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M. Prokopowicz

K. Lewandowska

A. Skwierawska

Andrzej Przyjazny

Jan F. Biernat

*See next page for additional authors*

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**Authors**

M. Prokopowicz, K. Lewandowska, A. Skwierawska, Andrzej Przyjazny, Jan F. Biernat, and J. Namiesnik

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# Synthesis and Characterization of Modified Silica Gel as an Intermediate in the Generation of Gaseous Standard Mixtures

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M. Prokopowicz / K. Lewandowska / A. Skwierawska / A. Przyjazny<sup>1</sup> / J. F. Biernat / J. Namieśnik\*

Chemical Faculty, Technical University of Gdańsk, Narutowicza 11/12 St., 80-950 Gdańsk, Poland

<sup>1</sup>GMI Engineering & Management Institute, Flint, MI, USA

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## Key Words

Gas chromatography  
Modified silica gel  
Gaseous standard mixtures  
FID calibration  
Methyl chloride

## Summary

A possibility of extending analytical applications of chemically modified silica gels is described. This involves their utilization for the generation of gaseous standard mixtures consisting of methyl chloride as the analyte and nitrogen as a carrier gas to be used for the calibration of the GC-FID system. N-methylmorpholine was chemically bonded to the propylsilylated surface of silica gel forming chloride of an appropriate immobilized compound which, under certain conditions, undergoes thermal decomposition yielding a single, volatile component (methyl chloride). Such a method of generating specific amounts of a standard substance can be used both for a single point calibration and for checking the accuracy of an analytical instrument in a relatively wide measurement range. It was found that  $3.40 \pm 0.081$  mg of methyl chloride can be generated per 1 g of the modified gel.

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## Introduction

Silica gel has found numerous applications both in analytical chemistry and in other areas of science. Chemical properties of this adsorbent depend on mutual orientation of edges of surface tetrahedra to which active hydroxyl groups are bonded [1]. Silica gel has been the material of choice in the manufacture of solid supports since the inception of chemically-bonded stationary phases due to its high mechanical strength and the advanced technology for the production of particles of specific size, surface area and pore size [1, 2].

Silica gel is commonly used as a stationary phase both in LC and in HPLC. By bonding a number of organic moieties to the silica gel surface, stationary phases with different separation properties can be obtained, including hydrophobic (utilized in reverse-phase chromatography), ion exchange or other, unique properties (e.g. the phase with bonded melanin or artificial biological membrane) [3–5]. Stationary phases employed in affinity chromatography, in which biomacromolecules such as proteins or polypeptides are chemically bonded to the surface of silica gel, belong to the last category [6].

The present paper deals with a different application of chemically modified silica gel – for the generation of measured components (analytes) of gaseous mixtures. This novel approach to the problem of generation of gaseous standard mixtures is based upon using thermal decomposition of compounds chemically bonded to the surface of silica gel. The process of chemical modification of silica gel surface results in the formation of so-called *immobilized compounds* [7]. Under proper conditions, such an immobilized compound undergoes thermal decomposition yielding a specific component or components which can be used as a gaseous standard or analytes in a gaseous standard mixture, which can in turn be utilized in model investigations, and primarily for the calibration of measuring devices (detectors, analyzers, monitors).

In order to assure high reproducibility and repeatability of calibration, it is important to obtain a uniform coverage of the silica gel surface with the immobilized compound. This requires solving a number of problems during the preparation of a batch of chemically modified silica gel.

Commonly used methods of generation of gaseous standard mixtures [8–19] require complex apparatus during both the preparation and storage of the mixtures. Using the proposed indirect method of generation of gaseous standard mixtures, an analytical instrument can be calibrated by connecting it directly to a furnace in which thermal decomposition of a sample of chemically modified silica gel takes place. In this case, the furnace acts as a sampling device. This approach has a number of advantages, such as the possibility of preparation of toxic

or malodorous analytes just prior to model investigations or calibration of a measuring device [20].

So far, this novel approach to preparation of gaseous standards have been used for the following analytes: thiols [21], isothiocyanates [22], amines [23], carbon dioxide [24] and a mixture of carbon monoxide and dioxide [25, 26].

It is very difficult to calibrate a measuring device using a gaseous mixture containing methyl chloride as the analyte due to its high volatility (boiling point  $-24\text{ }^{\circ}\text{C}$ ) which may lead to a significant error if the mixture is prepared by a direct method. A gaseous standard mixture must meet a number of requirements, one of them being the ability to maintain the analyte concentration at a constant level [17]; therefore, utilization of the method of thermal decomposition of immobilized compounds for the generation of unstable and highly volatile substances should be considered as a good alternative to a direct method.

## Experimental

### Reagents

Silica gel (MN-Kieselgel 60, 35–70 mesh; specific surface area  $200\text{ m}^2\text{ g}^{-1}$ ; Macherey-Nagel, Düren, Germany) was modified using the following procedure: 25 g of silica gel was dried for 8 h at  $120\text{ }^{\circ}\text{C}$  to remove the surface water. Next, 20 g of the gel was transferred into a round-bottom flask containing 100 mL of dry toluene. To this solution, 0.014 mol (1.96 mL) of (3-chloropropyl) trimethoxysilane was added. The mixture was refluxed for 6 h. After the reaction was complete, the silylated silica gel was carefully filtered and washed with toluene, methanol, methanol-water, water and acetone, and dried under vacuum. Then, the silylated silica gel was suspended in 100 mL of methanol and 0.014 mol (1.54 mL) of N-methylmorpholine was added. The mix-

ture was left at room temperature for two days. Afterwards, the product was collected, washed thoroughly and dried.

Chemical reactions involved in the preparation of modified silica gel are shown in Figure 1.

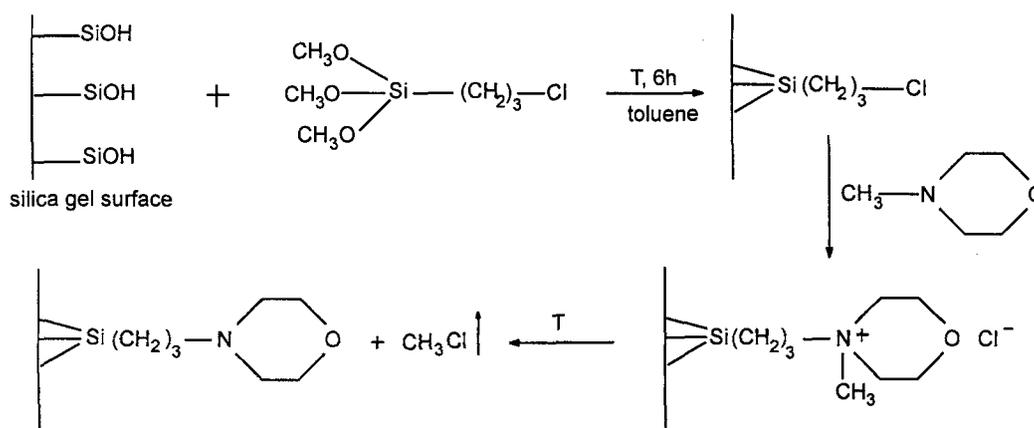
### Apparatus and Procedure

Samples of chemically modified silica gel of known mass ( $\pm 0.00001\text{ g}$ ) were placed in glass tubes (100 mm  $\times$  3.5 mm I.D.) and had been silanized prior to use in order to minimize interactions between the tube wall and the analyte.

The following silanization conditions were used [27]:

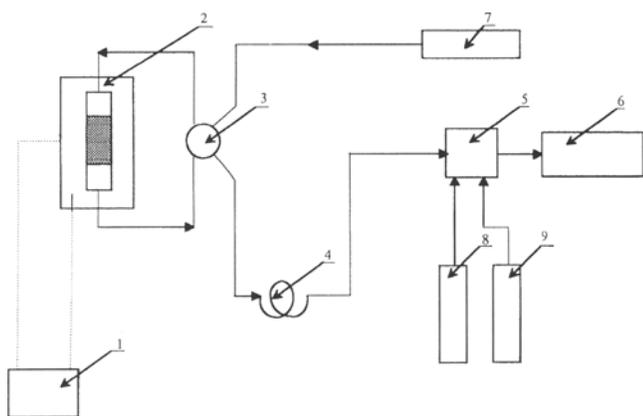
- silanizing mixture: hexamethyldisilazane-trimethylchlorosilane (5:1),
- silanization time 48 h,
- silanization temperature  $150\text{ }^{\circ}\text{C}$ .

The tubes with the gel were placed inside a desorber furnace of own design acting as a sampling device and connected to the GC-FID system through a six-port valve. The role of the valve was to include the desorber into the sample loop or to pass a stream of carrier gas directly to a GC column. The thermal desorber with the inserted tube containing the gel was heated electrically to a set temperature which was maintained at a constant level ( $\pm 2\text{ }^{\circ}\text{C}$ ). Airtight connection between the tube and the furnace was ensured by using PTFE washers. The process of thermal decomposition of the immobilized compound, during which the six-port valve cut off the flow of carrier gas through the desorber, began when the modified gel bed reached the set temperature. The time of thermal decomposition of a sample of the modified gel was 10 min after which the rotor of the six-port valve was switched for 1 min to a position in which the sample along with the desorber were filled with the carrier gas. As a result of these operations, a gas mixture (methyl chloride-nitrogen) was obtained at the thermal de-



**Figure 1**

Scheme of chemical modification of the silica gel surface resulting in the generation of methyl chloride upon thermal decomposition of the gel.



**Figure 2**

Schematic diagram of the apparatus used. 1 - temperature controller; 2 - desorber furnace; 3 - six-port valve; 4 - GC column; 5 - FID; 6 - recorder; 7 - tank with carrier gas (nitrogen); 8 - tank with hydrogen; 9 - tank with air.

sorber outlet which was then directed to the front of a GC column. After the mixture was introduced into the gas chromatograph, the desorber was cooled and, depending upon the type of investigation, the previous operations were repeated or a new sample of the modified gel was loaded into the desorber. The GC analysis proper lasted 4 minutes.

An HP 5830 A gas chromatograph equipped with a cold on-column, splitless injector, an FID detector (150 °C), a GC column (100 cm × 0.3 cm) Porapak Q 80–100 mesh (Hewlett Packard) (120 °C) were used in the investigations. In the first stage of investigations the GC-FID system was calibrated using a primary gas standard mixture prepared using a static low pressure method. The second stage of investigations involved finding experimental conditions providing complete liberation of methyl chloride from the silica gel surface and examining the dependence of the amount of methyl chloride generated on the mass of modified silica gel thermally decomposed.

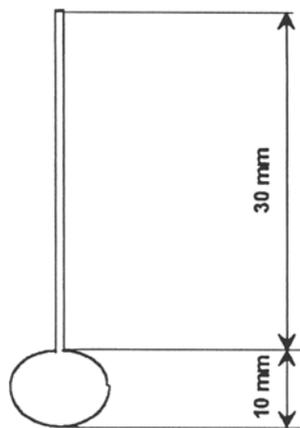
The apparatus used in the investigations is shown in Figure 2.

### Calibration of the GC-FID System

The GC-FID system used in the investigations was calibrated using a primary gas standard mixture prepared by a static method. The process of preparation of the primary gaseous standard mixture containing methyl chloride as the analyte included:

- Fabrication of a glass ampoule from glass capillary (Figure 3).
- Preparation of the gaseous standard mixture.

The fabricated ampoules were weighed to  $\pm 0.00001$  g. A commercial container (large glass ampoule) holding 25 mL of pure methyl chloride was cooled to  $-60$  °C using nitrogen vapor which enabled opening of the sealed end of the container. The open end of the capillary of a



**Figure 3**

Glass ampoule used for weighing known amounts of methyl chloride for the preparation of a primary gaseous standard mixture by a static gravimetric method.

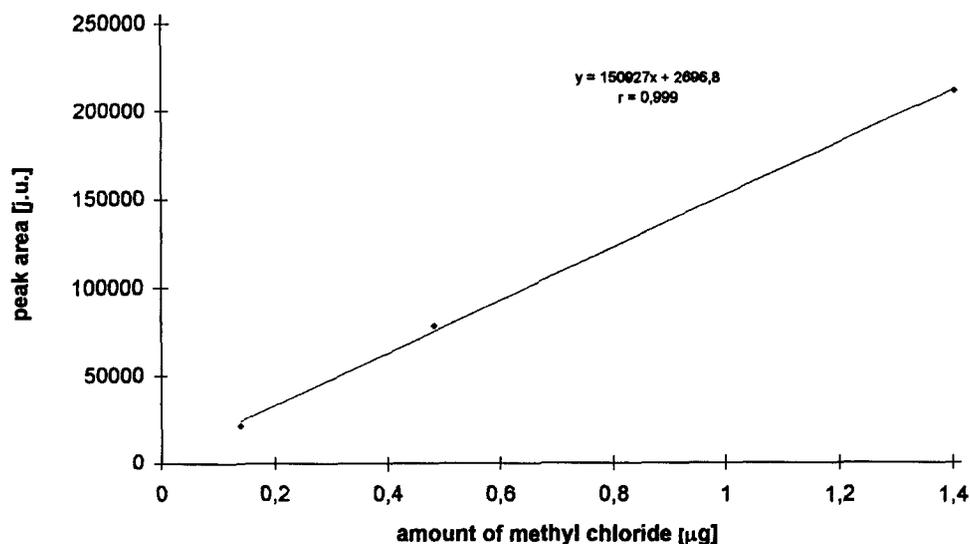
small glass ampoule was placed inside the opening of the large ampoule with methyl chloride and the bulb of the small ampoule was gently cooled which reduced the pressure inside the small ampoule and resulted in drawing methyl chloride into the small ampoule. Next, the end of the capillary of the small ampoule was sealed and the ampoule re-weighed, which permitted the determination of the exact mass of methyl chloride in the ampoule.

### Calibration of the GC-FID System by a Volumetric Method

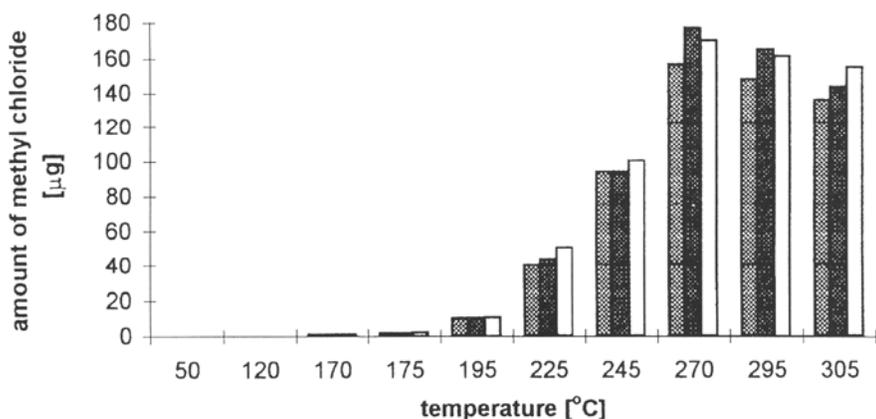
The ampoule with a known amount of methyl chloride was placed in a conical flask having a volume of 610 mL which had been previously purged with compressed air. The flask was closed with a PTFE stopper equipped with a silicone rubber septum. Next, the ampoule was broken by vigorous shaking of the flask and 20 mL of air was added using a gastight syringe to produce a slight overpressure in the flask. The process of homogenization of the mixture through evaporation and diffusion of methyl chloride lasted 2 hours. Next, a specific volume of the primary standard mixture was withdrawn from the flask through the silicone septum using a gastight syringe and injected onto the GC column. A calibration curve for the GC-FID system based on methyl chloride is shown in Figure 4.

### Optimization of Thermal Decomposition of Chemically Modified Silica Gel Samples

The process of thermal decomposition of the modified silica gel was optimized in terms of providing the maximum amount of the analyte liberated by varying the following parameters: decomposition temperature, decomposition time, and the diluent gas flow rate. The diluent gas flow rate was kept at  $15 \text{ mL min}^{-1}$  while the effect of other parameters on the amount of the analyte gener-



**Figure 4**  
Calibration curve for the GC-FID system based on a primary gaseous standard mixture containing methyl chloride as the analyte.



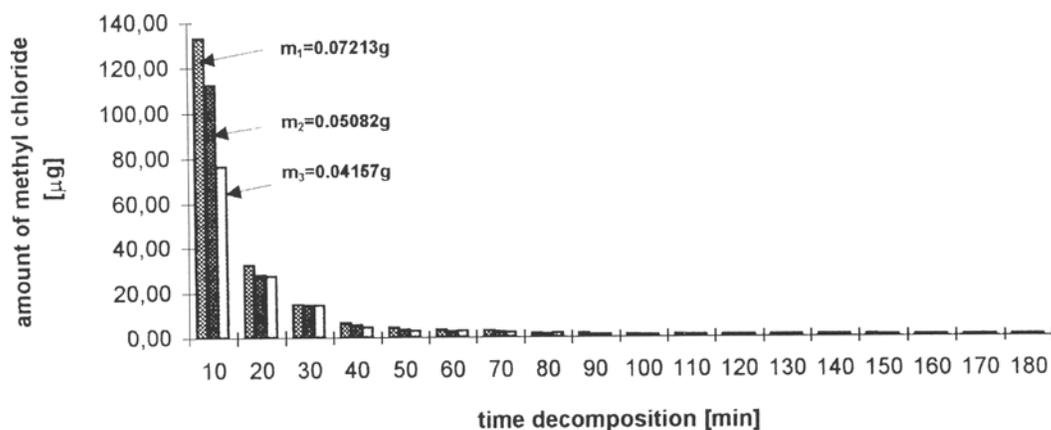
**Figure 5**  
Dependence of the mass of methyl chloride liberated on temperature.

ated during thermal decomposition of the modified gel was examined experimentally. For each of the temperatures investigated, a 10-minute thermal decomposition of the modified gel sample was carried in triplicate and the sample in the tube was changed after each decomposition. Initially, the decomposition temperature was varied from 50 °C to the value at which an uncontrolled thermal degradation of the immobilized compound was taking place while keeping the other two parameters (time and diluent gas flow rate) constant. Figure 5 shows the dependence of the amount of methyl chloride liberated on the temperature of thermal decomposition for three series of measurements. Next, at the experimentally determined temperature of thermal decomposition of the modified gel (called pyrolysis temperature), kinetics of the thermal decomposition process was investigated. To this end, the time required for complete liberation of methyl chloride from a given amount of the

modified gel (quantitative decomposition of the immobilized compound) was determined. This time was defined as the time after which the amount of the liberated analyte fell below the detection limit of the measuring device. The investigations were carried out for ten weighed samples of the modified gel at 270 °C (it was found that above 270 °C an uncontrolled degradation of the gel samples was taking place) and at a diluent gas flow rate of 15 mL min<sup>-1</sup>. The total time of thermal decomposition for a silica gel sample was counted from the moment of initiation of the decomposition process; the decomposition was interrupted every 10 minutes to carry out the GC analysis. A total of 18 measurements were carried out for each silica gel sample. Kinetics of the thermal decomposition of three samples of the modified silica gel (0.04157 g, 0.05082 g, 0.07213 g), i.e. the dependence of the amount of liberated methyl chloride on the time of thermal decomposition is shown in

**Table I.** Results of determinations of the amounts of methyl chloride liberated per unit mass of modified silica gel under given conditions of thermal decomposition

Conditions of thermal decomposition of modified silica gel		
Optimum temperature 270 °C	Total time of thermal decomposition 180 min	Carrier gas flow rate 15 mL min <sup>-1</sup>
Mass of gel [g]	Amount of the analyte per unit mass of gel [mg g <sup>-1</sup> ]	
0.04826	3.57	
0.04157	3.42	
0.02047	3.37	
0.07620	3.22	
0.09819	3.45	
0.08394	3.33	
0.02112	3.27	
0.07213	3.55	
0.05082	3.47	
0.04157	3.39	
3.40 ± 0.081		RSD = 2.4 %



**Figure 6**  
Dependence of the mass of methyl chloride liberated on duration of thermal decomposition.

Figure 6. The results of determination of total amounts of liberated methyl chloride for all investigated silica gel samples are listed in Table I.

### Investigation of the Dependence of the Mass of Liberated Methyl Chloride on the Mass of the Modified Silica Gel Used for its Generation

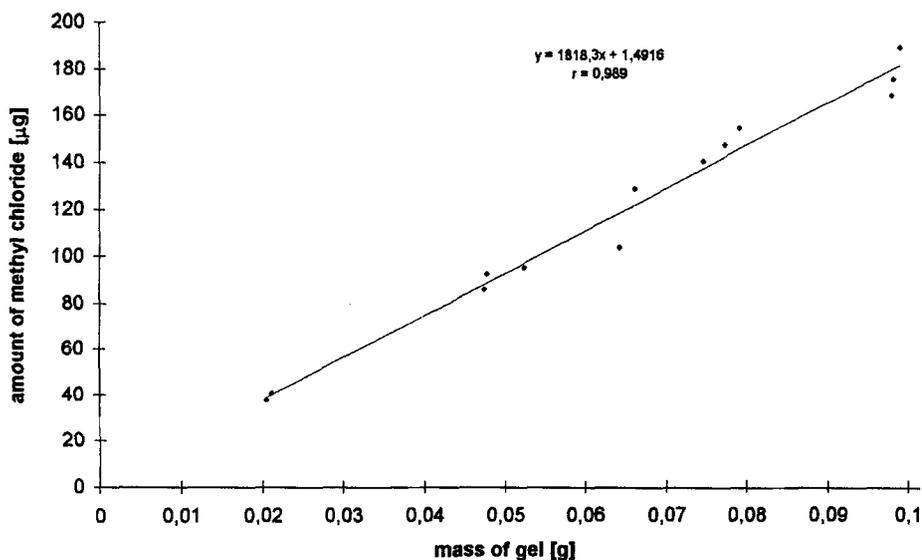
In the next stage of investigations, the modified silica gel was used to generate gaseous mixtures of methyl chloride for the calibration of the GC-FID system. Thermal decomposition of 13 samples of chemically modified silica gel with masses ranging from 0.02 g to 0.1 g ( $\pm 0.00001$  g) was carried out at 270 °C over a period of 10 min and at a diluent gas flow rate of 15 mL min<sup>-1</sup>. The results of determinations in terms of dependence of the amount of methyl chloride generated on the mass of modified silica gel are shown in Figure 7, while Figure 8 illustrates the dependence of the amount of methyl

chloride generated per unit mass of the silica gel on total mass of the gel used.

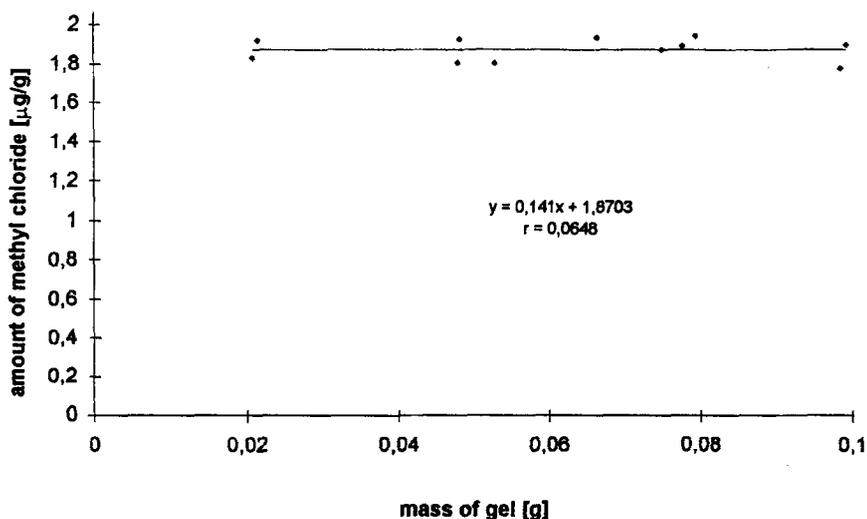
### Discussion

Examination of the dependence of the mass of methyl chloride liberated on temperature (Figure 5) reveals that the amount of the generated analyte increases with the decomposition temperature and reaches a maximum at 270 °C. Upon exceeding this temperature, a slight decrease in the amount of methyl chloride liberated is observed which can be attributed to a possible degradation of the silica gel bed as evidenced by the presence of trace amounts of other compounds.

Investigations of kinetics of thermal decomposition of the immobilized compound (Figure 6) revealed that the rate of generation of methyl chloride is highest during



**Figure 7**  
Dependence of the amount of methyl chloride liberated on total mass of the gel used.



**Figure 8**  
Dependence of the amount of methyl chloride liberated per unit mass of the silica gel on total mass of the gel used.

the initial period. After the first 10 minutes, the amount of liberated methyl chloride exceeds 50 % of the total amount of the analyte generated. Further decomposition takes place at a much slower rate, and after 90 minutes the amount of liberated methyl chloride is minimal and, for all practical purposes, constant. The dependence of concentration of the liberated analyte (C) upon the time of thermal decomposition (t) can be described by an exponential relationship:  $C = A \exp(-B t)$ , where A and B are empirical coefficients.

The experimentally determined average total amount mass of liberated methyl chloride per unit mass of the modified silica gel is:  $3.40 \pm 0.08 \text{ mg g}^{-1}$  (Table I).

There is a direct proportionality between the mass of liberated methyl chloride and the mass of modified sil-

ica gel (the correlation coefficient  $r = 0.989$ , Figure 7). Consequently, a wide range of concentrations of methyl chloride in the diluent gas can be conveniently generated by placing different amounts of the modified silica gel in the pyrolysis tube.

The slope of the straight line (Figure 8) is not significantly different ( $\alpha = 0.05$ ) from zero which indicates that the total amount of the analyte liberated per unit mass of the gel does not depend on the total mass of the gel used. The average mass of methyl chloride liberated per unit mass of the gel during the first 10 min of thermal decomposition is:  $1.88 \pm 0.040 \text{ mg g}^{-1}$  ( $n = 11$ ,  $\alpha = 0.05$ ).

For the moment there is no information on reproducibility of processes of chemical modification of silica gel

to obtain methyl chloride during controlled thermal decomposition of surface compounds. Therefore, the reproducibility has been studied in the case of other analytes (C<sub>3</sub>H<sub>7</sub>SH) [22] and the problem of obtaining and standardisation of chemically modified silica gel is described in a comprehensive review published in "Separation and Purification Methods" [7].

## Conclusion

Despite the fact that the concentration of the analyte in a gaseous mixture is not constant during the process of thermal decomposition of chemically modified silica gel, it can be calculated at any moment of the decomposition (as is the case in the exponential dilution method).

The developed method has a number of advantages, including:

- The developed procedure involves direct connection of the sampling device to the detector which minimizes losses of the analyte and the measurement errors associated with it;
- Temperature of thermal decomposition significantly exceeds room temperature which enables safe, long-term storage of chemically modified silica gel under ambient conditions;
- Suitability for generation of standard mixtures of reactive, toxic, unstable or malodorous components.

In further investigations, specially prepared glass rods with the surface coated with chemically modified silica gels generating upon thermal decomposition a gaseous standard mixture containing carbon monoxide and carbon dioxide will be used for the calibration of analytical instruments.

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