Use of porous glass and silica gel as support media of a surface compound for generation of analytes in gaseous standard mixtures. New method for the determination of the amount of analyte generated

Elżbieta Przyk[a], Piotr Konieczka[a], Jolanta Szczygelska-Tao[a], Roman Teschner[b],
Jan F. Biernat[a], Jacek Namieśnik[a],*

[a]*Chemical Faculty, Technical University of Gdańsk, 11/12 Narutowicza Street, 80-952 Gdańsk, Poland*
[b]*Johns Manville Europe GmbH, Faserweg 1, 97877 Wertheim, Germany*

Abstract

The paper presents a new method for the determination of a volatile component of a gaseous standard mixture obtained by thermal decomposition of a suitable surface compound. The amount of the analyte generated (under given conditions of thermal decomposition) per unit of mass of the chemically modified material has been determined exclusively on the basis of measuring generation time. Therefore, the total error of the determination of the amount of a standard compound depends solely on the respective errors of weighing the material and measuring its decomposition time (both being direct measurements). This new method permits obtaining a few measuring points on the basis of a single sample of the material with chemically modified surface.   © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Support medium; Silica gel; Porous glass; Surface compounds; Gaseous standard mixtures; Ethene

1. Introduction

Calibration of measuring devices and validation of analytical procedures, both require suitable standards, in which concentration of the analyte is known and/or has been determined with sufficiently high precision and accuracy. A trend towards analysis permitting determination of different analytes at lower and lower concentration levels, frequently in samples of complex composition [1], leads to the search for such methods of standard preparation which may be employed in the determination of concentrations of analytes at trace and ultra-trace levels with high accuracy and precision [2]. The task becomes particularly difficult when volatile and/or unstable substances are involved. To minimize the above-mentioned inconveniences, the methods of standard preparation are sought, which would permit: (i) calculation of the obtained concentration of an analyte on the basis of direct measurements (e.g., measurements of mass, time, temperature) and utilization of suitable, established before, mathematical relations between the variables [3,4]. Such an approach permits minimization of errors involved in the determination of the concentration of an analyte

in the standard, as the contributing errors of direct measurements are, by definition, significantly smaller than those of the indirect measurements; and (ii) obtaining the standards just before the calibration (or their utilization for other purposes). This virtually eliminates possible losses of the analyte (due to its volatility, adsorption and lability) that may occur between the generation of a standard and its introduction into the device being calibrated (short "lifetime" of an analyte). Hence, there is a strong preference for such methods of standard preparation, which utilize simple and unsophisticated equipment, thus being accessible in any laboratory.

A technique which fulfils the aforementioned requirements is the one, elaborated at the Chemical Faculty of the Technical University of Gdańsk (TUG), Poland, based on utilization of thermal decomposition of surface compounds to generate standard mixtures containing volatile analytes [5]. In the respective procedure, a suitable surface compound, bound to the surface of a support material (silica gel, porous glass) in a process of its chemical modification, undergoes thermal decomposition, yielding a volatile compound, which is the analyte of interest and whose amount closely depends on the conditions of thermal decomposition.

So far, two principal approaches towards this method have been developed, both permitting utilization of the generated gaseous mixtures as analytical standards:

(1) Mathematical equation, describing the kinetics of the generation of a given component of a gaseous standard mixture, (diluting gas flows continuously through the bed of the source material, i.e., a support material with its surface chemically modified, undergoing thermal decomposition) was found [5]. The equation expresses the relationship between the concentration of the analyte in the standard mixture and its generation time, temperature at which the decomposition is carried out, mass of the chemically modified bed and the diluting gas flow-rate. The most important advantage of this approach is the possibility of generation of gaseous standards of significantly varying concentrations, thus enabling multi-point calibration. The method is particularly suitable for calibration of integrating detectors in an "on-line" mode. The need to utilize complex mathematical equations to determine the concentration of

an analyte, at any moment of both the calibration and the thermal decomposition process, constitutes its major weakness.

(2) A dependence of the total amount of an analyte liberated, under optimum conditions, from the chemically modified bed since the beginning of thermal decomposition on the mass of the surface compound containing material was found (in this variant, the diluting gas is passed through the heated bed only when the sample must be passed from the generating apparatus to the instrument being calibrated) [5]. The method permits quick and easy preparation of the gaseous standard and the calculations involved are as simple as possible. The major limitation of this method is obtaining only one standard mixture from a single portion of the chemically modified material.

The study presented here permits one to combine the advantages of the both above described methods of carrying out the thermal decomposition and to eliminate their weaknesses and limitations. The new, practical approach, proposed here, is based on a simple mathematical relationship (function of a single variable) between the amount of an analyte liberated and time of its production – thermal decomposition of the suitable surface compound. The relationship is determined for, previously established, optimum conditions of the process of thermal decomposition of the surface compound. Such a relationship permits one to find the amount of the analyte liberated at any time interval (or intervals) during decomposition. Hence, the method allows preparation of standards of widely varying in concentration, while it is based on a simple mathematical function.

In this study, porous glass has been used for the first time as a support of the surface compound – the reactant in the decomposition reaction.

2. Experimental

2.1. Materials and apparatus

2.1.1. Materials

Materials used through the study as the support (substrate) of the surface compounds and their basic characteristics are listed in Table 1.

E. Przyk et al. / J. Chromatogr. A 928 (2001) 99–108

101

Table 1
Support materials used in the study and their basic parameters

Material	Manufacturer	Specific surface area (m^2/g)	Grain size (μm)	Pore size (nm)	Pore volume (mm^3/g)
1. Silica gel MN-Kieselgel 60	Macherey–Nagel & Co.	200.00	215–425		
2. Trisoperl porous glass	Johns Manville Corporation	104.54	100–200	63.2	1615.20
		39.00	100–200	99.8	1090.29
		29.91	100–200	126	940.57
		88.00	200–500	35.5	807.75

The materials were subjected to chemical treatment resulting in formation of a surface compound which, at elevated temperature (at least 85°C) decomposes with liberation of ethene. The details of the procedure of chemical surface modification and the scheme of the decomposition mechanism is presented in Fig. 1 [5,6].

Four types of porous glass, of different surface structure, were used in this study. For short and unambiguous notation, they were designated by giving in parentheses a numeral describing their pore volume (see Table 1), e.g., porous glass (1615).

2.1.2. Apparatus

A schematic diagram of the apparatus used in the study is shown in Fig. 2. Its basic element was a thermal desorber, whose furnace (1) was equipped with an Ni–NiCr thermocouple connected to an electronic temperature controller (3). This set up assured control of the furnace temperature within a 50–350°C range with ±3°C accuracy. A silanized glass tube (82 mm×1.6 mm I.D.), containing a sample of the surface modified material tested (2), was placed into the furnace. When the furnace cover was screwed tight, the tube was also sealed tight by pressing its tips into suitable PTFE gaskets. The furnace cover was equipped with a device to supply the diluting/carrier gas to the tube. Direction of the gas flow was controlled using a four-way valve (4) which also permitted an ''on-line'' mode connection with a gas chromatograph.

2.2. Procedures

2.2.1. Standard gaseous mixture preparation

A sample of chemically modified material,

weighed with ±10 μg accuracy was placed in the silanized glass tube (between silanized glass wool plugs). Subsequently, the tube was put into the furnace, pre-heated to the temperature required.
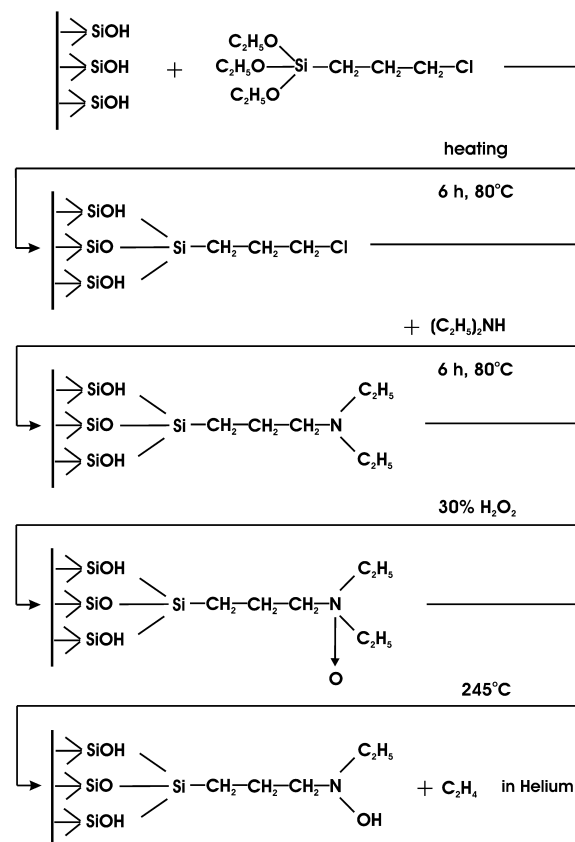

Fig. 1. Scheme of chemical modification of the surface of support material (silica gel or porous glass) resulting in the synthesis of immobilized compound, which ethene upon thermal decomposition yields [5,6].
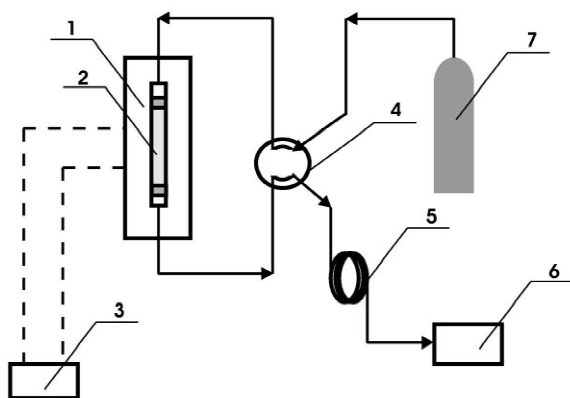
Fig. 2. Schematic diagram of the apparatus used in this study:
1 – thermal desorber; 2 – glass tube; 3 – temperature controller;
4 – four-way valve; 5 – GC column; 6 – detector (FID);
7 – cylinder with compressed carrier gas (helium).

During the heating period, the four-way valve was in position cutting the gas flow through the tube off. After the desired period of time, measured since the moment of sealing the tube after its insertion into the apparatus, the position of the valve was changed, thus directing the generated standard mixture onto the chromatographic column. After the required injection time, the valve was switched back to the initial position and, depending on the purpose of any particular series of measurements, either the dosage was repeated after another time interval at isothermal

decomposition conditions, or the furnace was cooled and another series started with a freshly prepared tube.

The amount of the analyte, introduced onto the chromatographic column, does not depend on the flow-rate of the diluting gas. Nevertheless, to ensure the stability of operating conditions, the following parameters were arbitrarily adopted in this study: diluting gas flow-rate=10 ml/min, mixture introduction time=20 s (volume of the diluting gas passed through the tube in 20 s exceeds the volume of the tube at least 10 times).

2.2.2. Chromatographic analysis

Gas chromatographic analysis of the gaseous mixture prepared in this way was performed under conditions given in Table 2.

3. Results and discussion

3.1. Determination of optimum conditions of thermal decomposition of the surface compound

The temperature range, within which ethene yielding thermal decomposition occurs, is 85–235°C. The high value of its lower limit (85°C) ensures the stability of the modified bed at room temperature. This fact is essential for save, long-term storage (at

Table 2
Conditions of gas chromatographic determination of ethene in obtained gaseous mixtures

Analytical procedure	
Gas chromatograph	HP 6890, Vectra XA
Detector	Flame ionization (FID)
Detector temperature	250°C
Injection system	Thermal desorber
Carrier gas	Helium
Elution temperature program	Isothermal 30°C
Integrating system	Chemstation
GC column (packed type):	
Stationary phase	Porapak Q
Support mesh size	80–100 mesh
Column length	100 cm
Column I.D.	0.3 cm
Calibration	ESD – methane gaseous standard mixtures prepared by static method (R_F=1.230 for methane; R_F=1.075 for ethene [7])
Detection limit	0.2 μg (per gram of bed)

room temperature) of samples and/or whole batches of the chemically modified material. Heating the samples of the studied material above the upper temperature limit of 235°C leads to uncontrolled degradation of the surface compound, as indicated by liberation of additional, undesired substances – other than the analyte of interest – and the bed colour turning brown.

During the measurements, the desorber temperature is maintained constant with ±3°C accuracy after reaching its preset value, while the amount of the analyte generated from a unit of mass of the bed depends on temperature of decomposition of the surface compound. Therefore, any variations in temperature of the desorber furnace during the decomposition can influence the analyte yield. It becomes necessary to determine a point, at which small variations in temperature result in the smallest possible variations in the amount of the analyte generated, ensuring the best reproducibility of the yield. To this end, a plot of the amount of the analyte liberated (ethene generation time in the series was kept constant and equal to 5 min) vs. decomposition temperature was prepared. The plots, determined for silica gel and one type of porous glass (1615), both modified in the same way, are shown in Figs. 3 and 4. On the basis of these curves, one can determine (for silica gel there is a maximum at 220°C), that so defined optimum temperature corresponds to 205–220°C range. Within this range, the differences in

yield between the neighbouring points are small, while the yield itself retains relatively high values. Taking into account the values of relative standard deviation (RSD) of the yield at all experimental points (temperatures), the optimum temperature of 210°C was chosen for subsequent experiments involving ethene yielding thermal decomposition of surface compounds. This temperature lies at the lower limit of the stability range, where the lowest RSDs were observed.

3.2. Possibility of utilization of porous glass as a support of the surface compound

The uniformity of surface coverage of the studied support material with the surface compound constitutes the necessary condition of the usage of the material for the standard generation purposes. It is essential in assuring reproducibility of the amount of the analyte generated, hence, high accuracy and precision of the gaseous standards prepared in this way.

Studies of the coverage of the silica gel surface with the ethene yielding surface compound have been described before [6]. For the purposes of this study, the uniformity of the coverage of the materials used was determined on the basis of RSD values calculated for five independent measurements (five independently weighed portions of the modified material) of the total amount of the analyte generated
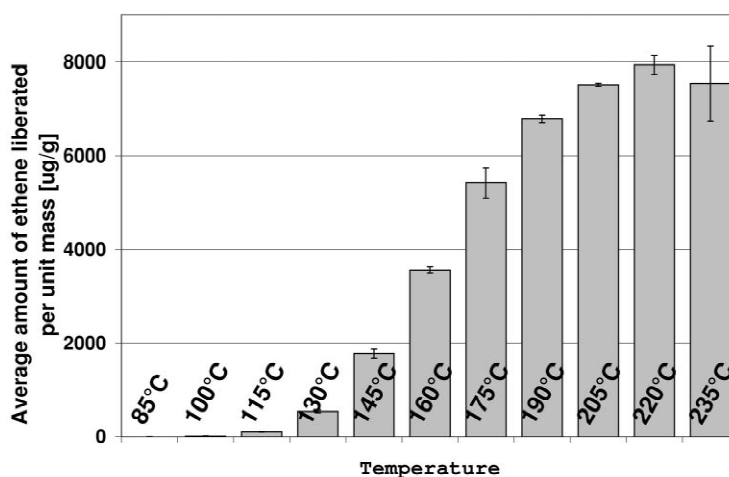
Fig. 3. Dependence of the amount of ethene liberated (per 1 g of the modified silica gel) on the temperature of the thermal decomposition.
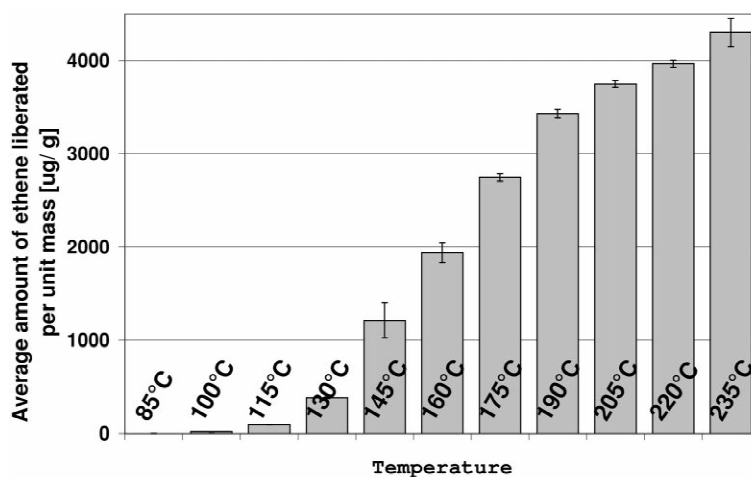
Fig. 4. Dependence of the amount of ethene liberated (per 1 g of the modified porous glass 1615) on the temperature of the thermal decomposition.

during the first hour of decomposition of the surface compound at 210°C. The results are collected in Table 3.

The results clearly demonstrate that the chemical modification of the studied materials was performed

uniformly. This is proved by a small value of the relative standard deviation (RSD<3%).

Additionally, comparing the results (mean values) obtained for individual types of granulated porous glass, one can conclude that there is a correlation

Table 3
Amount of ethene liberated from the tested materials with chemically modified surface (per 1 g of sample) during the first hour of thermal decomposition and the relevant statistical data

Mass of the sample of modified material (mg)					Mean (mg/g)	RSD (%)
Amount of ethene liberated (mg/g)						
Silica gel						
6.96	7.25	5.63	6.28	8.00		
8.57	8.59	8.61	8.46	8.53	8.55	0.68
Porous glass (1615)						
4.21	6.67	5.46	2.96	5.12		
4.16	4.19	4.21	4.21	4.13	4.18	0.87
Porous glass (1090)						
7.06	7.79	5.45	4.58	5.38		
0.419	0.394	0.394	0.394	0.394	0.399	2.9
Porous glass (940)						
10.94	7.34	6.76	9.19	9.75		
0.394	0.400	0.382	0.389	0.387	0.390	1.7
Porous glass (807)						
6.39	6.78	5.23	9.55	10.25		
2.23	2.22	2.29	2.21	2.24	2.24	1.4

Temperature of ethene generation: 210°C. Diluting gas flow-rate: 10 ml/min. Gaseous standard injection time: 20 s.

between the total amount of ethene liberated during the first hour of thermal decomposition and the specific surface area of the glass (Table 1).

3.3. Determination of a mathematical relationship between the amount of ethene generated and generation time

The previous studies conducted at Analytical Chemistry Department, TUG showed that the amount of the analyte generated during the course of the thermal desorption decreases exponentially in time [8]. Such a description of the reaction kinetics, however, is sufficient in the case of a continuous flow of the diluting gas through the bed. The different way of preparation of gaseous standard mixture based on modified material decomposition results in different kinetics of generation of measured components in the process of surface compound decomposition (Fig. 5). In the procedure adopted in this study, utilization of the integrated curve is more convenient. Therefore, bearing in mind practical applications, the relationship was sought between the total amount of ethene generated and time passing since the beginning of the generation process, to find the best mathematical description of the kinetics of the decomposition of the surface compound.

The generated gaseous mixture was introduced onto the GC column every 5 min during the first hour of thermal decomposition. Amount of ethene corresponding to each 5 min interval was defined as the total amount generated since the start of the generation process until the end of a given time interval.

Statistical analysis of the results led to the conclusion that the best suitable model of the ethene generation process is logarithmic curve. The regression equations found, together with corresponding correlation coefficients are presented in Table 4.

3.4. Verification of the mathematical equations describing the kinetics of decomposition of the surface compound

Correctness of the equations found by regression, describing the kinetics of thermal decomposition of the ethene yielding surface compound was verified by an independent series of measurements, performed at randomly selected time intervals. Subsequently, values found experimentally for each interval were compared with those calculated on the basis of the corresponding logarithmic curve. Results of these series are given in Table 5.

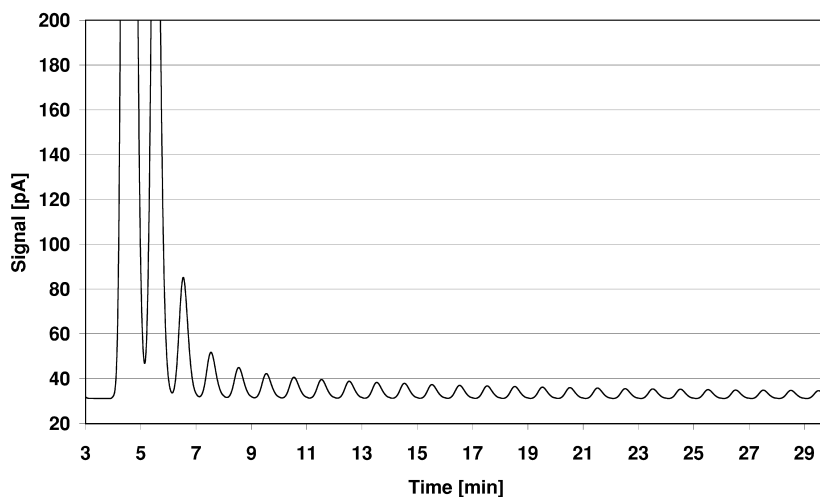On the basis of data presented in Table 5, one can

Fig. 5. Peaks of ethene obtained during thermal decomposition of the surface compound. This quasi-chromatogram was obtained for 1 min time intervals between the consecutive injections of the gaseous standard mixture. Support material of the surface compound: porous glass (1615). Temperature of ethene generation: 210°C. Diluting gas flow-rate: 10 ml/min. Gaseous standard injection time: 20 s. Thermal decomposition period: 30 min (sample injection at 1 min intervals).

Table 4
Mathematical equations describing the kinetics of decomposition of the surface compound yielding ethene found for the silica gel and granulated porous glass and the respective correlation coefficients

Support material	Equation found	Correlation coefficient
Silica gel	$y = 272 \ln(x) + 7428$	0.9994
Porous glass (1615)	$y = 136 \ln(x) + 3618$	0.9987
Porous glass (1090)	$y = 34 \ln(x) + 256$	0.9993
Porous glass (940)	$y = 36 \ln(x) + 239$	0.9973
Porous glass (807)	$y = 71 \ln(x) + 1945$	0.9989

Temperature of ethene generation: 210°C. Diluting gas flow-rate: 10 ml/min. Gaseous standard injection time: 20 s. y – Total amount of ethene liberated from 1 gram of bed material during time x (μg/g); x – time of the surface compound thermal decomposition process (min).

judge that the equations of curves describing the kinetics of thermal decomposition of chemically modified support material are correct. This is proven by high values of the respective correlation co-efficients ($R > 0.99$, see Table 4). Relative differences between the calculated (on the basis of the previously determined equations) and experimentally found

ethene yields at randomly selected time intervals did not exceed 5.6% (except the measurement after 1 min from the start of decomposition, see Table 5).

The applicability of the models found is also time limited:

(i) Minimum time of heating of the chemically modified support material, ensuring good agreement

Table 5
Experimentally measured and calculated amounts of ethene (per 1 gram of the modified support material) obtained in the course of thermal decomposition of the surface compound

Time (min)	Amount of ethene generated from unit of mass of the modified material (mg/g)														
	Silica gel			Porous glass											
				1615			1090			940			807		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
1				2.80	3.62	22.50									
2				3.69	3.71	0.62				0.272	0.264	2.8	1.97	2.02	2.8
3	7.31	7.73	5.4	3.80	3.77	1.02	0.301	0.294	2.4						
7	7.62	7.96	4.3	3.88	3.88	0.05							2.16	2.08	3.8
10							0.340	0.335	1.3				2.06	2.11	2.5
14				3.98	3.98	0.01				0.341	0.335	1.8			
19				4.03	4.02	0.22							2.10	2.15	2.5
25	7.86	8.30	5.4	4.07	4.05	0.46	0.371	0.367	1.2						
30	7.90	8.35	5.4				0.378	0.373	1.4	0.374	0.363	3.2	2.26	2.19	3.5
33	8.02	8.38	4.3				0.387	0.376	2.8	0.378	0.366	3.4			
34				4.13	4.10	0.79							2.27	2.20	3.4
35							0.384	0.379	1.4						
38							0.393	0.381	3.0				5.15	2.20	2.2
41	8.08	8.44	4.2										2.28	2.21	3.4
42	7.99	8.44	5.4							0.389	0.375	3.9			
45				4.19	4.13	1.24	0.392	0.387	1.2				2.29	2.22	3.5
46				4.15	4.14	0.40				0.393	0.378	4.0			
48										0.395	0.380	4.0	2.30	2.22	3.5
54	8.06	8.51	5.3							0.401	0.384	4.5			
57				4.19	4.17	0.52				0.404	0.386	4.7			
64	8.12	8.56	5.2										2.32	2.24	3.6

Temperature of ethene generation: 210°C. Diluting gas flow-rate: 10 ml/min. Gaseous standard injection time: 20 s. 1 – Experimental value; 2 – calculated value; 3 – relative error (%).

between the experimental and calculated value and permitting the use of the resulting mixture for calibration is equal to 2 min. This is indicated by the results, found for the porous glass (1615) after 1 min, when the relative error between the two values exceeded 22% (Table 5). For all times equal or longer than 2 min (and for all materials studied) the error did not exceed 5.6%. The most probable explanation of this discrepancy at 1 min is the method of data collection for the regression procedure, which were taken at 5 min intervals under assumption that the temperature of the material is constant since the very beginning of decomposition. Actually, directly after insertion of the tube with chemically modified material into the pre-heated furnace of the thermal desorber, the temperature is momentarily lowered and, apparently, it requires 1–2 min time to return to its preset value.

(ii) Maximum time may be defined as time after which there is no more generation of the desired analyte (or the resulting concentrations are too low for calibration purposes). Experiments indicate that after 1 h of heating (for each of the materials studied), the non-decomposed surface compound still exists on the support material, though, the slope of the curve decreases significantly. Hence, it would be necessary to perform some long lasting experiments to determine the value of the maximum time allowed. However, from the practical point of view, there is no need for longer use of a single bed, i.e., longer generation of the desired analyte. Therefore, 1 h was assumed as the maximum generation time for ethene.

It should be added that mathematical relationships describing kinetics of thermal decomposition of a surface compound are determined for a given batch of material and given conditions of decomposition process. For a new batch of chemically modified material mathematical relationships should be determined once again.

3.5. Validation of the proposed procedure

A comparison of quantitative results obtained using the proposed and a standard methods was performed. A static method of gaseous mixture preparation was used as a reference method. In the proposed method silica gel was used as a support material. Statistic analysis was carried out for the same ethene amount liberated (measured as a peak area) using both method of standard generation. The number of measurements in both methods was the same ($n_1=n_2=7$). The F-Snedecor test [9] was applied to compare the precision of two methods and Aspin and Welch test [9] for comparison of accuracy.

On the basis of the statistical evaluation of the obtained results it can be concluded that: (1) methods are statistically significantly different considering precision ($F_{crit}=4.28<F_{calc.}=6.52$; $r_1=r_2=6$, $\alpha=0.05$); (2) the proposed calibration method has better precision. The RSD for the proposed method was 0.19%, where for the standard method was RSD= 0.49%. (3) The methods are not statistically significantly different considering accuracy ($\nu_{crit}= 1.86>\nu_{calc.}=0.430$; $c=0.1$, $r_1=r_2=7$, $\alpha=0.05$).

The accuracy in the proposed calibration methods will be better when the degree of coverage of support material will be smaller. It comes from the fact that to obtain the same amount of a measured component it is necessary to weigh higher amount of a chemically modified material. In this case the porous glass as material with the smaller degree of coverage is more recommended then silica gel (Table 3).

4. Summary

Generation of gaseous standard mixtures utilizing thermal decomposition of suitable surface compounds is a simple and easy method of preparation of such standards in the case of volatile, toxic, chemically reactive, unstable and malodorous analytes.

The new method of determination of the amount of an analyte generated in the process of thermal decomposition of the surface compound, discussed in this paper, permits obtaining a few measuring points, while utilizing only a single sample of the chemically modified material. One should remember, however, that for determination of the amount of the analyte liberated during the second (and the following) time intervals the total amount of the analyte liberated since the start of decomposition until the beginning of a given time interval should be known.

The only errors involved in the described calibration method, depending on manual capabilities of

laboratory staff (human factor) are: weighing error and time measuring error. The former may be minimized by using a balance of suitably high sensitivity.

Additionally, the method offers wide opportunities of introducing innovations and modifications, first of all regarding the type and geometry of the support material used for preparation (by chemical modification of its surface) of the suitable surface compound, subsequently yielding the desired analyte in the process of its thermal decomposition.

Acknowledgements

References

[1] J. Namieśnik, Crit. Rev. Anal. Chem. 730 (2000) 221.
[2] J. Namieśnik, P. Konieczka, W. Chrzanowski, J.F. Biernat, Chem. Anal. (Warsaw) 39 (1994) 245.
[3] T.J. Bzik, D.L. Grieble, Am. Lab. 26 (1994) 20.
[4] J.N. Miller, Analyst 116 (1991) 3.
[5] P. Konieczka, M. Prokopowicz, B. Zygmunt, J.F. Biernat, J. Namieśnik, Chromatographia 51 (2000) 249.
[6] M. Prokopowicz, A. Przyjazny, J. Szczygelska-Tao, J.F. Biernat, J. Namieśnik, Microchem. J. 59 (1998) 437.
[7] R. Kaiser, in: Gas Phase Chromatography, Tables for Gas Chromatography, Vol. III, Butterworths, London, 1963, p. 101, Chapter 8.
[8] P. Konieczka, Fresenius J. Anal. Chem. 367 (2000) 132.
[9] J.B. Czerminski, A. Iwasiewicz, Z. Paszek, A. Sikorski, Metody Statystyczne dla Chemików, Butterworth & Co. Ltd., 1986, Chapter 2, pp. 103, 416; Chapter 3, pp. 130, 439.