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# Calibration of the thermal desorption-gas chromatography–mass spectrometry system using standards generated in the process of thermal decomposition of chemically modified silica gel

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## Abstract

A calibration method for the thermal desorption gas chromatographic–mass spectrometric (TD-GC–MS) determination of *n*-propanethiol based on a gas standard mixture generated in the process of thermal decomposition of chemically modified silica gel is proposed. The experimental results indicated that the total amount of *n*-propanethiol liberated from unit mass of the gel did not depend on the total mass of the gel used. A calibration curve for the TD-GC–MS system for *n*-propanethiol, determined for the relationship between the mass of *n*-propanethiol and the mass of the modified silica gel used, was found by a linear regression method and was characterized by a correlation coefficient  $r=0.99$ . This means that the amounts of liberated *n*-propanethiol are directly proportional to the mass of the modified gel used within the examined range of masses of silica gel samples. Consequently, the amount of the analyte (*n*-propanethiol) can be determined on the basis of mass of silica gel used and hence the modified silica gel can be treated as a standard of the liberated component (*n*-propanethiol in this case).

**Keywords:** *n*-Propanethiol; Silica gel

## 1. Introduction

One of the basic trends in analytics is to develop methods for the determination of ever lower concentration levels of analytes in more and more complex matrices. Consequently, such analytical steps as sampling and sample workup, sample introduction into an analytical system, and detector calibration are becoming increasingly important. At each of these steps, errors can be made which will

totally distort the results obtained, particularly at low concentration levels of the analyte(s). Hence, it is essential to minimize the probability of occurrence of errors at every step of the analytical procedure used. In the case of calibration, a major problem is the use of unstable, toxic, volatile or malodorous compounds. In addition, it is important that both the sample and the standard reach the detector in the same way, which eliminates the errors associated with the transport of samples and standards.

In the analysis of gaseous analytes, gaseous standard mixtures are used at a calibration step. The

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method, employing thermal decomposition of chemically modified silica gel, allows elimination of the sources of errors in the preparation of gaseous standard mixtures associated with using a different calibration of the system than that used in the analytical procedure [1–5].

The present paper discusses application of this method for the preparation of gaseous standard mixtures containing *n*-propanethiol as a measured component for the calibration of the thermal desorption gas chromatography–mass spectrometry (TD-GC–MS) system.

## 2. Experimental

### 2.1. Reagents

Silica gel used in the investigations (MN Kiesegel 60, 35–70 mesh (0.430–0.210 mm); Macherey Nagel, Düren, Germany) was dried at 120°C for 12 h and then modified as follows: a solution of 3 cm<sup>3</sup> of triethoxychloromethylsilane in 40 cm<sup>3</sup> of dry acetone was added to 20 g of the gel. Acetone was then evaporated from the mixture under reduced pressure and the product obtained was heated at 100°C for 12 h to complete the chloromethylsilylation reaction. The resulting product was washed with 50 cm<sup>3</sup> of methanol to remove the excess reactant and a mixture of 40 cm<sup>3</sup> of methanol and 4 cm<sup>3</sup> of aqueous ammonia was then added to the residue. After 12 h, the resulting aminopropylsilylated gel was isolated by filtration and washed with methanol, water and again with methanol. The modified gel was dried, and then 10 g of the product was suspended in a mixture of 20 cm<sup>3</sup> of acetone, 0.5 cm<sup>3</sup> of CS<sub>2</sub> and 1 cm<sup>3</sup> of dried pyridine. The resulting suspension was stirred for 0.5 h to complete the reaction of formation of pyridinium salt of dithiocarbamic acid. Next, 1 cm<sup>3</sup> of *n*-propyl iodide (bromide) was added to the mixture. The thus obtained mixture was left at room temperature and occasionally stirred. After 24 h, the solid product was filtered, washed with water and acetone and dried under vacuum at ambient temperature.

Chemical reactions used to prepare the modified silica gel which releases *n*-propanethiol as a volatile product are shown in Fig. 1 [1].

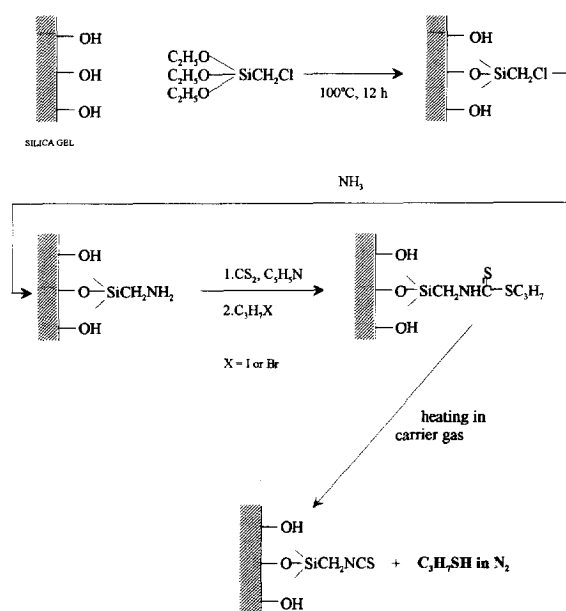


Fig. 1. Scheme of synthesis of a compound chemically bonded to the silica gel surface and its thermal decomposition resulting in the generation of a gaseous standard mixture of *n*-propanethiol.

### 2.2. Apparatus

The apparatus used for the generation of a gaseous standard mixture of *n*-propanethiol through thermal decomposition of the compound immobilized on silica gel is shown in Fig. 2.

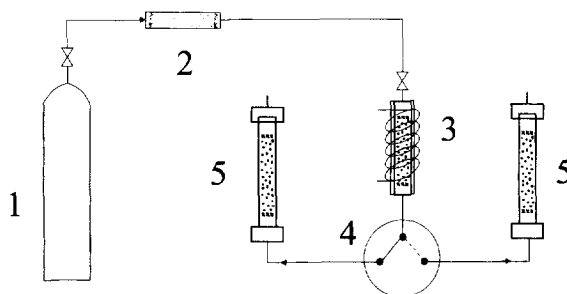


Fig. 2. Schematic diagram of the apparatus used for the generation of standard mixtures of *n*-propanethiol through thermal decomposition of the immobilized compound: (1) cylinder with compressed nitrogen; (2) deoxidizer; (3) tube with a gel sample; (4) tubes with Tenax TA; (5) six-port rotary valve.

The apparatus consists of:

1. tank with compressed nitrogen which is used as a diluent gas;
2. nitrogen purification system, comprising an oxygen remover (Omnisfera, Gdańsk, Poland) packed with Antyoxyo II bed (COBRABiD, Warsaw, Poland). Antyoxyo II is an oxygen scavenger of catalytic-sorption type; copper compounds coated on a ceramic support (kaolin, sodium silicate) are the active component. Other components are silver, iron, manganese and palladium compounds which play the role of activators and modifiers. The oxygen remover operated at about 200°C;
3. furnace for TD in which a tube with the modified silica gel is placed. The tube (I.D. 3.5 mm, length 80 mm) was previously silanized using the following conditions [6]: silanizing mixture, hexamethyldisilazane–trimethylchlorosilane (5:1); time of silanization, 48 h; silanization temperature, 150°C;
4. three-way valve which allows redirection of a stream of standard mixture;
5. sorption tubes packed with Tenax TA.

The process of TD of *n*-propanethiol trapped in the sorbent bed was carried out using a purpose-designed TD device [7].

The analysis of liberated thiol was performed by GC using the operating conditions listed in Table 1.

Table 1  
Operating conditions for the TD-GC-MS analysis

Thermal Desorption Unit	laboratory made
Trap	sorbent (100 mg Tenax TA)
Desorption time	2 min
Desorption temperature	255°C
Desorption gas	Argon (25 cm <sup>3</sup> min <sup>-1</sup> )
Microtrap	sorbent (12 mg Tenax TA)
Desorption time	1 min
Desorption temperature	260°C
Gas chromatograph	GC 8000 series (Fisons)
Column	SE-54 (30 m, 0.32 mm, 0.25 μm)
Carrier gas	Helium (35 kPa)
Column temperature	35°C
Detector	MD 800 (Fisons) SIM-mode

### 2.3. Kinetics of thermal decomposition of the immobilized compound

The process of thermal decomposition of an immobilized compound is initiated when the bed attains a certain temperature characteristic of a given compound and proceeds practically to completion. To investigate the kinetics of thermal decomposition of the immobilized compound generating *n*-propanethiol, a tube packed with a weighed amount of the modified silica gel was placed in a desorber furnace (Fig. 2) and a stream of diluent gas was passed through it at about 10 cm<sup>3</sup> min<sup>-1</sup>. Airtight connection of the tube was ensured by using PTFE washers. Prior to the bed reaching the temperature of thermal decomposition of the immobilized compound (170°C), the gas stream was passed through a bed of activated charcoal. Subsequently, the stream of standard mixture was passed alternately (every 5 min) through successive sorption tubes packed with Tenax TA. The change in concentration of *n*-propanethiol in the diluent gas as a function of time of mixture generation is shown in Fig. 3.

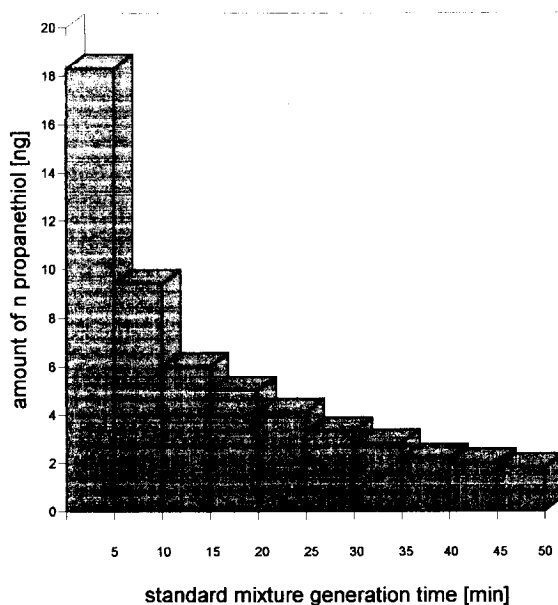


Fig. 3. The change in concentration of *n*-propanethiol in the diluent gas during the generation of a standard mixture: mass of the gel sample, 0.17427 g; temperature of thermal decomposition, 170°C; diluent gas flow-rate, 10 cm<sup>3</sup> min<sup>-1</sup>.

Table 2

Results of investigations of the dependence of mass of liberated *n*-propanethiol on the mass of the modified silica gel used

No	Mass of silica gel bed (g)	Amount of <i>n</i> -propanethiol in the sample of gel bed (ng)	Amount of the <i>n</i> -propanethiol per 1 g of silica gel bed (ng g <sup>-1</sup> )
1	0.06506	25.3	389
2	0.17712	82.5	466
3	0.11262	48.8	433
4	0.24712	100.8	408
5	0.23067	105.6	458
6	0.23462	92.9	396
7	0.23406	104.4	446
8	0.23142	103.9	449
9	0.23131	91.8	397
10	0.24824	108.7	438
11	0.44613	179.3	402
12	0.41611	164.8	396
13	0.15670	66.4	424
14	0.12775	54.8	429
15	0.11066	46.5	420
16	0.10767	46.0	427
Mean			420±12

#### 2.4. Investigation of the dependence of mass of liberated thiol on the mass of gel used for its generation

Various amounts of the modified silica gel were weighed into tubes. *n*-Propanethiol liberated at 170°C over a period of 50 min was transported in a stream of diluent gas at 10 cm<sup>3</sup> min<sup>-1</sup> to a sorbent bed (Tenax TA). The thiol was thermally desorbed in a purpose-designed desorber and analyzed by GC under the conditions listed in Table 1. The results of these investigations are compiled in Table 2.

### 3. Results

The studies of kinetics of decomposition of the immobilized compound revealed that under constant conditions (temperature 170°C, diluent gas flow-rate ca. 10 cm<sup>3</sup> min<sup>-1</sup>), the process of liberation of *n*-propanethiol can be related to the time of generation of the mixture by an exponential relationship [1–4]:

$$C = A \exp(-Bt) \quad (1)$$

where *A* and *B* are empirical coefficients dependent

on conditions of thermal decomposition (temperature, flow-rate of diluent gas, mass of silica gel) and *t* is time of generation of a standard mixture.

About 50 min after the beginning of generation of *n*-propanethiol, the amount of generated thiol becomes smaller than the error of determination of the total amount of the resulting thiol per unit mass of the silica gel bed. Consequently, in the following experiments aimed at determining the relationship between the mass of the liberated thiol and the mass of the modified silica gel used for the generation of the thiol, 50 min was used as the time of generation of the standard mixture.

The experimentally determined average mass of liberated thiol per unit mass of the modified silica gel is: 420±12 ng/g (Table 2).

The experimental results indicated that the total amount of *n*-propanethiol liberated per unit mass of the gel did not depend on the total mass of the gel used. Statistical analysis of the relationship between the mass of the liberated thiol per unit mass of the gel and total mass of the gel used in the studies based on the Student's *t*-test revealed that the slope of the straight line describing the above relationship (Fig. 4) is not significantly different ( $\alpha=0.05$ ) from zero.

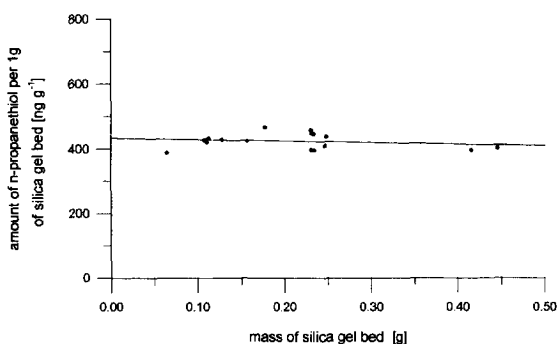


Fig. 4. Dependence of the mass of *n*-propanethiol liberated per unit mass of the silica gel on total mass of the gel used.

The following values were found:

the slope of the straight line:	-48.6
the standard deviation of the slope:	59.7
the calculated Student's <i>t</i> -value:	0.81
the critical <i>t</i> value ( $t_{crit}$ ):	2.1

In addition, the calculated value of the correlation coefficient (0.21) was compared with the critical value  $r_{crit}(16, 0.05)=0.47$ . Since  $r_{crit} > r_{calc}$ , the hypothesis that the two variables (mass of the thiol and mass of the modified silica gel) are interdependent has to be rejected. Hence, it follows that the bed of the modified silica gel is homogeneous and the amount of *n*-propanethiol liberated from 1 g of the gel is constant and independent of the mass of gel used.

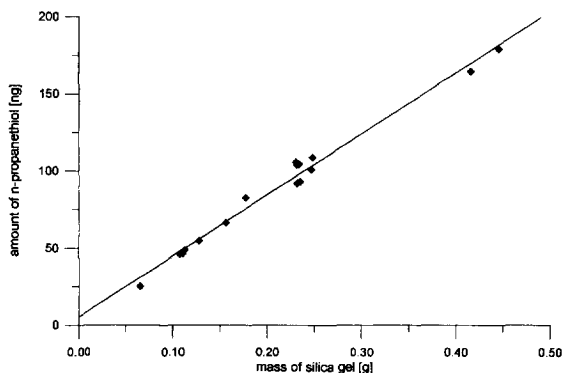


Fig. 5. Calibration curve for the TD-GC-MS system expressed as the mass of liberated thiol against the mass of the gel.

A calibration curve for the TD-GC-MS system for *n*-propanethiol, determined for the relationship between the mass of *n*-propanethiol and the mass of the modified silica gel used, was found by a linear regression method and yielded a correlation coefficient  $r=0.99$  (Fig. 5).

It should be noted that the results presented in this paper were obtained for one batch of the modified silica gel over a period of 7 months which demonstrates the stability of the gel bed prepared in the manner described here (no trend for the results was seen over those 7 months). This is very important especially for such unstable compounds as thiols.

#### 4. Conclusions

On the basis of experimental results, the following conclusions can be drawn. The proposed method is suitable for the preparation of standard mixtures of compounds that are unstable, toxic, reactive or malodorous. Also, the amounts of liberated *n*-propanethiol are directly proportional to the mass of modified gel used within the examined range of masses of silica gel samples. Consequently, the amount of the analyte (*n*-propanethiol) can be determined on the basis of mass of silica gel used and hence the modified silica gel can be treated as a standard of the liberated component (*n*-propanethiol in this case).

#### References

- [1] P. Konieczka, J. Namieśnik and J.F. Biernat, *J. Chromatogr.*, 540 (1991) 449.
- [2] J. Namieśnik, P. Konieczka, W. Chrzanowski and J.F. Biernat, *Chem. Anal.*, 39 (1994) 234.
- [3] P. Konieczka, J. Makarewicz, E. Luboch, J. Namieśnik and J.F. Biernat, *Chem. Anal.*, 39 (1994) 179.
- [4] P. Konieczka, E. Luboch, J. Namieśnik and J.F. Biernat, *Anal. Chim. Acta*, 265 (1992) 127.
- [5] J.F. Biernat, P. Konieczka, B.J. Tarbet, J.S. Bradshaw and R.M. Izatt, *Sep. Purif. Methods*, 23 (1994) 77.
- [6] M.L. Lee and B.W. Wright, *J. Chromatogr.*, 184 (1980) 235.
- [7] W. Janicki, L. Wolska, T. Górecki and J. Namieśnik, *Chem. Anal.*, 38 (1993) 423.