

## GC METHODS FOR QUANTITATIVE DETERMINATION OF BENZENE IN GASOLINE

**Instrument:** HP 5890 II GC with Dual FIDs, Split/Splitless Inlet and Purged Packed Inlet

### SUMMARY

GC–FID methods using two different capillary columns have been developed for the determination of benzene in gasoline samples and petroleum fractions. The methods were compared and evaluated. GC–FID with a PONA column is not appropriate for routine analysis. GC–FID with a TCEP column enables precise and accurate measurement of the benzene content of gasoline and petroleum fractions and can be widely used for analysis of petroleum products – there is no limitation of sample composition.

Results obtained from analysis of commercial samples of gasoline and petroleum fractions agree with those obtained by use of the IR spectroscopy reference method

### EXPERIMENTAL

Reagents and Calibration Solutions Benzene, isooctane, and 2-butanone (all 99.5% purity) were obtained from Fluka. Gasoline samples and petroleum fractions, each with different PONA values were obtained from Lukoil Neftochim Bourgas JSC. Five calibration solutions of benzene in isooctane, with and without internal standard, were prepared. The approximate concentrations of benzene were 0.1, 0.5, 1.0, 1.5, and 2.0% (v/v). 2-Butanone was used as internal standard.

**Table I**

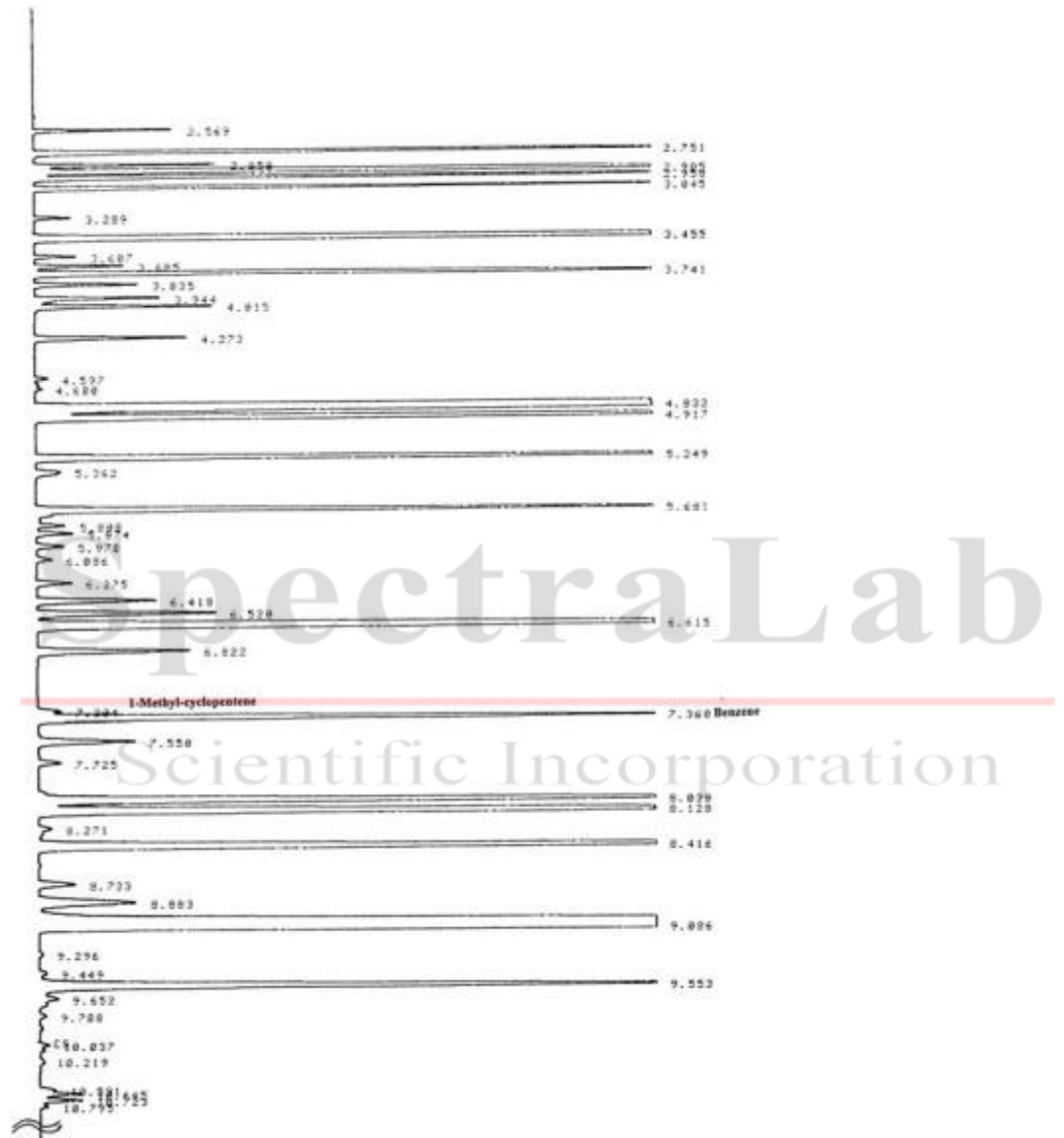
Test methods for determination of benzene in gasoline

Method	Technique	Scope	Repeatability		Reproducibility
			Range		
ASTM 3606	GC–TCD	0.1–5%(v/v) for finished motor and aviation gasoline	0.1–1.5% (v/v)	0.03(X) + 0.01	0.13(X) + 0.05
ASTM 4420	GC–TCD	0.1–5%(v/v) for finished motor gasoline	0.171 × measured value		0.408 × measured value
ASTM 5580	GC–FID	0.1–5%(v/v) for finished motor gasoline	Range 0.14–1.79% (v/v)	0.0265(X <sup>0.65</sup> )	0.1229(X <sup>0.65</sup> )
ASTM 5769	GC–MS	0.1–4% (v/v) for finished motor gasoline; gasoline containing oxygenated blending components	Range 0.09–4.0% (v/v)	0.046(X <sup>0.67</sup> )	0.221(X <sup>0.67</sup> )
IP 425	GC–FID	0.05–6.0% (v/v)	Concentration		
			0.02	0.002	0.003
			0.05	0.04	0.005
			0.1	0.06	0.008
			0.2	0.010	0.013
			0.5	0.019	0.025
			1.0	0.03	0.04
2.0	0.04	0.06			
EN 12177	GC–FID	0.05–6.0% (v/v) unleaded petrol	Range 0.05–0.15% (v/v)	0.005	0.01
			0.15–1.50% (v/v)	0.03	0.10
			1.50–6.00% (v/v)	0.05	0.25

## Chromatographic Systems and Conditions

Results were obtained by use of two different gas chromatographs. The first was a Hewlett–Packard 5890 series II model gas chromatograph (GC) equipped with a split/splitless injector, a flame ionization detector, and a 50 m × 0.2 mm i.d. PONA column coated with crosslinked polydimethylsiloxane gum. The injector temperature was 200°C and the detector temperature 250°C. The GC oven temperature was programmed from 35°C at 2° min<sup>-1</sup> to 200°C which was held for 10 min. Hydrogen was used as the carrier gas at a flow rate of 1.0 mL min<sup>-1</sup>; the split ratio was 1:100.

The second GC system was a Hewlett–Packard model 5890 series II GC with flame ionization detector and a 50 m × 0.25 mm i.d. column coated with a 0.4 µm film of CP-TCEP (Varian). The detector and injector temperatures were 275 and 250°C, respectively, and the oven temperature was maintained at 50°C for 10 min then programmed 10° min<sup>-1</sup> to a final temperature of 115 °C which was held for 10 min. Hydrogen was used as carrier gas at a flow rate of 1.0 mL min<sup>-1</sup>, the split ratio was 1:60.



**Fig. 1**

Partial chromatogram obtained from a gasoline sample on a PONA column

#### REFERENCES

- [1] Directive 98/70/EC of the European Parliament and of the Council, 13 October, 1998
- [2] ASTM D 3606-99. Standard Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography, Vol.05.02, 504, 2000
- [3] ASTM D 4420-94. Standard Test Method for Aromatics in Finished Gasoline by Gas Chromatography, Vol.05.02, 881, 2000

[4] ASTM D 5580-95. Standard Test Method for Determination of Benzene, Toluene, Ethylbenzene, p/m-Xylene, o-Xylene, C9 and Heavier Aromatics and Total Aromatics in Finished Gasoline by Gas Chromatography, Vol.05.03, 620, 2000

[5] ASTM D 5769-98. Standard Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasoline by Gas Chromatography/Mass Spectrometry, Vol.05.03, 760, 2000

[6] IP 425/96 Determination of Benzene Content of Petrol – Gas Chromatography Method

[7] EN 12177:1998 Liquid petroleum products – Unleaded petrol – Determination of benzene content by gas chromatography

[8] EN 238:1996E Liquid petroleum products – Petrol – Determination of the benzene content by infrared spectrometry

[9] E. Lopez – Anreus, S. Garrigues, and M. de la Guardia, Anal. Chim. Acta, 333, 157 (1996)

[10] G.S. Frysiner, R.B. Gaines, E.B. Ledford, J. High. Resol. Chromatogr., 22, 195 (1999)

[11] G.S. Frysiner and R.B. Gaines, J. High. Resol. Chromatogr., 22, 251 (1999)

[http://www.us.edu.pl/universytet/jednostki/wydzialy/chemia/acta/ac13/zrodla/18\\_AC13.pdf](http://www.us.edu.pl/universytet/jednostki/wydzialy/chemia/acta/ac13/zrodla/18_AC13.pdf)