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GAS CHROMATOGRAPHIC DETERMINATION OF THIOLS IN GASEOUS PETROLEUM FRACTIONS ON THE BASIS OF THIOL CONCENTRATION BY SODIUM *o*-HYDROXYMERCURIBENZOATE AND SODIUM *p*-CHLOROMERCURIBENZOATE

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SUMMARY

A method for the determination of individual thiols in gaseous petroleum fractions by gas chromatography, based on concentration of thiols by sodium *o*-hydroxy- and *p*-chloromercuribenzoate solutions, is described. The individual thiols in samples of propane-butane fractions determined by this method ranged in concentration from several tenths of 1 ppm to several parts per million. The results of qualitative analysis were confirmed by gas chromatography-mass spectrometry, while those of quantitative analysis were tested by determination of the total thiol sulphur content. This method can also be employed for the determination of much lower concentrations of thiols and for other types of gas samples.

INTRODUCTION

The gas chromatographic (GC) separation of individual thiols during their simultaneous separation from hydrocarbons is difficult and tedious or even impossible, with gaseous petroleum fractions, because these fractions contain only minute amounts of thiols and are mixtures of a number of hydrocarbons. Direct determination by GC can therefore be performed only by using detectors of high sensitivity to thiols that are virtually insensitive to hydrocarbons. Another possibility is to concentrate the thiols in gaseous petroleum fractions and thus achieve their separation from excess of hydrocarbons.

Fredericks and Harlow¹ have determined C₁-C₄ thiols in sour natural gas by using a non-linear programmed column in conjunction with a silver ion-generating microcoulometric detector. On injection of 30 cm³ of the sample, as little as 1 ppm of an individual thiol was determined with $\pm 2\%$ precision at 50 ppm. A flame photometric detector (FPD) was used to detect sulphur compounds in city gas² and to determine them in natural gas³. However, its response to sulphur compounds had been reported to be influenced by simultaneously emerging hydrocarbons⁴⁻⁷. A similar phenomenon was observed in our work. Accurate quantitative analysis of sulphur

compounds with an FPD is therefore possible only in certain instances. Cifrinovich and co-workers^{8,9} determined sulphur compounds, including thiols, in propane-propylene and ethane-ethylene fractions by using the concentration-based GC method. The sulphur compounds were sorbed at -80° on supported liquid phases, then desorbed by heating to ambient temperature and introduced into a GC column in a stream of carrier gas. Unfortunately, the desorbates contained considerable amounts of hydrocarbons. Staszewski and Zaslawska¹⁰ adsorbed thiols from a propane-butane fraction on a 13X molecular sieve and then liberated them into toluene as described by Staszewski¹¹. The hydrocarbons were, however, not completely separated from the thiols. Wardencki and Staszewski¹² also studied the concentration of sulphur compounds from liquid petroleum fractions by an analogous technique. The reactions of *o*-hydroxymercuribenzoate and *p*-chloromercuribenzoate with thiols have been studied by Wroński¹³. These mercurials are suitable for determining thiols and have been employed to determine sulphur in liquid^{14,15} and gaseous hydrocarbons¹⁶.

In this study, the concentration of thiols from gaseous hydrocarbons by means of sodium *o*-hydroxy- and *p*-chloromercuribenzoate has been investigated. Concentration was achieved by selective absorption of the thiols in aqueous solutions of the mercurials, followed by regeneration of the thiols and extraction with benzene. A concentration-based method for individual thiol determinations is described.

EXPERIMENTAL

Absorption system

The absorption of thiols in sodium *o*-hydroxymercuribenzoate (HMB) and sodium *p*-chloromercuribenzoate (PCMB) was investigated with the apparatus shown in Fig. 1. The liquefied gas of known total thiol concentration flows from the reservoir (1) into the valve (2), vaporizes and passes through the reducing valve (3), the hydrogen sulphide absorber (4), the thiol absorber (5) and finally through the control absorber (6). The valve (2) is heated with warm water at 60° flowing through the copper coil so as to maintain constant the vaporization rate and hence the flow-rate of the sample. The absorber (4) contains 10 cm^3 of acidified cadmium sulphate solution. Tests on model mixtures¹⁷ showed complete absorption of hydrogen sulphide and none of thiols in the absorber. The absorber (5) contains 2 cm^3 of HMB or PCMB

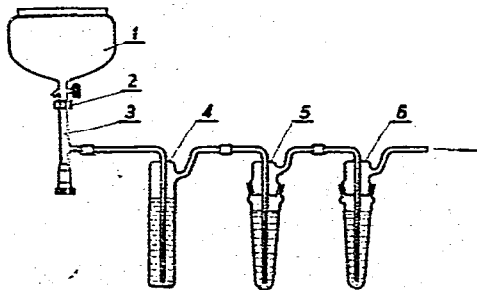


Fig. 1. Apparatus for examination of thiol absorption. 1 = Liquefied gas reservoir; 2, 3 = valves; 4 = hydrogen sulphide absorber; 5 = thiol absorber; 6 = control absorber.

solution. The height of the solution column is about 40 mm. The absorber (6) contains 5 cm³ of 0.25 M sodium hydroxide solution and about 5 · 10⁻⁴ mmole of HMB and thiofluorescein complex. If thiol absorption in the absorber (5) were not complete, the thiols would flow into the absorber (6) and liberate thiofluorescein and the previously colourless solution would turn blue.

Recovery of thiols from HMB and PCMB mercaptide solutions

The thiols converted during absorption into HMB or PCMB mercaptides are regenerated with thioacetamide and extracted with benzene. Because of the analytical use of the concentration process, it is necessary to know the percentage of the thiols recovered in the two-stage process (regeneration and extraction). In order to determine this recovery, the same volumes of mercurial (HMB or PCMB) solutions and model thiol solutions of initial concentrations C_i in benzene were shaken and centrifuged. The concentrations C_e of the thiols that remained in the benzene were determined by GC. Next, the mixture was treated with thioacetamide solution (1.5 molar excess) and acidified with orthophosphoric acid solution to about pH 6. After 5 min, it was shaken, centrifuged and the thiol concentrations (C_r) in the benzene layer were determined again.

The recovery of thiols (R , %) from aqueous mercaptide solution into benzene was calculated according to the equation

$$R = \frac{C_r - C_e}{C_i - C_e} \cdot 100 \quad (1)$$

Removal of interfering compounds from mercaptide solutions

In addition to thiols, certain amounts of hydrocarbons and possibly other components of the sample being analyzed are also retained in the mercurial solution. If not removed, they can be extracted with benzene. As those eluted from the GC column prior to benzene can interfere in the thiol determination, their removal by means of argon was investigated.

The samples of liquefied gas were passed through the mercurial solution and various amounts of argon were bubbled through the thiol absorber at ambient temperature and at 50°. Benzene was then added to the absorber and, after shaking, the benzene layer was analyzed by GC for the presence of interfering compounds.

Behaviour of unsaturated hydrocarbons

To ensure that unsaturated hydrocarbons do not interfere in the thiol determination, 25 cm³ of propylene was passed through 2 cm³ of the mercurial solution, which was then heated to 50°. Through this solution was passed about 1 l of argon, then 2 cm³ of benzene were added, the mixture was treated with thioacetamide and orthophosphoric acid as described above and the GC analysis for the presence of propylene was carried out.

Determination of individual thiols in samples of liquefied gas

Using the apparatus shown in Fig. 1, 20–25-g samples of liquefied gas (propane–butane fraction) were passed through the absorption system at a flow-rate of 100 cm³/min. The reservoir (1) containing the gas analyzed was disconnected and 500 cm³

of argon was bubbled through the absorbers. After disconnecting absorber (5) and placing it in water at 50°, argon was passed through it for 15 min at a flow-rate of 100 cm³/min. The cap of absorber (5) was detached, air was removed with argon and 2 cm³ of benzene were added. The contents of the absorber were treated with thioacetamide solution (1.5 molar excess) and subsequently acidified with orthophosphoric acid solution to about pH 6. After 10 min, the mixture was shaken and centrifuged. (Absorption, regeneration and extraction of thiols were carried out in one vessel so as to minimize the volume of mercaptide solution.)

The thiols in the benzene layer (concentrate) were analyzed by GC. Identification was based on retention indices and quantitative analysis on calibration. For the procedure described here, the concentrations of individual thiols in the analyzed samples were calculated according to the equation

$$C_{\text{RSH(S)}} = \frac{2C_{\text{RSH(C)}}}{m_p \cdot R} \cdot 10^5 \quad (2)$$

where $C_{\text{RSH(S)}}$ = concentration of a given thiol in the analyzed sample in parts per million of sulphur if the sample is expressed in grams, or in mg/m³ of sulphur if expressed in litres; $C_{\text{RSH(C)}}$ = concentration of a given thiol in the concentrate in mg/cm³ of sulphur; m_p = amount of sample expressed in grams or litres; and $R(\%)$ = recovery of a given thiol (Table I).

To confirm the results of the analysis, the concentrated compounds were identified by GC combined with mass spectrometry (GC-MS), and the total thiol sulphur content in the samples examined was determined by the coulometric method¹⁷.

Chromatographic conditions

The gas chromatograph used was a Fractovap 2200 Model (Carlo Erba, Milan, Italy) equipped with a flame ionization detector and a Spidomax recorder. The carrier gas was argon at a flow-rate of 50 cm³/min. A stainless-steel column, 200 × 0.4 cm, filled with 10% DC-200 silicone oil on Chromosorb W DMCS (80–100 mesh) was used. The thermostat was maintained at 60°.

Reagents and solutions

Solutions of 0.025 M HMB in 0.25 M sodium hydroxide and 0.025 M PCMB in 0.25 M sodium hydroxide were prepared by dissolving *o*-hydroxymercuribenzoic anhydride (Koch-Light, Colnbrook, Great Britain) and *p*-chloromercuribenzoic acid (pure, Chemapol, Prague, Czechoslovakia) in sodium hydroxide solution as described by Wroński¹³. Solutions of 3.8% of thioacetamide (pure, POCH, Gliwice, Poland) in water, 0.1% of thiofluorescein (indicator, POCH) in 0.1 M ammonia, 10% of cadmium sulphate (pure, POCH) in 0.005 M sulphuric acid and 1 M orthophosphoric acid and propylene (Fluka, Buchs, Switzerland) were employed. Use was made of solutions in benzene (for spectroscopy, Zakłady Koksochemiczne, Chorzów, Poland) of methanethiol (pure, Fluka), ethanethiol (pure, Schuchardt, Munich, G.F.R.), isopropanethiol (synthesized in this Institute), *tert*-butanethiol (synthesized in this Institute) and *n*-propanethiol (Fluka).

RESULTS AND CONCLUSIONS

Our investigations have shown that light thiols (methane, isopropane, *tert.*-butane and *n*-propanethiol) at concentrations up to 100 ppm of sulphur are absorbed quantitatively in HMB and PCMB solutions when the flow-rate of the samples is up to 100 cm³/min. Further, the recoveries of thiols from aqueous solutions of HMB or PCMB mercaptide are high and reproducible (Table I). There are no essential differences between the results obtained when using HMB or PCMB solutions, so that either of these mercurials can be used for concentrating thiols. Hydrocarbons and other interfering components retained in mercurial solution during absorption can be removed with argon or some other inert gas. It has been found that interfering components can be removed from the mercurial solution through which the samples of liquefied gas had been passed by heating the solution to 50° and passing argon through it for 15 min at a flow-rate of 100 cm³/min. Fortunately, there are no thiol losses during the above process. Also, unsaturated hydrocarbons do not interfere in the thiol determination, as they are not concentrated during the thiol concentration.

These results have shown that thiols can be selectively concentrated with HMB

TABLE I
RECOVERY OF THIOLS FROM MERCAPTIDE SOLUTIONS

Thiol	Initial thiol concentration in benzene (M)	Mercurial (0.025 M)	Number of measurements, n	Mean recovery, R (%)	Standard deviation, S _n	Confidence interval for P=95%
Methanethiol	0.015	HMB	8	89.2	1.03	89.2 ± 0.9
	0.003	HMB	7	89.4	0.98	89.4 ± 1.2
	0.015	PCMB	5	90.0	1.00	90.0 ± 1.2
Ethanethiol	0.015	HMB	7	96.1	0.90	96.1 ± 0.9
	0.003	HMB	5	97.2	0.84	97.2 ± 1.0
	0.015	PCMB	5	96.6	0.89	96.6 ± 1.1
<i>n</i> -Propanethiol	0.015	HMB	7	98.6	0.79	98.6 ± 0.7
	0.003	HMB	5	99.2	0.84	99.2 ± 1.0
	0.015	PCMB	5	98.8	0.84	98.8 ± 1.0
Isopropanethiol	0.002	HMB	6	99.2	1.00	99.2 ± 0.9
<i>tert.</i> -Butanethiol	0.002	HMB	6	100.0	0.89	100.0 ± 0.9

TABLE II
CONTENT OF INDIVIDUAL THIOLS IN PROPANE-BUTANE FRACTIONS
Eight measurements for sample 1, five measurements for sample 2.

Sample	Thiol	Average thiol concentration (ppm, w/w, of sulphur)	Standard deviation, S _n	Confidence interval for P = 95%
1	Methanethiol	8.2	0.33	8.2 ± 0.3
	Ethanethiol	9.4	0.37	9.4 ± 0.3
	<i>tert.</i> -Butanethiol	0.6	0.08	0.6 ± 0.1
	Isopropanethiol	<0.1	—	—
2	Methanethiol	8.3	0.29	8.3 ± 0.4
	Ethanethiol	9.2	0.41	9.2 ± 0.5
	<i>tert.</i> -Butanethiol	0.6	0.06	0.6 ± 0.1
	Isopropanethiol	<0.1	—	—

TABLE III
TOTAL CONTENT OF THIOL SULPHUR IN PROPANE-BUTANE FRACTIONS

Sample	Total thiol concentration (ppm, w/w, of sulphur)	
	Calculated on the basis of the individual thiol (Table II)	Determined by coulometric method
1	18.3	18.0
2	18.2	18.7

or PCMB from propane-butane and other hydrocarbon fractions, and that the concentration process can be employed in the analysis of thiols. GC analysis of the thiols concentrated from propane-butane fractions by the technique described showed that individual thiols can be determined accurately in these fractions (Table II). These results were confirmed by identification of the compounds concentrated by GC-MS and determination of the total thiol sulphur content by the coulometric method (Table III).

This method can also be employed for determining thiols in other gases when their concentrations are much lower than those of the thiols determined in our study, provided that, with a detector of equal sensitivity, the minimum samples are larger and hence the time of analysis is longer.

We have also studied the use of mercurials of this type for concentrating thiols from liquid petroleum fractions¹⁷.

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