

CHROM. 15,875

Note

Gas chromatographic identification of thiols in the naphtha cut from Libyan crude oil

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The concentration of thiols in different cuts from crude oils is usually so low that their direct determination is difficult even by gas chromatography (GC) with sulphur-specific detectors. This is mainly due to losses of thiols in the analytical system^{1,2} and hydrocarbon interferences during the analysis^{3,4}. Therefore, a pre-concentration step is usually included in the analytical procedure^{5,6}.

In this study, thiols from the naphtha cut from Libyan crude oil were extracted with a water-ethylene glycol solution of sodium *p*-chloromercuribenzenesulphonate. The regeneration of thiols into benzene was achieved by addition of thioacetamide. Thiols in the concentrate obtained were identified by GC with a flame photometric detector.

MATERIALS AND METHODS

Reagents and samples

Sodium *p*-chloromercuribenzenesulphonate (PMCS) (Sigma, St. Louis, MO, U.S.A.) was prepared as a 0.01 mol/dm³ solution in 0.25 mol/dm³ sodium hydroxide solution. The extraction solution was a mixture of ethylene glycol and the PCMS solution (1:1).

Thioacetamide solution (3.8%) and orthophosphoric acid solution (1 mol/dm³) were prepared.

Samples of the naphtha cut (b.p. 160–225°C) of Libyan crude oil (El-Zweitina) were obtained from the Gdańsk Oil Refinery; the total thiol sulphur in the samples was determined by volumetric titration with sodium *o*-hydroxymercuribenzoate⁷.

Preparation of thiol concentrate

A 10-cm³ sample and 2 cm³ of the extraction solution were shaken for about 5 min and then centrifuged. The upper hydrocarbon layer was removed with a syringe and discarded and then sample components that had been coextracted with thiols were reextracted from the remaining extract with hexane. Subsequently, hexane in the extraction centrifuge tube was replaced with benzene (1 cm³) and 1- μ l samples of the benzene layer were injected into a GC column to obtain a blank chromatogram. Finally, thiols were regenerated from the corresponding mercaptides by addition of thioacetamide solution (0.2 cm³) and acidifying the extraction solution to pH *ca.* 6

with orthophosphoric acid. When being regenerated thiols were simultaneously extracted with benzene. After regeneration was complete, the benzene layer constituting the thiol concentrate was analysed by GC for the presence of thiols.

Gas chromatographic analysis

A Pye Unicam 104 gas chromatograph, equipped with a Tracor flame photometric detector and a Philips chart recorder, was used. A pre-coiled glass column (150 × 0.4 cm I.D.) was packed with 3% OV-1 on 100–120-mesh Gas-Chrom Q. The carrier gas was argon at a flow-rate of 50 cm³/min. The column and detector temperatures were 130 and 150°C, respectively, and the instrument settings were range 10⁴ and attenuation 64.

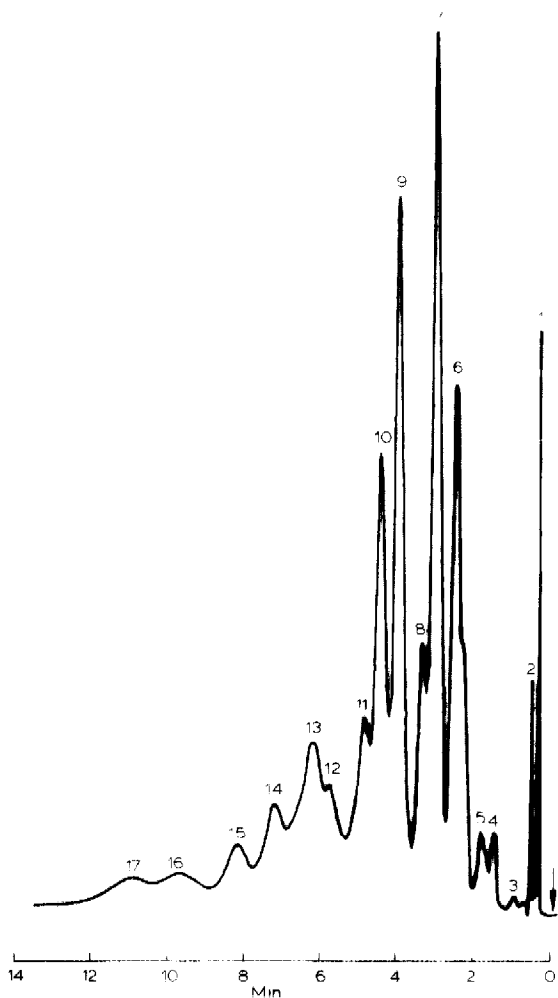


Fig. 1. Chromatogram of concentrate of thiols from naphtha cut (b.p. 160–225°C). Peak numbers refer to thiols listed in Table I.

TABLE I
RETENTION INDICES OF THE CONCENTRATE COMPONENTS (FIG. 1) AND REFERENCE THIOLS

Concentrate component		Reference thiols	
Peak No.	Retention index	Retention index	Compound
3	873	880	1,2-Propanedithiol
4	954	951	Thiophenol
5	1000	Presumably isoheptanethiol	
6	1050	α -Toluenethiol	
7	1097	Presumably isoctanethiol	
8	1114	1111	Cyclopentanedithiol
9	1147	1152	1,5-Pentanedithiol
10	1170	}	Nonanethiol isomers
11	1193		
12	1218	1219	<i>n</i> -Nonanethiol
13	1231	Presumably isodecanethiol	
14	1258	1255	1,6-Hexanedithiol
15	1271	}	Decanethiol isomers
16	1305		
17	1324		

RESULTS AND DISCUSSION

A chromatogram of a 1- μ l injection of the thiol concentrate is shown in Fig. 1. Peak 1 represents hydrogen sulphide and peak 2 the solvent (benzene). To identify other components of the concentrate, the retention indices of the peaks were determined and compared with either those of reference thiols or literature data (Table I). In a few instances only a tentative identification could have been made on the basis of the approximate relationship between elution times and boiling points.

As can be seen in Fig. 1, fifteen thiols in detectable amounts were present in the naphtha cut samples. The thiol sulphur (ca. 6 ppm) was represented mainly by α -toluenethiol (6), isoctanethiol (7), 1,5-pentanedithiol (9) and isononanethiol (10).

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