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STABLE STANDARD SOLUTIONS FOR GAS CHROMATOGRAPHIC DETERMINATION OF VOLATILE THIOLS

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SUMMARY

Pyrolysis of dithiocarbamates (DTCs) in the injection port of a gas chromatograph has been employed for *in situ* generation of volatile thiols. Long-term stability of DTC solutions has been studied and compared with the stability of standard solutions of respective thiols. The method enables at least two-month storage of standard solutions for gas chromatographic determination of thiols without checking their concentration. Pyrolysis efficiency of DTC and its temperature dependence has been examined. The precision and linear dynamic range of the developed method have been determined.
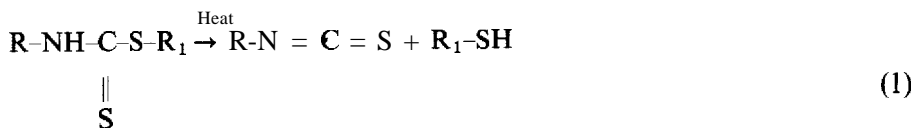
INTRODUCTION

Thiols (mercaptans) constitute an important group of organosulphur compounds owing to their abundance and properties, They are found in relatively large amounts and varieties in distilled and cracked petroleum products[1], in various natural products such as garlic, onions, coffee and tea and are a source of pollution of the atmosphere, water and industrial effluents. Thiols have become of increasing interest to analytical chemists due to their toxicity and reactivity even at trace levels.

Numerous methods have been employed for the determination of thiols[1,2], but most procedures make use of gas chromatography (GC), especially in the case of volatile compounds. Recently, a number of papers have described the GC determination of thiols in a variety of samples[3-25]. The determination of thiols at the ppb and sub-ppb levels is complicated by three main factors[16]: (1) sensitivity requirements; (2) the large number of compounds present and (3) adsorption.

Adsorption of thiols on the walls of the column or container results in perceptible loss of sample[9,16,18,26-28]. Additionally, owing to their reactivity, these compounds are easily oxidized both in the gaseous[14,29-31] and liquid[5] phases. For these reasons, gaseous and liquid standard solutions prepared by static methods are also unstable. For example, it was observed[5] that the loss of n-butanethiol from a dilute model solution in toluene amounted to *ca.* 8% after 1 week of storage, mainly due to oxidation giving di-n-butyl disulphide. As a result, dynamic methods of preparation of standard mixtures of thiols at low concentrations have frequently been em-

ployed[9,22,28]. However, these methods (mainly permeation or diffusion) suffer from several drawbacks[32]: (1) long initial induction period; (2) high cost; (3) need for precise temperature control (change of temperature by 1°C results in 10% variation of the permeation rate) and (4) impossibility of "shutting off" the device.

It has been found that dithiocarbamates (DTCs) derived from primary amines, i.e., having one hydrogen on the nitrogen, readily undergo pyrolysis to yield isothiocyanates and thiols[33-36]:

$$R\text{–}NH\text{–}\overset{\displaystyle \|}{\underset{\displaystyle S}{C}}\text{–}S\text{–}R_1 \xrightarrow{\text{Heat}} R\text{-}N = C = S + R_1\text{–}SH \qquad (1)$$

This reaction also occurs in the injection port of a gas chromatograph[35]. It was decided to utilize it to generate appropriate thiols directly in the injection chamber of a chromatograph, since dithiocarbamates can easily be synthesized[36-39] and form stable solutions in organic solvents.

EXPERIMENTAL

Apparatus

A Hewlett-Packard Model 5830 A gas chromatograph equipped with a flame ionization detector was employed for GC analysis. The chromatographic conditions were as follows: stainless-steel column (1.2 m × 2 mm I.D.), packed with Tenax GC (60-80 mesh) (Enka, The Netherlands); carrier gas, argon at 17 cm^3/min; column temperature, dependent on the compound; injector temperature, 250°C unless otherwise stated; detector temperature, 200°C.

A Model OH-404 coulometer (Radelkis, Hungary) equipped with an OP-Ag 7111 D silver ion-selective electrode and other standard accessories was used for coulometric determination of thiols.

Materials

Dithiocarbamates were synthesized by the method of Błotny[36]. Crystalline compounds were obtained for R = phenyl and R_1 = methyl, ethyl and n-butyl. The solvents used in the experiments, dimethyl sulphoxide (DMSO) (Reachim, U.S.S.R.), methanol (Reanal, Hungary), dimethylformamide (DMF) (POCh, Poland) and ethyl acetate (POCh), were purified by distillation. Methanethiol, ethanethiol and n-butanethiol (pure; Fluka, Switzerland) were further purified by distillation. The stock solutions of thiols and DTCs in various solvents were prepared in the mg/cm^3 range and their concentrations were tested during 60 days by GC and coulometric titration. Standard solutions were obtained by appropriate dilution of the stock solutions.

The buffer solution employed in coulometric titrations comprised 0.1 A4 NH_4NO_3 and 0.2 M NH_3 in 96% ethanol, pH 9.4.

Procedure

The degree of conversion of dithiocarbamates into thiols (pyrolysis efficiency) was investigated by injecting known volumes of standard solutions of DTCs in an

appropriate solvent into the gas chromatograph and measuring the peak area of the thiol formed by pyrolysis. First, the purity of the solvents used was determined chromatographically and it was established that no impurities interfering with the GC analysis of thiols were present. Subsequently, calibration of the detector was performed by injecting known volumes of standard solutions of thiols, the concentrations of which were determined by coulometric titration of 100 μl of solution with anodically generated silver ions in the ammonia buffer solution. The degree of conversion was calculated from the relationship

$$\text{degree of conversion} = \frac{m_{RSH} \text{ (found)}}{m_{RSH} \text{ (calc.)}} = \frac{\cot \alpha \cdot \bar{A}_{RSH}}{\dfrac{M_{RSH}}{M_{DTC}} \, m_{DTC(inj.)}} \tag{2}$$

where m_{RSH} (found) and m_{RSH} (calc.) are the experimental and calculated (from eqn. 1) masses of thiols, M_{RSH} and M_{DTC} are the molecular weights of the thiol and its corresponding dithiocarbamate, $m_{DTC(inj.)}$ is the injected mass of the dithiocarbamate (calculated as the product of the concentration and volume of the DTC solution), $\bar{A}_{RSH}$ is the average peak area of the thiol formed in the pyrolysis of DTC of mass $m_{DTC(inj.)}$ and $\cot \alpha$ is a calibration coefficient equal to

$$\cot \alpha = c_s V_{is}/\bar{A}_s \tag{3}$$

where $\bar{A}_s$ and V_{is} are the average peak area and the volume of the injected standard thiol solution and c_s is the concentration of the solution determined coulometrically.

The stability of the standard solutions of thiols and DTCs was studied over a period of 60 days by the procedure described above. The dependence of the decomposition rate on the type of solvents used for preparation of the solutions was examined by dissolving the compounds in various solvents and studying gas chromatographically the decrease in concentration of the thiols with time.

The effect of the injector (pyrolysis) temperature on the degree of conversion of DTCs into thiols was investigated by increasing the injector temperature from 200 to 280°C in 10°C increments and measuring the peak area of the thiol formed.

The applicability of the *in* situ generation of thiol standards was tested by determining its linear dynamic range and the detection limit through injections of various amounts of DTCs into the injection chamber of the chromatograph.

The precision of the method was estimated by repeated GC and coulometric determinations of thiols and calculation of the relative standard deviations of the results.

RESULTS AND DISCUSSION

The investigation of the degree of conversion (pyrolysis efficiency) of DTCs into the respective thiols showed that this reaction proceeds with high yield. The average degrees of conversion of N-phenyldithiocarbamates into methane-, ethane- and n-butanethiol during 60 days were 93 ± 1.6, 91 ± 1.8 and $85 \pm 2.1\%$, respectively. Additionally, it was established that the degree of conversion did not depend on the solvent used and did not change significantly with storage time. Incomplete

conversion of DTCs into thiols can probably be explained by the occurrence of side reactions, e.g.:

$$R-NH-\underset{\underset{S}{\parallel}}{C}-S-R_1 \xrightarrow{\text{Heat}} R-NH_2 + CS_2 + R_1H \tag{4}$$
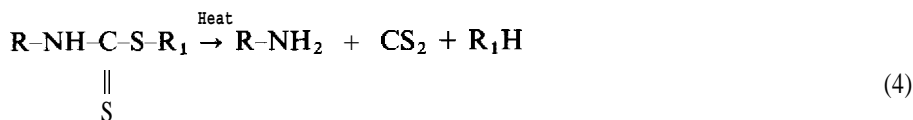
N-Aryldithiocarbamates were selected for the preparation of standard solutions owing to their crystalline form (which facilitates sample weighing) and higher stability in comparison with N-alkyl derivatives.

   The studies of the stability of standard solutions of thiols over a 60-day period indicated a continuous decrease in the concentration of the investigated thiols, monitored coulometrically. This decrease was equal to 37.6, 39.7 and 15.5% of the initial concentration for methane-, ethane- and *n*-butanethiol, respectively. In contrast, the decrease in concentration of thiols generated by pyrolysis of the appropriate DTC solutions was considerably lower, 3.6, 5.3 and <1%, respectively, after 60 days of storage. The decrease in concentration of methanethiol as a function of storage time is shown in Fig. 1. Curve 2 represents the corresponding behaviour of the thiol formed in the pyrolysis process, as determined by GC. It is seen that the prepared solutions of DTCs are fairly stable and may be employed as standards in the GC
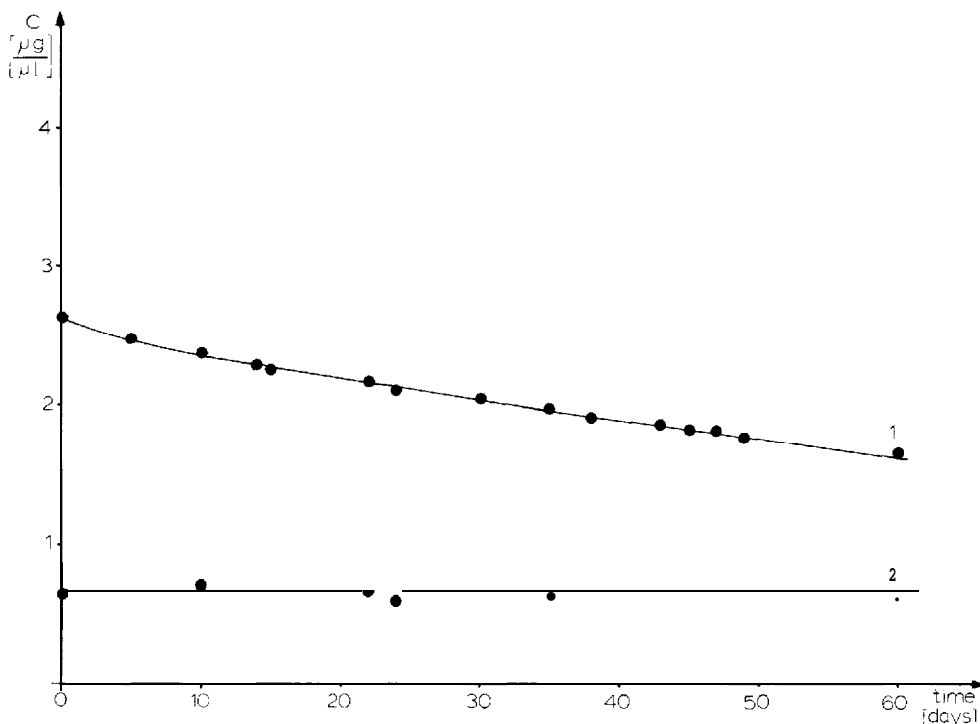

Fig. 1. Stability of standard solutions of methanethiol (curve 1) and methyl N-phenyldithiocarbamate (curve 2) in ethyl acetate as a function of storage time.
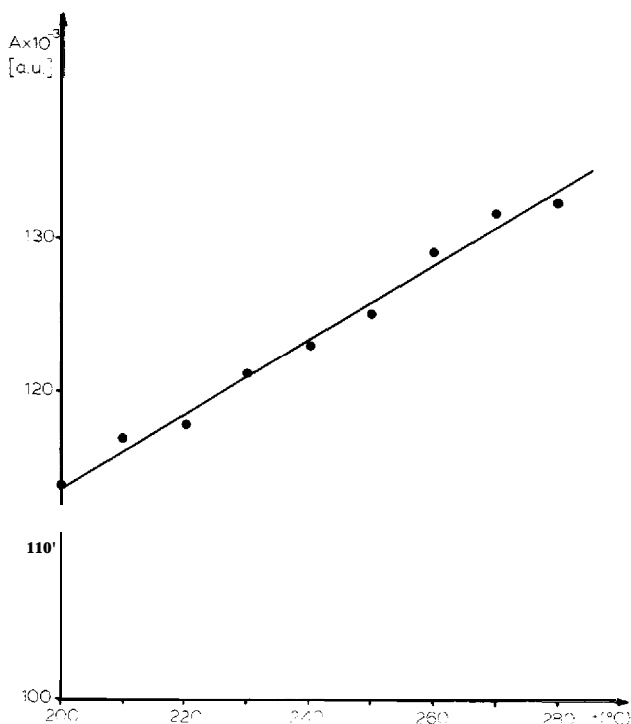
Fig. 2. The effect of the temperature of the injection chamber on the degree of conversion of methyl N-phenyldithiocarbamate into methanethiol, expressed as the peak area of the thiol. Concentration of di-thiocarbamate = 2.71 mg/cm^3. Volume injected: 1 μl. Solvent: DMF.

analysis of volatile thiols for a period of at least 2 months. In addition, it was found experimentally that the rate of decomposition of DTC did not depend on the solvent used.

The dependence on temperature of the degree of conversion of methyl N-phenyldithiocarbamate into methanethiol is shown in Fig. 2. It follows that the pyrolysis efficiency (expressed as the peak area of the thiol formed) depends to a large extent on the temperature. Hence, the temperature of the injection chamber should be controlled to ± 5°C in order to maintain the detector signal constant to ± 1% relative.

The precision of the method, expressed as the relative standard deviation of the peak areas of thiols measured during repeated injections of DTC solutions into the gas chromatograph, was good. The s_r values did not exceed 5%, and typical values ranged from 1 to 3% and were comparable with the respective values obtained for injections of standard solutions of thiols. The precision of the coulometric determination of the concentrations of standard thiol solutions was even better and the s_r values generally did not exceed 1%.

Injections of various amounts of DTCs permitted the determination of the linear dynamic range and detection limit of the method on the basis of the calibration curves constructed from experimental data. An example of a calibration curve for methanethiol generated by pyrolysis of a solution of methyl N-phenyldithiocarbamate is shown in Fig. 3. Similar curves were obtained for ethane- and n-butanethiol.
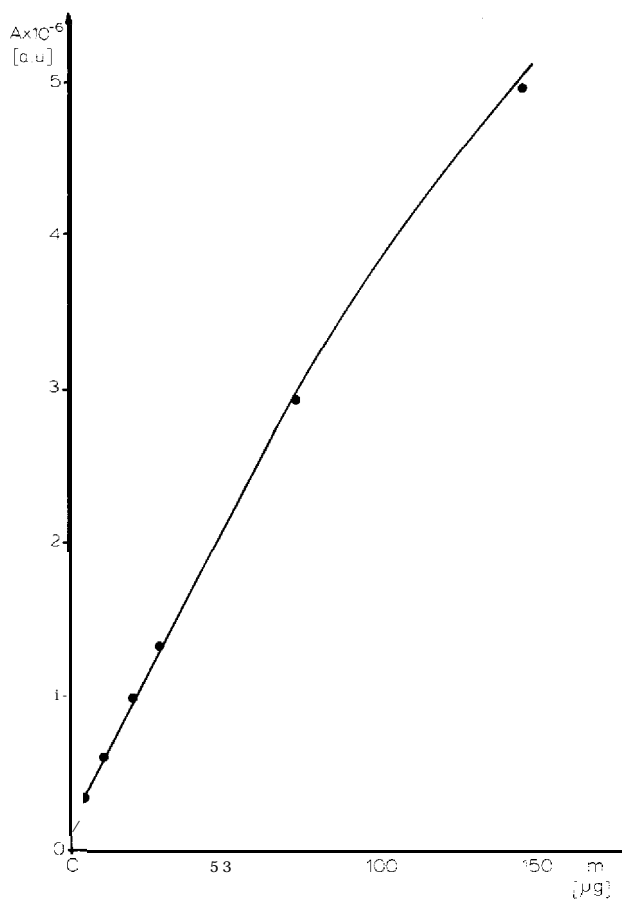
Fig. 3. Calibration curve, A = f(m), where is *m* the mass of methanethiol formed in the pyrolysis process, constructed on the basis of injections of a standard solution of methyl N-phenyldithiocarbamate in DMF.

The linear dynamic range estimated on the basis of calibration curves covered about three orders of magnitude (from hundreds of nanograms to *ca.* 100 μg) and the detection limit was of the order of hundreds of ng. Below this value, the results were irreproducible, presumably due to adsorption losses within the chromatographic system. Fig, 3 also illustrates that the degree of pyrolysis does not depend on the amount of DTC injected (up to 100 μg), as evidenced by the linearity of the calibration curve.

It was established that other products formed during pyrolysis of dithiocarbamates did not interfere in the GC determination of thiols. Phenyl isothiocyanate has a high boiling point (221°C) and, consequently, considerably larger retention volume than the examined thiols. Other possible products of side reactions also did not cause any problems in the analysis due to their high boiling points, e.g., for aniline, b.p. = 184°C, or lack of detector sensitivity, e.g. CS_2. No irreversible contamination of the chromatographic system by the products of pyrolysis was observed during 2 months of experiments.

On the basis of the experimental data the following conclusions can be drawn:

(1) the method enables at least 2-month storage of standard solutions for GC determination of volatile thiols

(2) the injector temperature should be maintained constant to ± 5°C to avoid changes in the pyrolysis efficiency larger than 1% relative

(3) the linear dynamic range of the method is about three orders of magnitude, from tenths to hundreds of μg, and the detection limit is cu. 0.1 μg

(4) the average relative standard deviation amounts to 1–3%, thus evidencing the high precision of the method

(5) the products of pyrolysis do not interfere with the chromatographic determination of thiols and do not irreversibly contaminate the chromatographic system.

ACKNOWLEDGEMENTS

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