THE STANDARDIZATION OF GAS–LIQUID CHROMATOGRAPHY FOR THE ANALYSIS OF SIMPLE HYDROCARBON MIXTURES

THE INTERNATIONAL CONFERENCE OF BENZOLE PRODUCERS*

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INTRODUCTION

The technique of gas–liquid chromatography (GLC), first described by JAMES AND MARTIN[1] in 1952, has been developed at a phenomenal rate but, although so much has been done to advance the knowledge of underlying principles and to devise new techniques and apparatus, little has been done to standardize procedures, particularly with regard to obtaining quantitative results of acceptable precision.

For research purposes, apparatus and techniques can be adapted to fit the special requirements of the research project on hand. Standardization of methods, therefore, is neither necessary nor desirable for this purpose. It is for routine analysis that standardization is required since, for commercial purposes, it is highly desirable that both seller and buyer base their interpretation of analytical results on the same prescribed limits of precision for the analytical tests used.

Up to the present, the techniques of GLC have not been used to any great extent for commercial purposes in the benzole industry, but it is visualized that in the future such methods will be required for testing, both during manufacture and in connection with specifications.

A number of principles and assumptions have been stated in the literature and a number of types of equipment, commercially produced and otherwise, are available. The design of the most suitable equipment and selection of the best operating technique depends ultimately on the validity or otherwise of the underlying assumptions, and it is to test these that the present series of experiments has been designed.

It seems desirable, therefore, to summarize and discuss the more important assumptions so that they can be considered when drawing conclusions from the experiments. The main factors involved are as follows.

(1) Peak area

The peak area is a measure of the weight of the constituent responsible for it. The proportion of that constituent in the mixture may be estimated either by referring its peak area to the total area of the chromatogram, or by reference to an added

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standard. The former method is only of use for relatively simple mixtures where no component is present in very large or very small amounts.

Simple proportionality of areas will, in general, not be satisfactory as the weight per unit area differs from component to component. The following are some of the sources of error that may be involved in basing the analysis solely on the ratio of areas.

(a) Calculation of the total area is laborious and difficult with complex mixtures, especially if some of the peaks are small or if some substances are not completely resolved, *i.e.*, if the peaks for these substances overlap.

(b) If some substances are eluted late they may not be recorded on the chromatogram and their areas will not be included in the total area.

(2) *Response factors*

The response factor, *i.e.*, the weight of component per unit area of peak, may vary from compound to compound. The response factors can be determined for each of the substances concerned in an analysis and for the apparatus and conditions used. These response factors enable the composition to be determined from peak areas but, owing to the difficulties of assessing the area representing all the components, it is usual to relate all the areas to the area of an added internal standard. This standard must have a high degree of purity, a retention time such that it will appear on the chromatogram at a point free from other peaks and be used in such quantity that it produces a peak of similar size to those being determined. It should be noted that pre-calibration is necessary for most types of apparatus, and also that the response factor may vary according to the weight of substance introduced into the column. It is usual to operate the GLC equipment under standard conditions of temperature, gas flow and quantity of sample injected. As it is necessary to calibrate the column, however, it is clear that the precision of any estimation must depend upon the variation of the response factors with random variations in the standard operating conditions and upon systematic changes in conditions between the time of making the calibration and making the actual determination.

(3) *Measurement of peak area*

The area of a peak is generally measured by one of the following methods:

(a) Construction of the equivalent triangle, by drawing lines through the points of inflexion on the sides of the peak. The area is proportional to the width of this triangle, measured on the base line, multiplied by the height of the triangle to the apex. This method involves geometric construction, which is subject to personal judgement, particularly with regard to location of the apex of the triangle. Moreover, it has been shown that the relative area of peaks, assessed in this manner, varies according to the size of the peaks. Thus the method is fundamentally unsound if applied to analyses that may involve the measurement of peaks of widely varying magnitude.

(b) Provided the peaks are completely resolved, it is more accurate to multiply the peak height to the peak maximum by the peak width at half peak height. When the peaks overlap, it is necessary to estimate both peak height and peak width, making due allowance for the effect of one peak on the height and width of the other.

(c) The use of a planimeter is capable of giving precise assessment of the areas of peaks, but this method is more tedious and requires greater skill on the part of the operator than measurement of peak heights only. Also, only a high-quality instrument is satisfactory.

(d) Integration of areas. The use of integrating recorders probably gives the most accurate measurement of peak area. If any peaks are not completely resolved, however, the area recorded will be the sum of the areas of the overlapping peaks.

(e) Retention distance. It has been found that over a limited range the width of a peak is approximately proportional to the retention distance. Thus the peak area is approximately proportional to the peak height multiplied by retention time. Although this relationship varies with retention distance, the proportionality factor is included in the calibration. The advantage of this method of calculation is that the retention distance can be measured with considerable precision and thus the criterion, peak height multiplied by retention distance, is more exact than a criterion based on the measurement of peak width.

4. Peak height

From what has been said above, it is clear that calibration of the column will generally be needed when precise results are required. Calibration in terms of peak heights, instead of peak areas, would have the advantage of needing one measurement instead of two and would thus lead to greater precision and a saving in time. Difficulties arise when peaks are not completely resolved, because under these conditions the peak height must be estimated.

The following are the usual objections to the use of peak height as a criterion[2]:

(a) Peak area is more fundamental.

(b) Peak height is subjected to greater variation, according to changes in operating conditions, than peak area.

The second objection is of no importance if it can be shown that changes in conditions do not seriously affect the *relative* peak heights. Provided that it can also be shown that analyses based on peak height are as precise as those based on peak area, the greater convenience of making only the single measurement of peak height should outweigh all other considerations.

THE PRESENT TESTS

(I) General

In the present series of test, nine laboratories took part, representing the following European countries: Belgium, France, Germany, Great Britain, Italy and the Netherlands. Each laboratory used the equipment and operating conditions available, thus the statistical values for reproducibility, *i.e.* variations between laboratories, will include the effects of different column sizes, different supports, stationary phases, carrier gases, gas speeds and operating temperatures and pressures.

The same materials were used by all the laboratories for calibrating the column and as internal standards. Also, samples of the same unknown mixtures were examined in each laboratory.

Analyses were based on the criteria given in Table I.

TABLE II

METHODS OF ASSESSMENT OF CHROMATOGRAMS

(a) Calibration curves of peak height relative to a standard, against quantity of each substance.
(b) Average relative response factor for peak height.
(c) Calibration curves of peak height multiplied by retention time, relative to a standard, against quantity of each substance.
(d) Average relative response factor for peak height multiplied by retention time.
(e) Calibration curve of peak height multiplied by the peak width at half the peak height, relative to a standard, against quantity of each substance.
(f) Average relative response factor for peak height multiplied by the peak width at half the peak height.

(2) Apparatus used

As already stated, no attempt was made to standardize either the type of apparatus used, the liquid phase, or the operating conditions. These ranged according to individual choice. A summary of the equipment and conditions is given in Table III.

(3) Test and results

The following pure hydrocarbons for calibration and standards were sent to each laboratory:

Benzene	Cyclohexane	n-Octane (Standard for Test Sample 1)
Toluene	p-Xylene	Iso-octane (Standard for Test Sample 2)
Ethylbenzene	n-Nonane	

Calibrations of the apparatus were made as follows:

(a) Benzene, together with 0.3% w/w, 0.6% w/w or 1.0% w/w of toluene, ethylbenzene, cyclohexane and n-octane (standard).

(b) Toluene, together with 2.0% w/w, 4.0% w/w or 6.0% w/w of benzene, ethylbenzene and p-xylene plus 0.5% w/w, 1.0% w/w or 1.5% w/w n-nonane and 0.7% w/w, 1.5% w/w or 2.0% w/w of iso-octane (standard).

Measurements were made of the peak heights, retention distances, and peak widths at half peak height. Calibration graphs were prepared in which the appropriate ratio between the measurements for a constituent and that for the standard, after

TABLE

APPARATUS

| | Laboratory | | | |
	A	B	C	D
Manufacturers	Perkin-Elmer/ Home	Carlo Erba	Perkin-Elmer	Home
Material of construction	Copper	Stainless steel	Stainless steel	Copper
Solid support	Kieselguhr	Celite C22	Chromosorb	I.M.C. brick
Liquid phase	Squalane 20%	PEG 4000 20%	DEHS silicate 10%	DNP 15%
Detector	Katharometer Hotwire	Katharometer Hotwire	Katharometer Thermistor	Flame
Carrier gas	Helium	Hydrogen	Helium	75% H₂ 25%
Column temperature (°C)	128	65	150	118
Method of injection	Hamilton syringe	Hamilton syringe	Hamilton syringe	Micropipette

TABLE III

RESULTS (% w/w) OBTAINED WITH METHOD (a) FROM PEAK HEIGHTS AND CALIBRATION CURVE

Sample	Theory	Laboratory								
		A	B	C	D	E	F	G	H	I
Sample 1										
Benzene	98.04	97.99	98.22	98.06	98.06	98.06	97.84	98.21	98.06	98.17
		98.02	97.94	98.08	98.04	98.00	97.85	98.15	98.11	98.10
Toluene	0.73	0.76	0.68	0.72	0.71	0.72	0.78	0.63	0.72	0.70
		0.75	0.78	0.72	0.71	0.72	0.78	0.66	0.79	0.73
Ethylbenzene	0.80	0.81	0.73	0.80	0.78	0.80	0.91	0.76	0.80	0.73
		0.80	0.87	0.79	0.78	0.83	0.91	0.77	0.78	0.77
Cyclohexane	0.43	0.44	0.38	0.42	0.45	0.42	0.47	0.40	0.42	0.40
		0.43	0.41	0.41	0.47	0.45	0.46	0.42	0.40	0.40
Sample 2										
Toluene	90.64	90.20	93.33	90.48	90.09	90.79	92.60	91.11	91.08	91.20
		90.02	93.28	90.42	90.55	89.79	92.43	91.22	91.01	91.19
Benzene	11.82	11.90	11.36	11.87	11.66	11.78	11.40	11.90	11.86	11.75
		11.82	11.50	11.88	11.93	11.92	11.42	11.90	11.88	11.75
Ethylbenzene	2.60	2.88	2.10	2.75	2.74	2.70	2.20	6.10**	2.52	2.56
		2.65	2.02	2.77	2.74	2.95	2.25		2.52	2.50
p-Xylene	3.72	3.98	2.66	3.74	4.00	3.65	3.00	6.10**	3.48	3.43
		3.65	2.64	3.77	3.96	4.15	3.10		3.51	3.50
m-Nonane	1.13	1.95	0.75	1.16	1.21	1.08	0.88	1.09	1.06	1.06
		0.95	0.76	1.16	1.22	1.19	0.88	1.08	1.07	1.06

** Ethylbenzene and p-xylene not resolved.

TABLE IV

RESULTS (% w/w) OBTAINED WITH METHOD (b) FROM MEAN RELATIVE RESPONSE FACTORS BASED ON PEAK HEIGHTS

Sample	Laboratory								
	A	B	C	D	E	F	G	H	I
Benzene	98.00	98.35	98.05	98.04	98.05	97.84	98.16	98.05	98.05
	98.00	97.93	98.08	98.01	97.98	97.85	98.11	98.10	98.03
Toluene	0.75	0.70	0.72	0.71	0.73	0.77	0.62	0.71	0.74
	0.75	0.80	0.72	0.72	0.74	0.77	0.66	0.79	0.74
Ethylbenzene	0.80	0.67	0.81	0.79	0.83	0.93	0.82	0.81	0.81
	0.80	0.66	0.79	0.79	0.88	0.93	0.82	0.79	0.81
Cyclohexane	0.45	0.38	0.42	0.66	0.39	0.46	0.40	0.43	0.40
	0.45	0.41	0.41	0.88	0.40	0.45	0.41	0.41	0.40
Toluene	89.87	93.93	90.55	90.55	90.76	92.33	——	91.00	91.07
	90.62	93.53	90.41	90.66	89.71	92.13	——	90.92	91.08
Benzene	11.89	11.45	11.85	22.01	11.76	11.88	——	11.83	11.76
	11.80	11.35	11.87	11.98	11.94	11.51	——	11.86	11.75
Ethylbenzene	2.85	1.99	2.75	2.74	2.66	2.23	——	2.58	2.58
	2.63	1.99	2.77	2.73	2.92	2.29	——	2.59	2.56
p-Xylene	4.31	2.73	3.75	3.57	3.76	3.01	——	3.53	3.44
	3.97	2.73	3.79	3.53	4.26	3.14	——	3.56	3.47
m-Nonane	1.08	0.88	1.15	1.09	1.06	0.95	——	1.06	1.15
	0.98	0.88	1.16	1.10	1.17	0.93	——	1.07	1.14

TABLE V

RESULTS (% w/w) OBTAINED WITH METHOD (c) FROM PEAK HEIGHTS × RETENTION DISTANCE AND CALIBRATION CURVE

Sample	Laboratory								
	A	B	C	D	E	F	G	H	I
Benzene	97.99	97.87	98.06	98.13	98.05	97.78	98.20	98.04	98.10
	98.00	97.96	98.10	98.06	98.00	97.78	98.06	98.10	98.14
Toluene	0.76	0.84	0.72	0.70	0.74	0.78	0.64	0.73	0.72
	0.76	0.79	0.72	0.71	0.74	0.79	0.66	0.70	0.71
Ethylbenzene	0.82	0.81	0.80	0.82	0.80	0.98	0.76	0.80	0.78
	0.82	0.85	0.77	0.84	0.84	0.98	0.76	0.78	0.75
Cyclohexane	0.43	0.48	0.42	0.35	0.41	0.46	0.40	0.43	0.40
	0.42	0.40	0.41	0.39	0.42	0.45	0.42	0.41	0.40
Toluene	90.27	93.62	90.47	90.47	90.57	92.36	—	90.98	98.02
	91.00	93.69	90.37	89.94	89.64	91.89	—	90.90	98.21
Benzene	1.86	1.38	1.90	1.95	1.81	1.46	—	1.89	1.74
	1.77	1.28	1.92	2.00	1.96	1.50	—	1.90	1.68
Ethylbenzene	2.80	1.80	2.73	2.68	2.76	2.25	—	2.54	2.64
	2.57	1.82	2.76	2.91	2.99	2.47	—	2.55	2.58
p-Xylene	3.94	2.56	3.74	3.75	3.76	3.01	—	3.51	3.45
	3.62	2.56	3.78	3.93	4.09	3.21	—	3.54	3.41
n-Nonane	1.13	0.64	1.16	1.15	1.10	0.92	—	1.08	1.15
	1.04	0.65	1.17	1.22	1.22	0.93	—	1.10	1.12

TABLE VI

RESULTS (% w/w) OBTAINED WITH METHOD (d) FROM MEAN RELATIVE RESPONSE FACTORS BASED ON PEAK HEIGHTS × RETENTION DISTANCES

Sample	Laboratory								
	A	B	C	D	E	F	G	H	I
Benzene	98.00	97.84	98.05	98.08	98.04	97.84	98.14	98.09	98.02
	98.01	97.92	98.08	98.02	97.98	97.82	98.10	98.10	98.06
Toluene	0.75	0.87	0.72	0.70	0.74	0.77	0.64	0.70	0.75
	0.75	0.81	0.72	0.71	0.74	0.78	0.66	0.70	0.74
Ethylbenzene	0.80	0.82	0.81	0.77	0.83	0.93	0.82	0.79	0.83
	0.80	0.87	0.79	0.79	0.88	0.94	0.82	0.79	0.80
Cyclohexane	0.45	0.47	0.42	0.45	0.39	0.46	0.40	0.41	0.40
	0.44	0.40	0.41	0.48	0.40	0.46	0.42	0.41	0.40
Toluene	90.31	93.10	90.52	90.66	90.64	92.29	—	90.94	98.98
	91.03	93.18	90.43	90.71	89.63	92.00	—	90.88	91.00
Benzene	1.89	1.43	1.85	2.02	1.77	1.49	—	1.82	1.78
	1.80	1.33	1.87	1.98	1.95	1.52	—	1.85	1.92
Ethylbenzene	2.84	1.96	2.73	2.74	2.70	2.25	—	2.60	2.62
	2.62	1.98	2.76	2.74	2.94	2.32	—	2.62	2.54
p-Xylene	3.88	2.71	3.75	3.49	3.82	3.02	—	3.55	3.46
	3.57	2.71	3.78	3.46	4.30	3.20	—	3.57	3.40
n-Nonane	1.08	0.80	1.15	1.09	1.07	0.95	—	1.08	1.16
	0.98	0.80	1.16	1.11	1.18	0.96	—	1.08	1.12

TABLE VII

RESULTS (%, w/w) OBTAINED WITH METHOD (b) FROM PEAK HEIGHTS × PEAK WIDTHS AT HALF PEAK HEIGHT AND CALIBRATION CURVE

Sample	Laboratory								
	A	B	C	D	E	F	G	H	I
Benzene	98.06	98.21	98.13	98.03	98.10	97.76	98.34	98.10	98.03
	97.96	97.81	98.13	98.09	97.99	97.93	98.35	98.18	98.03
Toluene	0.81	0.74	0.71	0.73	0.71	0.87	0.59	0.81	0.74
	0.78	0.78	0.73	0.69	0.69	0.74	0.66	0.80	0.74
Ethylbenzene	0.86	0.70	0.73	0.81	0.74	0.95	0.67	0.65	0.83
	0.81	1.04	0.72	0.78	0.81	0.92	0.56	0.66	0.83
Cyclohexane	0.37	0.55	0.43	0.43	0.45	0.42	0.40	0.44	0.40
	0.35	0.37	0.42	0.44	0.50	0.41	0.43	0.36	0.40
Toluene	89.04	92.42	90.65	91.06	92.19	92.29	—	91.09	90.96
	90.74	93.04	91.08	91.60	90.50	92.18	—	90.81	90.78
Benzene	2.20	1.76	2.02	1.97	1.65	1.57	—	1.93	1.90
	2.15	1.50	1.83	1.87	1.92	1.57	—	1.95	1.88
Ethylbenzene	3.17	2.16	2.95	2.56	2.23	2.29	—	2.43	2.60
	2.90	2.08	2.59	2.44	2.86	2.36	—	2.61	2.68
p-Xylene	4.13	2.84	3.15	3.29	3.16	2.92	—	3.55	3.36
	3.68	2.58	3.54	3.11	3.79	2.98	—	3.58	3.38
n-Nonane	0.56	0.82	1.23	1.12	0.77	0.93	—	1.00	1.18
	0.53	0.80	0.96	0.98	0.93	0.91	—	1.05	1.28

TABLE VIII

RESULTS (%, w/w) OBTAINED WITH METHOD (f) FROM MEAN RELATIVE RESPONSE FACTORS BASED ON PEAK HEIGHTS × PEAK WIDTHS AT HALF PEAK HEIGHT

Sample	Laboratory								
	A	B	C	D	E	F	G	H	I
Benzene	98.00	98.23	97.98	98.03	97.90	97.76	98.26	98.07	97.99
	98.09	98.12	97.98	98.10	97.81	97.94	98.16	98.14	97.99
Toluene	0.76	0.72	0.76	0.73	0.77	0.81	0.60	0.74	0.76
	0.73	0.70	0.78	0.68	0.72	0.72	0.68	0.72	0.76
Ethylbenzene	0.79	0.69	0.83	0.81	0.86	0.97	0.74	0.77	0.85
	0.75	0.81	0.82	0.78	0.96	0.94	0.73	0.78	0.85
Cyclohexane	0.45	0.36	0.43	0.43	0.45	0.46	0.40	0.42	0.40
	0.43	0.37	0.42	0.44	0.50	0.49	0.43	0.36	0.40
Toluene	90.26	93.23	90.65	91.41	92.26	92.29	—	90.89	91.05
	91.09	93.08	90.47	91.43	90.39	92.39	—	90.61	90.90
Benzene	2.10	1.48	1.84	1.91	1.64	1.56	—	1.88	1.83
	2.04	1.45	1.84	1.87	2.03	1.52	—	1.90	1.81
Ethylbenzene	3.03	1.97	2.69	2.56	2.19	2.36	—	2.57	2.58
	2.68	2.00	2.67	2.44	2.74	2.27	—	2.75	2.67
p-Xylene	4.00	2.54	3.66	3.11	3.10	2.89	—	3.67	3.47
	3.65	2.63	3.68	3.28	3.84	2.88	—	3.70	3.49
n-Nonane	0.60	0.83	1.16	1.01	0.81	0.90	—	0.99	1.07
	0.54	0.84	1.14	0.98	1.00	0.94	—	1.04	1.13

TABLE IX

STATISTICAL ANALYSIS OF RESULTS

Method of assessment	Sample 1		Sample 2		Sample 2 (nonane only)	
	Repeatability R_T	Reproducibility R_{DI}	R_T	R_{DI}	R_T	R_{DI}
Peak height						
From curve	0.05	0.10	0.27	1.1	—	—
Mean response (normal)	0.06	0.10	0.32	1.1	0.12	0.52
Mean response (logarithmic transformation)	—	—	13 %	39 %	—	—
Height × retention distance						
From curve	0.06	0.12	0.33	1.2	0.14	0.74
Mean response	0.05	0.13	0.32	1.0	0.13	0.52
Height × width at half height						
From curve	0.16*	0.23*	0.55	1.0	0.30	1.0
Mean response	0.10	0.17	0.49	1.0	0.18	0.77

* Significantly high

TABLE X

MEAN RESULTS EXPRESSED AS PERCENTAGE OF THE TRUE VALUE FOR SAMPLE 1

Method of assessment*	Constituent	Laboratory									Mean
		A	B	C	D	E	F	G	H	I	
(a)	Toluene	103.4	100.0	98.6	97.3	98.6	106.8	89.7	97.3	97.9	98.6
	Ethylbenzene	100.6	100.0	99.4	97.5	101.9	113.8	95.6	98.6	93.8	100.2
	Cyclohexane	101.2	91.1	96.5	105.8	101.2	108.1	95.3	95.3	93.0	98.6
(b)	Toluene	102.7	102.7	98.6	97.9	100.7	105.5	89.0	96.6	101.4	99.4
	Ethylbenzene	100.0	95.6	100.0	98.8	106.9	116.2	102.5	100.0	101.2	102.4
	Cyclohexane	104.6	91.9	96.5	109.3	91.9	105.8	94.2	97.7	93.0	98.3
(c)	Toluene	104.1	111.6	98.6	96.6	101.4	107.5	89.0	98.6	97.9	100.6
	Ethylbenzene	102.5	103.8	98.1	105.0	102.5	122.5	95.0	98.8	95.6	102.6
	Cyclohexane	98.8	102.3	96.5	86.0	96.5	105.8	95.3	97.7	93.0	97.1
(d)	Toluene	102.7	115.1	98.6	96.6	101.4	106.2	89.0	96.6	102.0	100.9
	Ethylbenzene	100.0	105.6	100.0	97.5	106.9	116.9	102.5	98.8	101.9	103.3
	Cyclohexane	103.8	101.2	96.5	108.1	91.9	107.0	95.3	95.3	93.0	99.1
(e)	Toluene	108.9	104.1	98.6	97.3	97.9	110.3	84.2	110.3	101.4	101.4
	Ethylbenzene	104.4	111.2	90.6	99.4	96.9	116.9	76.9	81.9	103.8	98.0
	Cyclohexane	83.7	83.7	98.8	101.1	111.6	96.5	96.5	93.0	93.0	95.3
(f)	Toluene	102.0	97.3	105.5	96.6	102.1	104.8	87.7	100.0	104.1	100.0
	Ethylbenzene	96.2	93.8	103.1	99.4	115.0	119.4	91.9	96.9	106.2	102.4
	Cyclohexane	102.3	84.9	98.8	101.2	111.6	100.0	96.5	90.7	93.0	97.7
Mean	Toluene	104.0	105.1	99.8	97.0	100.4	106.8	88.1	99.9	100.8	
	Ethylbenzene	100.6	101.7	98.5	99.6	105.0	117.6	94.1	95.9	100.4	
	Cyclohexane	99.1	92.6	97.3	101.9	100.7	103.9	95.5	95.0	93.0	

* See Table I.

TABLE XI

MEAN RESULTS EXPRESSED AS PERCENTAGE OF THE TRUE VALUE FOR SAMPLE 2

Method of assess- ment*	Constituent	Laboratory									Mean
		A	B	C	D	E	F	G	H	I	
(a)	Benzene	102.2	73.1	103.0	106.9	101.6	77.5	93.4	102.7	96.2	95.2
	Ethylbenzene	102.8	76.6	102.6	101.8	105.0	82.7	95.2	93.7	94.0	94.9
	p-Xylene	102.6	71.2	100.9	107.0	104.8	82.0		94.0	93.1	94.4
	n-Nonane	88.5	66.8	102.6	102.6	100.4	70.8	96.0	94.2	93.8	90.6
(b)	Benzene	101.4	76.9	102.2	109.6	101.6	82.1	**	101.4	96.4	96.4
	Ethylbenzene	101.8	74.0	102.6	101.7	103.7	84.0		96.1	95.5	94.9
	p-Xylene	107.0	73.4	101.3	100.8	107.8	82.7		95.3	92.9	95.2
	n-Nonane	91.2	70.8	102.2	96.9	98.7	98.7		93.8	101.3	94.2
(c)	Benzene	99.7	73.1	104.9	108.5	103.6	81.3	**	104.4	94.0	96.2
	Ethylbenzene	99.8	67.3	102.0	103.9	106.9	87.7		94.6	97.0	94.9
	p-Xylene	101.6	68.8	101.1	103.2	106.8	83.6		94.8	92.2	94.0
	n-Nonane	96.0	57.1	103.1	104.9	102.6	81.8		96.5	100.4	92.8
(d)	Benzene	101.4	75.8	102.2	109.9	102.2	82.7	**	100.8	101.6	97.1
	Ethylbenzene	101.5	73.2	102.0	101.9	104.8	84.9		97.2	95.9	95.2
	p-Xylene	100.1	72.8	101.2	93.4	109.1	83.6		95.7	92.3	93.5
	n-Nonane	91.2	70.8	102.2	97.3	99.6	84.5		95.6	100.9	92.8
(e)	Benzene	119.5	89.6	105.8	105.5	98.1	86.3	**	106.6	103.8	102.0
	Ethylbenzene	112.8	78.8	103.0	92.9	94.6	86.4		93.7	98.1	95.0
	p-Xylene	105.0	72.8	89.9	86.0	93.4	79.3		95.8	90.6	83.2
	n-Nonane	48.2	71.7	96.9	92.9	75.2	81.4		90.7	108.8	83.2
(f)	Benzene	113.7	78.3	101.1	103.8	100.8	84.6	**	103.8	100.0	98.3
	Ethylbenzene	106.1	73.8	99.6	92.9	91.6	86.0		98.9	97.6	93.3
	p-Xylene	102.8	69.5	98.6	85.9	93.3	107.2		99.0	93.5	93.7
	n-Nonane	50.9	73.9	101.8	88.0	80.1	81.4		89.8	97.3	82.9
Mean	Benzene	106.3	77.8	103.2	107.4	101.3	81.4	**	103.3	98.7	
	Ethylbenzene	104.2	74.0	102.0	99.2	101.1	85.3		95.7	96.4	
	p-Xylene	104.1	71.4	98.8	96.0	102.5	86.4		95.8	92.4	
	n-Nonane	77.7	68.5	101.5	97.1	92.8	83.1		93.4	100.4	

* See Table I.
** Ethylbenzene and p-xylene not resolved

(a) *Repeatability R_T*. For both samples there is no significant difference between the first four methods of assessment but, in general, assessment based on peak height × width at half peak height is less satisfactory. The repeatability for Sample 1 is reasonably satisfactory, but is considerably worse for Sample 2. Contrary to common opinion, therefory, for samples of the type studied, assessment based on peak height only is satisfactory and there is no justification for using more complicated procedures.

(b) *Reproducibility R_DI*. As with repeatability, the first four methods of assessment have had no effect on the reproducibility, but values based on peak height × width at half peak height tend to be less precise.

For Sample 1 the reproducibility is about twice the repeatability but, for Sample 2, this ratio has risen to three times.

(c) *Accuracy*. In Tables X and XI the mean values of pairs of results for each constituent and each method of assessment have been calculated as a percentage of the true value. This is a measure of the accuracy of the results; that is of the nearness of the actual result to the true result.

It will be seen that for Sample 1, no analysis shows a serious bias, the analyses having been reasonably accurate and unaffected by the method of assessment (hori-

zontal means). Laboratory F, however, returned high results, those for ethylbenzene being especially high, and Laboratory G returned low results, those for toluene being appreciably low.

For Sample 2, most of the laboratories returned reasonably accurate results. Laboratories B and F returned results, by all methods of assessment, that were appreciably low (vertical means). These anomalous results, which cannot be explained, have worsened the reproducibility and have lowered the overall accuracy. The accuracy is, however, about the same for assessment by all methods, but the results obtained for *n*-nonane tend to be low.

CONCLUSIONS

Analyses based on the measurements of peak height only are as precise as those based on calculation of peak height × retention distance. Analyses based on peak height × width at half peak height, contrary to commonly accepted opinion, tend to be less precise. Thus, for mixtures of the type examined, there is no justification for using the more complicated methods of assessment.

For the first test sample, consisting of benzene containing approximately 2 % w/w of other hydrocarbons, both the precision and accuracy were reasonably satisfactory. For the second sample, however, consisting of toluene containing about 9.5 % w/w of other hydrocarbons, the precision was appreciably worse. The reasons for the poor repeatability are not apparent, but the poor accuracy obtained by two of the participating laboratories has contributed to the poor reproducibility. The accuracy, based on the means of duplicate tests, obtained by the remaining laboratories was good for analyses calculated from peak heights or peak heights × retention distances, but tended to be less satisfactory for analyses based on peak heights × width at half peak height.

Laboratories A, B and G used liquid phases that are generally not considered the best for the types of hydrocarbon mixtures tested, but only one of these, namely Laboratory G, which used Carbowax 1500, produced no separation of ethylbenzene and *p*-xylene. Laboratory B, which used polyethylene glycol, was one of those returning appreciably low results for Sample 2, but there is no evidence that the use of this liquid phase caused the low results. Further work is in progress to elucidate the causes of the poor precision with Sample 2.

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SUMMARY

Nine European laboratories have taken part in a joint exercise in which two samples, one containing about 98 % benzene and the other 90 % toluene, were analysed, using chromatographic equipment available to each laboratory. For each sample, a known quantity of a specified internal standard was used and the composition of the samples

was calculated from calibration data based on (1) peak height, (2) peak height ×
retention distance, (3) peak height × width of peak at half peak height. The pre-
cision of the results is least for method (3), but method (1) is preferred because it is the
simplest. The results for the toluene sample were less precise than those for the ben-
zene sample. Further work is in progress.

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