

# New procedure of silica gel surface modification Preparation of gaseous standard mixtures for calibration purposes

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## Abstract

The new type of silica gel surface modification with using the trimethylamine as a reagent is described. The samples of chemically modified silica gel have been used for generation of gaseous standard mixtures (methyl chloride as a measurand) using the technique of thermal decomposition of the surface compound. The main aim of the research was to check the suitability of the new type of silica gel surface modification for obtaining methyl chloride as a measurand of gaseous standard mixture. The gaseous standard mixture obtained with using this technique was used for calibration of a thermal desorber–gas chromatography–flame ionization detector (TD–GC–FID) system. The homogeneity of coverage of silica gel surface with the immobilized compound has been evaluated. The full uncertainty budget of determination of liberated amount of methyl chloride has been calculated. The average amount of methyl chloride liberated from the unit sample of chemically modified silica gel is  $3.59 \pm 0.13 \text{ mg g}^{-1}$ . The influence of the modification way on the amount of liberated analyte has also been determined.

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**Keywords:** Thermal decomposition; Chemical modification; Methyl chloride; Silica gel; Gaseous standard mixtures

## 1. Introduction

Methyl chloride is a volatile organic compound with an average concentration in the atmosphere of 540 pptv [1].  $\text{CH}_3\text{Cl}$  is of environmental concern because it may be responsible for about 13% of the destruction of the stratospheric ozone layer [2]. The major identified sources of  $\text{CH}_3\text{Cl}$  include oceans, biomass burning, wood-rotting fungi, salt marshes and anthropogenic sources [3,4]. The highest allowable concentration and instantaneous concentration in air are 20 and  $160 \text{ mg m}^{-3}$ , respectively.

It is very difficult to calibrate a measuring device using a gaseous standard mixtures containing chloride methyl as a measured component due to its high volatility (boiling point:  $-24^\circ\text{C}$ ) which may lead to a significant error if the mixture is prepared by a direct method. One of the requirement which a gaseous standard mixture should meet is the ability to maintain the analyte concentration at the constant level [5]. Utilization of the technique of thermal decompo-

sition of surface compound for the generation of unstable and highly volatile substances ought to be considered as a good alternative to a direct method [6]. The preparation of gaseous standard mixture this way is based on using thermal decomposition of compounds chemically bonded to the surface of silica gel. Under proper conditions, surface compound undergoes thermal decomposition yielding a specific analyte(s) which can be used for calibration of analytical device. So far, this technique has been used for generation of gaseous standard mixtures containing very different analyte(s) (thiols, isothiocyanates, amines, carbon dioxide and monoxide, acetaldehyde) [7–12]. The gaseous standard mixture of chloride methyl has been prepared also, but this time the procedure of silica gel modification was different. It has been planned to check how the type of modification of support material (silica gel) influences on the amount of liberated chloride methyl.

Usually in the air, methyl chloride can be analyzed by Method 1001 of the US National Institute for Occupational Safety and Health (NIOSH) [13]. Analysis is performed by gas chromatography (GC), and the sample detection limit is  $3.1 \mu\text{g m}^{-3}$  (1.5 ppb). The use of carbon disulfide at dry ice temperature for desorbing the analyte has also been

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described, as well as a thermal desorption technique as an alternative [14]. For monitoring methyl chloride in the work place, a thermally desorbable diffusional dosimeter has been used [15]. Very low concentration ( $0.006\text{--}0.1\ \mu\text{g m}^{-3}$ ) of methyl chloride (in an ambient air) can be analyzed by the use of photoionization, flame ionization, and electron capture detector in series [16].

Stratospheric air samples are often concentrated by a cryogenic procedure, at liquid nitrogen or argon temperature, followed by GC analysis employing electron capture detection [17] or with GC/MS [18]. The GC may be equipped with a flame ionization detector [19] or a mass selective detector [20]. Almasi et al. [21] described a modified version of a method commonly used by the US Environmental Protection Agency (EPA) to analyze low levels of volatile organic compounds in air (EPA Method TO-14). It includes samples concentrations on glass beads at  $-160\ ^\circ\text{C}$ , thermal desorption, separation on a GC capillary column, and detection with ion trap MS. The detection limit is about  $0.06\ \mu\text{g m}^{-3}$  ( $0.03\ \text{ppb}$ ) for methyl chloride.

The main goal of the investigation was to find the temperature at which the most repeatable and large amount of methyl chloride could be liberated. The homogeneity of coverage of silica gel surface with the immobilized compound was going to be determined also.

## 2. Experimental

### 2.1. Materials

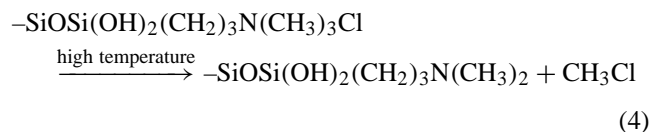
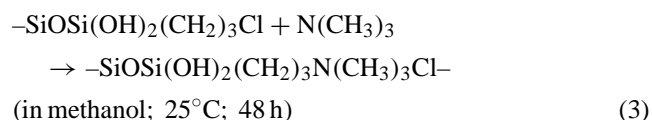
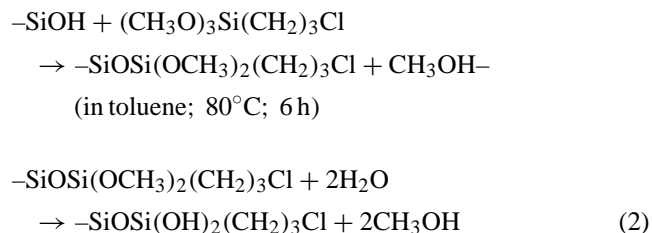
The silica gel characterized by specific surface area of  $480\text{--}520\ \text{m}^2/\text{g}$  and particle diameter of  $0.063\text{--}0.2\ \text{mm}$  (Macherey, Nagel & Co.) has been used as a support material in the technique of thermal decomposition of the surface compound for the generation of gaseous standard mixture of methyl chloride.

Trimethoxysilane was bought from *Aldrich*, (Milwaukee, WI, USA); toluene, trimethylamine and methanol were

purchased from *POCh* (Gliwice, Poland). Hydrogen peroxide (p.a. 30%) was supplied by *Chempur* (Piekary Śląskie, Poland).

### 2.2. Procedure of silica gel surface modification

The following reactions describe the synthesis of the surface compound and its thermal decomposition with the formation of methyl chloride:



The scheme of generation of gaseous standard mixture with using the technique of thermal decomposition of the surface compound is presented on the Fig. 1.

The usefulness of the chemically modified silica gel as a source of methyl chloride was tested by determining the conditions of thermal decomposition of the surface compound ensuring complete (or higher than 70%) release of methyl chloride, followed by statistical evaluation of the results of determination of the amount of methyl chloride generated as a function of the mass of the sample of modified gel taken for the analysis.

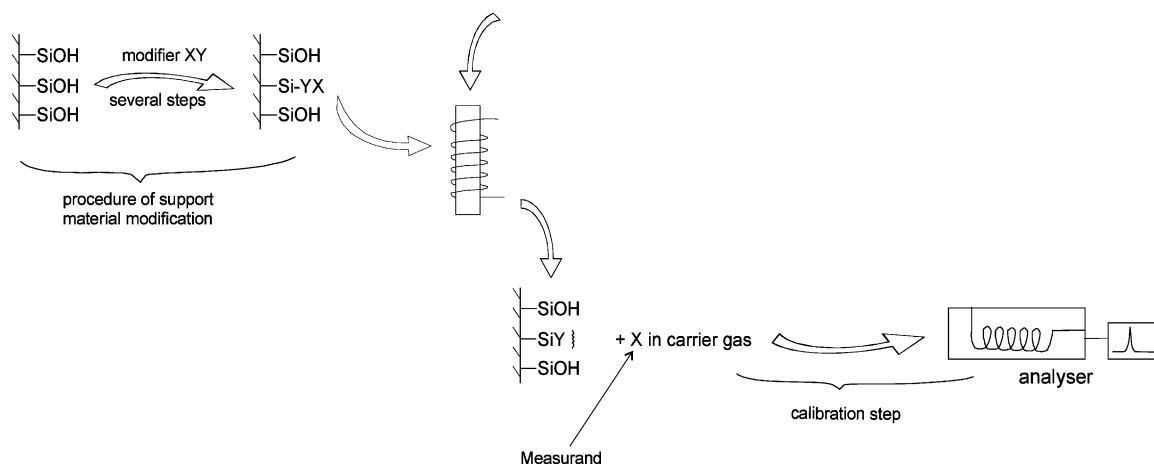


Fig. 1. The scheme of generation of gaseous standard mixtures with using the technique of thermal decomposition of the surface compounds.

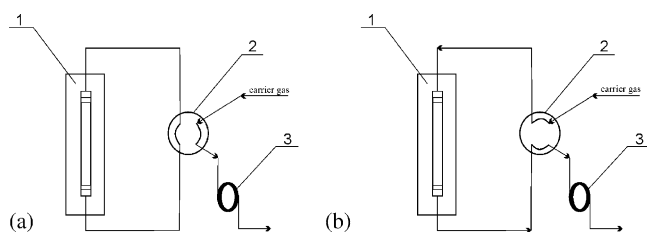


Fig. 2. Schematic diagram of positions of the valve: (a) thermal decomposition of surface compound; (b) chromatographic analysis, (1) thermal desorber, (2) four-port sampling valve, (3) GC column [22].

### 2.3. Apparatus

Samples of chemically modified silica gel were placed in glass tubes (82 mm long; 1.6 mm i.d.) between silanized glass wool plugs. The glass tubes were silanized prior to use to minimize interactions between the tube wall and the analyte [5].

The tube with modified silica gel was placed into thermal desorber which served as a sampling device and was connected to the gas chromatography–flame ionization detector (GC–FID) system via a four-port valve. Depending upon its position, the valve directed a stream of carrier gas either through the thermal desorber or directly onto the front of a GC column. The schematic diagram of different positions of the valve is shown on Fig. 2. The desorber was heated electrically to suitable temperature which was maintained constant ( $\pm 2^\circ\text{C}$ ) using a temperature controller. The time of decomposition process was measured since the start of heating of the thermal desorber. After a specified (depending on the type of investigation) period of heating, the four-port valve was switched for 1 min to the position in which the carrier gas purged the sampling loop including the desorber. The gaseous standard mixture generated in the desorber outlet was then directed to the front of a GC column. The hydrogen has been used as a carrier and flammable gas. The important advantage of proposed technique in the possibility of choosing the diluent gas. During the sampling of the standard mixture the desorber was heated continuously. GC analysis conditions are given in Table 1.

Table 1  
Conditions of GC analysis of gaseous standard mixtures containing methyl chloride obtained during thermal decomposition of suitable surface compound

Gas chromatograph	GC 6000 Vega Series; Carlo Erba Instruments
Detector	FID, $250^\circ\text{C}$
Injection mode	Thermal desorber
Dosage time	60 s
Carrier gas	Hydrogen at $20\text{ ml min}^{-1}$
Temperature program	Isothermal, $40^\circ\text{C}$
GC column	20% Squalane on Chromosorb P, 80–100 mesh, diameter 1/8 inch, length 95 cm
Calibration	External standard

## 3. Results and discussion

### 3.1. Calibration of the GC–FID system using gaseous standard mixtures prepared by a static method (reference technique of calibration)

In the first step of the investigations, a TD–GC–FID system was calibrated by using a primary gaseous standard mixtures prepared by a static technique [6]. 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 desorber. Next, a gaseous standard mixture was directed into the chromatographic column.

In the range from 1 ng to  $13\ \mu\text{g}$  FID, which was used in the study, retains linearity, as proven by calibration ( $y = 284x - 4.86$ ;  $r = 0.999$ ).

### 3.2. Investigation of optimum temperature of thermal decomposition process

Examinations consisted in analysis of the process of the decomposition and distribution—in different temperatures—of successive samples of modified silica gel and determining the amounts of the analyte released each time.

Examinations were started at room temperature, and next, the temperature was increased by increments of  $20^\circ\text{C}$  to a temperature of  $330^\circ\text{C}$ , and it was checked whether degradation of the examined deposit takes place. Each analysis was carried out following an 11 min period of decomposition at a given temperature (10 min of heating + 1 min of dosage at constant heating of the sample). For each temperature, three measurements were performed (using new samples of silica gel each time). The amounts of analyte released were converted to a unit of mass of chemically modified silica gel, which was necessary due to the application of weighed amounts of gel in the analysis, that differed from each other in mass. In Fig. 3, the relation between the amount of methyl chloride released from a unit of silica gel mass and the

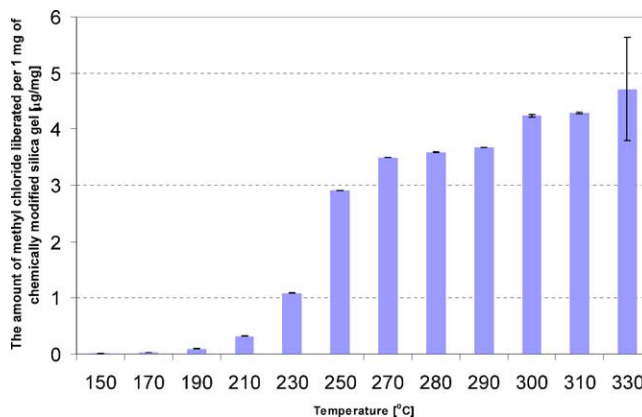


Fig. 3. Dependence of the amount of methyl chloride liberated per 1 mg of the modified silica gel on the thermal decomposition temperature. Error bars represent a standard deviation.

process of thermal decomposition of the surface compound while retaining constant values of: carrying gas flow rate and duration of the thermal decomposition process is shown. Thermal decomposition was performed for samples of silica gel with masses range of 0.69–4.57 mg for a period of 11 min (the duration was determined on the basis of earlier investigation [6]) and at flow rate of the carrier gas at  $20 \text{ ml min}^{-1}$ .

The lowest temperature of thermal decomposition process, at which measurable amounts of methyl chloride begin to appear is  $150^\circ\text{C}$ . Examination of the process was finished at a temperature of  $330^\circ\text{C}$ , at which a browning of the deposit was noted. At  $330^\circ\text{C}$ , uncontrolled degradation process of modified silica gel took place and influences on high value of standard deviation. At the temperature range  $270\text{--}290^\circ\text{C}$  the large and the most reproducible amount of methyl chloride was generated. It is very important that at  $280^\circ\text{C}$  the temperature variations even  $\pm 10^\circ\text{C}$  did not indeed influence on the liberated amount of methyl chloride.

### 3.3. Investigation of kinetics of thermal decomposition of surface compound on silica gel

At the experimentally determined temperature of thermal decomposition of the modified silica gel, kinetics of the thermal decomposition process was investigated.

The investigations were conducted under optimum process conditions (temperature  $280^\circ\text{C}$ , the flow rate of a stream of diluent gas  $20 \text{ ml min}^{-1}$ ) by determination the dependence of the liberated amount of compound on the time of thermal decomposition process. The sample of modified silica gel was being heated for 10 min in the desorber, then the stream of generated gaseous standard mixture was directed

onto the chromatographic column. After 1 min of sampling, the sample was heating for next 9 min and dosing over again. The procedure for specified sample was repeated for every 9 min period of time (after every 9 min, the sample was introducing to the chromatographic column for 1 min) until the amount of methyl chloride was lower then 1% of the total amount liberated so far (it could provide the ending of the thermal decomposition process). The dependence of the amount of methyl chloride liberated from the sample of chemically modified silica gel (the mass of silica gel was known) on the time of thermal decomposition process is presented in Fig. 4. Three series of measurements of the methyl chloride amount (masses of silica gel samples were: 2.07; 1.60 and 1.48 mg) were done.

One hundred and twenty minutes were assumed as the total duration of the decomposition of samples of the modified silica gel, which was the source of methyl chloride in the given range of masses and in certain measurement conditions. On the basis of data presented in Fig. 4, it can also be noted that the amount of methyl chloride released in the model gaseous mixture is the highest (over 70%) after 11 min of the process of thermal pyrolysis of the chemically modified silica gel sample.

### 3.4. Investigation of homogeneity of coverage of silica gel surface with the immobilized compound

The investigation of coverage homogeneity of silica gel surface with the immobilized compound was based on the results of measurements of the amount of methyl chloride liberated during first 11 min of thermal decomposition process (the liberated amount of methyl chloride was

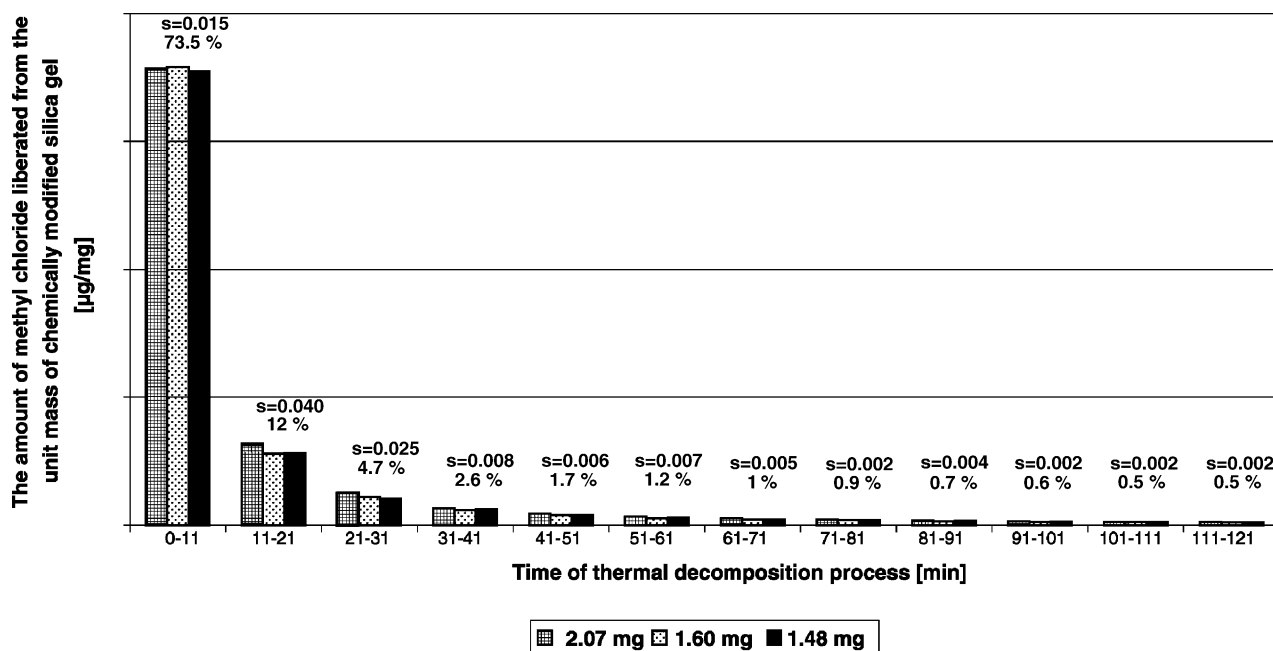


Fig. 4. Dependence of the amount of methyl chloride liberated from the unit mass of chemically modified silica gel on duration of thermal decomposition process. Labels represent the percentage of the amount of methyl chloride liberated. S: standard deviation.

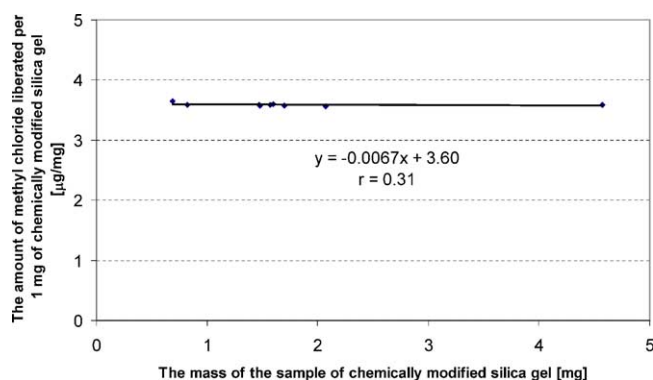


Fig. 5. Dependence of the amount of methyl chloride liberated per 1 mg of the silica gel on total mass of the gel sample used.

recalculated from one unit mass of silica gel sample). Eleven minutes of thermal decomposition process was the most useful time for the investigation because at this time the largest amount of methyl chloride was liberated. The investigation of degree of coverage homogeneity of silica gel surface with the immobilized compound was estimated through the statistical evaluation of the results of measurements of analyte amount liberated from one unit mass of silica gel sample.

The dependence of the amount of methyl chloride liberated from a unit mass of silica gel bed during first 11 min of the thermal decomposition process on the mass of silica gel samples was examined under optimum measurement conditions and presented in Fig. 5.

### 3.5. Uncertainty budget

The influence of all parameters on uncertainty of average amount of methyl chloride liberated per unit mass of silica gel is schematically presented in Fig. 6 using Ishikawa diagram [23].

The uncertainty budget has been done for a given batch of modified silica gel, so influences of the modification procedure and a batch of silica gel used were not taken account.

The uncertainty for a given batch of modified silica gel was calculated according to GUM [24] using formula as follows:

$$U = kx \sqrt{u(c_{\text{cal}})^2 + u(m_{\text{sample}})^2 + \frac{1}{n}(\text{R.S.D.}_{\text{results}})^2} \quad (5)$$

where  $U$  is the expanded uncertainty,  $k$  the coverage factor (usually 2),  $x$  the average amount of methyl chloride liberated per unit mass of silica gel,  $u(c_{\text{cal}})$  the uncertainty of calibration step (using gaseous standard mixtures prepared by static method),  $u(m_{\text{sample}})$  the uncertainty of sample of modified silica gel,  $\text{R.S.D.}_{\text{results}}$  the relative standard deviation of results, and  $n$  is the number of independent determinations.

For calculation of every standard uncertainties, the GUM Workbench version 1.3 (Metrodata GmbH, Ger-

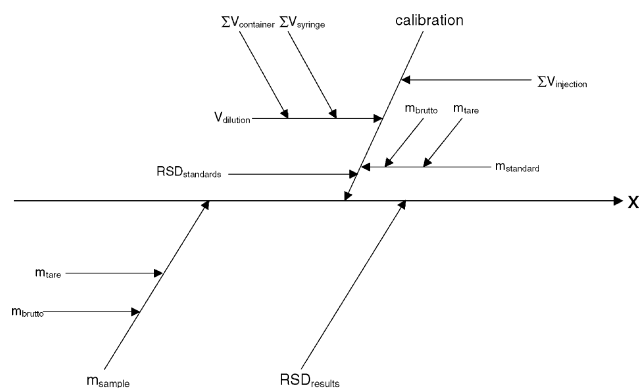


Fig. 6. Ishikawa diagram [23] presented uncertainty contributions for determination of the average amount of methyl chloride liberated per unit mass of modified silica gel.  $m_{\text{sample}}$ : mass of sample of modified silica gel;  $m_{\text{tare}}$ : net weight;  $m_{\text{brutto}}$ : brutto weight;  $\text{R.S.D.}_{\text{results}}$ : relative standard deviation of results;  $m_{\text{standard}}$ : mass of standard (pure substance) used for preparation of gaseous standard mixtures using static method;  $V_{\text{dilution}}$ : dilution of standard;  $V_{\text{container}}$ : volume of container(s) used for dilution;  $V_{\text{syringe}}$ : volume of syringe(s) used for dilution;  $V_{\text{injection}}$ : volume of standard(s) injected;  $\text{R.S.D.}_{\text{standards}}$ : relative standard deviation of determinations of gaseous standard mixtures prepared by static method.

many) software has been used. The following values were obtained:

$$u(c_{\text{cal}}) = 1.4\%, \quad u(m_{\text{sample}}) = 1.2\%,$$

$$\text{R.S.D.}_{\text{results}} = 0.69\%, \quad n = 9, \quad U(k = 2) = 3.7\%$$

and finally:

$$x \pm U(k = 2) = 3.59 \pm 0.13 \text{ mg g}^{-1}$$

The statistical evaluation of the results is presented in Table 2. The average amount of methyl chloride liberated from a unit mass of silica gel sample during first 11 min of the thermal decomposition process at 280 °C and the flow rate of the carrier gas stream 20 ml min<sup>-1</sup> is 3.59 ± 0.13 mg g<sup>-1</sup>.

On the basis of the results of the determination of the amount of methyl chloride which can be released per unit

Table 2

Statistical evaluation of the measured quantities of the methyl chloride released from the unit mass of chemically modified silica gel during the first 11 min of thermal decomposition process

The average mass, $x \pm U$ (mg g <sup>-1</sup> )	3.59 ± 0.13
The standard deviation, $S_{n-1}$	0.025
The slope of the straight line, $a$	-0.0067
The standard deviation, $S_a$	0.0079
The calculated Student's $t$ -value, $t_{\text{calc}} = a/S_a$	0.85
The critical Student's $t$ -value, $t_{\text{crit}}(0.05, 7)$	2.36
The intercept, $b$	3.60
The standard deviation, $S_b$	0.016
The calculated Student's $t$ -value, $t_{\text{calc}} = (b - x)/S_b$	0.74
The critical Student's $t$ -value, $t_{\text{crit}}(0.05, 7)$	2.36
The correlation coefficient, $r_{\text{calc}}$	0.31
The critical $r$ value, $r_{\text{crit}}(0.05, 7)$	0.67



mass of modified silica gel the following conclusions can be made:

1. there is no statistically difference between slope of the line ( $a$ ) and value 0—for significance level  $\alpha = 0.05$  calculated parameters of Student's  $t$ -test is smaller than its critical value ( $t_{\text{calc}} < t_{\text{crit}}$ );
2. there is no statistically difference between intercept of the line ( $b$ ) and value equals to average amount of  $\text{CH}_3\text{Cl}$  liberated—for significance level  $\alpha = 0.05$  calculated parameters of Student's  $t$ -test is smaller than its critical value ( $t_{\text{calc}} < t_{\text{crit}}$ );
3. calculated correlation coefficient is smaller than its critical value ( $r_{\text{calc}} < r_{\text{crit}}$ , calculations were made for significance level  $\alpha = 0.05$ )—no statistically significant correlation is observed.

Due to that it is possible to notice that amount of methyl chloride liberated from unit mass of modified silica gel does not depend on mass of silica gel used. For given batch of silica gel, the coverage of their surface will be homogenous.

### 3.6. Reproducibility of modification procedure

In the method of generation of volatile analytes based on thermal decomposition of surface compounds an amount of measurand obtained depends on:

- parameters of thermal decomposition process;
- coverage of surface of modified support.

The amount of available hydroxyl groups on the surface influences the coverage of surface of modified support and depends on:

- type of support;
- efficiency of modification reaction.

For utilization of surface compound for generation a specific amount of analyte it is very important to obtain (under specific and controlled conditions) reproducible amount of a measurand. Due to that it is necessary that modification procedure is reproducible. The support material used for modification has to have the reproducible characteristics as well.

During our investigation three different samples of silica gel from the same unit have been modified. The surface coverage for each of them has been determined (as a average of eight independent determinations). The results obtained are presented in Fig. 7. Based on the data obtained, it can be concluded that, for a given batch of silica gel, the modification procedure is reproducible.

The coverage of silica gel surface has to be determined for each new batch of modified silica gel—immediately after modification procedure. Taking into account the high stability of modified silica gel, surface coverage of the newly modified silica gel can be determined on the basis of the coverage of the previously studied support material.

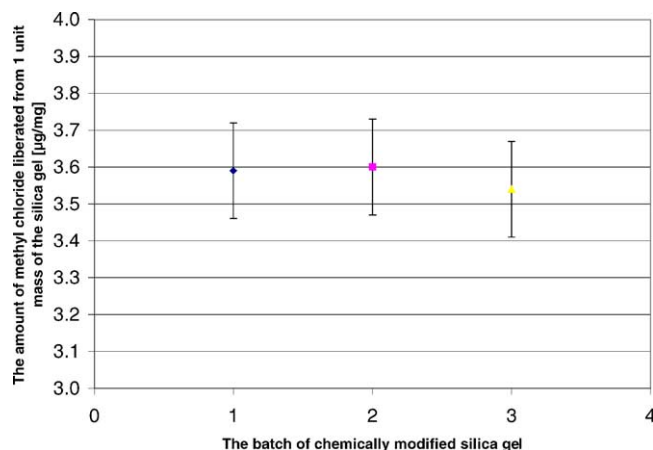


Fig. 7. Results of reproducibility determination of silica gel surface modification procedure. Error bars represent an expanded uncertainty.

### 3.7. Calibration of the TD–GC–FID system using gaseous standard mixtures prepared by the technique of thermal decomposition of the surface compounds

During the next stage, the gaseous standard mixture obtained during thermal decomposition of the surface compound was used for calibration of the TD–GC–FID. During tests, nine samples of chemically modified silica gel (masses of the weighed samples were from 0.69 to  $4.57 \pm 0.01$  mg) under optimal measurement conditions (each sample was heated for 10 min, and next, the methyl chloride released, was directed—in a stream of a carrying gas—to the head of a chromatographic column (1 min)) have been used in the experiment.

Linear relationship between the amount of methyl chloride ( $\mu\text{g}$ ) and the mass of a sample of chemically modified silica gel (mg) has been observed ( $y = 3.59x - 0.0057$ ;  $r = 0.999$ ).

## 4. Conclusions

On the basis of the results obtained, we can draw the following conclusions:

1. The optimum temperature for conducting the process of thermal decomposition of a surface compound (formed on the surface of silica gel) is  $280^\circ\text{C}$ ; at higher temperatures ( $330^\circ\text{C}$  and higher), gradual degradation of the deposit takes place. Temperature  $280^\circ\text{C}$  was chosen as optimal because the amount of methyl chloride liberated is high, and the temperature variation of even  $\pm 10^\circ\text{C}$  does not influence (statistically significant) the amount of measurand liberated (in the case of temperatures 270, 290, 300 and  $310^\circ\text{C}$  smaller variations of temperature have significant influence on an amount of methyl chloride liberated).

- High value (150 °C) of the minimum temperature of decomposition of the surface compound ensures stability of the modified deposit in room temperature. This is very important, due to the possibility of safe storage, transport and analysis of samples.
- Examinations of the kinetics of the thermal decomposition process of the surface compound have shown that the greatest and the most repeatable amount of methyl chloride is released during the first 11 min of heating of the sample material with the chemically modified surface. It is very important that both of these requirements (the greatest and the most repeatable amount of a measurand) have to be fulfilled.

Statistical analysis of the results of assays obtained during examination of the relation between the amount of analyte released and the mass of the examined gel sample shows that the amount of generated compound from a unit of modified silica gel does not depend on the mass of the gel sample taken for analysis. It can, then, be said that the degree of homogeneity of silica gel surface coverage by the examined surface compound—for given batches of modified silica gel—is satisfactory.

The modification procedure for a given batch of silica gel is reproducible. However, it is necessary to point out that the coverage of silica gel surface has to be determined for each new batch of modified silica gel (it means immediately after modification procedure). The modified silica gel can be used as a calibrant only after determination of its surface coverage on the basis of calibration using standards prepared by gravimetric (absolute) method.

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