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Note

Rapid high-performance liquid chromatographic method for the analysis of benzene in gasoline

HELGE STRAY

Norwegian Institute for Air Research, P.O. Box 130, N-2001 Lillestrom (Norway)

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The authorities of many countries have decided to reduce the lead content of automobile gasoline. This has forced the producers to look for other ways of maintaining a high octane number. One possibility is to increase the content of benzene and alkylbenzenes in gasoline. Because of the toxic properties of benzene, Norwegian authorities have set a maximum limit for this compound of 5% (v/v) in automobile gasoline. Different techniques such as gas chromatography¹ nuclear magnetic resonance spectroscopy² and infrared spectrometry³ have been used for the determination of benzene in gasoline. In addition the retention behaviour of benzene and some alkylbenzenes using high-performance liquid chromatography (HPLC) with different reversed-phase columns has been studied⁴.

Both high-resolution capillary gas chromatography (HRGC) and HPLC have been investigated. A simple method based on a single dilution step and quantification by HPLC has been developed for benzene. The results were controlled by HRGC which was used as an independent method. Except for one sample the agreement of the measuring values was better than $\pm 4\%$. This special gasoline sample contained an unknown compound which interfered strongly with the gas chromatographic determination. Using HRGC-mass spectrometry this compound was tentatively identified as an isomer of hexadiyne.

EXPERIMENTAL

Standards and reagents

All reagents used were at least of analytical-reagent grade. Benzene standard solutions were prepared from analytical-reagent grade benzene (E. Merck, Darmstadt, G.F.R.; No. 1783) which was diluted in isooctane for HPLC determination or in light petroleum (b.p. 40–60°C) for quantification by HRGC. 2-Butanone (E. Merck, No. 9708) was used as an internal standard for the HRGC method.

Apparatus

The HPLC system consisted of a CCM control module, a Constametric III and I pump and a UV III monitor Model 1203 with a fixed wavelength of 254 nm (all from Laboratory Data Control, Division of Milton Roy Co., FL, U.S.A.). The injector was a Rheodyne 7125 with 20- μ l loop which was completely filled. A Supelcosil LC-8

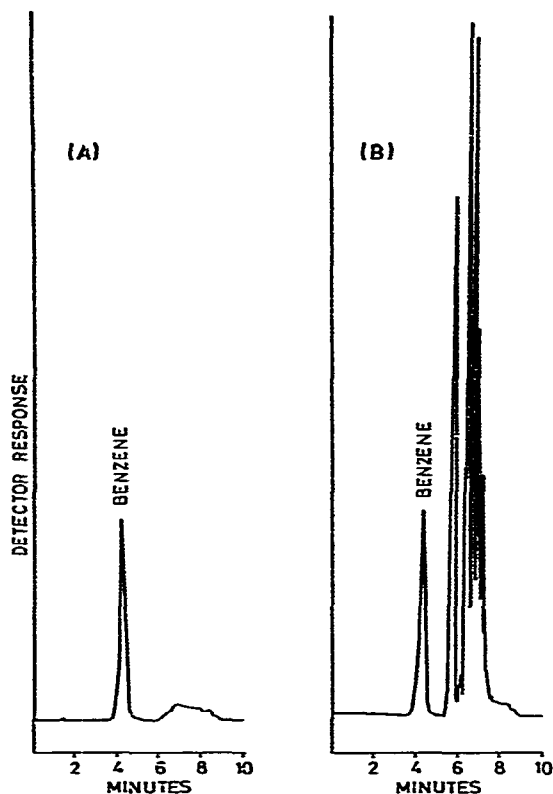


Fig. 1. Chromatograms from HPLC analysis showing (A) a standard of 0.3% benzene and (B) a gasoline sample.

column (150×4.6 mm; Supelco, Bellefonte, PA, U.S.A.) was used. The gas chromatographic analysis was carried out on a Carlo Erba Fractovap 2150 equipped with an electrometer type Type 180, a LT programmer 232, a flame-ionization detector, a Grob-type split/splitless injector and a Spectra-Physics system I computing integrator. A glass capillary column ($25 \text{ m} \times 0.3 \text{ mm I.D.}$) coated with OV-225 (film thickness $0.2 \mu\text{m}$) was used.

Analytical procedure

HPLC method. Prior to the HPLC analysis the gasoline samples were diluted (1:9) in methanol. Base standards of 1, 3 and 5% benzene content were diluted further with methanol to working standards of 0.1, 0.3 and 0.5% respectively. After injecting a $20\text{-}\mu\text{l}$ sample a solvent mixture of methanol-water (70:30) was used to elute benzene at a flow-rate of 1 ml/min. Afterwards all other compounds were washed out using pure methanol at a flow-rate of 2.5 ml/min. A new sample could be injected after 11 min. The benzene concentration was calculated from the peak area using the external-standard method. The relationship between area and concentration was linear in the actual measuring range. A 0.3% benzene standard was injected after every five samples for control and correction of the response factor. Fig. 1 shows a chromatogram of a standard and a gasoline sample.

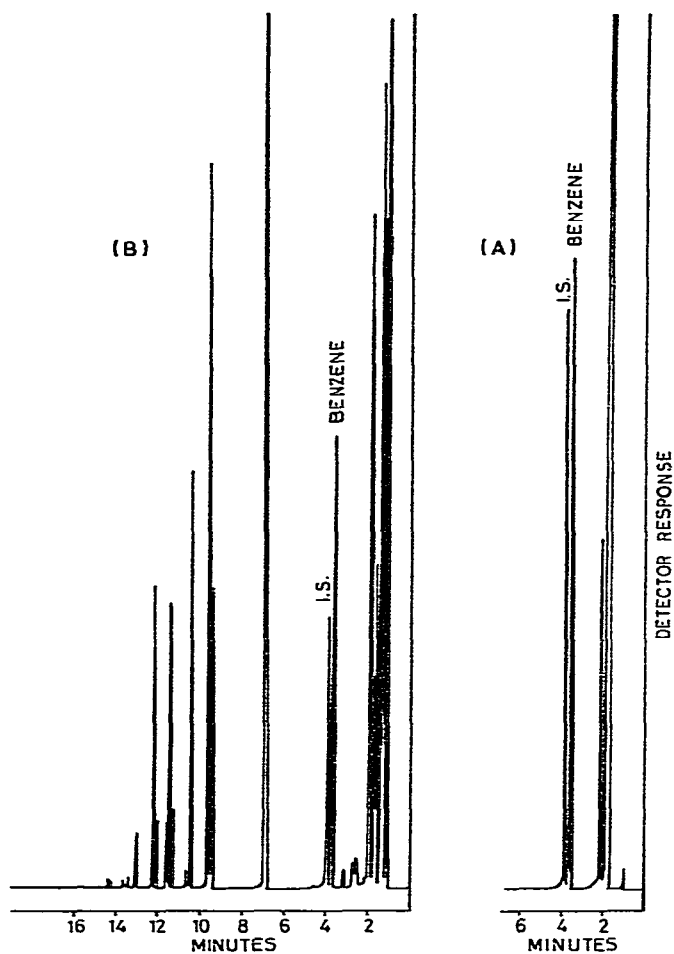


Fig. 2. Chromatograms from HRGC analysis showing (A) a standard of 3.0% benzene and (B) a gasoline sample.

HRGC method. A 4% sample of the internal standard (I.S.) was added to the undiluted gasoline sample and to standard solutions containing 2 or 4% benzene in light petroleum. A 0.1- μ l aliquot was injected with a split ratio of 1:100. The oven was kept at 30°C for 5 min, then the temperature was raised at a rate of 15°C/min to 150°C. At least two standard solutions were injected each day for calculation of the relative response factor. The resin OV-225 is a polar stationary phase which gives benzene a relatively long retention time. This results in a better separation from other less polar compounds in the same range of boiling point than with less polar stationary phases.

Fig. 2 shows a chromatogram of a standard and a gasoline sample.

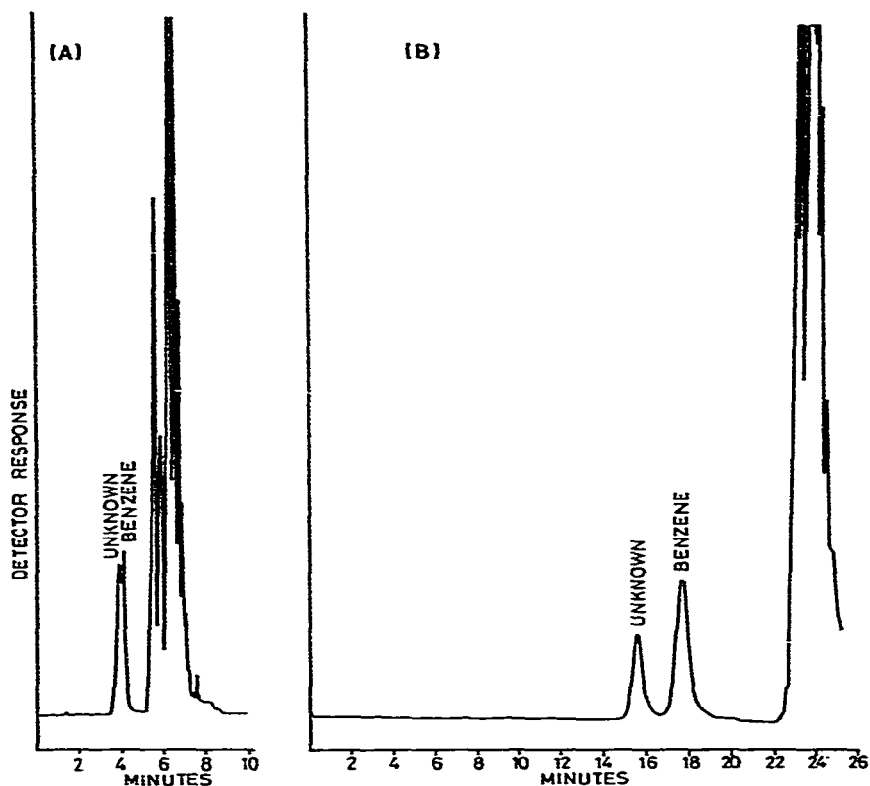


Fig. 3. HPLC chromatograms of a gasoline sample containing an interfering compound eluted at (A) 70% and (B) 50% methanol.

RESULTS AND DISCUSSION

Table I compares the results from both HRGC and HPLC quantification of thirteen samples from six oil companies. The results of both methods are the average of two analyses each. Except for sample no. 8, the results from the HRGC and the HPLC method are in good agreement and no systematic deviation is observed.

Sample No. 8 showed a considerably higher value when analysed by HRGC. This also was the only sample showing an unknown component as an unresolved peak in front of the benzene peak when analysed by HPLC (see Fig. 3). A better separation was obtained by reducing the methanol concentration in the eluent from 70 to 50%, and the benzene content could be measured without any interference from the first peak.

The undiluted sample No. 8 was injected on to the HPLC column and both the unknown and the benzene was collected separately. The two solutions were extracted with hexane and the extracts were analysed by HRGC. This revealed that the two compounds had the same retention on the OV-225 column. HRGC-mass spectrometric analysis of the two extracts using the same HRGC column showed that the two compounds had identical mass spectra using electron-impact ionization. A reasonable proposal for the structure of the unknown is 1,4-hexadiyne.

TABLE I

COMPARISON OF THE RESULTS FROM HGRC AND HPLC ANALYSIS OF THIRTEEN GASOLINE SAMPLES

Sample No.	Oil company	Octane number	Concentration (%, v/v)		Difference (%)
			GC	HPLC	
1	A	98	4.33	4.29	+ 0.9
2	A	93	3.67	3.64	+ 0.8
3	B	98	3.37	3.35	+ 0.6
4	B	93	3.22	3.14	+ 2.5
5	C	98	3.17	3.25	- 2.5
6	C	93	3.27	3.21	+ 1.9
7	D	99	5.10	5.00	+ 2.0
8	D	99	2.80	2.20	+27.3
9	D	93	4.45	4.29	+ 3.7
10	E	98	1.78	1.76	+ 1.1
11	E	93	1.55	1.59	- 2.5
12	F	98	4.44	4.40	+ 0.9
13	F	93	4.35	4.33	+ 0.5

Until now, 42 gasoline samples have been analysed by the HPLC method and only two samples, both coming from the same supplier, showed this interfering peak. This study indicates that apart from being faster and demanding less pretreatment, the HPLC method is less exposed to interferences than the HRGC method.

ACKNOWLEDGEMENT

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