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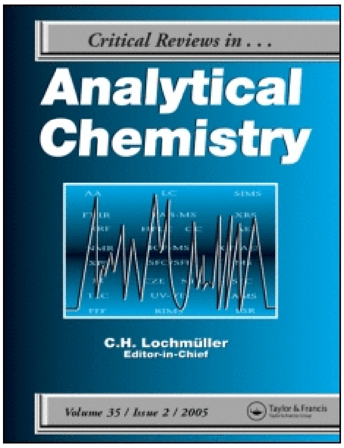

Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

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Online publication date: 18 June 2010

To cite this Article Przyk, Elzbieta , Świtaj-Zawadka, Anna , Szczygelska-Tao, Jolanta , Przyjazny, Andrzej , Biernat, Jan F. and Namieśnik, Jacek(2003) 'Preparation of Gaseous Standard Mixtures: Methods for Controlling the Amount of Components Generated in the Process of Thermal Decomposition of Immobilized Compounds', Critical Reviews in Analytical Chemistry, 33: 3, 249 — 267

To link to this Article: DOI: 10.1080/713609165

URL: http://dx.doi.org/10.1080/713609165

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Critical Reviews in Analytical Chemistry, 33(3):249–267 (2003)

Preparation of Gaseous Standard Mixtures: Methods for Controlling the Amount of Components Generated in the Process of Thermal Decomposition of Immobilized Compounds

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ABSTRACT: Gaseous standard mixtures play an important role in characterizing and checking the applicability of new analytical procedures. In this case gaseous standard mixtures can be treated as a special kind of reference material (validation process requires the use of so-called matrix reference materials).

The selection of a method of generation of gaseous standard mixtures with the desired characteristics depends on the nature of the analyte and diluent gas, as well as on the required concentration of analytes in the mixture. Recently, dynamic methods of generation of gaseous standard mixtures are becoming more and more common. These include the method based on thermal decomposition of immobilized compounds. The generation of the measured component takes place as a result of heating of a sample of solid support with chemically modified surface. During a chemical reaction initiated by sufficiently high temperature, the immobilized compound undergoes decomposition or rearrangement accompanied by the release of a specific volatile compound. Various amounts of the analyte per unit time can be obtained by adjusting the conditions of the thermal decomposition process.

This article describes the possibility of varying the amount of a measured component through the adjustment of conditions of drying the solid support or of the process of chemical modification of its surface. The principle of this technique is exemplified by the generation of a mixture containing ethene as the analyte. Porous glass was used as a solid support. The proposed technique was used for the generation of gaseous standard mixtures for the calibration of a thermal desorber-gas chromatograph-flame ionization detector (TD-GC-FID) system.

KEY WORDS: gaseous standard mixtures preparation, thermal decomposition process, chemically modified supports, immobilized compounds, surface hydroxyl groups.

I. INTRODUCTION

Rapid progress in processes of chemical modification of surfaces of inorganic supporting materials has been observed since the 1970s.[1] It was due to the creation of new immobilized complexes of metals, the development of methods of immobilizing enzymes, and, primarily, to the process of preparation of new stationary phases for HPLC.[2]

An ideal support for many chromatographic and other purposes should possess the following properties:[3]

- uniform and/ or spherical shape of particles with a narrow size distribution,
- high specific surface area with evenly distributed reactive sites,
- porosity to allow free passage of molecules, thus allowing rapid diffusion and rapid equilibration,
- mechanical stability.

Almost all of the properties mentioned above are met by silica gel. On the basis of a literature search, it can be concluded that silica gel is the support used most frequently (after chemical modification for the

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generation gaseous standard mixtures using the techniques of thermal decomposition of the surface compound.[4-14] Its widespread use can be explained by ready availability and the ease of preparation of different kinds of silica gel (differing with respect to pore size, total porosity, specific surface area. and particle size) through an adjustment of conditions of synthesis. In addition, silica gel has favorable physicochemical properties, such as:[15,16]

- insolubility in mobile phase liquids,
- mechanical stability (it is not destroyed at pressures up to 65 MPa),
- chemical inertness in a relatively wide range of pH values (2 to 8),
- thermal stability up to 250°C,
- the possibility of replacement of silicon atoms in silica gel with other atoms, such as boron, magnesium, or aluminum,
- the possibility of surface modification and the modification of geometric structure of pores through hydrothermal treatment or chemical phase binding,
- the possibility of adsorbing or binding large amounts of compounds as a result of high specific surface area relative to other beds (such as polymers) and a large number of active sites per unit surface area,
- highly uniform structure of the surface.

Also, some kinds of glass have physicochemical properties useful for surface modifications. High chemical inertness over a wide pH range toward both organic and aqueous solvents, and even aggressive reagents allows that the glass is suitable for a variety of applications in the industry, for example, pharmaceutics or biotechnology. Examples of the application of porous glass *Trisoperl,* depending on its chemophysical properties are listed in Table 1.[17]

These materials (silica gel, porous glass, and glass fiber) are also applied as supports of

TABLE 1
The Examples of Applications of Porous Glass *Trisoperl* with Its Chemophysical Properties[17]

Affinity chromatography	♣	♦	♠	⊗	⊕	∇	*	ℵ	
Inorganic analysis	♦	♥	×	ℵ					
Antidoby purification	♣	⊗	⊕	∇					
Plasma depletion	♦	⊗	⊕	∇	+	ℵ			
Biotechnology	♣	♦	♥	♠	⊗	∇	+	*	ℵ

♣- narrow pore distribution;
♦- mechanical strength;
♥- broad pH-stability;
♠- low abrasion;
⊗- low non specific adsorption;
⊕- toxicol. harmless;
∇- high reproducibility;
×- thermal stability;
+- simple decontamination;
*- easy scale-up;
ℵ- reusability.

so-called “surface compounds” in a technique of generation of gaseous standard mixtures. This technique, developed at the Chemical Faculty of Gdansk University of Technology (GUT), is based on thermal decomposition of a surface compound, bound to the surface of support material in the process of its chemical modification. At high temperature (above 40°C), the surface compound undergoes thermal decomposition, yielding a volatile compound that is an analyte of interest. The process of generation of the measured component of a gaseous standard mixture can be carried out, for example, in a thermal desorber, and the amount of the analyte strongly depends on:

- surface structure of support material,
- parameters of the chemical modification process,
- mass of a sample of the chemically modified support,
- conditions of thermal decomposition (time and temperature of thermal decomposition, diluent gas flow rate).

This article is a review of the available literature and practical experience in the area of generation of gaseous standard mixtures by the process of thermal decomposition of immobilized compounds. The review emphasizes the possibility of the adjustment of the concentration of a measured component in the generated gaseous standard.

II. CHEMICAL MODIFICATION OF SURFACE OF A SOLID

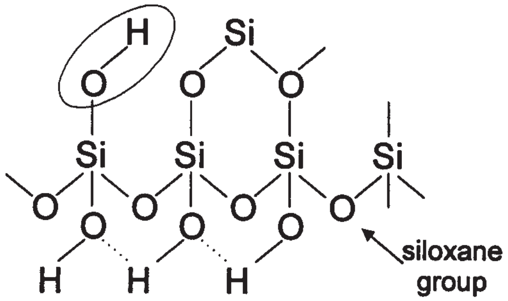
During chemical modification of a solid, the skeleton of a matrix remains unchanged, while the physicochemical character of the surface, where chemical properties depend on the nature of compounds bound through strong covalent bonds with active sites, undergoes a change.

Active sites in materials originating from silica are silanol groups (*silanols*; –SiOH). However, not all the silanol groups present on the solid surface are chemically active. For example, LiChrosorb SI-100 has 4.6 –SiOH groups per 1 nm^2, of which only 2.95 groups per 1 nm^2 are chemically active.[3,18] In general, the density of active sites decreases with an increase in specific surface area of a solid, which in turn is accompanied by an increase in average pore size.[3]

The total number of all hydroxyl groups in amorphous silicas (silica gel, porous glass, aerogel), differing with respect to conditions under which they were prepared, surface area, or porosity, is constant. This means that the density of silanol groups is a physicochemical constant, characterizing the surface of a solid of silica origin; it is approximately equal to 8 µmol/ m^2.[19]

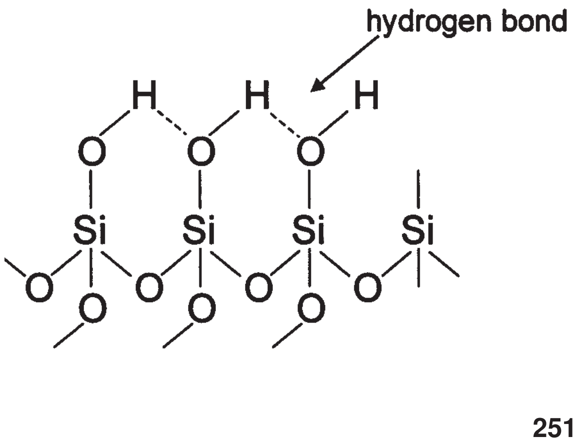
There are three fundamental types of surface hydroxyl groups:[3,16,20]

1. *single unbound silanols (free, isolated)* – the hydroxyl groups occurring on different silicon atoms at a distance preventing the formation of hydrogen bonds; the distance from nearest -OH groups is 5 to 5.2 Å:

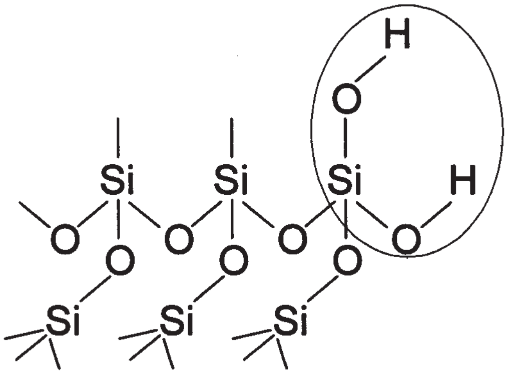


2. *active silanols* — the hydroxyl groups are present on the same or adjacent silicon atoms at a distance enabling the formation of hydrogen bonds; the distance between closest –OH groups is 2.52 to 2.6 Å, that between –OH groups further apart-5.2 Å:

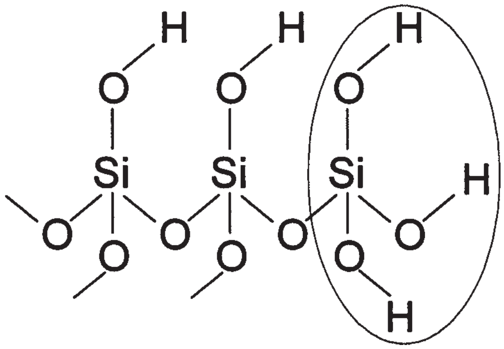
Single bound silanols (vicinal)



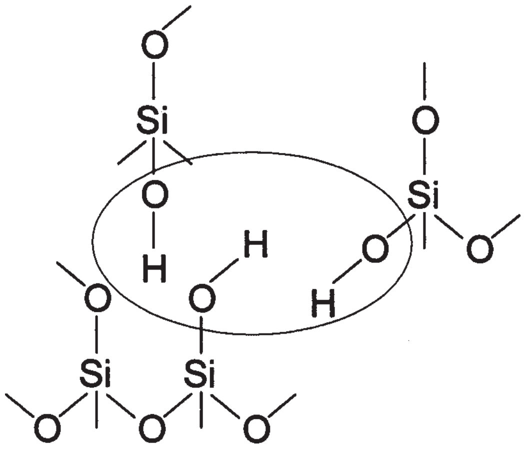
Double silanols (geminal)



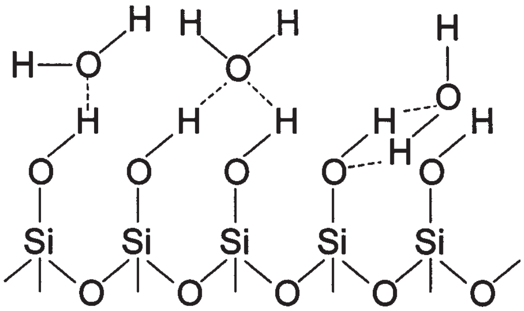
Triple silanols



3. *bound silanols* — the hydroxyl groups having in their vicinity two, three, or four –OH groups at a distance of 2.52 to 2.6 Å:



Polar nature of hydroxyl groups results in high hygroscopicity of the material:



However, only single hydroxyl groups have a decisive effect on all chemical reactions taking place on the surface of material supporting an immobilized compound.

An inorganic material can be modified using either inorganic or organic reagents. Modification with inorganic reagents results in coverage of the surface of a solid with mono- or polymolecular layers, for example, Al_2O_3, Fe_2O_3, Cr_2O_3, B_2O_3, TiO_2, etc.[3]

Most common organic reagents include:[3]

- amines — resulting in formation of Si-NR_2 bonds,
- alcohols — resulting in formation of Si-OR bonds,[21–23]
- Grignard reagents, alkyl derivatives — resulting in formation of Si-CR_3 bonds,
- chlorosilanes, alkoxy(alkyl)(aryl)silanes — resulting in formation of Si-O-SiR_3 bonds.[21–23]

Among the bonds listed above, the Si-C bond has the greatest stability. Consequently, the first step in the process of the chemical modification of a support material usually involves the formation of a Si-C bond. Thus, a chemical moiety bonded to the support surface becomes in turn a substrate in following chemical reactions, a proper combination of which allows the introduction onto the surface of support of any functional group.

A review of the available literature reveals[1–3] a wide applicability of materials with chemically modified surface in a variety of areas of science and technology. We are particularly interested in a new approach to the problem of the generation of gaseous standard mixtures by thermal decomposition of immobilized compounds obtained through chemical modification of the surface of solid supports. This is a new area of application of such materials.

III. PREPARATION OF GASEOUS STANDARD MIXTURES USING THE PROCESS OF THERMAL DECOMPOSITION OF IMMOBILIZED COMPOUNDS

A general procedure for generating a gaseous standard mixture by using a support with chemically modified surface and the process of thermal decomposition is shown in Figure 1.

The ease of generation of a gaseous standard mixture over a wide range of concentrations of a measured component is not the only advantage of this technique. Another important advantage, resulting from the use of a thermal desorber, is the possibility of performing the calibration of a measuring device both *off-line* and *on-line*. In the latter case, a thermal desorber plays a dual role: that of a generator of the measured component as well as of a dispensing device. A schematic diagram of connection of a thermal desorber with a measuring device *off-line* and *on-line* is shown in Figure 2.[24]

Since in this technique gaseous standard mixtures can be generated immediately prior to use, the approach based on the use of controlled pyrolysis of immobilized compounds also solves the problem of the generation of chemically reactive, toxic, unstable, volatile, or malodorous substances. The use of this new technique in analytical practice enables generation of a specific amount of the analyte on "as-needed" basis. In addition, there is a possibility that this amount can be determined by simple and yet accurate measurements of mass (samples of modified support in the form of beads or granules), a length of rod or fiber (made of glass or quartz), or the number of particles in a sample of material (provided that they will be of the same size). Thus far, we investigated the use of this technique for the generation of gaseous standard mixtures of thiols, isothiocyanates, ammonia, methyl chloride, carbon monoxide and carbon dioxide, ethene, and acetaldehyde. A list of immobilized compounds obtained so far through chemical modification of the support surface is presented in Table 2.

IV. HOMOGENEITY OF COVERAGE OF THE SUPPORT SURFACE BY THE IMMOBILIZED COMPOUND

Each modified support intended for the generation of a measured component through controlled thermal decomposition should have a high degree of homogeneity of coverage of its surface by the immobilized compound. In other words, there should be a linear relationship between the amount of a measured component obtainable from a given sample of modified support $\mathbf{M}$ and the mass of the sample $\mathbf{m}$, according to the equation: $\mathbf{M} = \mathbf{bm} + \mathbf{a}$; the straight line should pass through the origin of the coordinate system.

The degree of homogeneity of coverage of the surface of a support by an immobilized compound depends on three factors, namely:

- homogeneity of physical structure of the material surface,
- homogeneity of coverage of the material surface by active sites participating in the process of chemical modification of the surface,
- homogeneity of chemical modification of the surface on an entire sample of material.

The significance of this parameter in the technique of preparation of standards results from its direct effect on the reproducibility of the generation of measured components. In addition, a constant value of the ratio of the amount of generated measured component to the mass of sample subjected to thermal decomposition enables an accurate determination of the mass of a generated compound from the mass of a sample of modified support or the length of a glass fiber.[26] Such a way of controlling the amount of a generated measured component in a gaseous standard mixture is closely related to a degree of coverage of the support surface by an immobilized compound.

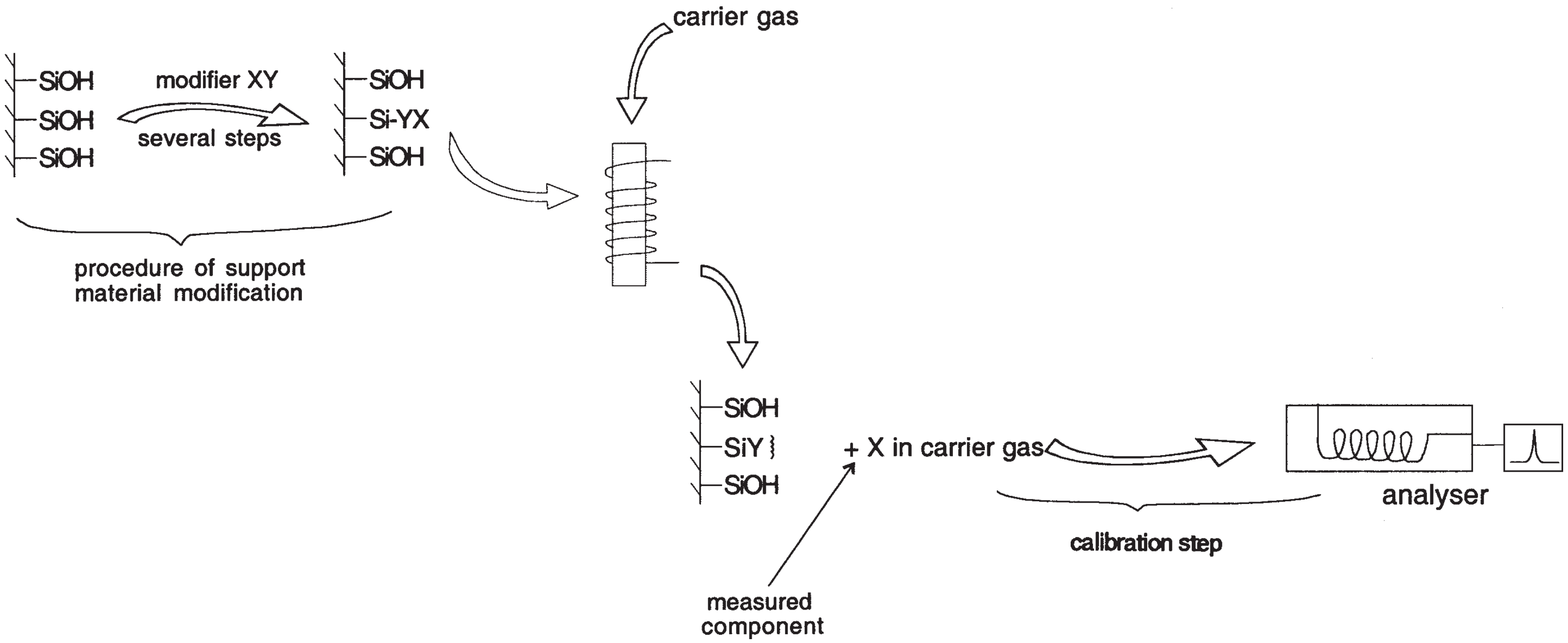


FIGURE 1. The scheme of generation of gaseous standard mixtures with using the technique of thermal decomposition of the surface compound.

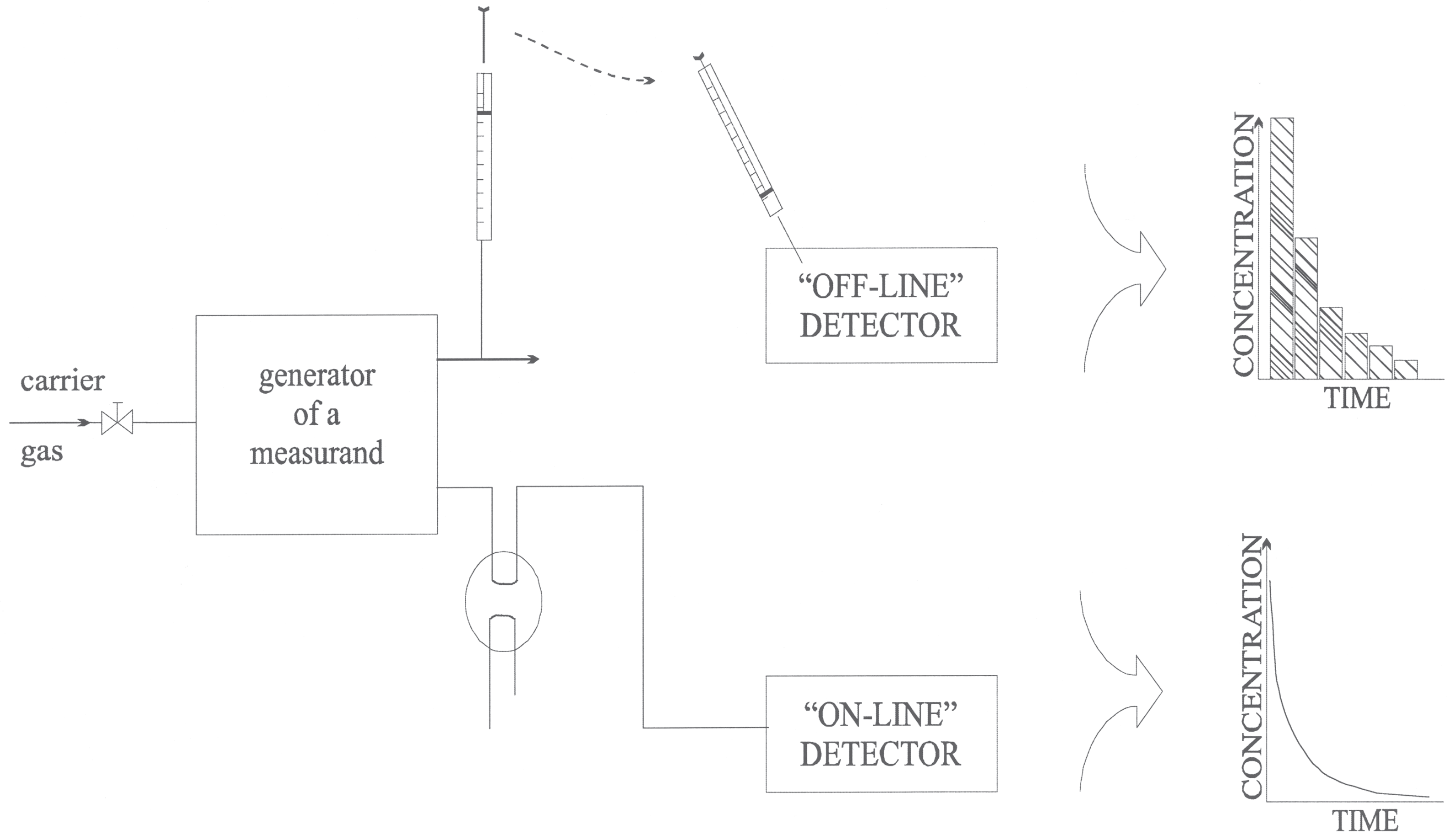
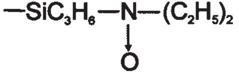
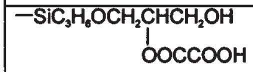
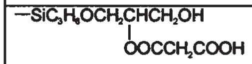
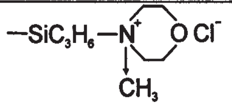
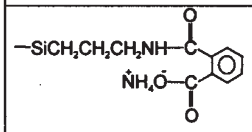
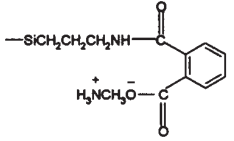
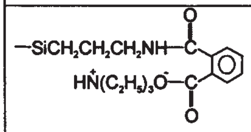
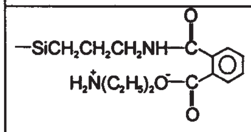
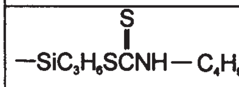
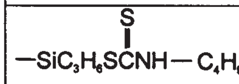
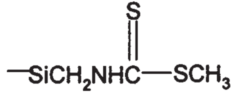
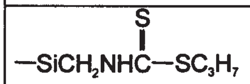


FIGURE 2. The scheme of the apparatus working in "off-line" and "on-line" mode.[24]

TABLE 2
The Area of Application of Chemically Modified Support as a Source of Measurands Generated with using Technique of Thermal Decomposition of Surface Compound

Surface Compound	Measurand	Support Material	Calibrated Detector	Literature
 $-SiC_3H_6-\underset{\overset{\downarrow}{O}}{N}-(C_2H_5)_2$	C_2H_4	Porous Glass	FID	25
		Silica Gel		4
		Glass Fiber		26
 $-SiC_3H_6OCH_2\underset{OOCCOOH}{CH}CH_2OH$	CO	Porous Glass	FID	27
	CO_2	Silica Gel	FID, NDIR	5-7
$-Si(OH)_2C_3H_6N(OH)C_2H_4OH$	CH_3CHO	Silica Gel	FID	8
 $-SiC_3H_6OCH_2\underset{OOCCH_2COOH}{CH}CH_2OH$	CO_2		NDIR	9
	CH_3Cl		FID	10
	NH_3		Photometric Detector- SQ 118 (after absorption in solution)	11
	CH_3NH_2			11
	$(C_2H_5)_3N$			11
	$(C_2H_5)_2NH$		NPD Photometric Detector- SQ 118	11
 $-SiC_3H_6S\overset{S}{C}NH-C_4H_9$	CH_2CHCH_2NCS		FID	12
 $-SiC_3H_6S\overset{S}{C}NH-C_4H_9$	C_4H_9NCS		FID	12
 $-SiCH_2NH\overset{S}{\overset{\parallel}{C}}-SCH_3$	CH_3SH		FID	13
 $-SiCH_2NH\overset{S}{C}-SC_3H_7$	C_3H_7SH		FID, FPD, MS	13, 14

V. DEGREE OF COVERAGE OF THE SUPPORT SURFACE BY AN IMMOBILIZED COMPOUND

The total amount of analyte(s) that can be released from unit mass of a chemically modified support depends on the density of a chemical moiety on its surface, which in turn depends on the preparation procedure. Optimization (i.e., the determination of reagent concentrations, duration and conditions of chemical reactions) of individual steps of the process of chemical modification allows obtaining a maximum degree of coverage of the surface of a given support by an immobilized compound. Because in the modification process chemically active hydroxyl groups present on the surface of a support play a key role, the ability of the support to form chemical bonds with various chemical groups depends on their number. Chemical activity (the number of active sites) of a support can be modified by subjecting the material to thermal processing.[16,28,29] Drying a support at a temperature of 150 to 200°C results in the desorption of the majority of adsorbed water molecules, without a decrease in the number of –OH groups present on its surface. At 200 to 400°C, condensation of the majority of active –OH groups takes place, yielding water. A subsequent temperature increase results in a rapid decrease of number of hydroxyl groups due to condensation of free hydroxyl groups. A strongly dehydrated surface of a support is obtained at about 1000°C. The effect of temperature on surface hydroxyl groups is schematically illustrated in Figure 3. Figure 4 shows the dependence of the amount of a measured component (ethene) on temperature and drying time of a support (porous glass). The degree of activation of a support also depends on the structure of its surface, which is shown in Figure 5. Characteristics of materials used in our investigations as supports for immobilized compounds are presented in Table 3.

The amount of generated analyte also strongly depends on the kind of used support, which is shown in Table 4. The largest amount of a measured component per unit mass of a modified support is released from silica gel. Compared with silica gel, porous glasses in most cases have a significantly smaller extent of surface coverage by an immobilized compound. However, based on the results obtained, it cannot be unequivocally concluded that there is a clear relationship between the amount of generated measured component and any of the parameters describing geometry of the support surface.

A distinct advantage resulting from different degrees of coverage of the support surface by an immobilized compound is the possibility of preparing standard mixtures *off-line*. In this mode of preparation of standards, there is a substantial dilution of a mixture generated in a thermal desorber, dependent on the volume of a container used. Hence, the generation of a mixture, in which the concentration of measured components will be above the detection limit of the measuring device requires the use of a considerably larger sample of modified support (compared with the generation of a standard mixture *on-line*). Because the volume of a glass tube through which a modified support is fed to a desorber is limited, silica gel is recommended as a support for this method of generation of standard mixtures.

VI. DECOMPOSITION TEMPERATURE OF IMMOBILIZED COMPOUND

The dependence of the amount of analyte(s) released on the temperature of thermal decomposition of an immobilized compound is shown in Figures 6 and 7.[5–8,27]

It is evident that in case of a reaction initiated by a given parameter, its magnitude will affect the rate of the process; hence, the observed increase in amounts of generated measured components at higher temperatures of their generation.

In case of the immobilized compound that releases both carbon monoxide and carbon dioxide on heating, the temperature of a thermal desorber also affects the ratio of both compounds, although the amount of carbon dioxide is always larger. This can be explained by the mechanism of decomposition of the immobilized compound (see Figure 8). Because the decarboxylation process requires lower activation energy than the decarbonylation process, only carbon dioxide is released at lower temperatures (see Figure 7).

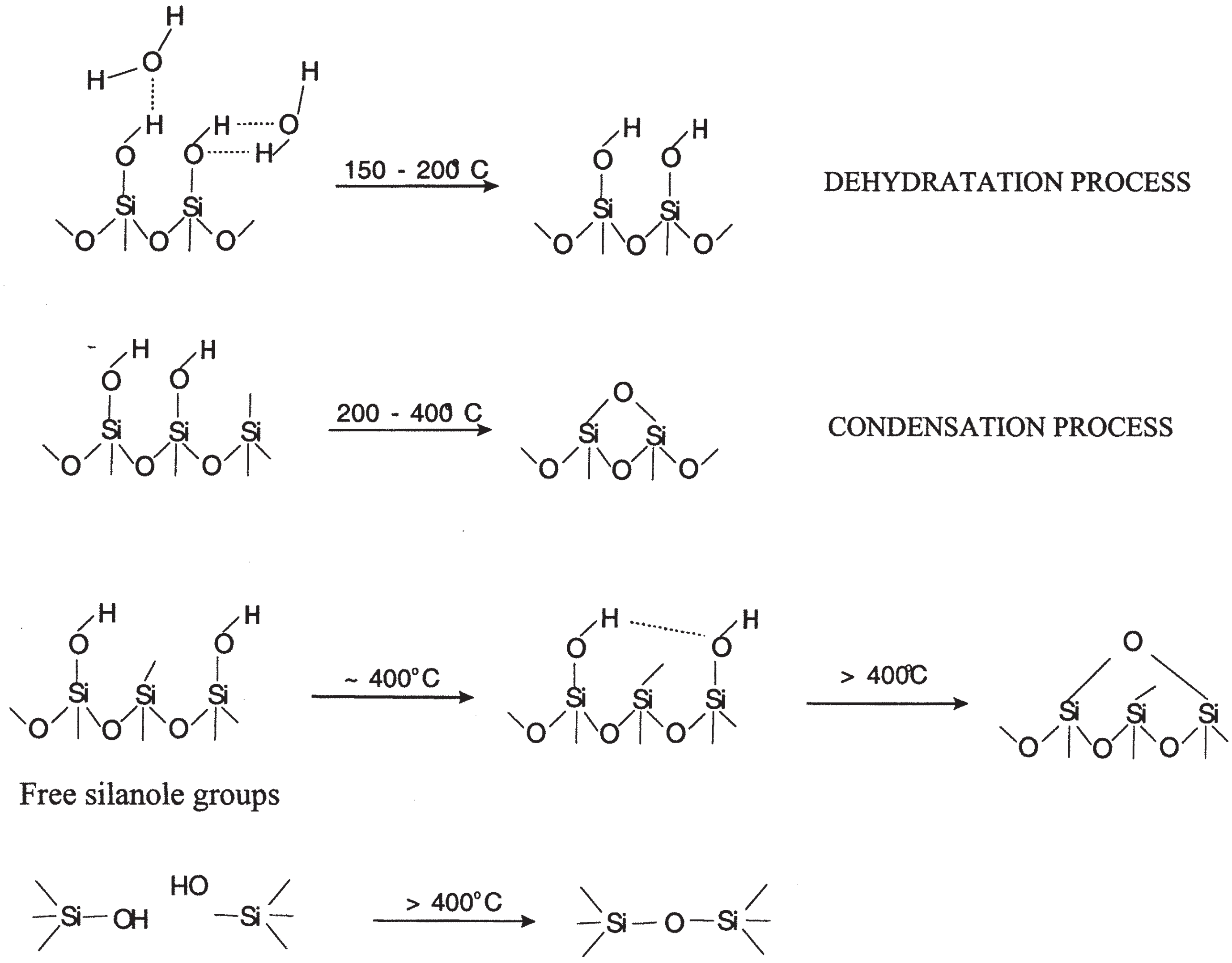


FIGURE 3. The influence of the thermal treatment on the support activation.

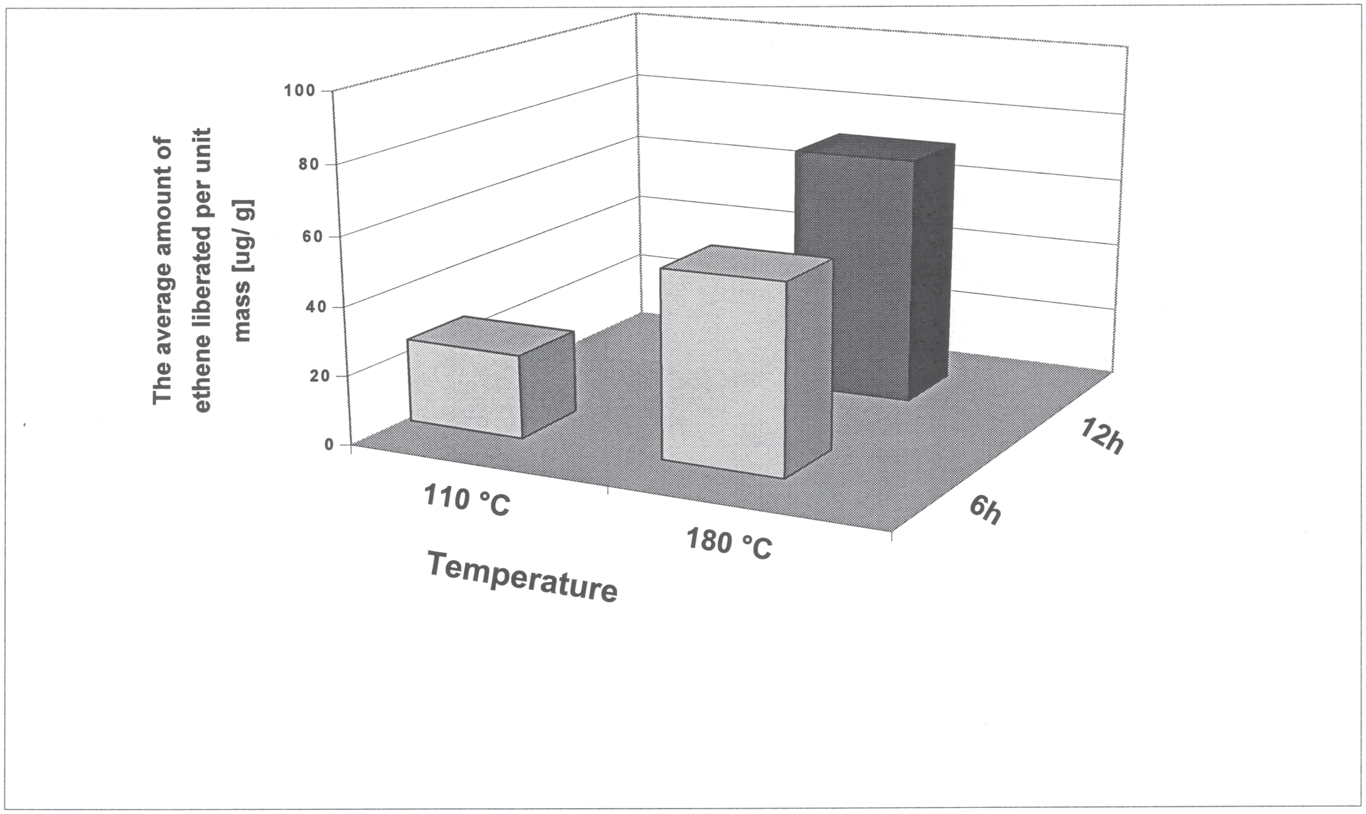


FIGURE 4. Dependence of the amount of ethene liberated per 1 gram of the modified porous glass (1615) on temperature and time of support drying before chemical modification of its surface. Temperature of ethene generation: 210 [°C]. Time of thermal decomposition process: 10 min.

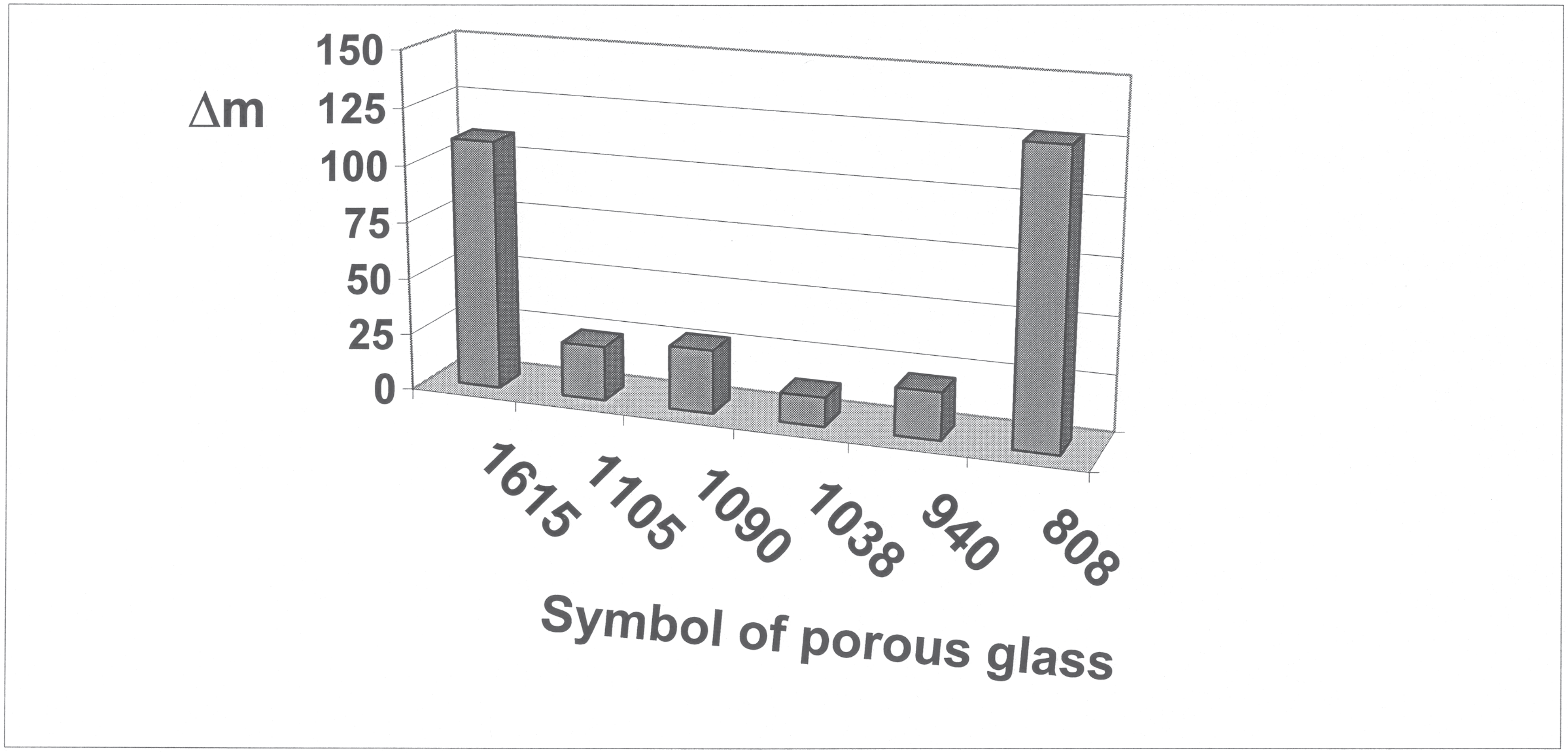


FIGURE 5. The influence of activation time of different type of porous glass on the amount of ethene liberated. Δm — calculated as: $m_{24} - m_{12}$, where m_{24} and m_{12} are average amount of ethene liberated from support that was heating at 110°C prior chemical modification for 24 and 12 h, respectively.

TABLE 3
Materials Used as Supports for Surface Compounds

	Supplier	Specific Surface $[m^2/g]$	Bead [μm]	Pore size [nm]	Pore volume $[mm^3/g]$
1. Silica Gel *MN-Kieselgel 60*	Macherey, Nagel & CO	200.00	215 ÷ 425		
2. Porous Glass *Trisoperl*	Johns Manville Europe GmbH	104.54	100 ÷ 200	63.2	1615.20
		32.83	100 ÷ 200	152.1	1104.80
		39.00	100 ÷ 200	99.8	1090.29
		20.02	100 ÷ 200	292.1	1038.23
		29.91	100 ÷ 200	126	940.57
		88.00	200 ÷ 500	35.5	807.75
3. Glass Fibers	They were prepared in the Laboratory of Optical Fibers Technology from Faculty of Chemistry, Maria Curie Skłodowska University in Lublin. The lengths of glass fibers were 2 and 3 cm. The diameter was 100 μm.				

TABLE 4
The Amount of Carbon Monoxide and Dioxide Liberated per Unit Mass of Modified Supports in the First 15 Min of Process of Thermal Decomposition of Surface Compound

		The amount of liberated measurand [μg/ g]					
		Ethene	**RSD [%]**	**Carbon monoxide**	**RSD [%]**	**Carbon dioxide**	**RSD [%]**
	Silica Gel	545	1.0	27.4	3.1	333	2.7
Porous Glass	**(1615)**	244	2.0	3.3	2.3	43	2.5
	(1104)	5.2	1.8	2.7	2.5	77	2.2
	(1090)	33	3.0	1.4	1.8	32	2.0
	(1038)	9.4	2.7	1.5	2.7	24	2.4
	(940)	16	1.5	4.1	2.6	60	3.3
	(807)	66	1.0	9.6	2.0	106	1.6

VII. CARRIER GAS FLOW RATE

So far, in our investigations of the technique of generation of gaseous standard mixtures based on thermal decomposition of immobilized compounds two different solutions regarding the flow of diluent gas were used:

- during the process of thermal decomposition of an immobilized compound the diluent gas flowed continuously through a heated bed of a chemically modified support,
- the flow of a diluent gas through a bed heated in a thermal desorber took place only during feeding of the generated standard to a measuring device.

In the latter case, the flow rate of a diluent gas has no effect on the amount of measured components in a mixture. In the former case, however, the concentration **c** of a measured component in a diluent gas after time **t** of its generation can be described by the exponential equation: c = Aexp(Bt). The diluent gas flow rate

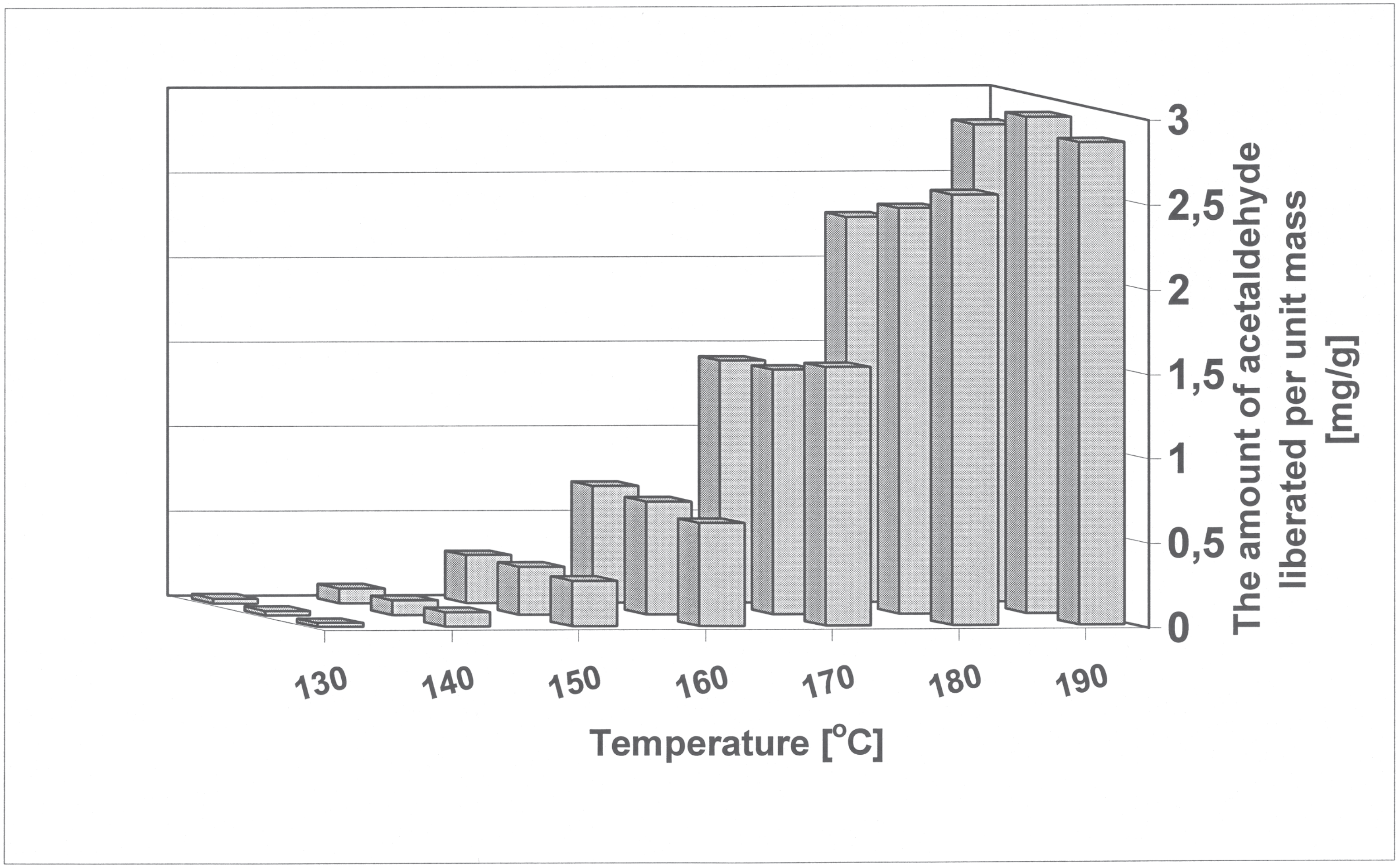


FIGURE 6. Dependence of the amount of acetaldehyde liberated per 1 gram of the modified silica gel on thermal decomposition temperature.[8]

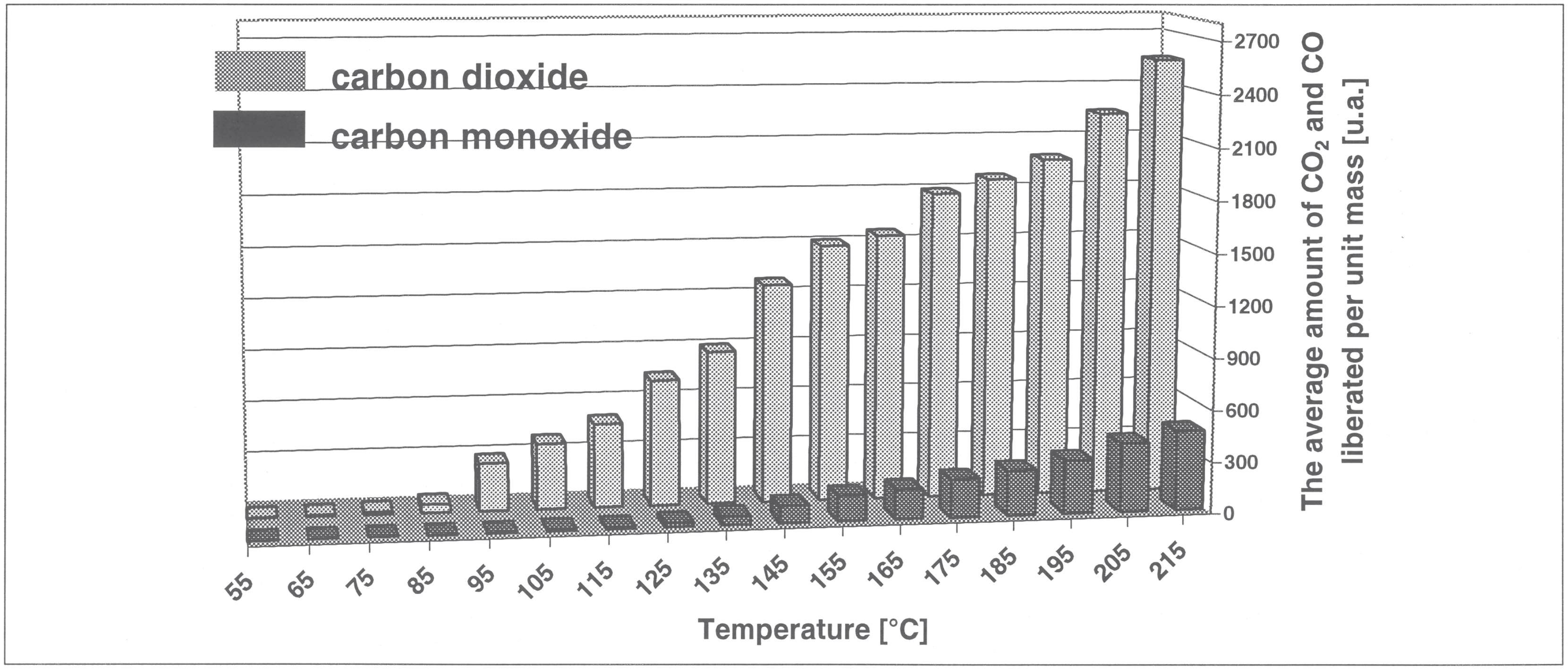


FIGURE 7. Dependence of the average amount of CO_2 and CO liberated per unit mass of the modified silica gel on temperature of decomposition of surface compound.[5–7,27]

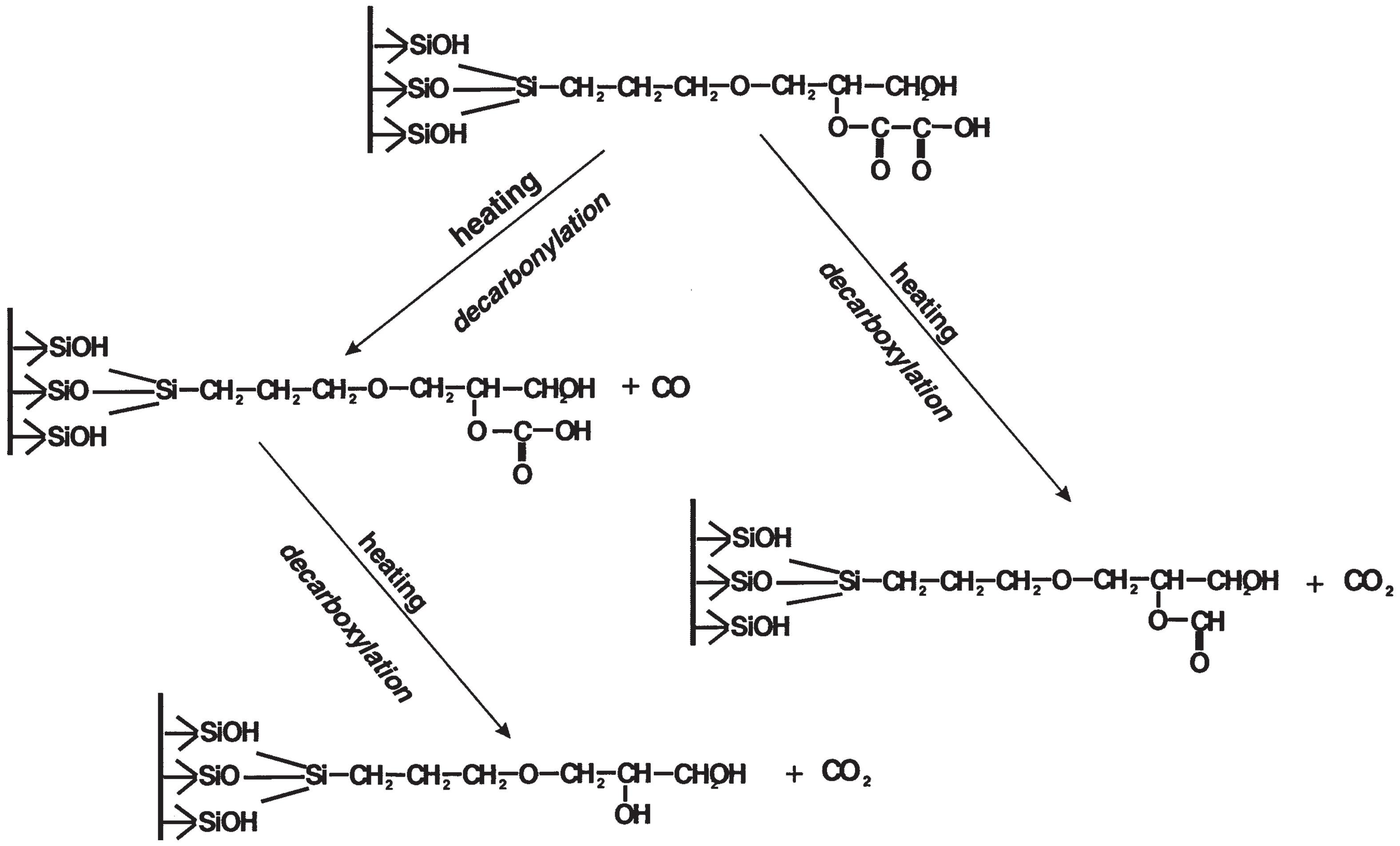


FIGURE 8. The scheme of the decomposition of surface compound yields to the liberation of carbon monoxide and dioxide.

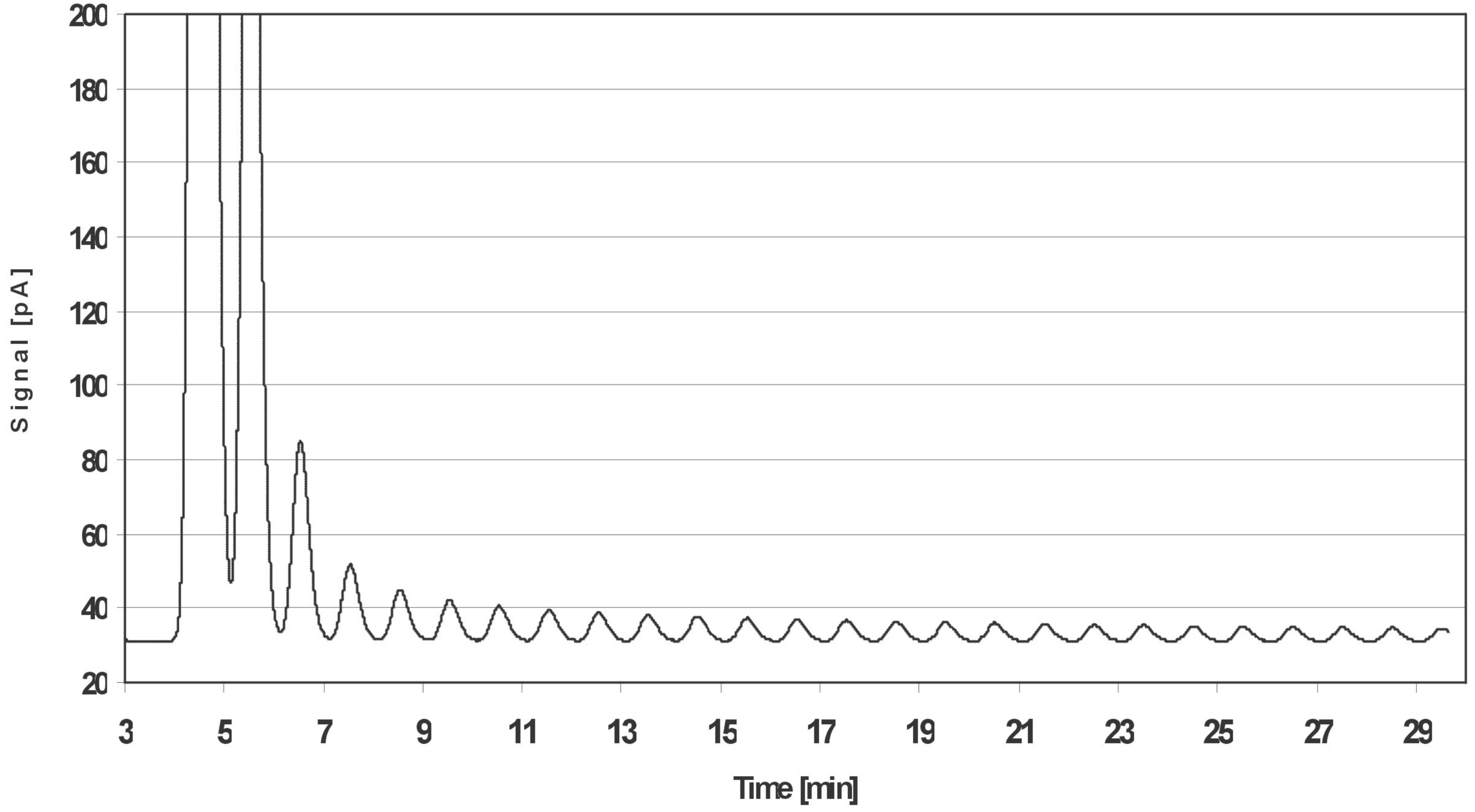


FIGURE 9. Peaks of ethene obtained during thermal decomposition of the surface compound. This quasi-chromatogram was obtained for 1-minute time intervals between the consecutive injections of the gaseous standard mixture. Support material of the surface compound: pourous glass (1615). Temperature of 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).

significantly affects the values of both coefficients (**A** and **B**) in this equation.

VIII. DURATION OF THERMAL DECOMPOSITION OF AN IMMOBILIZED COMPOUND

The rate of generation of measured components during thermal decomposition of immobilized compounds decreases with time, a substantial fraction of the total amount that can be obtained from a given sample of modified support (ca. 80 to 95%) being released during the first 10 min of the process. Thus, the amount of a measured component released during the heating of one sample can decrease even by four orders of magnitude, depending on the duration of the process and the frequency of sampling of a mixture generated in a desorber. The dependence of the amount of a generated measured component on duration of thermal decomposition is shown in Figure 9 (from the preceeding page).[25]

In the variant with the flow of a diluent gas taking place solely during sample introducing, the kinetic of the termal decomposition process (reaction) can be described by an equation being a function of one variable, that is, the time of the process: M = Aln(t) + B; M — total amount of a measured component released from unit mass of a sample during time (t) [μg/g]; t — duration of the process of thermal decomposition of an immobilized compound (min).

The knowledge of this equation allows carrying out multipoint calibration of a measuring device *on-line* on the basis of one sample of chemically modified support. Furthermore, it is possible to calculate the time after which the generated mixture should be sampled to obtain the desired amount of a measured component in the mixture. It should be obvious that, unless special design measures are undertaken, the generation of a substantially larger amount of a measured component during the first sampling cannot be avoided. Examples of calculations are shown in Table 5.

IX. SUMMARY

The possibility of control and rapid change of the amount of a measured component in a generated gaseous standard makes the technique presented in this article useful for both single-point and multipoint calibration using one sample of chemically modified support. The amount of a measured component in a gaseous mixture can be adjusted by the selection of conditions of thermal decomposition of modified support as well as of the conditions of chemical modification of its

TABLE 5
The Amount of Ethene (Per Unit Mass of Chemically Modified Support Material) Liberated in a Specified Time Interval of Thermal Decomposition of the Surface Compound

Time interval [min]	Amount [μg/ g]	Time interval [min]	Amonut [μg/ g]
0 - 3	293	0 - 3	293
3 - 16	57	3 - 6	24
16 - 19	5.8	6 - 10	17.4
19 - 22	5.0	10 - 15	13.8
22 - 26	5.7	15 - 21	11.4
26 - 30	4.9	21 - 28	9.8
30 - 35	5.2	28 - 35	7.6
35 - 41	5.4	35 - 41	5.4

Support material: Porous glass (1090)
The temperature of the thermal decomposition process: 210°C
Mathematical equation: M = 34ln(t) + 256
M – the total amount of ethene liberated per unit mass of support sample in a specified time interval (t) [μg/ g];
t – time of thermal decomposition process: [min].

surface, because the method of chemical modification of the support surface and the kind of support used determine the degree of surface coverage by an immobilized compound.

A clear advantage to this approach to the generation of gaseous mixtures is the minimization of errors, because the amounts of measured components in a generated mixture are calculated on the basis of absolute measurements of mass or length of a modified support used. In addition, the technique can be used for the generation of multicomponent gaseous mixtures. t

In summary, it can be concluded that the technique of preparation of gaseous standard mixtures based on thermal decomposition of immobilized compounds may be used as an alternative to other methods of preparation of such mixtures, particularly commonly used static techniques.

ACKNOWLEDGMENTS

This work has been partially supported by the Polish State Committee on Scientific Research (KBN).

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