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GAS–LIQUID CHROMATOGRAPHIC ANALYSIS OF HYDROCARBON MIXTURES

A REPORT ON THE WORK OF THE INTERNATIONAL CONFERENCE OF BENZOLE PRODUCERS

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SUMMARY

From a series of international testing programmes, the precision attainable in the analyses of hydrocarbon mixtures with components present in the range 0.001–30% has been established. Only the minimum standardization of procedure and equipment has been demanded in these programmes. Conclusions are drawn on the relative precision of katharometers and flame ionization detectors, methods of chromatogram assessment and methods of calibration. Recommendations are made on procedures necessary to minimize errors in gas–liquid chromatographic techniques without complete standardization of equipment and procedure.

INTRODUCTION

To obtain the highest possible precision in gas–liquid chromatographic (GLC) analyses, it is not unreasonable to assume that all factors that may effect the precision should be rigorously standardized. The result should be a single apparatus, defined in detail, and a carefully described procedure for each application of the technique. Unfortunately, this doctrine of perfection often proves to be impractical, particularly when comparative tests may be on an international basis. With this situation in mind, the International Conference of Benzole Producers (ICBP) has completed an extensive series of cooperative testing programmes with the object of determining the precision attainable with the minimum standardization of apparatus and procedure.

Since 1962, there have been nine such programmes, all of which have been concerned with the analysis of hydrocarbon mixtures of the types encountered in the aromatic hydrocarbons industry. The first programme in this series has already been described in detail[1] and the others have followed a similar pattern. The sixteen laboratories that have participated are located in Austria, Belgium, France, Germany, Great Britain, Italy, The Netherlands, Spain and Sweden.

Each testing programme has been planned and the results analysed statistically and the precision has been calculated as follows:

TABLE I

APPARATUS AND CONDITIONS

Key to stationary liquid phases: A = polyethylene glycol; B = polypropylene glycol (Ucon LB 550X); C = polyethylene glycol 400 dibenzoate; D = 1:1 Bentone 34–didecyl phthalate.

Conditions	*Laboratory*						
	A	*B*	*C*	*D*	*E*	*F*	*G*
Detector	Flame ionization	Flame ionization	Flame ionization	Flame ionization	Flame ionization	Flame ionization	Flame ionization
Column length (m)	50	6.1	4	7	6	8	4
I.D. (mm)	0.25	2.2	4.0	4.0	4.0	4.65	3.1
Material	Stainless steel	Stainless steel	Stainless steel	Copper	Copper	Copper	Stainless steel
Operating temperature (°C)	30–70	50	65	70	69	52	70
Carrier gas	He	N_2	He	He	N_2	N_2	N_2
Inlet pressure (bar)	1.0	2.8	1.5	1.5	1.0	2.0	1.9
Flow rate (ml/min)	1.3	20	40	—	20	50	25
Support	Capillary	Johns-Manville C22 brickdust	Acid-washed Chromosorb W	C22 brickdust	Chromosorb W	Celite 54	Chromosorb W
Mesh size	—	60–80	60–80	—	—	60–100	—
Stationary liquid phase	B	C	D	D	D	A	D
Amount of stationary phase (%, w/w)	—	7.5	20	10	10	15	5
Sample size (μl)	2.0 (split 1:200)	1.0	4.0	1.0	1.5	1.0	0.2
Standard	*n*-octane or *n*-hexane	*n*-octane	2-methyl pentane	*n*-octane	2-methyl pentane	*n*-octane	2-methyl pentane
Chart speed	0.5 in./min	3.0 cm/min	0.5 in./min	50 cm/h	15 cm/h	30 cm/h	0.5 in./min

The *repeatability* (r) is the difference between duplicate results on the same sample, by one operator using one set of apparatus, that would be equalled or exceeded in the long run in only one case in twenty.

The *reproducibility* (R) is the difference between a single result by one operator at one laboratory and a single result on the same sample by another operator at another laboratory that would be equalled or exceeded in the long run in only one case in twenty.

The samples, which ranged from two to five per programme, were sent to each of the participating laboratories, where they were tested in duplicate by the same operator using the same apparatus. The apparatus was not specified in detail but it was required to give a specified resolution for the components being measured. An indication of the range of apparatus and conditions used can be judged from Table I, which refers to the ninth programme. In earlier programmes, other types of detector were included.

When response factors were required, they were obtained from blends of the components to be determined and the standards. Four chromatograms were run on each blend. The mean response factors for the four runs were calculated and used in the calculations for the sample.

No test results are included in this report, but detailed reports of each programme have been submitted to members of ICBP. This report summarizes the main features of each programme and presents the precision figures obtained. It also makes certain recommendations on the preferred techniques.

Throughout the course of the ICBP programmes, there has been liaison in Great Britain with the Standardization of Tar Products Tests Committee (STPTC) and the Institute of Petroleum (IP), and particular note has been taken of "Principles of Gas Chromatography"[2] and "Specification for Gas Chromatographic Methods"[3].

MIXTURES EXAMINED

The hydrocarbon mixtures that have been examined can be summarized as follows.

A. Main component = benzene

Other components	*Concentration range (%, w/w)*	*Programme no.*	*No. of samples*
Toluene	0.01–0.03	4	3
Cyclohexane	0.4	1	1
Toluene	0.7		
Ethylbenzene	0.8		
Toluene	0.36	3	1
n-Hexane	0.40		
n-Heptane	0.15		
n-Heptane	0.5–1.8	2	3
n-Hexane	0.01 –0.03	8 and 9	2 and 3
Methylcyclopentane	0.001–0.05		
Cyclohexane	0.002–0.01		
n-Heptane	0.001–0.04		
Methylcyclohexane	0.002–0.05		

B. Main component = toluene

Other components	*Concentration range (%, w/w)*	*Programme no.*	*No. of samples*
Benzene	0.2–0.9	6	5
Benzene	0.11	3	1
n-Octane	0.48		
n-Nonane	0.27		
Benzene	0.5 –1.0	2	3
Ethylbenzene	0.08–0.2		
p-Xylene	0.19–0.25		
Benzene	1.8	1	1
Ethylbenzene	2.7		
p-Xylene	3.7		
n-Nonane	1.1		

C. Main component = p-xylene

Other components	*Concentration range (%, w/w)*	*Programme no.*	*No. of samples*
o-Xylene	3.1–30.0	2	3
Mesitylene	2.1– 5.0		
Isopropylbenzene	2.1–7.75		
Toluene	0.5–1.5	5	3
Ethylbenzene	4.0–6.0		

D. C_8-aromatic isomers

Component	*Concentration range (%, w/w)*	*Programme no.*	*No. of samples*
Ethylbenzene	15–20	7	2
p-Xylene	16–20		
m-Xylene	44–49		
o-Xylene	15–22		

The dates of the programmes were as follows: programme no. 1, 1962; 2 and 3, 1963; 4, 1964; 5, 1966; 6, 1967; 7, 1968; 8, 1970; and 9, 1971.

EVOLUTION OF PREFERRED TECHNIQUES

In the course of the nine years of joint testing programmes, a variety of techniques have been examined, the precisions compared and the procedures modified to minimize the errors.

Detectors

In programmes 1 and 2, only katharometers were used; in programmes 4, 8 and 9, only flame ionization detectors were used. In the other programmes, both types of detector were used and the precisions obtained were compared. There was no significant difference between the precisions of the results obtained with the two types down to the 0.1% (w/w) level. Katharometers were not suitable below this level.

Standardization

It was demonstrated that a substantial proportion of the reproducibility error was associated with the addition of internal standards and the preparation of volatile synthetic mixtures either for the determination of response factors or for comparison. This information was obtained by comparing the precision of the results obtained when each laboratory when each laboratory prepared its own standards with that obtained when the same laboratories used standards prepared in bulk and circulated by a single laboratory.

Provided that the errors associated with the preparation of standards are eliminated, there is little difference in the precision obtained by using internal standards or by comparing the chromatogram of the sample with that of a similar synthetic mixture.

Recommendations on determining response factors are included in this paper.

In programmes 8 and 9, comparisons were made between the precisions obtained when internal standards were added to the sample by weighing and by use of a microsyringe. There was no significant difference in precision and the microsyringe procedure is therefore preferred because of the saving in time.

Peak assessment

Comparison of the precision of results showed that it was more precise to use peak area than peak height. Area assessment using the product of peak height and peak width at half-height has proved satisfactory.

PEAK RESOLUTION

If two components are separated sufficiently to permit a satisfactory determination of their peak widths and the curves are approximately Gaussian, as shown in Fig. 1, then the resolution is

$$\frac{2\Delta y}{Y_a - Y_b}$$

where Y_a and Y_b are the peak widths of peaks A and B, respectively, and Δ_y is the horizontal distance between the verticals through the peak maxima.

The minimum resolution that is necessary to avoid significant interference by either of the peaks on the other depends on their relative peak areas and on the method of peak measurement. A minimum resolution of 1.5 should be sufficient for area measurements of peaks differing by a factor of up to ten in their respective areas.

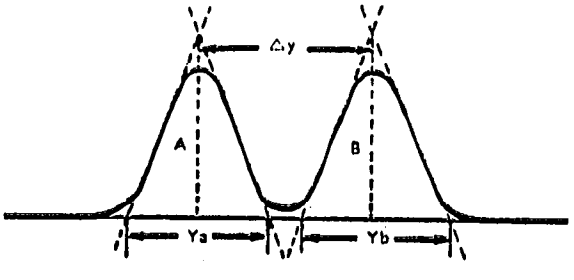

Fig. 1. Peak resolution.

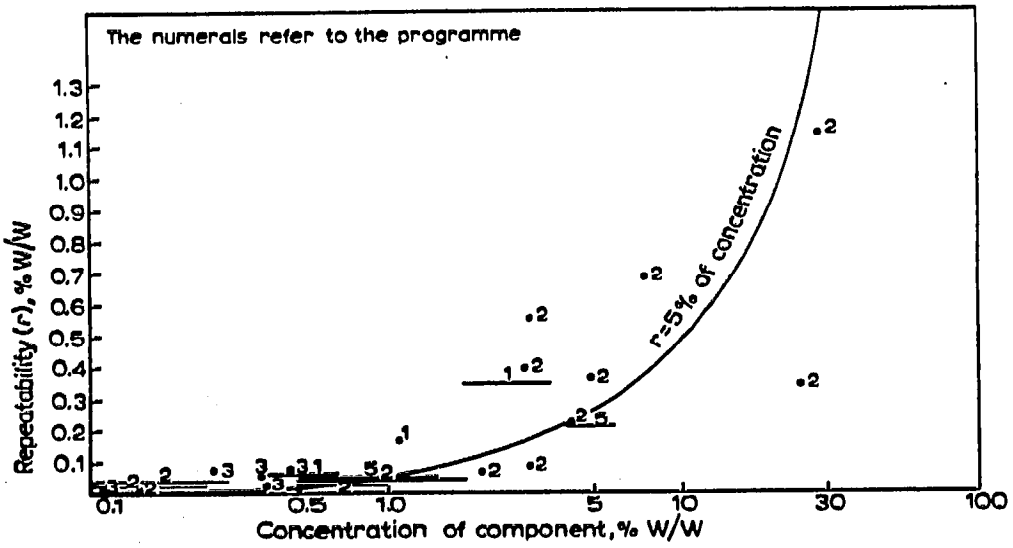

Fig. 2. Repeatability.

PRECISION

An over-all analysis of the results of all the programmes has not been attempted and the value of such an analysis would be limited owing to the improvements in technique from programme to programme. The repeatability and reproducibility figures for programmes 1 to 5 have been plotted in Figs. 2 and 3. If a generalization on the precision obtained in these programmes were required, the values would be:

Repeatability (r) = 5%
Reproducibility (R) = 10%
} of the concentration being determined.

In programme 7, most of the improved techniques were used and the precision was better than that for the earlier programmes.

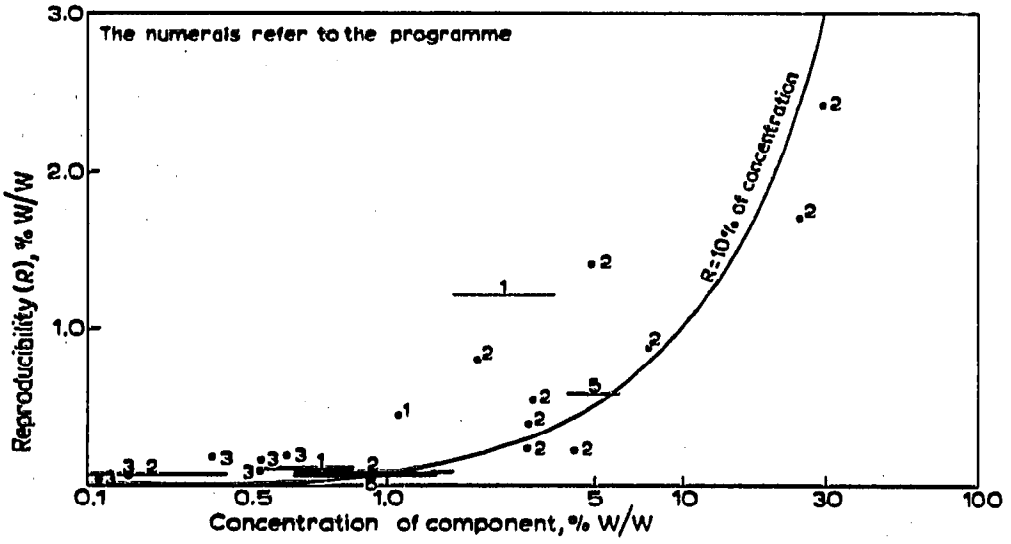

Fig. 3. Reproducibility.

TABLE II

PRECISION DATA

The precision figures are quoted in the units of the test, *i.e.*, % (w/w) (no parentheses) and as a percentage of the mean concentration determined (in parentheses).

Component (in order of elution)	*Level (%, w/w)*	*Repeatability (r)*	*Reproducibility (R)*
Ethylbenzene	15–20	0.4 (2%)	1.1 (6%)
p-Xylene	16–20	0.5 (3%)	1.4 (8%)
m-Xylene	44–49	1.3 (3%)	1.5 (3%)
o-Xylene	15–22	0.5 (3%)	1.4 (8%)

The results are given in Table II.

Programme 6 was concerned with the determination of benzene in toluene. Unfortunately, the reproducibility was inflated owing to errors in the preparation of standards. In view of the interest in this particular analysis, however, it seems desirable to quote the results obtained.

Over the range 0.2–0.9% (w/w) of benzene, the precision values were:

Repeatability (r) = 4%
Reproducibility (R) = 12%
} of the concentration being determined.

Programmes 8 and 9 provided precision data for the concentration range 0.001–0.1%. These are presented in Tables III and IV and compared with published precision data for some IP and ASTM methods.

ABLE III

EPEATABILITY

ource of precision data	*Level (%, w/w)*							
	0.001	*0.002*	*0.01*	*0.015*	*0.02*	*0.03*	*0.07*	*0.10*
CBP Programme 9	W^a	0.0001	0.00025	0.001	0.0015	0.0025	0.002	0.004	0.011
ion-aromatics in benzene)	M^b	0.0001	0.0003	0.001	0.004	0.0025	0.004	0.005	0.010
CBP Programme 8 ion-aromatics in benzene)		—	—	—	0.002	0.003	—	—	—
CBP Programme 4 enzene in toluene)		—	—	0.001	—	0.002	—	—	—
STM D 2600/67T enzene in non-aromatics)		—	—	0.0015	0.002	0.003	0.004	0.010	0.015
P 262/70T enzene in non-aromatics)		0.0001	0.0002	0.001	0.002	0.0025	0.004	0.009	0.015
P 184/66 ion-aromatics in crude oil)		—	—	—	—	—	—	—	0.03
P 214/66T sopropylbenzene in xylene)		—	—	—	—	—	—	—	0.03

[a] W = internal standard added by weighing.
[b] M = internal standard added by microsyringe.

TABLE IV

REPRODUCIBILITY

Source of precision data	*Level (%, w/w)*								
		0.001	*0.002*	*0.01*	*0.015*	*0.02*	*0.03*	*0.07*	*0.10*
ICBP Programme 9 (non-aromatics in benzene)	W[a]	0.0003	0.0005	0.004	0.0065	0.007	0.009	0.016	0.017
	M[b]	0.0003	0.0006	0.003	0.006	0.0055	0.009	0.014	0.020
ICBP Programme 8 (non-aromatics in benzene)	*Average*	—	—	—	0.004	0.005	—	—	—
ICBP Programme 4 (benzene in toluene)		—	—	0.002	—	0.004	—	—	—
ASTM D 2600/67T (benzene in non-aromatics)		—	—	0.002	0.003	0.004	0.006	0.014	0.020
IP 262/70T (benzene in non-aromatics)		0.0004	0.0009	0.0045	0.0065	0.009	0.015	0.030	0.045
IP 184/66 (non-aromatics in crude oil)		—	—	—	—	—	—	—	0.11
IP 214/66T (isopropylbenzene in xylene)		—	—	—	—	—	—	—	0.06

[a] W = internal standard added by weighing.
[b] M = internal standard added by microsyringe.

RECOMMENDATIONS ON GLC PROCEDURES

ICBP consider that detailed specifications of equipment and procedures are unnecessary when describing a GLC method. It is recommended, however, that the following general requirements are met in a manner appropriate to the particular analysis.

(1) If an internal standard is used, it must be adequately resolved from the components being determined and impurities in the sample under test.

(2) An internal standard should, whenever possible, be so chosen that it is not present as an impurity in the sample.

(3) The quantity of internal standard must be such that the peak it produces has an area of the same order as that of the components being determined. A peak at least 5.0 cm high and 0.5 cm wide at half-peak height is preferred.

(4) The purity of internal standards and components of synthetic mixtures must be specified so that any impurities have a negligible effect on the result.

(5) When synthetic mixtures of volatile hydrocarbons are prepared (*e.g.*, for the determination of response factors), there must be full duplication, including weighing or pipetting by microsyringe, to enable rogue results to be eliminated and to minimize the errors associated with this stage.

(6) Response factors should be the mean of values calculated from chromatograms on the two synthetic mixtures and should differ by less than 4%.

(7) The peak resolution required should be defined.

(8) The peak assessment can be made by any established measurement procedure or by integrator provided that the over-all accuracy and precision are obtained when the procedure is checked with a synthetic mixture.

CONCLUSIONS

(1) Results sufficiently precise for most commercial purposes can be obtained by GLC analysis of hydrocarbon mixtures without detailed specification of the equipment to be used.

(2) Katharometers and flame ionization detectors give equally precise results down to the 0.1% (w/w) level. Flame ionization detectors give satisfactory precision down to 0.001% (w/w).

(3) Peak assessment methods based on peak area are preferable to those using peak height.

(4) A major source of error can be associated with the preparation of synthetic mixtures for determining response factors. Special precautions are required.

(5) Methods using internal standards and those involving comparison with a synthetic mixture are equally precise.

(6) There is no significant difference in the precisions obtained when internal standards are added by microsyringe or by weighing. The former is the quicker procedure.

(7) At concentration levels above 0.2%, a repeatability of 5% and reproducibility of 10% of the concentration being determined can be obtained without detailed specification of the equipment to be used. By following strictly the instructions for the determination of response factors, these figures can be reduced to 3% and 8%, respectively.

(8) At concentration levels in the range 0.001–0.10%, the precision of the ICBP results compares favourably with the corresponding precision figures for IP and ASTM standard methods.

REFERENCES

1 International Conference of Benzole Producers, *J. Chromatogr.*, 12 (1963) 293.
2 P. V. WATKINS (Editor), *Standard Methods of Testing Tar and its Products*, 6th Ed. STPTC, Gomersal, Yorks., 1967, p. 94.
3 G. R. PRIMAVESI, N. G. Mc TAGGART, C. G. SCOTT, F. SNELSON AND M. M. WIRTH, *J. Inst. Petrol., London*, 53 (1967) 367.