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

THE INTERNATIONAL CONFERENCE OF BENZOLE PRODUCERS*

Paris (France)**

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INTERODUCETION

The technique of gas-liquid chromatography (GLC), first described by James and Martin¹ 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

^{*} The International Conference of Benzole Producers, which represents all the major producers of aromatic hydrocarbons from coal sources in Europe, has carried out a series of co-operative tests, summarized in this paper, with a view to standardizing techniques for the analysis of aromatic hydrocarbon mixtures.

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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 tilbe 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 tilbe natio of areas.

- (a) Calculation of the total area is laborious and difficult with complex unixtumes, 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 warw from compound to compound. The response factors can be determined for each of the substances concerned in an analysis and for the apparatus and condittions used. These response factors enable the composition to be determined from peak areas built, owing to the difficulties of assessing the area representing all the components, iit 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 iit will appear on the chromatogram at a point free from other peaks and be used in such quantiity tilhat iit produces a peak of similar size to those being determined. It should be motted tiliat 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 themperatume, gas flow and quantity of sample injected. As it is necessary to callibrate the column, however, it is clear that the precision of any estimation must depend upon the waniation of the response factors with random variations in the standard operating conditions and upon systematic changes in conditions between the time of smalking 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, wanies according to the size of the peaks. Thus the method is fundamentally unsound iff applied to analyses that may involve the measurement of peaks of widely warying 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 operation than measurement of peak heights only. Also, only a high-quality instrument is sattisfactiony.
- (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. All though this relationship varies with retention distance, the proportionality factor is included in the calibration. The advantage of this method of calculation is that the netention 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. Paak haight

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, imstead off peak areas, would have the advantage of needing one measurement instead off 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:

- ((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 amen, the greater convenience of making only the single measurement of peak height should outsweigh all other considerations.

((II)) Gamanall

THE PRESENT TESTS

Im the present series of test, nine laboratories took part, representing the following Europeam countries: Belgium, France, Germany, Great Britain, Italy and the Netherlands. Each laboratory used the equipment and operating conditions awaillable, 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.

TOWERDE II

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- (a) Caliibuatiion curves of peak height relative to asstandhad againstop motitiy offeadhsubstance.
- ((b)) Average relative response flactor for peak height.
- (c) Calibration conves of peak beight moultiplied by retention time, relative to a standard, against quantity of each substance.
- ((d)) Average relative response flaction (for peak likelight modified like rettertion time.
- (e) Calibration conve of peak height multiplied by the prek widthatthalf the peak height, relative to a standard, against quantity of each substance.
- (f) Average relative response factor for peak theight multiplied by the peak will at half the peak beight.

((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. Whese manged 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:

Ethylbenzene m-Noname

Calibrations of the apparatus were made as ffollows:

- (a) Benzene, together with 0.3 % w/w, 0.6 % w/w or 11.00 % w/w off tolliene, etilyil-benzene, cyclohexane and m-octane ((standard)).
- (b) Toluene, together with 200% w/w, 400% w/w or 600% w/w off benzere. ethylbenzene and p-ylene plus 05% w/w, 1100% w/w or 15% w/w nonnere and 0.7% w/w, 15% w/w or 20% w/w offiso-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

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Detector	Hotwine	Heatwine	Ikadilaranetur Ililaranistan	Hilame
Carrier gas	[Hielingan	Hillyallangen	FREE Fingeron	7/50% HILL 250/00
Column temperature (°C)): n=25	65	III-	nings
Method of imjection	"Hammiltom syringe	FH annilltoms sydinge	Hamiltonswinge	Micropipatte

correction for the quantity of standard, were plotted against concentration in the calibrating mixture free from standard. For peak heights, for example, the ratio:

$$\frac{p_z \times S \times 100}{p_s (100-S)}$$
 was plotted against $\frac{1000 t}{(100-S)}$

where p_t and p_s are the peak heights for toluene and standard, t and S are the quantity of toluene and standard in the calibrating mixture. Separate calibration graphs were prepared for each of the six criteria mentioned above under "The Present Tests: ((1)) General".

Test Samples I and 2, the compositions of which are shown in Table III, were then analysed in duplicate in each laboratory and the peak heights and widths at half peak heights and retention distances were reported. The compositions of the two unknown samples were then assessed from these data, according to the six methods (a) to (f). The results are given in Tables III to VIII inclusive.

For each of the methods of assessment of the composition of Samples I and 2, a statistical calculation has been made of the Repeatability R_T and the Reproducibility R_{DL} . These may be defined as follows:

Repeatability R_T is the difference between duplicate results, on the same sample, by one operator, using one set of apparatus, that would be equalled or exceeded, im the long run, in only one case in twenty.

Reproducibility R_{DI} 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.

No significant differences were found in the precision of the determination of the components within Sample 1, but for Sample 2 it was found that the results for m-nonane had to be considered separately. Overall precision figures have therefore been calculated for Sample 1 and for Sample 2 excluding m-nonane. The precision figures for Sample 1 are applicable to impunities present in quantities less than 1 % and those for Sample 2 for the range 1.5-4%. These results are given in Table IX.

The following points emerge from an examination of this table:

DITIONS-

		Laboratory		
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Glass-	Stainless steel	Copper	Соррет	Statimiless steell
Celite 545	Chromosorb P	Cellite C22	Chromosorb	4.W. C22
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20.0/	30%	25%	20 % / m	யம் ^இ ற
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**RESULIS_((%)\w/\w))_GUBLAINIDAWTEHNMETHODD((A))FROMPEAKHEIGHTSANDCALLBRATION\CURVES

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TABILE W

RESULUS ((% W/W)) (OBICALINED WITH METHOD ((C)) TROW FEAR HULIGHUS % RELEASING IDESTANCE: AND CALIBRATION CURVE

15°					Acids matern	ay .			
Sample -	ना	<i>IB</i>	C	<i>II</i> D)	Œ	Œ	(Gr	<i>IIII</i>	Æ
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	ത്യൂട്ടു.തര	97.96	றுவாம	98.00 6	ത്രി	977:778	ுற்கு.யடு	ஞ் பாம்	் இது ப
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	·076	O79	(D.:7722	Ф.7T	· Ø7741	(മു.;779)	ന്ത. (തിത ്	(0).77,111	(0).77.1
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	O.82	©.\$55	ത.777	യ8341	ത 84	ത.ത്രങ്ക	(0).776)	(D).7/8	(0):775
Cyclohexane	· Ø43	ത.ഷ്ട്	(0).2422	· co335	നും.എന	താഷത്	ത്രാന്റ്	തപ്പുങ്ങു	(D): 44(
	(O.42	ത.എത	ம.அம	· @399	மு.அ2	 Ф. 11 22	(0) il 2:	(ao-Him	തഷം
Toluene	90.27	93.62	90.47	90.417	·900.577	(<u>9)2233</u> 66		ത്രതാത്രി	ு இத் ம
	ூர்மூ	93.69	90.37	89.94	89.64	ுறா. இரு		(മാന)(മാന)	98.21
Benzene	п.:86	п3/8	пфю	JI. 995	ur.\88\n	மு:#1@		ம்.ஆம்	ш.7/
	п77	п28	п.992	22.00 00	ம#ூ∕டு	ar.,5500		முற்ற	nr.(6)
Ethylbenzene	2.80	п80	2.73	22.66 8	2.76	2.25		22.5541	22.65
	2.57	п.,82	22.766	22.991	2:00	2.417		22.555	22.55
p-Xylene	33.94	22.5/6	33-7741	3-75	3.76	33,000		33.570	33-11
	3.62	2.56	3.78	3:93	44.7199	33,:2011	-	33-554	33-11
m-Nomane	ппз	ത66#	пп65	11.1155	பா.பாம	(0)(9)22		III.(00/88)	п.п
	IIO.H	യ.6 5 5	п1177	II.22	II.222	ത്രത്രു		III.IIIO)	IL.II

TABLE WI RESULTS ((% W//W)) (OBTAINED WITH MEDHOD ((d)) PROM MEAN RELATIVE RESPONSE PACHORS BASED ON PEAK BEIGHTS % RELEASING IDENTIFIES

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Sample -	भा	IB	C	270)	Œ	Æ.	(G)	IH I	II.
Benzene	തയ്യു.	97.84	9 8.05	· 98.08	௵8.ஶ்௮	977.84	ுக்.ர்	തുങ്കുന്തു	(0) (02
	ற8.ரா	97.92	ௐ ® ௐ	· ගු 8ග <u>ଅ</u>	'977.19 8	97.82	இது.பால	முக்கிற்	(D) B. (D) (
Foluene	· 075	©87	O.72	· @7@	· (D.: 7/4)	(O.7////	மு.(ந்யு	(D).77III	(D).775
	· Ø75	ம்.ஆா	O.72	· (D.:771	· Ø.:77#	'O.,778'	(D)(O)	((0). 777 (0)	(0).774
Ethylbenzene	(O. (8 0	യ82	ு.88π	O.777	ത.ജ്ജ	ത്യത്തുട്ടു	ന്തു.	(@ \.\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	ලකියගා
	(O.:80	·87	യ.79	(D. 779)	ത്തിങ്ങ	എ.തുഷ	ത്തിക്കു	(D).77(9)	താഷ്ട്രദ
Cyclohexame	(O.445)	O.4177	(D.4)22	መ-45	ത.:3399	എഷ്ക	(CO)-TH(CO)	(@ >−#im	(D): #0
	(O##	ത.ഷത	ம்.≄π	ത.ഷൂക്	തഷ്യത	ு க்கு	ത്ര <u>ച്ചുമ</u>	(क)- मिं ग्रा	(D) 140
Toluene	ுற்.தா	93.10	go.52	. 900666	ത്തുത്ഷ	(9)229)	·	ർത്ത തു	@ B :@f
	னாத	93.18	ത്രമ.പ്പട്ട	900.71	8 9.63	തുമ.ത്ത		രാനു ജൂജ്.	னுமு
Benzene	п. 89	114133	п.885	22.002	u////	TT-14169)		III. (#1)22:	п.76
	п80	113333	11.887	119 %	m.:9055	ш.5522		III. (8)55	III.(Q)1
Ethylbenzene	2.84	пனுக	22.73	2.74	2.70	2.25		:22.(6m	22.6 0
-	2.62	n98	2.76	2:74	22.00)41	2.32		: 2: (62:	22.56
<i>p</i> -Xylene	3.88	2.71	33-775	3-49	3.82	3,002		33-355	33:-11
	3.57	2.71	33.7788	3.416	44.300	33200		33-577	33°-#
m-Nonane	பம்8	ത.ജന	IIII 55	01.00g	UI ((CD) 77	ത്യമുട്ട		TII.(00)(E)	п.п
	@.98	തജ്മ	п.л66	п.пп	வக	ത്ത്ര		TIL ACOUNTE	m.m

TABLE WILL

HERENUMES $(\binom{(0)}{N}, \mathbf{W}/\mathbf{W})$ Coeximined With Method (\mathbf{b}) from hear; heights \times peak; widths at half heartheight and cameration curve:

1. 55 (A) 1					Labbentoes	ώ.			
- Sample -	.441	EB.	Œ	D)	Æ	F i	G;	H!	I
Hierozene	38336	GB 2211	98 133	ඉතිරනු	983 m	97,76	9S:34(98.10	98.03
	C077-C000	937, SSU	ஷ்ணாலு	98309)	97,99)	977933	98:35	98.18	98.0
III colinazione	co SSE	00:7744	00.771	00723	O) 7/30	02877	0259	0.81	0.7
	$\mathbf{co}_{77}\mathbf{S}$	0.778	00.733	യർളു	O169)	0:74	0:66	0.80	0.74
HEifflyd Il berozeroe	00.536	007/00	00.7733	oo Sin	027/44	02955	0:67/	0.65	0.83
	co.\$33cm	IE CO24:	00 7722	o.,7 5 8	018 10	01922	0.56	0.66	0.83
(Civallo linesseeme	CO:3377	CD 3355	00.483	CD.483	014 <u>5</u> 5	0142	0:40	0.44	0.40
	(CO 3355)	co 3377	യഷമ	क्याना	0155U	O) tir	02433	0.36	0.40
Hirotherence	8890944	कुछ-भूष्ट	990655	gmats	92:19)	92:29)		91109	90.90
	(90)7714	(1332044)	ggra 0258	ரோடும ்	901501	92.18		90.SI:	90.7
HRICE TRANSPORTER	ושוגביונב	11:77.15	22022	11.977	11.655	II.557/		1193	1.90
	22:055	115500	\mathbf{n} SS333	11.877	nge	IL 577		1195	1.88
HEfflhyill berozerne	33:1177	22.1165	22925	22,555	2:233	2129)		2:43	2.60
	55000	22:058	22,500	22.4141	22 S65	2236		2:61	2.68
the Ministerne.	44,1133;	22.SS44	33.1155	3320)	33 1160	22922		3-55	3.39
	33:1158	22:558	33.5544	33 1111	33 7/9)	2298		3.58°	3.38
m-Noneme	முன்	ගානික:	11.233	11, 1122	02777	01933		ILOO	1.18
	CO 5533	con Silono	യയ്ക്ക	യമുട	01933	01911		1105	1.28

TABLE VIIII

FRESULTE: (((%), w/w)) CORTAINED WITH METHOD (()) FROM MEAN RELATINE RESPONSE FACTORS BASED

(ON PERANCHETURES × PERANCWIDTHS AUTHALIS PERANCHETURE)

corrections.					Llabbenstory	ù.			
Siample -	.41	<i>B</i> 3:	æ	D)	Æ	B	G;	H.	1
IR emzeme	്യൂട്ട അത	956233	93779338	ള്ളവുള	977.9900	97,76	98:26	98:07	97.99
	ത്രമാത്ത	998 1122	93779388	988 100	977.Sm	97/94	98:16	98:14:	97.99
III collegeners:	(D) 77.60	00:772:	90.76 6	00.733	90777	O.Stu	0260)	0.74	0.76
	(0:7733)	00:7700	00788	co 638	01722	0.72	o₂6 S ∂	0.72	0.76
HEtilayi II berozaeree	(0)77.9)	00.000	ගා නිසු	oo,88aa	0)88 8	01977	01731	0.77	0.85
	00:7/50	00 SSEE	യട്ടു	ou7/88	თვნ ნ	01934	01733	0.78	0.8
Cycillothessenre	(0)455	രം ജ്ഞ	മാച്ചുട്ടു	വച്ചുട്ട	00.455	0.46	0240	0:42:	0.40
	CO:483	œ <u>3377</u>	00.422	00. 1 1 1	0) 571	0.40	02433	0.36	0.40
Ilfollosoe	ത്തായര	933233	9900 GG55	் பா4ரா	92:26 5	92:29)		90:89:	91.0
	COLUCTORIO)	933 ca 18	9900.497	GTT.433	900390	92:39)		90:61:	90.90
Hammerne	22:1100	II.483	11 SE44	поп	11.64	n.56		1.88	1.8
	22,0014	II 455	II 884	11.8877	22033	11.52		1190	1:8
HE this I be present	33,0033	11.0077	22600	22.5 <u>5</u> 66	22,1000	2236		2:57	2:5
	22:0638	22,0000	22,6677	22.414	22.7741	2:27		2:75	2.6
A Skyllene	44:0000	22:5514:	33066	33.77	33.100	22 S9)		3:67	3:4
	33055	22.00gg:	336688	33288	33834	2488		3:70	3:49
m-Montanne	C12.6660	യം ക്രൂട്ട	111111111111111111111111111111111111111	II. On II.	00.89m	0290)		0.99	I.O
	ത്തു	CO 5844	III II41	00.9988	ILOO)	0194		I104:	ILI

TABLE IX
STATISTICAL ANALYSIS OF RESULTS

18 -12 - 2 -4	Sam	rpic z	Sampl	c z	Sample 2 (nonane only	
Method of assessment	Repea- tability R _T	Repro- ducibility R _{D1}	R_T	R_{D1}	R _T	R_{D1}
Peak height						
From curve	0.05	0.10	0.27	1.1		
Mean response (normal)	0.06	0.10	0.32	I.I	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

 $\begin{tabular}{ll} TABLE\ X \\ \hline \end{tabular}$ Mean results expressed as percentage of the true value for sample 1

Method	C1:1					Laboratory					Mean
of essess-	- Constituent -	A	В	С	D	E	F	G	Н	I	Jul ensi
(a)	Toluene	103.4	100.0	98.6	97-3	98.6	106.S	89.7	97-3	97-9	98.6
	Ethylbenzene	100.6	100.0	99-4	97-5	101.9	213.8	95.6	98.6	93.8	100.2
	Cyclohexane	101.2	91.1	96.5	105.8	101.2	1.801	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	9S.Š	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	Sg.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.S	98.0
	Cyclohexane	83.7	83.7	98.8	101.1	111.6	96.5	96.5	93.0	93.0	95-3
(£)	Toluene	102.0	97.3	105.5	96.6	102.1	104.8	87.7	100.0	104.1	100.0
1-7	Ethvlbenzene	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.S	97.0	100.4	106.8	SS.I	99.9	8.001	
pr	Ethylbenzene	100.6	101.7	98.5	99.6	105.0	117.6	94.I	95.9	100.4	
•	Cyclohexane	99.1	92.6	97-3	101.9	100.7	103.9	95.5	95.0	93.0	to prove

^{*} See Table I.

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

Method	- Constituent -					Laboratory	•				
eff assuss-	- Conseiluene -	A	B	С	D	E	F	G	H	r	- Mean
(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		93.7	94.0	94.9
	p-Xylene	102.6	71.2	100.9	107.0	104.8	82.0	95.2	94.0	93.1	94.4
	m-Nonane	SS-5	66.8	102.6	102.6	100.4	70.8	96.0	94.2	93.8	90.6
(b)	Benzene	IOL.4	76.9	102.2	109.6	101.6	82.1		101.4	96.4	96.4
-	Ethylbenzene	IOI.S	74.0	102.6	101.7	103.7	84.0	**	96.i	95.5	94.9
	p-Xylene	107.0	73-4	101.3	100.8	107.8	82.7		95.3	92.9	95.2
	m-Nonane	91.2	70.8	102.2	96.9	98.7	98.7		93.8	101.3	94.2
(c)	Benzene	99-7	73.I	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	IOI.I	103.2	106.8	83.6		94.8	92.2	94.0
	m-Nonane	96.o	57.I	103.1	104.9	102.6	81.8		96.5	100.4	92.8
(d)	Benzene	IOI-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.I	72.8	101.2	93-4	109.1	83.6		95.7	92.3	93.5
	m-Nonane	91.2	70.8	102.2	97-3	9g.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.Ś	102.0
- "	Ethylbenzene	112.8	78.S	103.0	92.9	94.6	86.4	**	93.7	98.1	95.0
	p-Xylene	105.0	72.S	89.9	86.o"	93.4	79.3		95.8	90.6	83.2
	m-Nonane	48.2	71.7	96.9	92.9	75.2	81.4		90.7	108.8	83.2
(f)	Benzene	п13-7	78.3	101.1	103.8	100.8	84.6		103.8	0.001	98.3
	Ethylbenzene	106.1	73.8	99.6	92.9	91.6	86.o	**	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
	m-Nonane	50.9	73.9	101.8	88.o	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	
	#-Xylene	104.1	71.4	98.8	96.0	102.5	86.4		95.8	92.4	
	m-Nonane	77-7	68.5	101.5	97-1	92.8	83.1		93.4	100.4	

^{*} See Table I.

(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 \times 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_{Dl} . As with repeatability, the first four methods of assessment have had no effect on the reproducibility, but values based on peak height \times width at half peak height tend to be less precise.

For Sample I 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 I, no analysis shows a serious bias, the analyses having been reasonably accurate and unaffected by the method of assessment (hori-

^{**} Ethylbenzene and p-xylene not resolved

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

For Sample 2, most of the laboratories returned measonably accurate mesults. Laboratories B and F returned results, by all methods of assessment, tihat were appreciably low (vertical means). These anomalous results, which cannot be explained, have worsened the reproducibility and have llowered the overall accuracy. The accuracy is, however, about the same for assessment by all methods, but tihe 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, then 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 measurably satisfactory. For the second sample, however, consisting of troluene containing about 9.5% w/w of other hydrocarbons, the precision was appreciably worse. The measure 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 memaining laboratories was good for analyses calculated from peak heights or peak heights meteration 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 off these, mandly Laboratory G, which used Carbowax 1500, produced no separation of ethylbenzene and p-xylene. Laboratory B, which used polyethylene glycol, was one off those meturning 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 (I) peak height, (2) peak height \times retention distance, (3) peak height \times width of peak at half peak height. The precision of the results is least for method (3), but method (I) is preferred because it is the simplest. The results for the toluene sample were less precise than those for the benzene sample. Further work is in progress.

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