg/l As(III) in ^b 1.0 M HCl, ^c 0.01 M HCl.

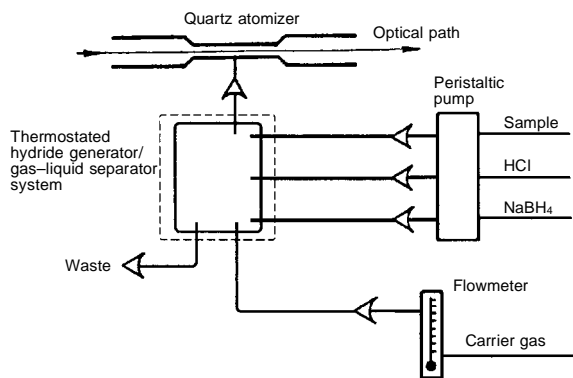


FIG. 1
Apparatus for continuous generation of the hydrides

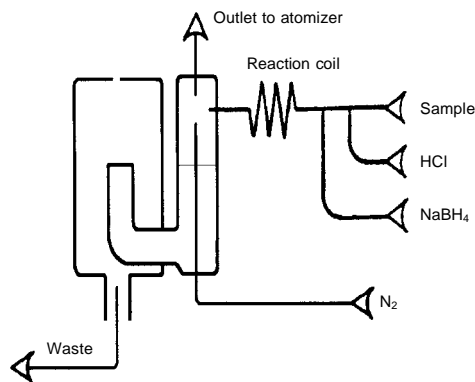


FIG. 2
VGA-76 separator (A)

The connection between the exit from the given separator and the entrance into the absorption cell consisted of a 50-mm polyethylene tube (inner diameter 1.5 mm; dead volume minimization) in all cases.

A water thermostat (type U-15, MLW, Medingen, Germany) was used to maintain constant temperature (mostly 25 °C) of the studied systems.

Hydride Generation Gas-Liquid Separator Systems

The following six hydride generator/gas-liquid phase separator systems were selected and used in this work.

*Commercial type of separator from the Varian VGA-76 apparatus*⁶ (system A, Fig. 2) (U-shaped gas-liquid phase separator); the separator was combined with the reaction coil of length of 3 000 mm.

Combined generator/separator system (system B, Fig. 3). This system is characterized by different means of generation and principle of separation of the gas phase. The reaction occurs inside the system through mixing of reagents at the ends of the inlet capillaries and the mixture drips onto the frit. This generator-separator system was first used in the DCP-AES method⁷ and was modified for this study.

After acidification with HCl, the sample is fed under the surface of the reaction mixture through a narrow capillary (i.d. 0.5 mm) and a NaBH₄ solution is fed to the immediate vicinity through a second capillary (i.d. 0.5 mm). The bottom of the separator consists of a microporous glass frit, through which the carrier gas flows into the system. The separator is widened at the top to limit passage of foam (formed at high carrier gas flow rates) into the quartz atomizer. After reacting, the reaction mixture is continuously transferred by a peristaltic pump into the waste outlet through a side opening in the separator and thus its volume is maintained at a constant level in the system. The volume of this reaction space can be changed by changing the liquid level in the separator; the maximum volume of the reaction space is 36 ml.

*The combined generator/separator system with a fixed volume*⁸ (internal volume 25 ml and reaction volume 3 ml) (system C, Fig. 4) has a design similar to the previous type. It consists of a funnel-shaped inner vessel and external cylindrical glass jacket. The bottom of the funnel once again consists of a microporous frit. AsH₃ is formed in the small funnel space, into which reagents are continuously added close to the frit surface. The carrier gas, similar to the previous case, flows into the apparatus through a frit and then flushes the gas phase formed into the atomizer. The waste solution overflows over the edge of the funnel into the space of the external cylinder and then through a side arm connected to an open reservoir.

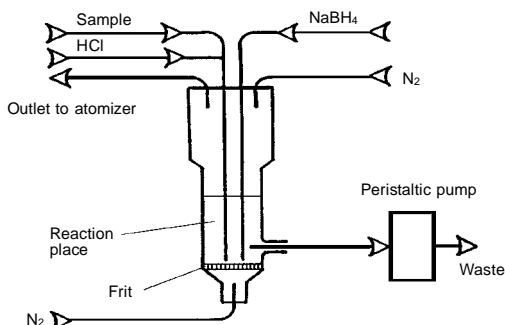


FIG. 3
Combined generator-separator (B)

The tube hydride generator/separator system is based on the diffusion of the gas through the thin wall of a silicone tube⁹ (system D, Fig. 5). Into an external PE tube of a given length (i.d. 5 mm), a special separation silicone tube is fitted with the same length (i.d. 2 mm, wall thickness 0.3 mm). This inner silicone tube is also the reaction coil into which the reagents are fed (NaBH_4 , HCl , sample). The carrier gas feed is at the one end of the external tube, that is used for counter-current (relative to the direction of flow of the reaction mixture) flushing of gases passing through the wall of the silicone tube from the space between the two tubes. This type of equipment was originally used for the determination of As, HCO_3^- , I, Se, Sn and S by the ICP-AES method^{11,12}. It was later used to determine As through generation of AsH_3 in the ICP-MS method¹³.

In the hydride generator/membrane separator system¹⁰ (system E, Fig. 6), the separation is based on diffusion of the gas through a membrane consisting of a Teflon strip with a thickness of 0.075 mm (11 mm in width, 1 μm pore size, ZeFluor, Gelman Sciences). The separator consists of two blocks of poly(methyl methacrylate) with a groove in the middle of their largest sides. The reaction mixture is fed through the first block using a groove of dimensions of $1.0 \times 3 \times 50$ (90) mm. The hydride formed and excess hydrogen are fed into the atomizer through the second block with a groove of dimensions of $3 \times 3 \times 50$ (90) mm. A nylon grid with a thickness of 0.1 mm (100×10 mm) is used to fix the Teflon membrane. The two blocks are fitted tightly together and sealed with a thin rubber seal fitted between the two blocks. The system using the gas-liquid membrane separator was combined with the reaction coil length of 2 000 mm.

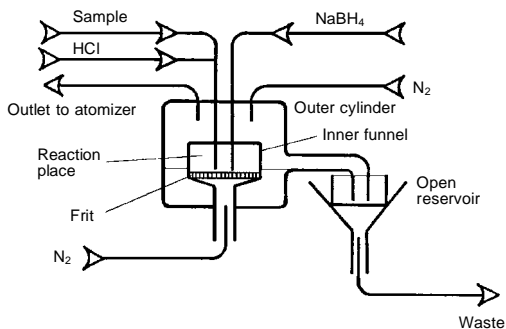


FIG. 4
Combined generator-separator with
fixed volume (C)

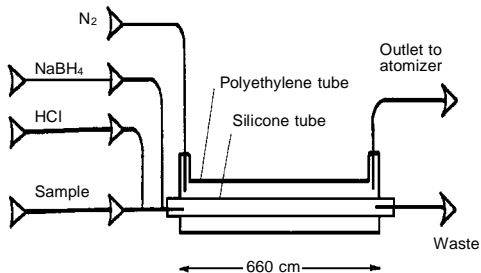


FIG. 5
Tube separator (D)

The combined hydride generator/separator system (system F, Fig. 7) utilizes the advantages of the classical separator (U-tube) A and the combined generator-separator B. The reaction coil length was chosen 2 000 mm.

Reagents

A standard As solution (1.0000 g/l) (Analytika, Prague) was used to prepare the 10 $\mu\text{g/l}$ As(III) working solution. The working standard was prepared daily from the standard solution. The hydrochloric acid used was Suprapur[®] grade (Merck, Darmstadt).

Solution of sodium tetrahydroborate NaBH_4 (Merck, Darmstadt, content >96%) in 0.4 wt.% NaOH was always prepared fresh from the powdered substance.

Hydrofluoric acid (38–40 wt.%, Analytika, Prague, semiconductor grade purity) was used to clean the quartz atomizer.

Deionized water was prepared using the Milli Q+ deionizer from the Millipore Co., U.S.A. The carrier gas was 99.999% purity nitrogen.

Procedure

Working conditions for all the hydride generator/separator systems were tested on a 10 $\mu\text{g/l}$ As(III) sample prepared in 1 M HCl. The effect of the acid concentration (HCl) was studied on a sample of 10 $\mu\text{g/l}$ As(III) in 0.01 M HCl.

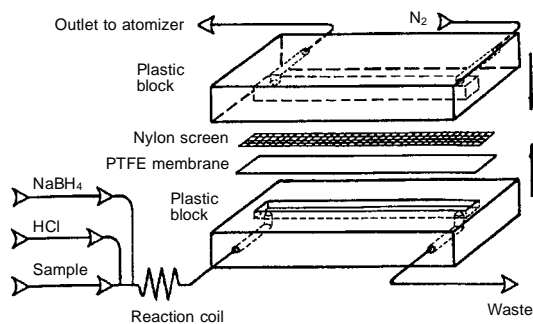


FIG. 6
Membrane separator (E)

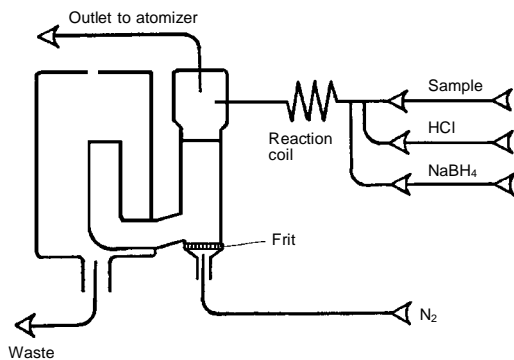


FIG. 7
Combined separator (F)

The absorbance values given in the graphs of the basic characteristics were always read off after attaining a stationary state in the system and are the average of three recorded values with an integration time of 10 s.

The delay time was found for each system; this is defined as the time required for the signal to attain a steady value after a change in the analyte concentration.

For each system the characteristic concentration and the limit of detection were determined, the latter being defined as $3 s/m$, where m is the slope of the linear portion of the calibration graph and s is the standard deviation for ten identical measurements near the blank signal level.

RESULTS AND DISCUSSION

The following six hydride generator/gas-liquid separator systems were selected for comparison of their characteristics in the hydride generation technique in AAS.

As a basic system the commercial separator in VGA-76 apparatus (A) was chosen, representing the classical separation method. In addition, two combined generator/separator with microporous glass frits (B, C), two separators based on the principle of diffusion of a gas through a membrane (D, E) and the newly designed combined separator (F) were tested.

Working Conditions for All the Tested Separators

First, working conditions were studied for all the tested hydride generator/gas-phase separator systems. All the measurements were carried out using the apparatus depicted in Fig. 1.

The concentration of the reducing agent, NaBH_4 , concentration of hydrochloric acid, sample flow rate, carrier gas flow rate and, where pertinent, the length of the reaction coil and its temperature were found for each system.

The dependences for each tested parameter obtained for all the systems are depicted in a separate graphical plot for a better comparison of the results obtained. At the same time, these graphical dependences also give the values obtained by measuring the newly designed separator. The working conditions are discussed separately for each of the separators. All the graphical dependences are plotted as the dependences of absorbance vs the given parameter; the criterium for the optimum working conditions is thus the absorbance value.

The effect of the concentration of NaBH_4 (Fig. 8), concentration of HCl (Fig. 9), flow rate (Fig. 10), the carrier gas flow rate (Fig. 11) and the length of the reaction coil (Fig. 12) at 25 and 45 °C are illustrated for systems A-F.

Table I gives the working conditions for all the separators.

System A

It follows from Fig. 8 that the measuring sensitivity is highly dependent on the NaBH_4 concentration required for conversion of the analyte to the hydride. A NaBH_4 concentration of 1.0% was found to be optimum for separator A (for a reaction coil temperature of 45 °C). The decrease in the absorbance beyond the maximum is apparently caused by dilution of the hydride by excess generated hydrogen. It was found that the temperature of the system has a significant impact on the process of generation of AsH_3 and thus on the sensitivity of measurement. It was also verified that the optimum NaBH_4 concentration is dependent on the temperature of the system (reaction mixture). At a temperature of 25 °C, the optimum NaBH_4 concentration is 1.7 wt.%, whereas for 45 °C a value of 1.0% was obtained (with a simultaneous increase in the signal by about 0.06 A).

Figure 9 yielded an optimum concentration of added HCl of 6 mol/l at a flow rate of 1.8 ml/min (the concentration of HCl in the reaction mixture is then 1.2 mol/l for a flow rate of 7.0 ml/min and HCl concentration in the sample of 0.01 mol/l, and 2.0 mol/l for a flow rate of 7.0 ml/min and HCl concentration in the sample of 1.0 mol/l).

Figure 10 depicts the effect of the flow rate of the sample on the measured signal; a flow rate of 7.0 ml/min was chosen as an optimum. Figure 11 depicts the dependence of the absorbance signal on the carrier gas flow rate into the separator. It is apparent from the dependence that a certain carrier gas flow rate (≈ 40 ml/min) is necessary for a maximum separation of the hydride formed; the excess hydrogen formed is insufficient and flushes most of the hydride away from the separator. However, higher carrier gas flow rates decrease the noise in the measured signal.

Figure 12 depicts the effect of the reaction coil length at 25 °C and for the selected optimum temperature of 45 °C. It can be seen that even a very long reaction coil cannot

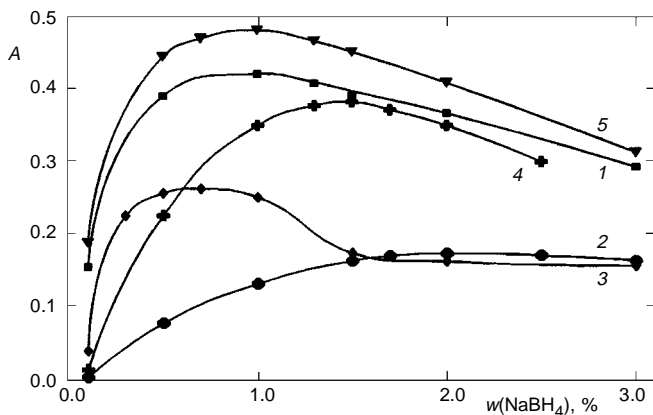


FIG. 8

Dependence of absorbance ($\lambda = 193.7$ nm) on NaBH_4 content. System: 1 A, 2 C, 3 D, 4 E, 5 F

have such a strong impact on the measurement sensitivity as an increase in the temperature of the reaction coil. The higher sensitivity at higher temperatures is also caused by a rapid decrease in the solubility of AsH_3 in water with increasing temperature (the solubility of AsH_3 in water at 25 and 100 °C is 28 and 0 ml per 100 ml, respectively; the solubility of hydrogen in water at 25 and 50 °C is 1.91 and 1.89 ml per 100 ml, respectively, and the solubility of nitrogen at 25 and 40 °C is 1.52 and 1.42 ml per 100 ml, respectively)¹⁴. At reaction coil lengths greater than 350 cm, a strong pulsation of the reaction mixture occurs, producing oscillations in the measured signal. Lengthening of the reaction coil leads both to a significant increase in noise levels and also to increased delay times and thus increased sample consumption.

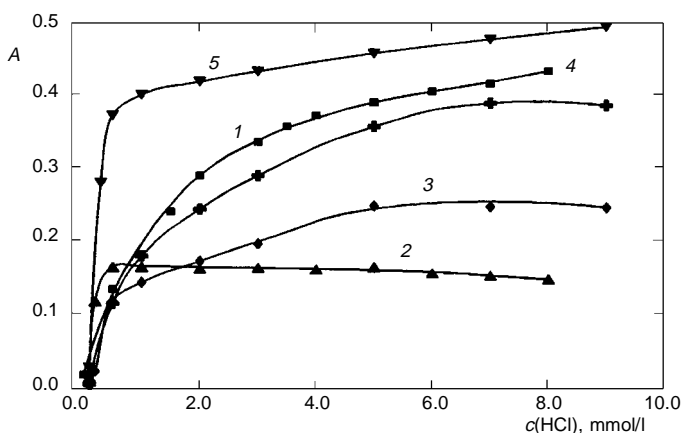


FIG. 9

Dependence of absorbance ($\lambda = 193.7$ nm) on HCl concentration. System: 1 A, 2 B, 3 D, 4 E, 5 F

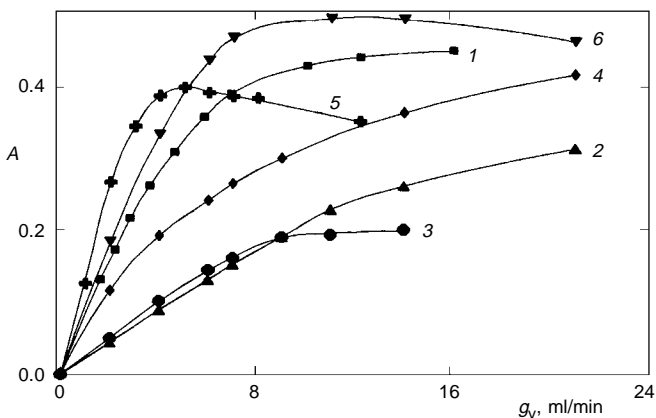


FIG. 10

Dependence of absorbance ($\lambda = 193.7$ nm) on sample flow rate. System: 1 A, 2 B, 3 C, 4 D, 5 E, 6 F

As it was found that the temperature of the reaction coil has a marked effect on the generation of AsH_3 , this dependence was measured in detail. It can be seen from Fig. 13 that the effect of the temperature increases to approximately 50°C ; at higher temperatures, the noise level in the measured signal increases considerably.

System B

An optimum concentration of the acid feed of about 0.5 mol/l was found from Fig. 9 (corresponding to an analytical concentration of HCl of about 0.1 mol/l in the reaction

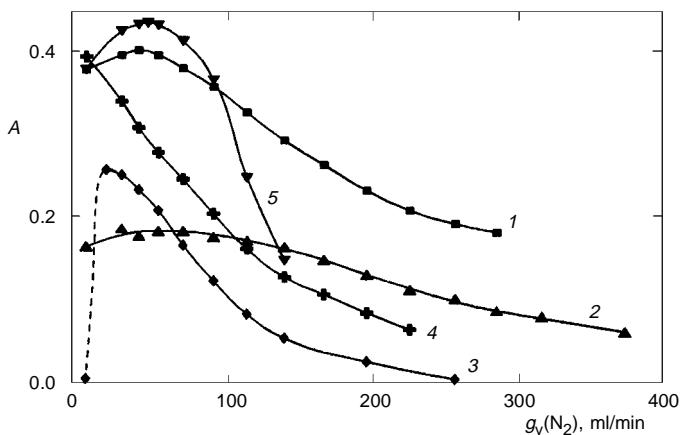


FIG. 11

Dependence of absorbance ($\lambda = 193.7\text{ nm}$) on carrier flow rate. System: 1 A, 2 B, 3 D, 4 E, 5 F

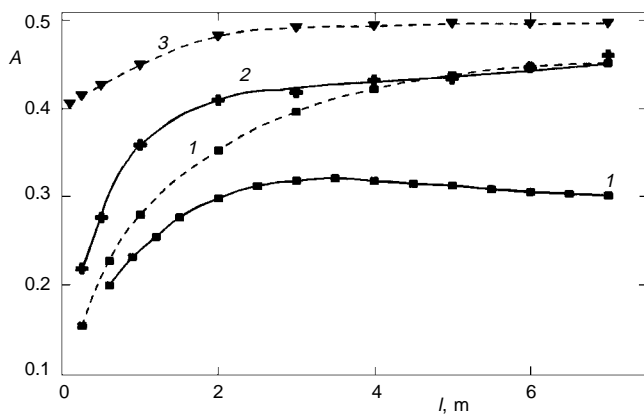


FIG. 12

Dependence of absorbance ($\lambda = 193.7\text{ nm}$) on reaction coil length at 25°C (—) and 45°C (---). System: 1 A, 2 E, 3 F

mixture). Thus the acidity of the sample is sufficient for the measurement and the acid feed channel need not be used. The dependence of the signal on the acid concentration exhibits a sharp increase up to a value of about 0.5 M HCl (maximum hydride generation occurs practically at the stoichiometric ratio of the NaBH_4/HCl concentrations); the signal value then remains nearly constant and finally decreases slightly at acid concentrations above 5 mol/l. The requirement of low sample acidity for the generation can be explained by the relatively large reaction volume (of the order of several tens of ml; an amount of 10.5 ml, maximum 35 ml was used) compared with the volume of the reaction coil (e.g., 1.96 ml for system A). The second reason is the design of this system with a frit through which the carrier gas flows, which efficiently stirs the reaction mixture and also forms a large liquid–gas interface for the fastest possible passage of the hydride into the gas phase. At low acidities, the bubbles of the gas phase formed are very small and produce a practically homogeneous liquid–gas mixture, so that the contact time of the two phases is greatly prolonged.

The dependence of the absorbance on the sample flow rate for this system (Fig. 10, curve 2) is linear up to a flow rate of 11 ml/min. Even at higher flow rates, the loss in efficiency of hydride formation is not as great as for the previous system, once again because of the large reaction volume of the system (a volume of 10.5 ml used), and thus the sufficiently long reaction time. The reaction time here is determined by the time during which the given amount of liquid remains in the reaction space (equal to 72 s for flow rates of 7.0 ml/min for sample, 1.8 ml/min for NaBH_4 and reaction volume of 10.5 ml; this time decreases to 28 s for a higher sample flow rate of 21 ml/min being still at least an order of magnitude greater than in system A with a sample flow rate of 7.0 ml/min).

The dependence of the absorbance on the nitrogen flow rate through the frit is given in Fig. 11, curve 2. The relatively broad plateau is apparently a result of two opposite

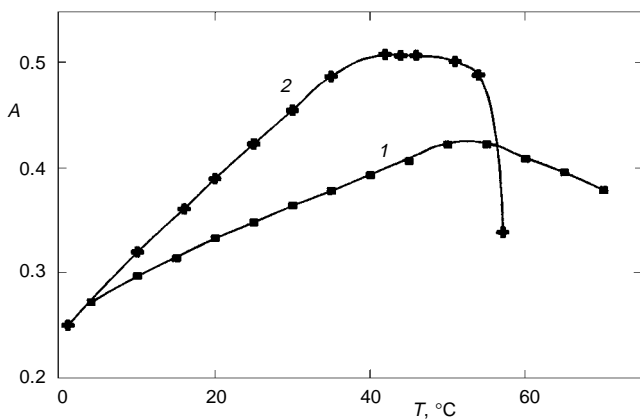


FIG. 13

Dependence of absorbance ($\lambda = 193.7$ nm) on temperature of reaction coil. System: 1 A, 2 F

tendencies: the first is the dilution of the hydride with increasing flow rate (decreased sensitivity); the second is the more efficient stirring of the reaction mixture and faster passage of the hydride into the gas phase with increasing nitrogen flow rate (the measurement sensitivity increases); the former tendency begins to predominate above a flow rate of about 100 ml/min of nitrogen. As the nitrogen flow rate increases, the noise level of the measured signal decreases. This is also one of the reasons for the choice of the higher nitrogen flow rate of 138 ml/min accompanied by a slight decrease in sensitivity (the highest sensitivity of measurement was achieved at 50 ml/min of nitrogen). The higher flow rate was also chosen because of a relatively large dead volume of the system (*e.g.*, for a flow rate of 24 ml/min, the delay time is 120 s; this time equals 70 s at the flow rate used here). The inlet of the carrier gas through the frit was only used in the system. Nitrogen feed through the second inlet (for a given nitrogen flow rate below the frit) only led to decreased sensitivity caused by dilution of the hydride. Similarly, the same nitrogen flow rate only through the second inlet led to a small response compared with the inlet only through the frit.

System C

The system does not provide a sufficiently large reaction volume for the reaction to occur efficiently in such weakly acidic medium like in the previous system, and requires a separate inlet channel for the HCl solution. It is apparent from the comparison of all the measured dependences of the absorbance on the HCl concentration that the dependence has the slowest increase towards the maximum sensitivity (absorbance) value for the smallest reaction volume (reaction coil). In contrast, the dependence increases rapidly to this absorbance value for the largest reaction volume (generator with variable reaction volume of 10.5 ml). The dependence for system C lies between these two curves.

System D

Figure 8 (curve 3) depicts the effect of the amount of NaBH_4 from which an optimum value of 0.7% was obtained. However, a value of 1.0% was chosen for the measurement because the gas production is so low and uneven at lower NaBH_4 concentrations that the mixture in the inner silicone tube pulsates. At an NaBH_4 concentration greater than 3%, the reaction mixture again begins to pulsate and the walls of the silicone tube are deformed. The efficiency of the separation of the hydride in this system greatly depends on both the magnitude of overpressure of the gas phase as well as on the period of contact of the gas with the silicone membrane. In contrast to the previous system, this interface forms considerable resistance to the separated gas phase. The time of contact with the separation interface is determined not only by the flow rate of the reagents and the sample, but also by the NaBH_4 concentration (the amount of hy-

drogen released and thus the velocity of the passage of the gas phase through the silicone tube). Thus, the sensitivity is decreased at NaBH_4 concentrations greater than 1.0%, combined with dilution of the gaseous hydride by excess hydrogen.

A sample flow rate of 7.0 ml/min was found to be an optimum. In this system, the flow rate of the reaction mixture has a certain critical level above which the flow of the mixture in the tube begins to pulsate. This flow rate can be affected primarily by the concentration of the NaBH_4 solution used and also by the sample flow rate. At NaBH_4 concentration of 1.0%, a stable signal is obtained at flow rates of at least 7.0 ml/min.

The nitrogen carrier gas acts only as a transport medium in this system. The system has a relatively large dead volume and the amount of gas phase passing through the membrane is much smaller than for all the systems studied previously. It can be seen from the graph that, at zero flow rate of the carrier gas, the hydride is not flushed into the atomizer at all (nor is the excess hydrogen formed). Even a very small flow rate of the carrier gas transports the hydride from the system into the atomizer, which is reflected in a sharp increase in the signal. (Among other things, this dependence confirms that the amount of gas phase passing through the membrane is very small.) The separation efficiency in this system can be affected primarily by the choice of the membrane wall thickness (a wall thickness of 0.3 mm was used in the system). However, a silicone tube with a thinner wall (0.25 mm) cannot be used because of complete deformation of the silicone tube – membrane. The response to a change in the analyte concentration is very slow and decreases further with a decrease in the carrier gas flow rate. However, an increase in the nitrogen flow rate leads to a considerable decrease in the sensitivity (dilution of the hydride by the carrier gas). No change in the magnitude of the noise in the signal was observed after a change in the flow rate. Similarly, the direction of flow of the carrier gas has no effect on the measured signal. The length of the system has a considerable effect on the separation of the hydride as it determines the contact time of the reaction mixture with the membrane and thus the amount of hydride passing through the membrane. The magnitude of the signal increases almost linearly with increasing length of the system up to a value of about 550 cm; a system length of 660 cm was chosen for the measurements. Reliable measurements cannot be carried out with a system longer than 660 cm as a further increase in the tube length leads to an ever-increasing resistance to pumping of the reagents and the mixture begins to pulsate strongly in the system. Increasing the length also increases the delay time; this value increases to 500 s for a tube length of 660 cm.

System E

The reaction site in this system is once again the reaction coil and this separator is used only to separate the gas phase. The dependence of the absorbance signal on the NaBH_4 concentration (Fig. 8, curve 4) exhibits a sharp maximum around 1.5% NaBH_4 . The rapid decrease in the sensitivity beyond this value is not only a result of dilution of the

analyte hydride by an ever-increasing amount of hydrogen, as found for all the separation systems without a membrane, but rather of the increase in the overall flow rate of the reaction mixture. This leads to a decrease in the contact time of the reaction mixture with the membrane. In contrast to the previous separator with an active separation surface of about 414 cm^2 (length 660 cm), this system has an active separation surface of only 1.5 cm^2 (groove length 50 mm) or 2.7 cm^2 (groove length 90 mm). At NaBH_4 concentrations higher than 2.5%, the flow rate of the reaction mixture through the system becomes very fast and its functioning can be permanently disturbed (a great pressure of the reaction mixture on the membrane leads to passage of a certain amount of liquid; as soon as the liquid enters the space between the membrane and the Nylon grid, the surface tension of the liquid leads to blockage of the grid openings and the active surface of the separator decreases).

Because of the very small dead volume of this separator (0.45 ml for a groove 50 mm long and 0.81 ml for a groove 90 mm long), the system has a very fast signal response. The hydride is transported sufficiently rapidly to the atomizer by the excess hydrogen formed in the reaction of NaBH_4 with HCl (the amount of hydrogen formed under these optimum working conditions corresponds to a flow rate of about 71 ml/min under ideal conditions). This is also reflected in the dependence of the absorbance signal on the carrier gas flow rate given in Fig. 11 (curve 4). Thus, a carrier gas was not used for this system. No change was observed in the noise signal level while changing the nitrogen flow rate.

Changes in the temperature have various effects on the generation and separation of the gas phase and on the overall functioning of this system. Increasing temperature has a favorable effect on the generation and separation of the gas phase, reflected in an increase in the sensitivity up to a value of about $45 \text{ }^\circ\text{C}$. However, increasing temperature has a detrimental effect on the separator lifetime (the PTFE membrane). The higher the temperature of the reaction mixture, the shorter the lifetime of the separator; this time decreases to only a few minutes around $40 \text{ }^\circ\text{C}$ and only a few seconds at $50 \text{ }^\circ\text{C}$ (the values strongly depend on the kind of membrane used). The change in the separation efficiency is irreversible. When the separator is used for longer periods of time at elevated temperatures, the signal values become irreproducible and the measured value gradually decreases at a rate dependent on the experimental temperature. Thus the graph of the absorbance signal vs the temperature of the reaction mixture (Fig. 13, curve 2) is of no significance for practical measurements as the signal of the analyte cannot be reproduced at higher temperatures. Thus, in practical measurements using this system with a given PTFE membrane, it is necessary to work at laboratory temperature.

The efficiency of separation in this system can be changed to a certain extent only by changing the size of the active surface area of the PTFE membrane. However, the membrane surface area must not be too large to avoid a detrimental increase in the dead volume of the separator and also to avoid mechanical deformation of the membrane.

Thus, the groove cannot be broader, but can be lengthened. In these measurements, a separator with a groove length of 50 or 90 mm was employed. Under optimum conditions (sample flow rate 4 ml/min, 1.5% NaBH₄ and 1 ml/min of 7 M HCl), a separation length of 50 mm is not sufficient for complete separation. However, a separation length of 90 mm is adequate.

System F

This next test system has not yet been studied (Fig. 7). It was prepared on the basis of the knowledge obtained from the study of the previous apparatus for the generation and separation of the gas phase as described in this work. The design of this apparatus includes the favorable features of the previous equipment.

It can be seen from Fig. 9, curve 5 that the variation of the absorbance signal with increasing HCl acid concentration has similar features for both systems (curves 1 and 2, respectively), from which their advantages were taken. The sharp increase in the sensitivity for concentrations up to 0.5 M HCl is a result, similar to separator B, of the existence of a larger reaction volume (5.6 ml used) in the separator (in addition to the reaction volume of 1.57 ml in the reaction coil), in which the chemical reaction of hydride formation can be finished at low acid concentrations (effect of acidity on the kinetics of hydride formation). The nitrogen flowing through the porous frit, similarly to system B, thoroughly stirs the reaction mixture and forms a large liquid-gas phase interface for easier passage of the analyte hydride into the gas phase. However, after this rapid increase, the signal attains a maximum value (as for system B) as the low flow rate of nitrogen through the frit is not sufficiently intense for the reaction above the frit to occur with maximum efficiency. As the acidity of the reaction mixture increases, the formation of the gas phase is accelerated and occurs practically only in the reaction coil at high acidities. The dissolved hydride is then only released in the separator space.

Figure 12 (curve 3) gives the variation of the absorbance signal with the increasing reaction coil length at a reaction mixture temperature of 45 °C. In this system, with nitrogen bubbling through the reaction mixture, there is a certain correction for losses in efficiency of conversion of the analyte to the hydride (caused by the insufficiently long reaction coil) due to the possibility of completion of the reaction in the separator space (in contrast to system A).

Comparison of the Separation Systems

For all the test systems, in addition to determination of the optimum working conditions, the calibration curve was constructed and the detection limits and the measurement sensitivity were determined. In addition, the measurement reproducibility was found for each system (using a sample of 10 µg/l As); the necessary delay times were measured

and the sampling rates were found from these values. The results are summarized in Table II.

It follows from the table that the lowest limits of detection were obtained for systems of types E and F. Similarly, the highest measurement sensitivities were found for these systems. The sensitivities for these systems increase in the order: B, C, D, A and E.

All the systems exhibit approximately the same linear calibration ranges with the exception of system B. The high dynamic concentration range of system B is associated with the large reaction volume in the separator.

Similarly, all the systems exhibit the same reproducibility. The noise level in systems using a reaction coil is affected primarily by fluctuations in the flow rate of the reaction mixture inside the reaction coil, caused by uneven production of bubbles of the gas phase (systems A, E and F). Similarly, the noise level for the systems using porous frits (B, C) is caused by uneven separation of the gas phase from solution. The values of typical measurement delay times are, however, variable. A very different value is obtained for system D, because of its great length which is, however, also necessary for attaining at least a comparable measurement sensitivity. On the other hand, the smallest value is attained for membrane separator E. The highest analyzing frequency is also obtained for this system. Because of its small dead volume and thus short delay time, system E and proposed system F are very useful for the flow-injection mode.

System E has the fastest signal response to a change in the analyte concentration. The relatively small overall flow rate of the gas phase in system E, which is the lowest of all the test systems, permits the use of small-diameter (1 mm) connecting tubes for passage of the gas phase from the separator into the atomizer. This further decreases the dead volume of the apparatus and thus also the time response. This tube diameter could

TABLE II
Comparison of characteristics of the studied systems

Parameter	System					
	A	B	C	D	E	F
Limit of detection, $\mu\text{g/l}^a$	0.060	0.060	0.075	0.093	0.050	0.050
Sensitivity of measurement, $1/\mu\text{g}$	0.042	0.017	0.018	0.024	0.048	0.050
Linearity of the calibration graph, $\mu\text{g/l}$	0-5	0-20	0-10	0-10	0-10	0-10
Reproducibility, %	0.5	1.3	1.4	1.9	0.9	0.8
Typical delay time, s	40	70	60	500	25	35
Sampling rate, s/h^b	65	36	40	7	90	72

^a $3 s/m$ (m is slope of the linear portion of the calibration graph and s is an estimation of standard deviation of 10 replicate measurements near the blank level); ^b integration time 3×10 s was used for measurement of one sample.

not be used for the other test systems because of the elevated overpressure in the separator, which led in the narrow tube to greater resistance to the flow of the gas phase.

In general, it can be expected that the hydride generation can reach 100% for membrane systems D and E; however, the separation is less efficient here because there is a greater resistance to the gas phase passage across the membrane. In contrast, it can be expected for the systems without membranes that the efficiency of separation of the gas phase is the same as the generation efficiency. However, the gas generation need not attain a maximum efficiency (especially for system A). It is thus assumed for these systems that all the gas phase produced enters the atomizer. This is certainly not true of the membrane separation. It clearly follows from the experiments that the most efficient generation of the gaseous hydride is achieved for combination of prior location of the reaction coil with a frit separator (F). The use of a reaction coil for the chemical reaction is the most efficient means of generation. The use of the reaction coil greatly improves the measurement response time (the small internal volume of the coil is flushed very rapidly and the signal stabilizes in a short time). The frit feed of the carrier gas in system F ensures completion of the reaction in the reaction mixture (especially at higher analyte concentrations). At the same time, the carrier gas fed into the separator frit located at the bottom (F) clearly facilitates the second step – separation of the hydride from the reaction solution. The fine stream of bubbles of the carrier gas passing through the reaction mixture probably also assists in even stirring of the carrier gas with the released hydride. This appears as even transport of a completely homogeneous gas mixture into the atomizer leading to a lower noise and lower detection limit. The use of a reaction coil also permits the use of higher temperatures for the reduction reaction.

Both the systems with a porous frit without a reaction coil (B, C) have the disadvantage of the high carrier gas flow rate (necessary for efficient reaction), which greatly dilutes the generated gaseous hydride and thus decreases the sensitivity of the determination.

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