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## GENERATION OF TRACE AMOUNTS OF ALKANETHIOL STANDARD GASES USING REACTION GAS CHROMATOGRAPHY

KOUICHI ISHIKAWA, TOSHIYUKI HOB0\* and SHIGETAKA SUZUKI

*Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, 2.1.1 Fuka-sawa, Setagaya-ku, Tokyo 158 (Japan)*

and

KATSUNORI WATABE

*Department of Organic Chemistry, The Weizmann Institute of Science, 76100 Rehovot (Israel)*

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### SUMMARY

A method for the generation of alkanethiol standard gases is described. It is based on the hydrolysis of S-alkylisothiurea sulphate or S-alkylisothiurea hydrogen bromide by sodium hydroxide. The alkanethiols generated were methane-, ethane- and *n*-butanethiols. Each thiol was quantitatively generated in the range of  $10^{-11}$ – $10^{-9}$  mol. The relative standard deviation for the reproducibility of generation of each compound was about 1%.

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### INTRODUCTION

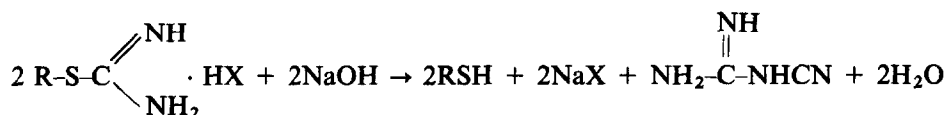
There is an increasing need for reliable standards in various fields of analysis. In gas analysis, standard gases are required in order to draw calibration curves and to examine the functioning of analytical instruments and procedures employed.

Generally, the methods employed for the preparation of standard gases are either static or dynamic ones. The static method is easy to employ, but it lacks reliability due mainly to the adsorption and reaction of constituents on the container walls, particularly at low concentrations. The dynamic, usually dilution method is more reliable, but needs a large quantity of diluent gas and most of the prepared gas is wasted. Further, in the case of reactive, toxic and/or malodorous gases, great care should be taken during the preparation and storage.

Recently, it was proposed to use chemical reactions in a gas chromatographic (GC) system for the generation of standard gases<sup>1-3</sup>. Vinyl chloride, acrolein, acrylonitrile and nitrosamines were generated quantitatively through oxidation or thermal decomposition reactions<sup>1,2</sup>. Aldehydes was also prepared through the stoichiometric decompositions of alcohols<sup>3</sup>. We have reported a new method for the preparation of acrolein standards through the dehydration of glycerol<sup>4</sup>. These results show that the chemical reaction method can provide an accurate, reproducible and simple means of supplying desired amounts of standards.

In this report, a method for the generation of alkanethiol standard gases using a reaction gas chromatographic system is described. Alkanethiols are typical malodorous pollutants in air and arise from many sources: kraft pulp industry, petroleum refining, sewage treatment, etc. When the concentration of these thiols exceeds a level of not more than 1 ppb, in air, everybody has a feeling of disgust. Their concentrations are usually measured by a GC method which utilizes a flame photometric detector. In that case, diluted standard solutions of the malodorous thiols are used for identification and quantification purposes.

Here, we propose to use odourless and stable S-alkylisothioureia salts as the source of the thiol standards. The gases can be generated through a chemical reaction in a GC system whenever they are required. The reactions proceed as follows:



Each alkanethiol was quantitatively generated in the range of  $10^{-11}$ – $10^{-9}$  mol. The reproducibility of generation of each compound was satisfactory.

Another advantage of this method which should be mentioned is that since S-alkyl-isothioureia salts have molecular weight about four times larger than corresponding thiols, their low concentration solutions can be easily prepared.

## EXPERIMENTAL

### Apparatus

The GC system used is shown in Fig. 1. A Shimadzu Model GC-5A gas chromatograph equipped with a flame photometric detector was employed after modification of its carrier gas line by the installation of a four-way valve. Pure nitrogen gas was used as the carrier gas. During the investigation of the reaction conditions, the

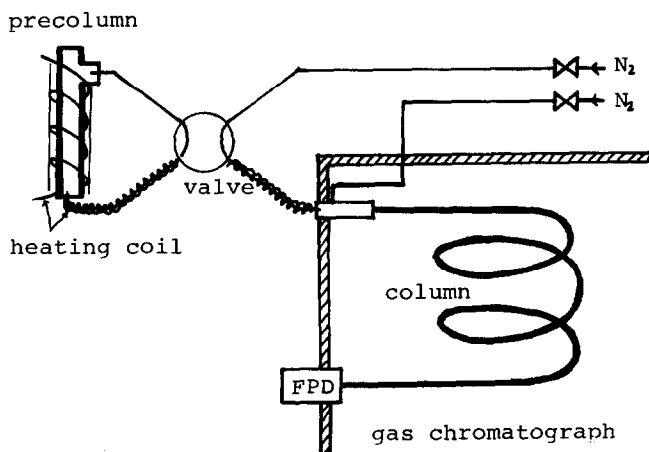


Fig. 1. Schematic flow diagram of the system.

carrier gas flow-rate into the detector was kept constant by controlling the flow-rate of the carrier gas added at the injection port. The other carrier gas can be led either directly into the injection port or by way of the reaction precolumn by adjustment of the four-way valve. The GC conditions employed for the separation of alkanethiols were as follows: separation column, glass (1.5 m  $\times$  3 mm I.D.), packed with 25% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb W AW DMCS (80–100 mesh); column temperature, 56°C; flow-rates of total carrier gas, hydrogen and air, 70, 45 and 40 ml min<sup>-1</sup> respectively.

#### Reaction precolumn

A Pyrex glass column (6 mm I.D.) packed with sodium hydroxide-impregnated Gas.Chrom R (60–80 mesh) was used as the reaction precolumn (Fig. 2). The front end of the precolumn was packed with Gas-Chrom R and behind it about 2 cm of the reagent powder. Both ends were plugged with silica wool. The precolumn was surrounded by a cylindrical heater, and its temperature was controlled by a Variac.

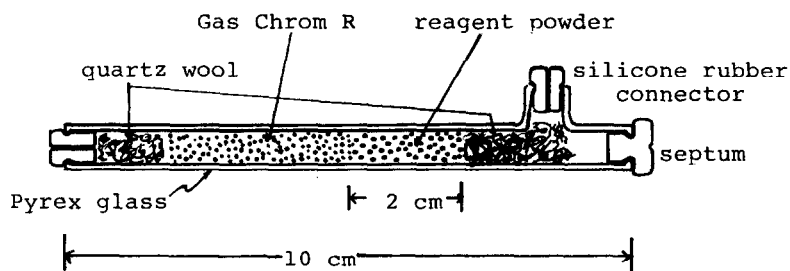


Fig. 2. Reaction precolumn.

#### *S*-Alkylisothiourea salts

The raw materials, *S*-alkylisothiourea salts, for the generation of alkanethiols were prepared according to procedures of Shildneck and Windus<sup>5</sup> and Urquhart *et al.*<sup>6</sup> as briefly described below.

*S*-Methylisothiourea sulphate. Seventy six grams (1 mol) of finely powdered thiourea and 35 ml of water were mixed in a 500-ml flask. Immediately after addition of 66 g (0.55 mol) of dimethyl sulphate a reflux condenser was attached to the flask and stirring was started. The reaction was allowed to proceed spontaneously with occasional cooling. After the initial vigorous reaction had ceased, the mixture was heated under reflux for about 1 h. Crystallization of the product occurred. The flask was cooled, 200 ml of ethanol were added and then the contents were filtered under aspiration. The remaining solid was washed with methanol and dried in air. Pure *S*-methylisothiourea sulphate was obtained by reprecipitation.

*S*-Ethylisothiourea sulphate. Forty grams (0.53 mol) of finely divided thiourea and 46 g (0.3 mol) of diethyl sulphate were mixed in a 500-ml flask. The reflux condenser was attached, and the mixture warmed to *ca.* 70°C with stirring. The thiourea dissolved slowly; after complete dissolution, the temperature was raised to the refluxing point. Crystallization occurred gradually; when it was complete the flask was cooled and the contents filtered with suction. The product was washed with

methanol and allowed to dry in air. Pure S-ethylisothiourea sulphate was obtained by recrystallization.

*S-Butylisothiourea hydrogen bromide.* In a 300-ml flask, 15.2 g (0.2 mol) of finely divided thiourea, 27.4 g (0.2 mol) of *n*-butyl bromide and 100 ml of ethanol were mixed. The mixture was refluxed for 7 h. S-Butylisothiourea hydrogen bromide was crystallized upon evaporation of the solvent. It was dried with diethyl ether.

#### *Response characteristics of flame photometric detector*

For the quantitative evaluation of the method, the response characteristics of the detector, namely the relationship between the concentration of sulphur compound and the peak height, should be known. In this experiment, dimethyl sulphide in *n*-hexane was used as the test solution and the slope, *n*, of the logarithmic plot was measured. The corrected peak area, *A*, can be obtained from

$$A = h^{1/n} W_h$$

where *h* and  $W_h$  are the peak height and peak width at  $h/2^n$  from the baseline. Under the conditions employed in this investigation *n* was 1.81.

#### RESULTS AND DISCUSSION

Aqueous solutions of each S-alkylisothiourea salt at various concentrations (S-methylisothiourea,  $7.2 \cdot 10^{-2}$ – $7.2 \cdot 10^{-4}$  mol l<sup>-1</sup>; S-ethylisothiourea,  $6.5 \cdot 10^{-6}$ – $1.6 \cdot 10^{-3}$  mol l<sup>-1</sup>; S-butylisothiourea,  $1.1 \cdot 10^{-5}$ – $1.4 \cdot 10^{-3}$  mol l<sup>-1</sup>) were prepared and the generation of alkanethiols was examined upon direct injection of the solutions into the precolumn.

A typical chromatogram of alkanethiols generated using mixed S-alkylisothiourea salts is presented in Fig. 3. The conditions employed were the optimum ones as shown later.

#### *Precolumn packing and its position*

Fixing the packing length of sodium hydroxide-impregnated Gas-Chrom R at 2 cm, and varying the amount of sodium hydroxide on the support from 5 to 30%, the evolved amount of methanethiol was investigated. In all cases, the generated amount of methanethiol was similar and satisfactory. Therefore, considering the durability of the column, 20% sodium hydroxide was chosen for the following experiments.

The generated amounts of alkanethiols, however, changed with the position of the reagent powder in the precolumn. Therefore, the effect of varying the distance from the front of the reagent powder to the needle point of the microsyringe at injection upon the yield of methanethiol was investigated. The results are shown in Fig. 4. The injected amount of S-methylisothiourea sulphate was  $3.6 \cdot 10^{-10}$  mol. A distance of 0 cm means that the needle point at injection just touches the front surface of the reagent powder. As is seen, when the distance exceeds 1 cm the generated amount decreases, possibly because the methanethiol reacts further with sodium hydroxide to form a sodium salt. A distance of less than 5 mm should be employed. Further investigation revealed similar trends with ethanethiol and butanethiol.

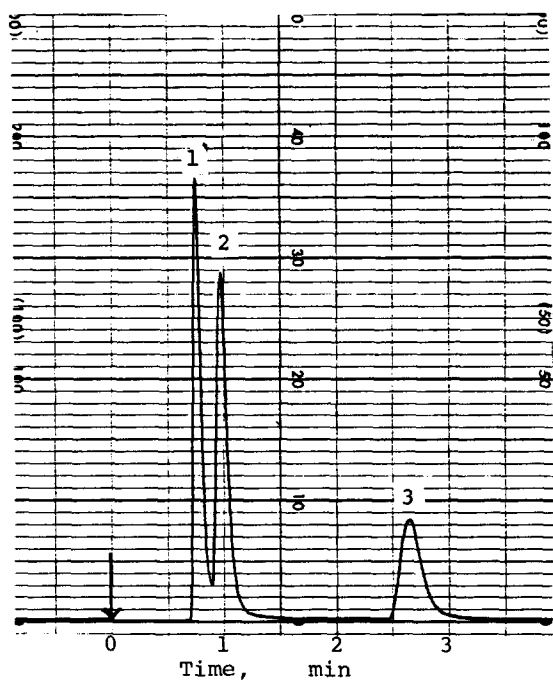


Fig. 3. Typical gas chromatogram of thiols generated. Peaks: 1 = methanethiol; 2 = ethanethiol; 3 = *n*-butanethiol (each  $1.0 \cdot 10^{-9}$  mol). Precolumn temperature:  $210^{\circ}\text{C}$ . Carrier gas flow-rate through pre-column;  $50 \text{ ml min}^{-1}$ . Total carrier gas flow-rate:  $70 \text{ ml min}^{-1}$ . Separation column temperature:  $56^{\circ}\text{C}$ .

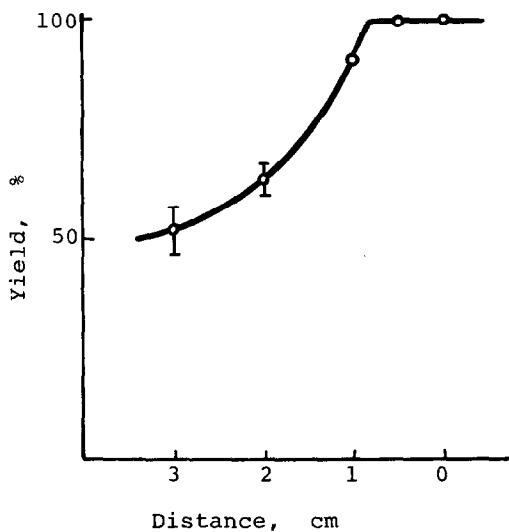


Fig. 4. Yield vs. distance between the reagent front surface and needle point. Reagent powder: 20% NaOH on Gas-Chrom R. Amount of *S*-methylisothiourrea sulphate injected:  $3.6 \cdot 10^{-10}$  mol. Precolumn temperature:  $180^{\circ}\text{C}$ .

### Reaction temperature

The effect of reaction temperature on the yields of thiols is shown in Fig. 5. In the case of methanethiol, the injected amount of S-methylisothiurea was  $3.6 \cdot 10^{-10}$  mol and the carrier gas flow-rate was  $50 \text{ ml min}^{-1}$ . As can be seen, the generated amount of methanethiol was maximal and constant when the reaction temperature was higher than  $120^\circ\text{C}$ . The optimum temperature was chosen to be  $180^\circ\text{C}$ .

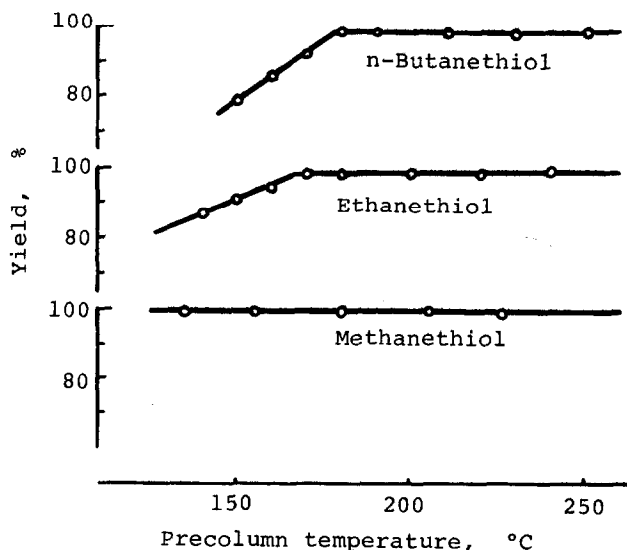


Fig. 5. Yields of thiols vs. the precolumn temperature. Injected amount: S-methylisothiurea,  $3.6 \cdot 10^{-10}$  mol; S-ethylisothiurea,  $1.6 \cdot 10^{-10}$  mol; S-*n*-butylisothiurea,  $4.7 \cdot 10^{-10}$  mol. Carrier gas flow-rate through precolumn:  $50 \text{ ml min}^{-1}$ .

Under similar conditions, maximum and quantitative generation of ethanethiol and butanethiol was attained when the temperature was higher than  $170$  and  $180^\circ\text{C}$  respectively;  $200$  and  $210^\circ\text{C}$ , respectively, were chosen as the reaction temperatures for these compounds.

### Carrier gas flow-rate

The effect of carrier gas flow-rate on the generation of each alkanethiol was also examined. The results are shown in Fig. 6. At the optimum reaction temperature, carrier gas flow-rates higher than  $30$ ,  $40$  and  $40 \text{ ml min}^{-1}$  for methane-, ethane- and butanethiols respectively gave maximum and quantitative yields. Therefore,  $50 \text{ ml min}^{-1}$  was chosen as the carrier gas flow-rate.

### Quantitative aspects

Under the optimum conditions described, the relationship between the injected amount of each S-alkylisothiurea salt and the amount of the corresponding alkanethiol generated was examined. The results are summarized in Table I. In each case, a dynamic range of at least 1:50 at the pmol level was obtained. Further, the yields were almost quantitative and the reproducibilities were also satisfactory.

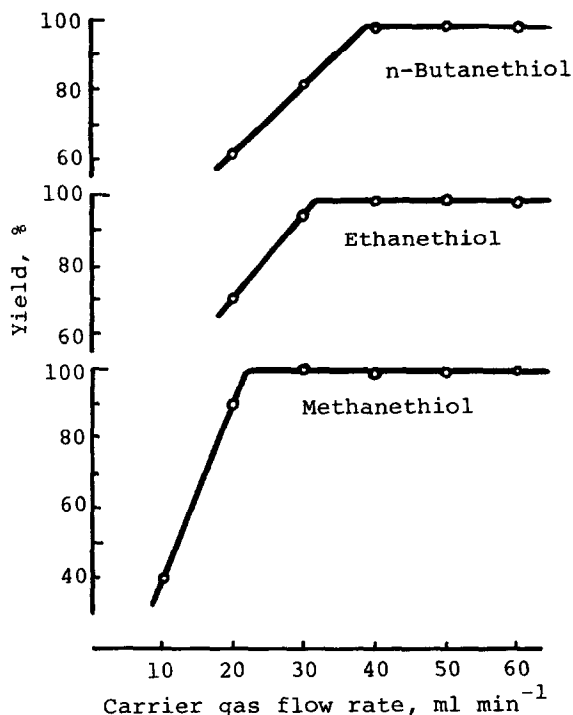


Fig. 6. Yields vs. the carrier gas flow-rate. For injected amounts of S-alkylisothiouras see Fig. 5. Precolumn temperatures for methane-, ethane- and *n*-butanethiols: 180°, 200 and 210°C respectively. Carrier gas flow-rate through precolumn: 50 ml min<sup>-1</sup>.

TABLE I  
QUANTITATIVE ASPECTS OF THE RESULTS

Product	Raw material	Linear range (mol)	Yield (%)	Rel. std. dev.* (%)
Methanethiol	S-Methylisothiourasulphate	$1.4 \cdot 10^{-11}$ – $1.4 \cdot 10^{-9}$	99	1.3 (at $2.8 \cdot 10^{-11}$ mol)
Ethanethiol	S-Ethylisothiourasulphate	$1.3 \cdot 10^{-11}$ – $6.5 \cdot 10^{-10}$	98	1.7 ( $7.2 \cdot 10^{-11}$ mol)
Butanethiol	S-Butylisothiourasulphate hydrogen bromide	$1.1 \cdot 10^{-11}$ – $1.4 \cdot 10^{-9}$	98	0.95 ( $1.5 \cdot 10^{-10}$ mol)

\* Number of runs = 20.

## CONCLUSION

The method proposed can be recommended as a simple and reliable means for the preparation of trace amounts of alkanethiol standard gases. It gives high yields, and excels in quality and reproducibility. Besides, the S-alkylisothiouras salts used

as the raw materials are odourless and so stable that they can be stored for a long time. It is also thought to be possible to prepare several other thiols by the proposed method using corresponding S-alkylisothiourea salts.

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