

Short Communication

Generation of standard gaseous mixtures by thermal decomposition of surface compounds

Standard mixtures of thiols

PIOTR KONIECZKA, JACEK NAMIEŚNIK and JAN F. BIERNAT*

Institute of Inorganic Chemistry and Technology and Corrosion, Faculty of Chemistry, Technical University of Gdańsk, 80-952 Gdańsk (Poland)

(First received August 23rd, 1990; revised manuscript received November 19th, 1990)

ABSTRACT

A new concept has been introduced for the generation of standard gaseous mixtures which is based on the thermal decomposition of surface-bonded residues and leads to the production of a single volatile product. An example is demonstrated which makes use of the ease with which silica gel-anchored dithiocarbamate groups decompose to form thiols.

INTRODUCTION

The preparation of accurate, reproducible and controllable standard concentrations of gaseous or vapour-phase pollutants at ppm (v/v) or ppb^a (v/v) levels is essential in environmental and occupational health sciences. In recent years, the development of several highly sensitive instruments has complicated the calibration problem. The improvements in the detection limits of many analytical methods and the demand to measure lower concentrations of toxic gases have also increased the need to prepare accurate standards at low levels for calibration [1–3].

Many methods have been developed for the generation of gas standards with very good accuracy. In general, these methods can be divided into two categories, *viz.*, static and dynamic methods. In static methods, a known amount of pure gas or vapour is added to a known volume of diluent gas in closed devices (vessels) such as bags, stainless-steel cylinders or glass vessels in which they are mixed and stored until use. Static methods are simple and inexpensive; however, they suffer from a number of disadvantages such as losses due to adsorption and condensation on the walls of the

* Throughout this article, the American billion (10⁹) is meant.

container. Only limited volumes can be prepared, leaks can occur and pressure changes can exert an effect.

In dynamic methods, pure gas or vapour at a known generation rate is introduced continuously into a known flow-rate of diluent gas. Although more complex and relatively more expensive equipment is involved, the dynamic systems offer several advantages over the static methods. Because standards are generated continuously, losses due to adsorption on the walls of the system are negligible after equilibration. Large volumes of gas standards can be generated and concentrations can be varied to provide a wide dynamic range. Flexibility in concentration range, volume and flow-rate of the generated standards is especially important for calibration and the evaluation of analytical instruments or sampling devices.

The dynamic methods can be divided with respect to the method of generation and introduction of the stream of the measured component into the stream of the diluent gas. Hence, methods basing on mixing of the stream [4] (including methods based on autodilution [5]), injection, evaporation, electrolysis [6], diffusion [7-9], permeation [10,11] and based on chemical reactions [12,13] can be distinguished.

Thermal decomposition reactions constitute a fundamental type of reaction that can be employed for the preparation of certain components of standard gaseous mixtures. Using these reactions it is possible to obtain standard gaseous mixtures of unstable and/or highly reactive components in the diluent gas at a desired moment. Methods allowing the generation of standard gaseous mixtures containing acrolein [14], formaldehyde [15], aldehydes [16], vinyl chloride, acrylonitrile, nitrosoamines [17,18] and thiols [19,20] have been reported.

In this work, to obtain volatile thiols we made use of the ease with which dithiocarbamates undergo thermal decomposition to form thiols and isothiocyanates [21]. Solutions of the respective dithiocarbamates were used to generate thiols in a previous study [20]. In the present method, dithiocarbamates were used as surface compounds. To our knowledge, this is a first example of the use of such a method to generate components for preparing standard gaseous mixtures. The surface-bound compound may be prepared in such a way that its decomposition may deliver only one volatile compound. The residual or side products, being chemically bonded to the silica gel surface, are non-volatile and may be removed under much more drastic conditions. On the other hand, such surface-bound compounds may be easily prepared using silylation reactions [22-24], which, in general, are fast, selective and easily applicable, and make accessible virtually all types of surface-bound compounds. Silica gel is most frequently used as the support because of its highly standardized properties.

EXPERIMENTAL

Reagents

An outline of the synthesis of surface-bound compounds possessing dithiocarbamate moieties is shown in Fig. 1. The surface of the dried (200°C) silica gel (MN-Kieselgel 60, 35-70 mesh; Macherey, Nagel & Co.) was chemically modified in the following way.

Triethoxychloromethylsilane [23] (3 ml) was added to a suspension of 20 g of dried silica gel in 40 ml of dry acetone [24]. The mixture was evaporated to dryness under reduced pressure and the residue was heated at 100°C overnight to terminate

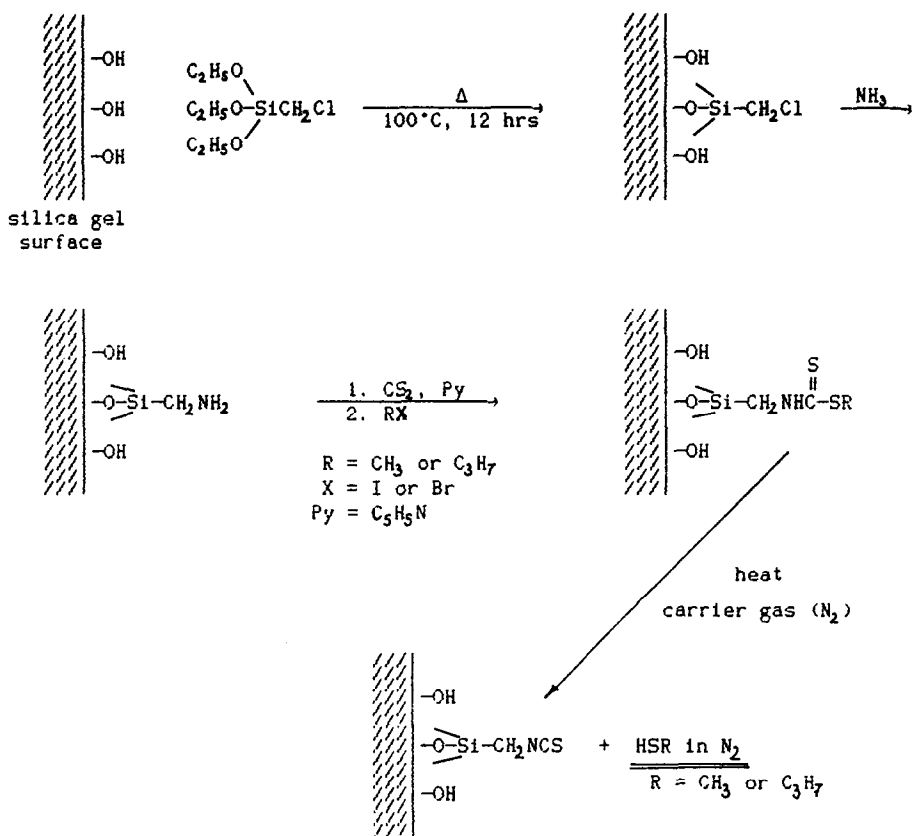


Fig. 1. Scheme of the synthesis of compounds chemically bonded to the silica gel surface and of the generation of standard gaseous mixtures by thermal decomposition of the compounds formed in a stream of carrier gas.

chloromethylsilylation of the surface. The product was washed with 50 ml of methanol and then suspended in 40 ml of methanol and 4 ml of concentrated ammonia were added. After standing overnight, the aminomethylsilylated silica gel obtained was collected and washed with methanol. The product when dried under reduced pressure at 100°C weighed 21.55 g. Next, 0.5 ml of carbon disulphide and 1 ml of dry pyridine were added to a suspension of 10 g of the aminomethylsilylated silica in 20 ml of dry acetone. The mixture was stirred for 0.5 h and then 1 ml of methyl iodide was added. The mixture was occasionally shaken at room temperature. The next day the product, methylthio-thiocarbonamidomethylsilylated silica gel, was collected and washed with water and acetone and dried under reduced pressure at room temperature. During thermal decomposition the product yields methanethiol.

To obtain propanethiol, the *n*-propyl bromide (or iodide) in an equivalent amount was added instead of methyl iodide. Other alkyl dithiocarbamates can be obtained analogously.

Apparatus

The sample of chemically modified silica gel (*ca.* 0.35 g) was placed in a glass tube of (200 mm × 3 mm I.D.) between glass-wool stoppers. The interior of the glass tube was silanized prior to the first use. The silanization conditions were as follows [25]: silanizing mixture, hexamethyldisilazane-trimethylchlorosilane (5:1); silanization time, 48 h; and silanization temperature, 150°C.

The tube with the sample was placed in a tube furnace, the temperature of which was kept constant with $\pm 2^\circ\text{C}$. Nitrogen from a cylinder was passed through the tube at a certain flow-rate. Oxygen-free nitrogen was obtained by passing the stream of gas through a layer of the sorptive-catalytic deoxidizing agent Antyoxo II (COBRABiD, Poland) placed in the tube and heated to 180°C. The thiol formed as a result of thermal decomposition of the compound chemically bonded to the silica gel surface was carried out of the tube and a certain volume of the nitrogen-thiol mixture was injected by means of a six-port valve into a gas chromatograph equipped with a flame ionization detector. A column (2 m × 3 mm I.D.) packed with 10% diethylene glycol succinate on Chromosorb W AW DMCS (80–100 mesh) was used. The column temperature was 60°C. The flow-rate of the gas in the system was measured using bubble flow meters.

Determination of the total amount of thiol that can be liberated from the silica gel

The outlet of the tube in which the thermal decomposition process took place was connected to a glass capillary immersed in a test-tube containing 40 ml of 0.2 *M* sodium hydroxide solution (absorbing medium for thiols). The tube, containing *ca.* 0.60 g silica gel, was heated to 150°C and a nitrogen stream (4 ml/min) was passed through it for 3 h. In this time the compound bonded chemically to the silica gel surface was thermally decomposed, and the thiol formed was quantitatively absorbed in an absorbing medium. The absorbed thiol was titrated with a 0.02 *M* solution of sodium *o*-hydroxymercuribenzoate, $\text{C}_6\text{H}_4(\text{COONa})(\text{HgOH})$, using 1% dithizone in 0.2 *M* sodium hydroxide solution as an end-point indicator. The results are given in Table I.

Utilization of the thiols formed for the generation of standard gaseous mixtures

A stream of deoxidized nitrogen (4 ml/min) was passed through the tube heated to a certain temperature in the range 40–80°C. The gaseous mixture formed was then

TABLE I

RESULTS OF TITRATION OF THIOLS LIBERATED FROM SILICA GEL SURFACE COMPOUNDS

Thiol	Expt. No.	Amount of silica gel compound (g)	Titration volume (ml)	Amount of thiol liberated (g/g)
Methanethiol	1	0.62033	8.4	0.013008
	2	0.62917	8.5	0.012960
	3	0.65143	9.3	0.013728
				Mean: 0.0132 \pm 0.00067
Propanethiol	1	0.59319	6.8	0.017404
	2	0.56590	6.4	0.017176
	3	0.61193	7.1	0.017632
				Mean: 0.0174 \pm 0.00084

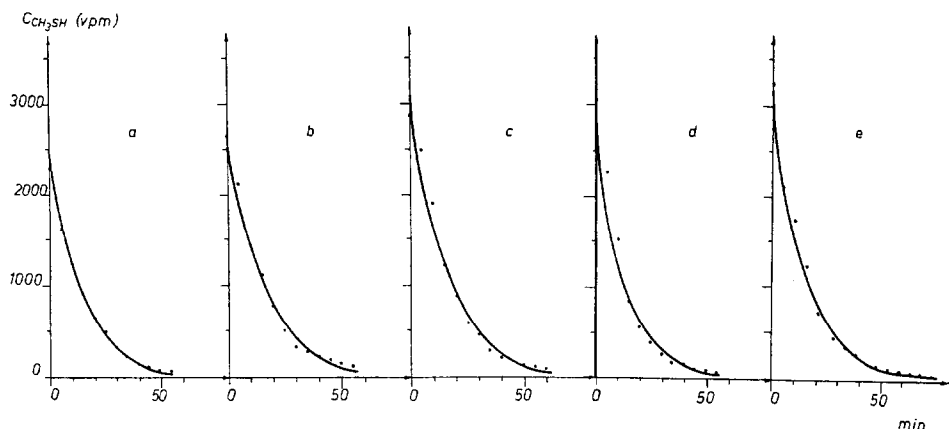


Fig. 2. Dependence of the methanethiol concentration ($C_{\text{CH}_3\text{SH}}$) in the generated mixture on the time (t) from reaching the maximum concentration (C_0) for various pyrolysis temperatures ($V_{\text{nitrogen}} = 4$ ml/min). (a) 45°C, $C = 1.10C_0 \exp(-0.0178 Vt)$; (b) 60°C, $C = 0.96C_0 \exp(-0.0150 Vt)$; (c) 72°C, $C = 1.06C_0 \exp(-0.0160 Vt)$; (d) 77°C, $C = 0.91C_0 \exp(-0.0186 Vt)$; (e) 86°C, $C = 0.93C_0 \exp(-0.0164 Vt)$.

passed through a sampling loop (PTFE tube) of 1.8-ml volume. The contents of the sampling loop were transported by carrier gas (argon) to the gas chromatograph at certain time intervals. Investigations of this type were carried out for two kinds of modified silica gel, yielding methane- and propanethiol standard mixtures. To determine the concentration of the thiol in the generated mixture, the chromatograph was calibrated using standard thiol mixtures prepared by a static pressureless method.

The results obtained in the form of the dependence of the thiol concentration in the mixture on the time from reaching the maximum concentration (C_0) are presented in Figs. 2 and 3. It has been established that the thiol generated during the pyrolysis is

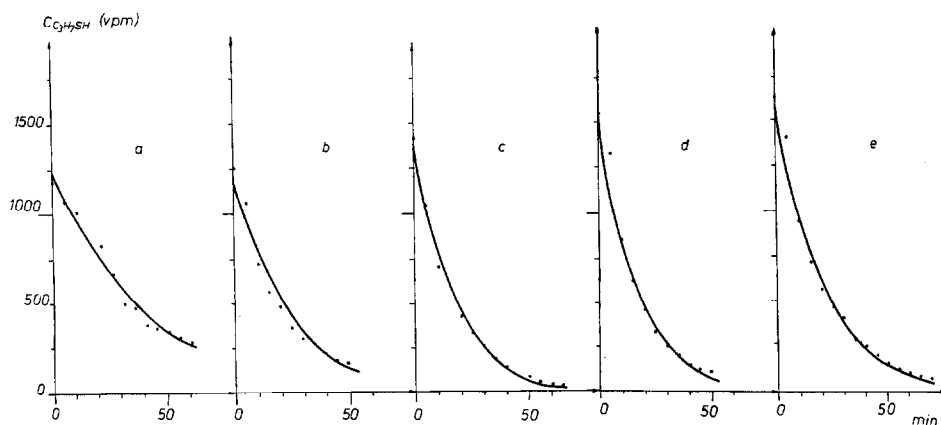


Fig. 3. Dependence of the propanethiol concentration ($C_{\text{C}_3\text{H}_7\text{SH}}$) in the generated mixture on the time (t) from reaching the maximum concentration (C_0) for various pyrolysis temperatures ($V_{\text{nitrogen}} = 4$ ml/min). (a) 48°C, $C = 1.03 C_0 \exp(-0.0062 Vt)$; (b) 55°C, $C = 0.91C_0 \exp(-0.0106 Vt)$; (c) 67°C, $C = 0.94C_0 \exp(-0.0140 Vt)$; (d) 75°C, $C = 0.96C_0 \exp(-0.0142 Vt)$; (e) 86°C, $C = 0.97C_0 \exp(-0.0120 Vt)$.

TABLE II

DEPENDENCE OF MAXIMUM CONCENTRATION OF THIOLS (C_0) ON THE PYROLYSIS TEMPERATURE

Methanethiol		Propanethiol	
Temperature, T ($^{\circ}\text{C}$)	Concentration (vpm) ^a	Temperature, T ($^{\circ}\text{C}$)	Concentration (vpm) ^a
45	2311	48	1176
60	2670	55	1255
72	2902	67	1412
77	3081	75	1551
86	3243	86	1627
$C_0 = 23.2T + 1266$		$C_0 = 12.5T + 581$	

^a The units vpm (volumes per million) and vpb (volumes per billion) are commonly used as ppm and ppb equivalents for gases; they are the respective volume concentrations.

first adsorbed at the silica gel layer and is completely liberated from the layer only after the desorption step. Owing to this, before the gel is saturated with the thiol, the concentration of the thiol in the mixture gradually increases until it reaches a maximum value (C_0) under given conditions, then it decreases. It is only from this moment that the generated mixture can be used for the calibration of, *e.g.*, detectors. Both the value of C_0 and the time necessary to reach this concentration (from the beginning of passing the carrier gas at a certain flow-rate through the gel) depend on the pyrolysis temperature. The $C_0 = f(T)$ dependence is presented in Table II and the $tC_0 = f(T)$ dependence in Table III.

The above investigations were repeated after a 3-month period. No changes were observed either in the dynamics of thermal liberation of thiols or in the total amount of the compounds liberated.

TABLE III

DEPENDENCE OF THE TIME NECESSARY FOR REACHING THE MAXIMUM CONCENTRATION OF THIOLS (C_0) (CALCULATED FROM THE BEGINNING OF PASSING THE CARRIER GAS STREAM THROUGH THE SILICA GEL LAYER) ON THE PYROLYSIS TEMPERATURE

Methanethiol		Propanethiol	
Temperature, T ($^{\circ}\text{C}$)	Time (min)	Temperature, T ($^{\circ}\text{C}$)	Time (min)
45	34	48	44
60	29	55	38
72	24	67	26
77	23	75	20
86	20	86	14
$C_0 = -0.35T + 49.5$		$C_0 = -0.81T + 82.1$	

CONCLUSIONS

These investigations confirmed the suitability of the proposed method for the generation of standard gaseous mixtures of compounds that are volatile and readily oxidizable such as methane- and propanethiol. Elimination of the necessity to have pure thiols for the generation of standard mixtures is the basic advantage of this method. Generation of the thiols starts only after heating the gel. No generation of thiols was observed at the sensitivity level of the detector used at ambient temperature (25°C). The thiol concentration in the mixture can be significantly reduced either by using a sampling loop of a smaller volume, or by increasing the carrier gas flow-rate through the apparatus. From the practical point of view it seems unnecessary to determine the physical sense of the determined empirical coefficients of the curves in Figs. 2 and 3. We plan to continue the investigations on the application of the described method to the generation of standard gaseous mixtures of other components.

ACKNOWLEDGEMENT

These investigations are part of research project "Environment Protection in the Marine Region" sponsored by the Technical University of Gdańsk.

REFERENCES

- 1 R. S. Barrat, *Analyst (London)*, 106 (1981) 817.
- 2 J. Szulc and Z. Witkiewicz, *Chem. Anal. (Warsaw)*, 26 (1981) 375.
- 3 J. Namieśnik, *J. Chromatogr.*, 300 (1984) 79.
- 4 C. Lefevre, P. Ferrari, J. P. Guenier and J. Muller, *Chromatographia*, 27 (1980) 37.
- 5 J. Namieśnik and P. Konieczka, *Chem. Anal. (Warsaw)*, in press.
- 6 J. N. Harman, III, *ASTM Spec. Tech. Publ.*, No. 598 (1976) 282.
- 7 R. A. Glaser and J. E. Arnold, *Am. Ind. Hyg. Assoc.*, 50 (1989) 112.
- 8 J. Namieśnik, L. Torres, E. Kozłowski and J. Mathieu, *J. Chromatogr.*, 208 (1981) 239.
- 9 U. Giese, H. Stenner and A. Kettrup, *Staub Reinhalt. Luft*, 49 (1989) 159.
- 10 K. Lechnitz, *Pure Appl. Chem.*, 55 (1983) 1239.
- 11 J. Namieśnik, L. Torres and J. Mathieu, *Analisis*, 13 (1985) 46.
- 12 D. Grosjean, K. Fung, J. Collins, J. Harrison and E. Breitung, *Anal. Chem.*, 56 (1984) 569.
- 13 K. L. Geisling and R. R. Miksch, *Anal. Chem.*, 54 (1982) 140.
- 14 K. Ishikawa, K. Watabe, T. Hobo and S. Suzuki, *Bunseki Kagaku*, 32 (1983) E321.
- 15 J. Godin, G. Bouley and C. Boudene, *Anal. Lett.*, A11 (1978) 319.
- 16 W. Tsang and J. A. Walker, *Anal. Chem.*, 49 (1977) 13.
- 17 D. J. Freed and A. M. Majsce, *Anal. Chem.*, 49 (1977) 139.
- 18 D. J. Freed and A. M. Majsce, *Anal. Chem.*, 49 (1977) 1544.
- 19 K. Ishikawa, T. Hobo, S. Suzuki and K. Watanabe, *J. Chromatogr.*, 295 (1984) 445.
- 20 A. Przyjazny, *J. Chromatogr.*, 292 (1984) 189.
- 21 G. Błotny, *Justus Liebigs Ann. Chem.*, (1982) 1927.
- 22 D. E. Leyden and W. T. Collins (Editors), *Silylated Surfaces*, Gordon and Breach, New York, London, Paris, 1978.
- 23 I. B. Slinyakova, M. G. Voronkov and I. E. Krot, *Kolloidn. Zh.*, 35 (1973) 480.
- 24 P. Roumeliotis, A. A. Kurganov and V. A. Davankov, *J. Chromatogr.*, 266 (1983) 439.
- 25 M. L. Lee and B. W. Wright, *J. Chromatogr.*, 184 (1980) 235.