Detailed analysis of sulfur compounds in gasoline range petroleum products with high-resolution gas chromatography–atomic emission detection using group-selective chemical treatment

Árpád Stumpf*, Krisztina Tolvaj, Miklós Juhász

MOL Hungarian Oil and Gas Co., R&D Analytical Department, P.O. Box 1, 2443 Százhalombatta, Hungary

Abstract

This paper describes a method for detailed analysis and group-type identification of sulfur compounds in gasoline range petroleum products. Separation and detection was provided by coupled capillary gas chromatography–atomic emission detection (GC–AED). Chemical treatment of the samples was carried out using selective reactions for group-type classification of the peaks. Over 100 sulfur peaks were classified and compound names were assigned to many of them. Various types of naphthas were analyzed and their sulfur distributions are presented. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Quantitative and qualitative analysis of sulfur compounds in gasolines and gas oils has become an area of great interest according to the increased tendency to regulate the sulfur level in these kinds of fuels. Before final refining and blending of gasolines, the most reactive and damaging sulfur compounds (generated by hydrotreating and destructive technologies) must be eliminated or converted in order to protect automotive emission control catalysts and to meet the new specifications on gasoline composition according to the environmental requirements.

Detailed analysis (speciation) of heteroorganic compounds in hydrocarbon matrix is very difficult. GC separation of sulfur compounds cannot be accomplished because of the similar boiling points and polarity of analytes and matrix components.

Element-selective detection methods [flame photometric detection (FPD), (SCD), atomic emission detection (AED), etc.] simplify this problem a great deal [1,2]. Several works have been published dealing with the analysis of individual sulfur compounds in gasoline and an American Society for Testing and Materials (ASTM) method was established for the analysis of about 16 sulfur compounds [3–8].

Nevertheless, lots of questions remain. Sulfur-selective chromatograms of gasolines can be very complicated, and element-selective detectors tell nothing about molecular structure. Gas chromatography–mass spectrometry (GC–MS) tends to be the ultimate tool when identifying peaks but, in the case of petroleum matrices, such attempts are usually destroyed by the disturbing effect of co-eluting hydrocarbons.

Sulfur compound analysis of gas oils and higher distillates is a bit of a harder job. Fortunately, sulfur compounds in these fractions are incomparably less

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*Corresponding author.

reactive and corrosive than those in the gasoline range. So detailed analysis and group-type sulfur distribution data are important especially in gasoline range fractions.

Middle distillates contain mainly dialiphatic sulfides, alkyl-substituted benzothiophene and dibenzothiophene isomers. However, the variety of compounds is so wide that even with high-resolution (HR) GC, only poor separation can be achieved. For this reason, detailed component analysis is hopeless. On the other hand, a benzothiophene and dibenzothiophene distribution profile of gas-oil range fractions can be easily determined, for it apparently does not depend on either total sulfur content or geographical origin of the sample [9].

Going even higher in the boiling point range, that is in case of heavy distillates and residues, only determination of the boiling-point distribution of sulfur (sulfur-SIMDIS) has any real possibility.

Petrochemical samples contain a limited number of compound classes but uncountable individual compounds, so characterization of process streams or products via comprehensive analysis of that many species is a virtually impossible task. It is also hardly reasonable because, in most cases, group type analysis provides ample information about a sample.

According to this philosophy, our goal was to separate sulfur compounds of different naphthas and classify them, at the very least. Success in compound identification was considered the best result but, when it was beyond our abilities, we were satisfied with classification. Our approach described here uses chemical treatment, namely two sulfur-group selective reactions. In order to achieve a good separation and to obtain sulfur selective chromatograms, we used high resolution capillary GC with AED.

In gasoline-range products and process samples, almost the whole sulfur content is represented by H_2S, COS, CS_2, and three groups: mercaptanes, sulfides and thiophenes (including benzothiophenes). One of the two reactions mentioned above was a selective oxidation of mercaptanes with iodine (forming disulfides), which resulted in a chromatogram of sulfides and thiophenes. The other was the oxidation of mercaptanes and sulfides with H_2O_2 (forming sulfonic acids and sulfones), which resulted in a chromatogram of thiophenes (and benzothiophenes), exclusively.

The classification was carried out through comparing these chromatograms with that of the original sample.

The method development was based on a visbroken naphtha, in which about 120 individual sulfur peaks were found and their group-type determined. Where standard compounds, previously published fingerprint chromatograms and retention data [3–8], or other sources of information were available, identification resulted in exact compound names.

The selective reactions, described in this paper, had been tested on a model mixture of eight sulfur compounds, and their effectiveness has been experimentally confirmed.

Other gasoline range samples [fluid catalytically cracked (FCC), straight-run and delayed coker naphtha] were also analyzed, differences and similarities concerning their sulfur distributions are illustrated.

2. Experimental

2.1. Chemicals

Visbroken (VB) naphtha, the gasoline-range product of visbreaker plant was selected for our experiments, because this stream is exceptionally rich in sulfur compounds produced by the thermal cracking process of heavy stocks.

The VB naphtha used for our experiments was a product of VisBreaker Plant, Danube Refinery, MOL Hungarian Oil & Gas, Százhalombatta, Hungary, with total sulfur content of about 2500 mg/dm^3. Iodine (puriss), sodium thiosulphate (purum), hydrogen peroxide (30%, w/w, puriss), acetone (>puriss), sodium hydroxide (puriss) and acetic acid (96%, w/w, puriss) were used for reagent purposes, each of them a product of Reanal, Budapest, Hungary, except acetic acid, which was a product of Erdõkémia, Budapest, Hungary. For standard purposes we mostly used a kit of 15 different sulfur compounds, a product of Polyscience, Niles, IL, USA (distributed by Supelco, Cat. No. 4-4605). Other than that, only thiophene (purum) and ethyl methyl sulfide (purum) were applied, both produced by Fluka, Buchs, Switzerland. Sulfur-free naphtha, produced by Danube Refinery, MOL Hungarian Oil

& Gas, Százhalombatta, Hungary was used as a diluting chemical when making the model mixture.

2.2. Instrumentation

GC was performed with an HP5890A Series II chromatograph equipped with an HP7673A automatic liquid sampler and an HP5921A AED system. All instruments were from Hewlett–Packard, Palo Alto, CA, USA.

2.3. GC conditions

The chromatograph was fitted a 100-m$\times$0.25-mm, 0.50-μm Petrocol DH-100 (Supelco) column, which was installed directly into the discharge tube. The temperature program had two isothermal and two heating periods. First, the oven was held on 35°C for 28 min, then heated by 1.9°C/min up to 64°C, then by 2.2°C/min up to 200°C, finally another isothermal for 24 min. As carrier gas, high-purity (6.0) helium was used at 300-kPa constant head pressure. The injected volume was 1 mm^3 with a split ratio of 1:60.

2.4. AED conditions

Sulfur detection was performed at 361 nm. This is very important, because at 181 nm, iodine lines interfere with the sulfur signal background correction. This recipe requires both H$_2$ and O$_2$ reagent gases, pressures were set to 550 kPa and 340 kPa, respectively. Cavity pressure was 10 kPa. Helium supply pressure 200 kPa and make up gas flow was about 100 cm^3/min.

2.5. Model mixture

Eight different standard compounds were diluted in 4 cm^3 of sulfur-free naptha, all of them in the sulfur concentration range of 200–400 mg/dm^3. The eight compounds were as follows: thiophene, diethyl sulfide, n-butylmercaptane, tert.-amylmercaptan, di-n-propyl sulfide, n-hexylmercaptan, n-heptylmercaptan and di-n-butyl sulfide.

2.6. Oxidation with iodine (Reaction I)

First, 0.32 g of I$_2$ was diluted with 8 cm^3 of acetone, which was meant to be a reagent mixture, referred to as Solution I. Then another reagent, referred as Solution II, was made by dissolving 0.8 g of Na$_2$S$_2$O$_3$ in 10 cm^3 of 0.05 M NaOH solution. Two cm^3 of Solution I was added to a 3-cm^3 sample in a 8-cm^3 screw-cap vial. The mixture was vigorously shaken from time to time for 10 min at room temperature.

This step was the oxidation of mercaptans (with iodine in definite excess), according to the following equation:

$$R\text{-}SH + R'\text{-}SH + I_2 \rightarrow 2\,HI + R\text{-}S\text{-}S\text{-}R'$$
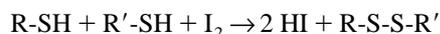
The unreacted iodine was converted to hydrogen iodide by adding 2 cm^3 of Solution II to the mixture. The NaOH content of Solution II enhanced the extraction of HI from the organic (naphtha) phase.

The phases were then separated, and the naphtha was washed four times with 2 cm^3 of distilled water.

2.7. Oxidation with hydrogen peroxide (Reaction II)

A 3-cm^3 sample was added to the mixture of 3 cm^3 H$_2$O$_2$ and 1 cm^3 acetic acid in a 8-cm^3 screw-cap vial. About 1 cm^3 of acetone was added to act as a transmitter between the phases, thus allowing a relatively quick, 1-h reaction. The mixture was vigorously shaken from time to time for 1 h at 60°C. Mercaptanes and sulfides reacted in the following way:

$$R\text{-}SH + H_2O_2 \rightarrow R\text{-}SO_3H$$

$$R\text{-}S\text{-}R' + H_2O_2 \rightarrow R\text{-}SO_2\text{-}R'$$

The phases were then separated, and the naphtha washed four times with 2 cm^3 of distilled water.

3. Results and discussion

3.1. Identification

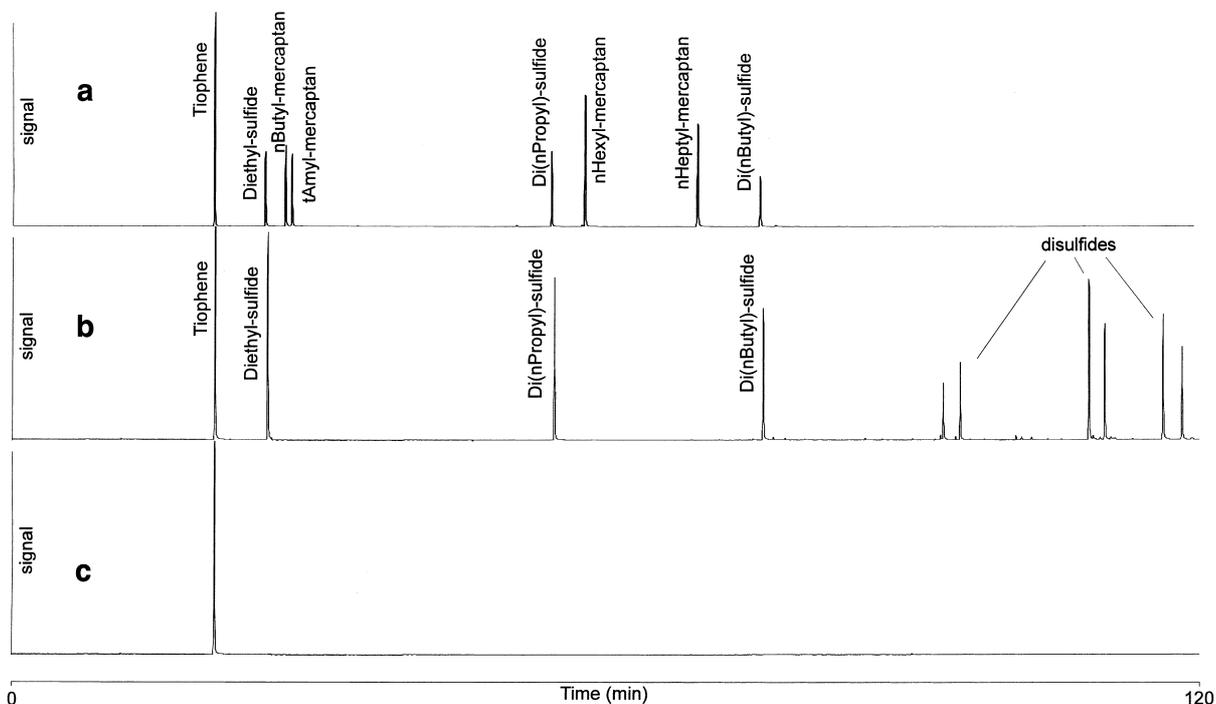Fig. 1 illustrates the results of testing group

Fig. 1. The effect of oxidation on sulfur compounds with iodine and hydrogen peroxide. (a) Original model mixture; (b) model mixture oxidized with iodine; (c) model mixture oxidized with H_2O_2.

reactions on the model mixture. Apparently, oxidation with iodine cleared out the peaks of all mercaptans. Meanwhile disulfides, which occurred in Reaction I, appeared on the chromatogram, eluting well after the last model compound. (Fig. 1b).

Hydrogen peroxide, as a more reactive agent, eliminated all mercaptanes and sulfides and only thiophene was left behind. Sulfonic acids and sulfones, formed in Reaction II, have no trace in the chromatogram. (Fig. 1c).

These test results proved the power and group-selectivity of Reactions I and II, so we applied them to real naphtha samples as well.

Fig. 2 shows sulfur chromatograms of VB naphtha before (Fig. 2a) and after oxidation with iodine (Fig. 2b) and with H_2O_2 (Fig. 2c).

Comparing the three chromatograms, we classified the peaks as mercaptan, sulfide or substituted thiophene isomers. After that we proceeded with compound identification. In general, standard compounds and published retention data were used to assign names to peaks. However, most referred publications use GC conditions, where lots of co-elutions occur. In some cases, we were able to achieve better separation. Then it was our job to decide, if possible, which of the separated peaks represents the relevant compound. Results of this identification process are presented in Table 1.

In order to carry out quantitative analysis, it is required to know whether or not the detector response is linear and compound dependent. We added various amounts of five different sulfur compounds to sulfur-free naphtha to obtain standard solutions covering the concentration range of 0.1–1000 mg/dm^3.

Sulfur-selective chromatograms of these standard mixtures were used to evaluate the AED response. Each peak in each calibration mixture, regardless of compound type, was found to fit to a line described by the following equation:

Sulfur peak area [count $\times$ s] =

$1.2465 \times$ concentration [mg sulfur/dm^3] + 6.1408

$(R = 0.99836)$

Therefore, we assumed compound independent signals in the gasoline range samples, and linearity over the whole range mentioned above.

The limit of detection (LOD) was calculated to be about 0.5 mg/dm^3 sulfur for a particular compound in gasolines, using the conditions summarized in the experimental part.

According to these quantitative aspects, sulfur group-type composition data can be obtained by summation of the corresponding individual concentrations. The same holds for total sulfur content, where concentrations of all the peaks are to be summed.

Total sulfur contents of various naphthas were calculated by means of peak summation, as well as measured according to the ASTM D545-93 method. The results show a good agreement between the two methods (Table 2).

3.2. Sulfur distribution profile of gasolines

Fig. 3 shows a sulfur distribution profile of some gasoline range process streams. FCC naphthas (Fig. 3a) contain mainly CS_2 and thiophenes, benzothiophene and methyl-benzothiophene isomers showing up at the end of the chromatogram. Sulfides are present at a very low level, and we were not able to detect mercaptanes.

The sulfur content of a straight-run naphtha (Fig. 3b) mostly consists of light mercaptanes and H_2S,
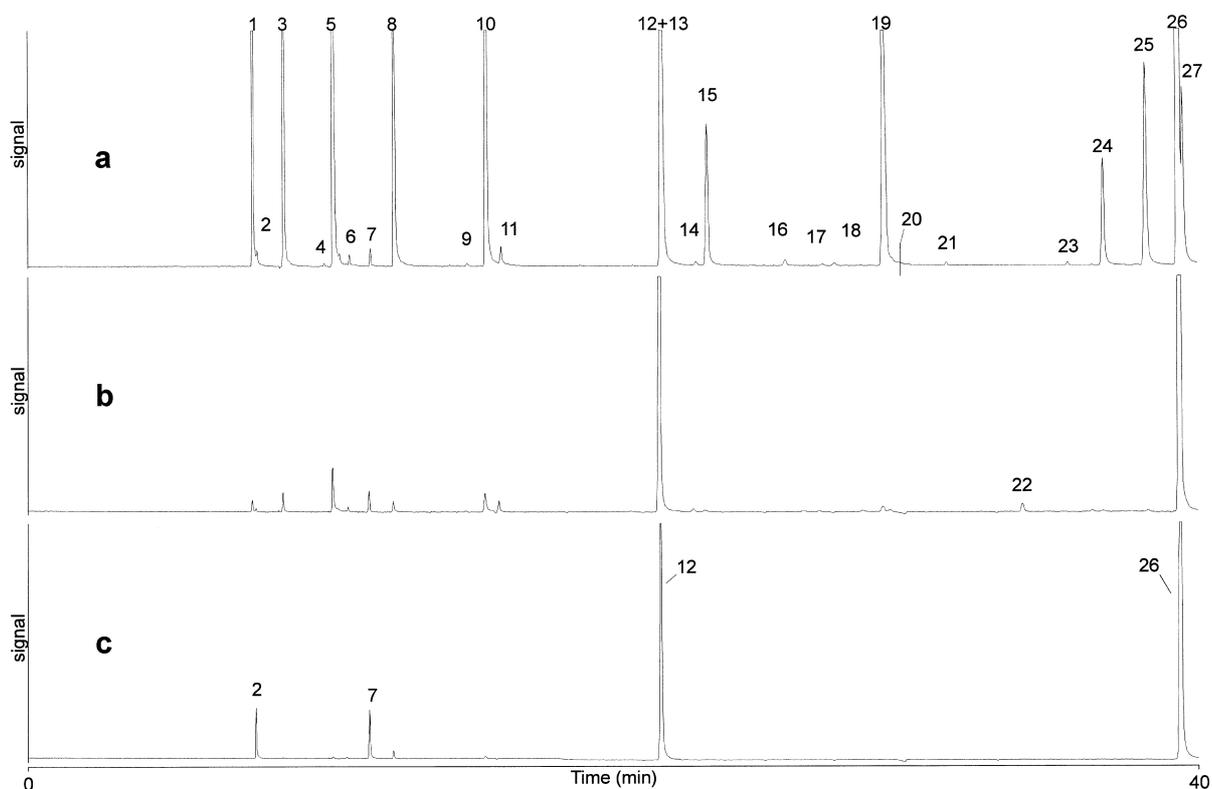

Fig. 2. The effect of selective oxidation on VB naphtha. (a) Original VB naphtha; (b) VB naphtha oxidized with iodine; (c) VB naphtha oxidized with hydrogen peroxide.
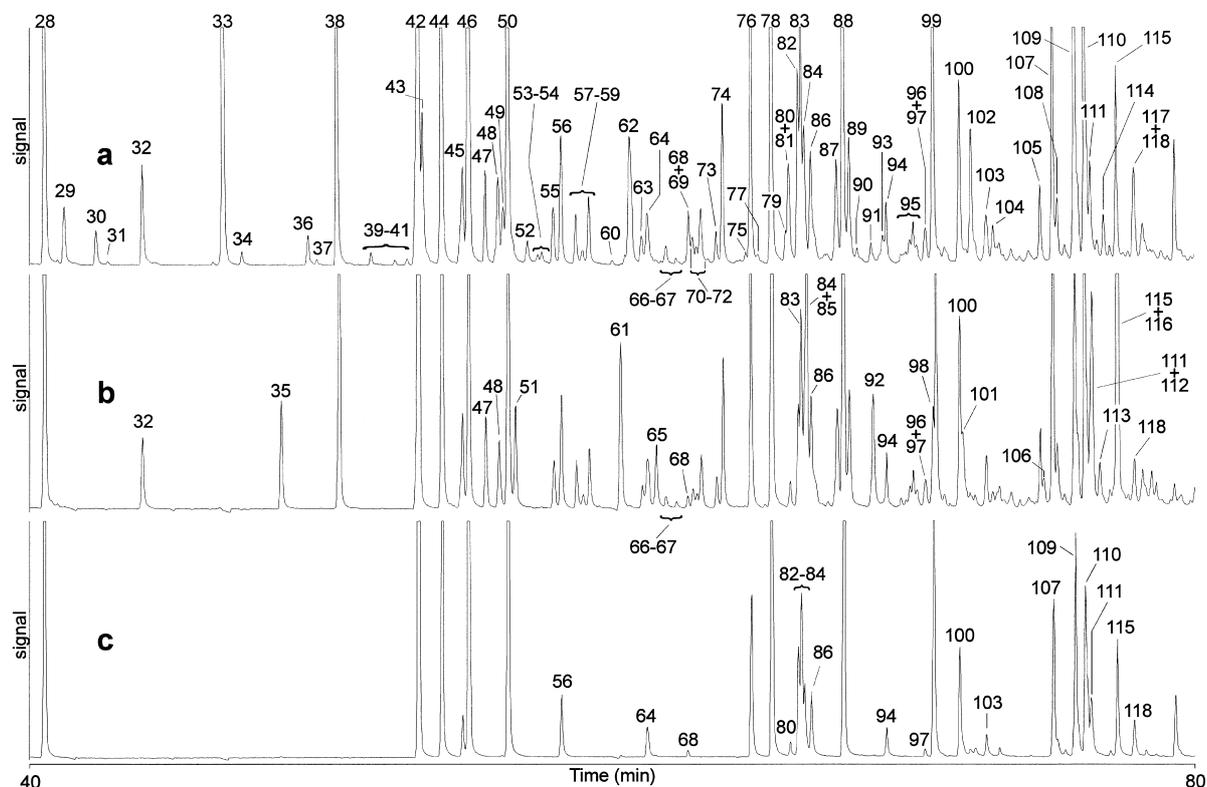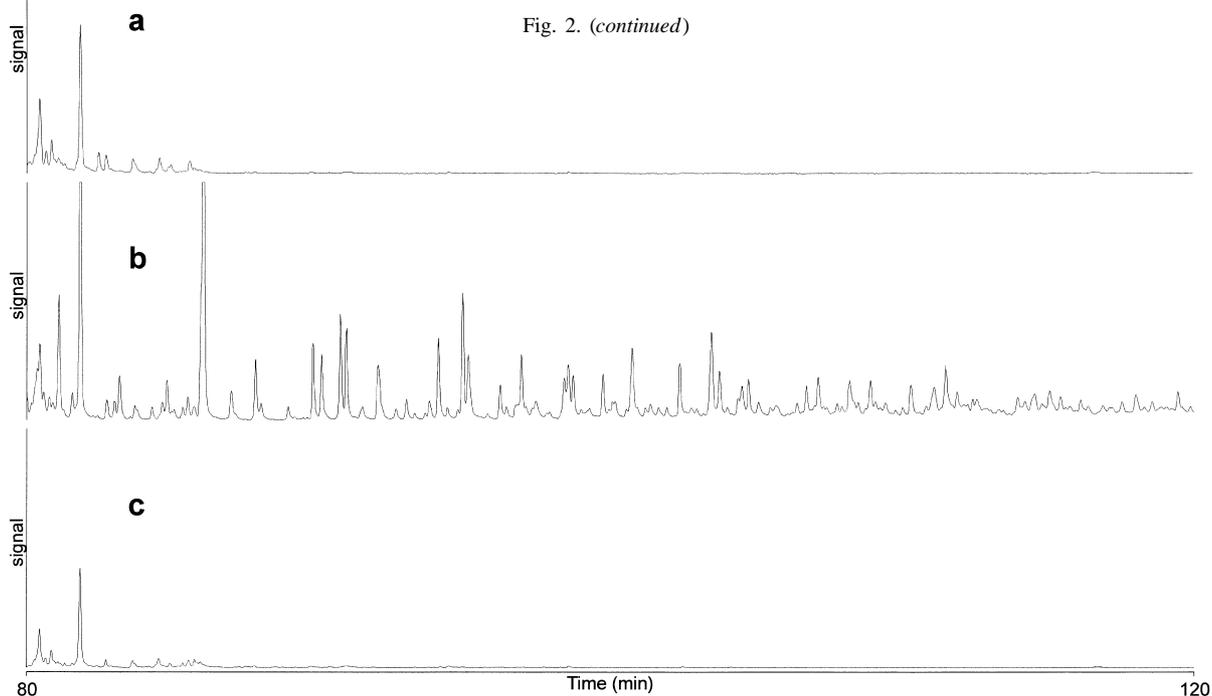
Fig. 2. (continued)

Fig. 2. (continued)

Table 1
List of compounds

1	Hydrogen sulfide	41	C_6 mercaptan	81	C_7 mercaptan
2	Carbonyl sulfide	42	2-Ethyl thiophene	82	unident. thiophene
3	Methyl mercaptan	43	C_6 mercaptan	83	unident. thiophene
4	Unidentified	44	3-Ethyl thiophene	84	unident. thiophene
5	Ethyl mercaptan	45	C_2 thiophene	85	unident. disulfide
6	Dimethyl sulfide	46	2,5-Dimethyl thiophene	86	unident. thiophene
7	Carbon disulfide	47	C_6 sulfide	87	sulfide
8	Isopropyl mercaptan	48	C_6 sulfide	88	unident. thiophene
9	*tert.*-Butyl mercaptan	49	C_6 mercaptan	89	sulfide
10	*n*-Propyl mercaptan	50	2,4-Dimethyl thiophene	90	C_7 mercaptan
11	Ethyl methyl sulfide	51	unident. disulfide	91	C_7 mercaptan
12	Thiophene	52	C_6 mercaptane	92	unident. disulfide
13	*sec.*-Butyl mercaptan	53	C_6 mercaptane	93	C_7 mercaptan
14	???sulfide???	54	C_6 mercaptane	94	unident. thiophene
15	Isobutyl mercaptan	55	C_6 mercaptane	95	group of sulfides
16	C_4 sulfide	56	2,3-Dimethyl thiophene	96	unident. sulfide
17	C_4 sulfide	57	C_6 sulfide	97	unident. thiophene
18	Diethyl sulfide	58	C_6 sulfide	98	unident. disulfide
19	*n*-Butyl mercaptan	59	C_6 sulfide	99	unident. thiophene
20	*tert.*-Amyl mercaptan	60	C_6 mercaptan	100	unident. thiophene
21	???sulfide???	61	unident. disulfide	101	unident. disulfide
22	Methyl disulfide	62	*n*-Hexyl mercaptane	102	*n*-Heptyl mercaptan
23	C_5 mercaptan	63	C_7 sulfide	103	unident. thiophene
24	C_5 mercaptan	64	3,4-Dimethyl thiophene	104	C_8 mercaptan
25	C_5 mercaptan	65	unident. disulfide	105	unident. sulfide
26	2-Methyl thiophene	66	C_7 sulfide	106	unident. disulfide
27	C_5 mercaptan	67	C_7 sulfide	107	unident. thiophene
28	3-Methyl thiophene	68	C_3 thiophene	108	unident. sulfide
29	C_5 mercaptan	69	C_7 mercaptan	109	unident. thiophene
30	C_5 mercaptan	70	unident. sulfide	110	unident. thiophene
31	C_5 mercaptan	71	unident. sulfide	111	unident. thiophene
32	Tetrahydrothiophene	72	unident. sulfide	112	unident. disulfide
33	*n*-Amyl mercaptan	73	unident. sulfide	113	unident. disulfide
34	C_6 mercaptan	74	unident. sulfide	114	C_8 mercaptan
35	Ethyl disulfide	75	C_7 mercaptan	115	unident. thiophene
36	C_6 mercaptan	76	C_3 thiophene	116	unident. disulfide
37	C_6 mercaptan	77	C_7 mercaptan	117	C_8 mercaptan
38	C_6 sulfide	78	C_3 thiophene	118	unident. thiophene
39	C_6 mercaptan	79	C_7 mercaptan	119	Benzothiophene
40	C_6 mercaptan	80	C_3 thiophene	120	Methyl benzothiophene isomers

Table 2
Comparison of GC–AED and ASTM D545-93 in terms of total sulfur content measurement

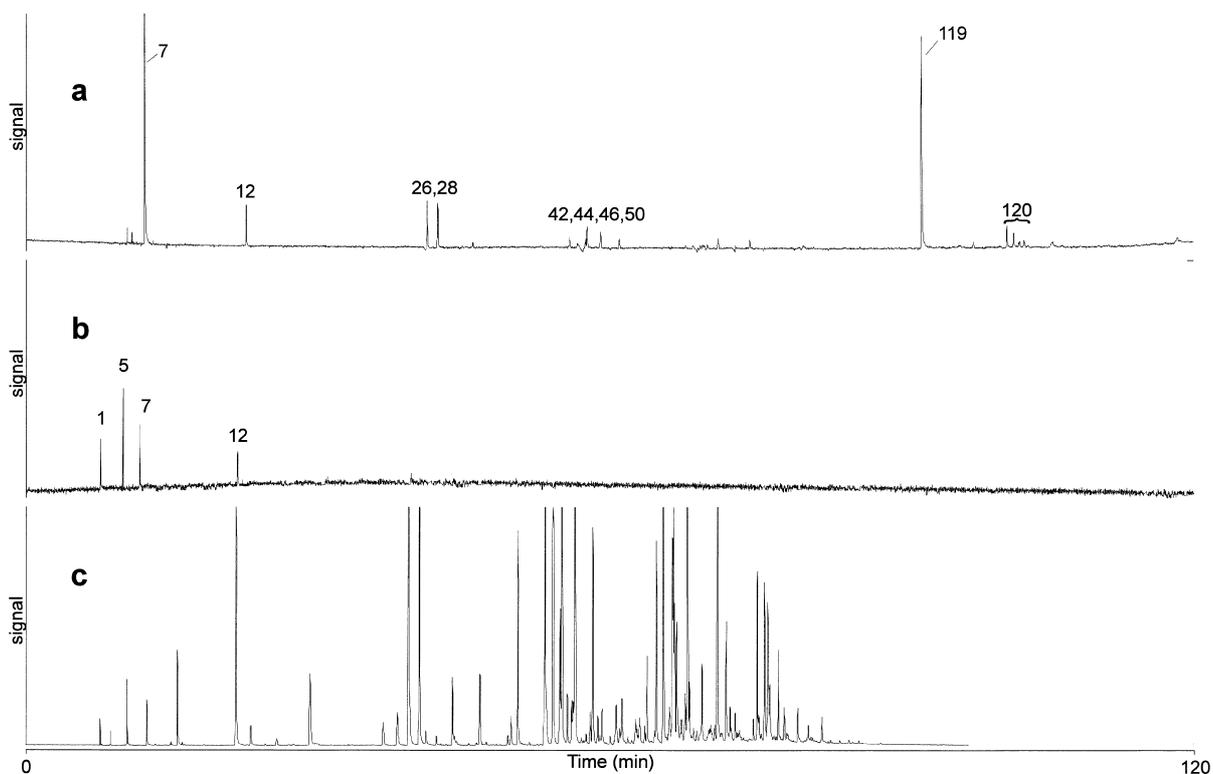| Naphtha	Total sulfur content by GC–AED (mg/dm^3)	Total sulfur content by ASTM D545-93 (mg/dm^3)
FCC	1498	1567
Straight run	82	79
Delayed coker	8241	8422

Fig. 3. Fingerprint chromatograms of various naphthas. (a) FCC naphtha; (b) straight run naphtha; (c) coker naphtha.

even if these are only present in a little amount. Thiophene and thiophene isomers might be present, depending on the boiling range, sulfides are not typical.

Both coker (Fig. 3c) and VB naphthas are products of thermal cracking processes, so their fingerprint chromatograms are very similar, practically matching each other.

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