Study of the relative response factors of various gas chromatograph–flame ionisation detector systems for measurement of C_2–C_9 hydrocarbons in air

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Abstract

The assumption of an instrument response that is linear with carbon number is frequently used to quantify atmospheric non-methane hydrocarbons (NMHCs) when using gas chromatography (GC) and detection by flame ionisation detector (FID). In order to assess the validity of this widely used method the results of intercomparison measurements by 14 laboratories across Europe were evaluated. The intercomparison measurements were made on synthetic, gravimetrically-prepared, gas mixtures containing 30 hydrocarbons (C_2–C_9) in the low ppbv range, using various different GC–FID systems. The response per carbon atom of GC–FID systems to individual NMHCs, relative to that of butane, were found to differ by more than 25% across different systems. The differences were mostly caused by analytical errors within particular GC–FID systems and to a more minor degree by systematic deviations related to the molecular structure. (Correction factors due to the molecular structure would lessen the differences, e.g. by about 5% for olefin compounds.) The differences were larger than 10% even after elimination of obvious outliers. Thus, calibration of GC–FID systems with multicomponent NMHC mixtures is found to be essential whenever the accuracy of NMHC measurements is required to be better than about 10%. If calibration by multicomponent gas mixtures is not possible and effective carbon atom response factors are used to quantify the individual NMHC compounds then the particular analytical system should be carefully characterised and its responses to individual compounds be verified.
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Keywords: Air analysis; Hydrocarbons; Gas chromatography; FID

1. Introduction

Hydrocarbons play an important role in atmospheric chemistry [1–3], especially as precursors for photochemical formation of tropospheric ozone and other photo-oxidants [4]. Some of the hydrocarbons are toxic, such as aromatic compounds like benzene. Due to their differences in reactivity and toxicity the measurement of individual hydrocarbons is necessary. Typically, about 50 individual hydrocarbons with chain lengths between C_2 and C_9 are found in the air at concentrations ranging from a few ppbv (parts per 10^{-9} by volume) in urban air to sub-ppbv in rural and background

air [5,6]. Measurements of individual hydrocarbons are also required for other purposes, such as the control of indoor air quality and the determination of the composition of natural gas and petroleum distillates.

Four steps are usually involved in a typical analysis of individual NMHCs in air: sampling, pre-concentration, separation and detection. Air samples analysed off-line may be collected in special containers and pre-concentrated in the laboratory prior to the analyses or air samples may be directly adsorbed onto suitable adsorbents during collecting. Alternatively, air may be sampled directly by an on-line instrument. Because of the limited sensitivity of current detectors and the usually low NMHC concentrations in ambient air (lower ppb and sub-ppb range), air analysis requires an initial pre-concentration of the NMHCs before their separation

and detection. After pre-concentration, the individual NMHC compounds are usually separated using a capillary gas chromatography (GC) column and then detected by a flame ionisation detector (FID) or by a mass spectrometer [5,6].

The FID is the most frequently used detector because of its low purchase and running costs, robustness, high sensitivity, large linear range and relatively simple operation. In addition, the nearly linear dependence of its response on the number of carbon atoms in the hydrocarbon molecule is considered to be a major advantage, because it enables the measurement of almost all NMHCs with only one or two component calibration gas mixtures. This linear dependence has been reported for both lower and higher hydrocarbons [7–14]. Perkins et al. [9] found for C_6–C_{20} alkanes a maximum difference from strict linearity of less 1%. Dietz [12] measured relative sensitivities for C_1–C_{10} hydrocarbons and found a maximum difference of 12%, for benzene, whilst the majority of hydrocarbons showed differences of about 2–3%. Tong and Karasek [14] determined the carbon number responses of 16 alkanes (C_{14}–C_{32}) and found them to have a relative standard deviation of 1.4%. Apart from ethyne, which usually shows an anomalous FID response [15], the calibration of FIDs using one or two compounds as a standard (e.g. butane and benzene) has become a common method for the quantification of NMHCs [6,16].

A common feature of the reports mentioned above is the use of an optimised gas chromatographic system by a highly qualified research laboratory. In addition, all measurements of the FID response factors (except that by Apel et al. [16]) were made by the injection of highly concentrated NMHC mixtures without the pre-concentration and cryo-focussing which are normally used for air analysis. If, however, linearity of response to carbon number is to be assumed in the measurement of NMHC from air matrices then there are, at the least, several prerequisites: a quantitative preconcentration, desorption, and transfer of NMHC analytes to the analytical column; a sufficient separation of the compounds without co-elution with unknown compounds, and optimum working conditions of the FID. The results of recent intercomparisons of NMHC determination in air [16–18,20,21] suggest, however, that these prerequisites are frequently not being fulfilled completely in the routine monitoring of NMHCs in air.

The results of the recent AMOHA intercomparison measurements (Acurate Measurements of Hydrocarbons in the Atmosphere [18], partially funded by the EU) provide a unique data base to study the viability of the assumed linear carbon number response for monitoring of NMHCs in ambient air. During each of the second and third AMOHA intercomparison measurements in 1998 and 1999 a group of 14 European laboratories analysed synthetic 30-component hydrocarbon gas mixture of unknown concentration in the low-ppbv range by using different GC–FID systems. The analytical results were then calculated in two different ways. One method of calculation (and that one used in the main AMOHA report) relied on the specific calibration of all of the hydrocarbons being analysed by the GC–FID systems,

using a multicomponent standard gas mixture containing the same hydrocarbons that were in the unknown mixture but whose concentrations were known (and were also in the same general range as the unknown mixture). The other method of calculation used only a single component standard (butane), with the assumption of strict linearity between the GC–FID response and the carbon number of each hydrocarbon.

The results of these two methods of calculation are shown in Fig. 1 for the second intercomparison and in Fig. 8 of reference [18] for the third intercomparison. In Fig. 1 the value for the difference for each hydrocarbon is the difference between the gravimetric concentration and the measured concentration obtained by each laboratory as then averaged across all of the laboratory results, after 86 outliers identified by Nalimov test [22] had been removed from a total of 390 values. It can be seen from Fig. 1 that the great majority of the mean absolute differences resulting from butane calibration are significantly higher than those that are based on the substance-specific calibration using all the hydrocarbons in the calibration mixture. The standard deviations of the differences, indicated by a line along each bar, are also significantly higher for the butane calibration than for the substance-specific calibration in a large majority of cases. The results of the third intercomparison presented in Fig. 8 of reference [18] are very similar and, therefore, are not presented here.

The aim of this study is to utilise the data obtained in the second and third AMOHA measurements to check the validity of the assumption that the response of GC–FID systems is linear with carbon number, as commonly used in the routine monitoring of NMHCs in ambient air, and to specify any potential error sources. The following data analysis is based on the assumption of a high accuracy of the gravimetrically prepared synthetic mixtures. The uncertainty of the NMHC concentrations in the synthetic mixtures was better than 0.5% (see the following section).

2. Experimental

The structure of the AMOHA intercomparisons and the gravimetric preparation of the synthetic test and standard gas mixtures are described in detail elsewhere [18]. Table 1 lists the participants of the second and third intercomparisons and Table 2 summarises the measurement techniques used. Laboratories are coded by letters in Table 2 to ensure confidentiality.

The preparation of the synthetic test and standard mixtures, conducted by the National Physical Laboratory (NPL) can be summarised briefly as follows [18]: the normally-gaseous hydrocarbons were weighed in suitable quantities into a number of different cylinders. The contents of these cylinders were combined in stages into a single cylinder, with further weighing at each stage. The normally-liquid hydrocarbons were mixed as liquids, with an individual weighing of each one, to produce a single mixture of liquids.
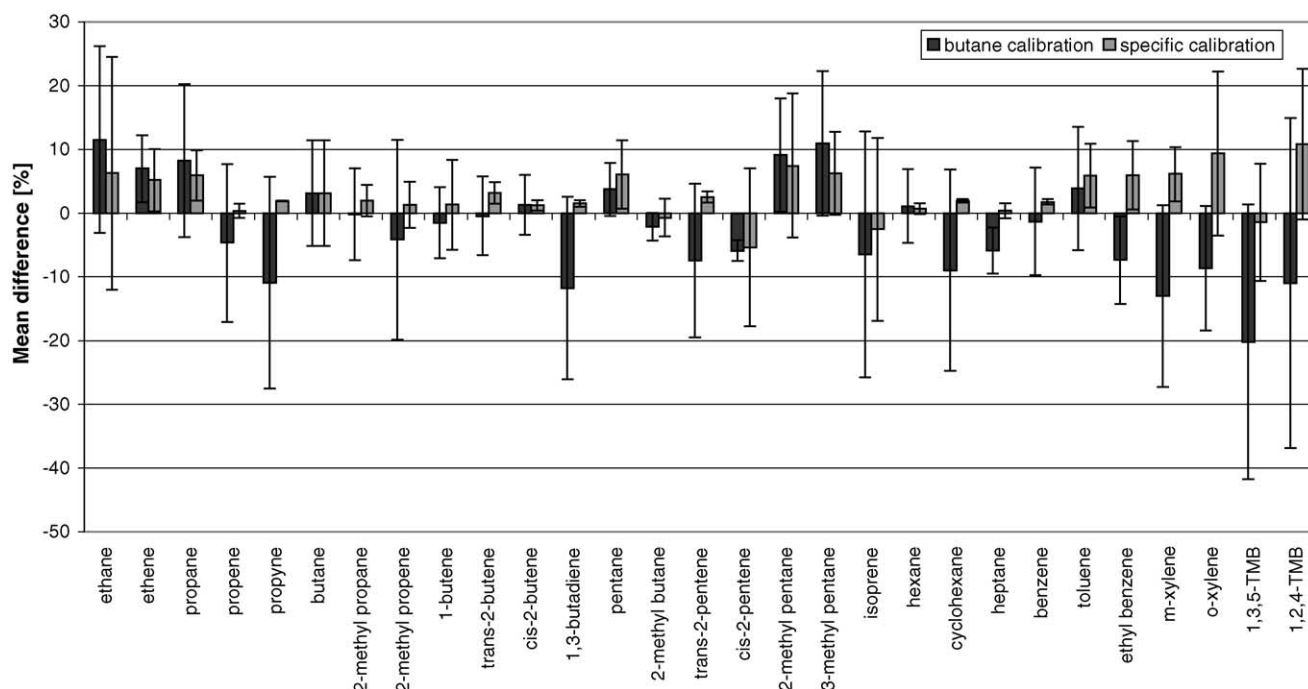
Fig. 1. Differences from gravimetric values as averaged across all laboratories for substance-specific calibrations and for calibrations using butane as a single calibrant for the second AMOHA intercomparison using a 30-component synthetic test mixture. Outliers identified by Nalimov test [22] are eliminated. The line along each bar indicates the standard deviation of the values that were averaged to produce the bar value. TMB stands for trimethyl benzenes.

A weighed portion of this mixture was injected into a cylinder and diluted with nitrogen in such way that all hydrocarbons evaporated. Finally, the normally-liquid and normally-gaseous hydrocarbons were combined into a single cylinder, in which the individual hydrocarbons had concentrations in the low ppm (parts per million by mole fraction) range. The resulting mixture in the ppm range was reduced to the required concentration in the low-ppb (parts per billion by mole fraction) range by two successive gravimetrical dilutions with freeze-dried high-purity nitrogen to produce a single parent cylinder of each mixture. Two different gas mixtures were used in each of the second and third intercomparisons: one was used as a calibration and the other as a test gas mixture. The compositions of all gas mixtures are given in Table 3.

The analytical measurements were carried out as blind intercomparisons. Each laboratory was asked to report at least five successive measurements of each test and calibration

Table 1
Institutions participating in the second and third AMOHA intercomparisons

Institution	Country	Intercomparison
Messer Griesheim (MG), Duisburg	Germany	2
University of East Anglia (UEA), Norwich	United Kingdom	3
Slovak Hydrometeorological Institute (SHMU), Bratislava	Slovakia	2, 3
Istituto sull'Inqinamento Atmosferico del C.N.R. (CNR), Monterotondo Stazione	Italy	2, 3
Instituto de Salud Carlos III (ISC), Madrid	Spain	2, 3[a]
Fraunhofer Institut für Atmosphärische Umweltforschung (IFU), Garmisch-Partenkirchen	Germany	2, 3
Ministry of Environment and Energy (MEM), Roskilde	Denmark	2
TNO, Appeldoorn	The Netherlands	2, 3
Czech Hydrometeorological Institute (CHMU), Prague	Czech Republic	2, 3
Forschungszentrum Jülich GmbH (ICG3), Jülich	Germany	2, 3
Leeds University (UL), Leeds	United Kingdom	2, 3
Norwegian Institute for Air Research (NILU), Kjeller	Norway	2, 3
Deutscher Wetterdienst (DWD), Hohenpeißenberg	Germany	3
Finnish Meteorological Institute (FMI), Helsinki	Finnland	3
Eidgenossische Material- und Prüfanstalt (EMPA), Dübendorf	Switzerland	2, 3
Vlaamse Milieumaatschappij (VMM), Gent	Belgium	2
Institut National de l'Environnement Industriel et des Risques (INERIS), Verneuil-en-Halatte	France	2, 3

[a] Due to technical problems no measurements reported.

Table 2

Methods used by the AMOHA participants in the second and third AMOHA intercomparisons

Institution	GC system	Column(s)	Preconcentration trap	Detector	Dryer
D (second)	Siemens Sichromat II	ASTEC Gas Pro GSC, 0.32 mm dia., 60 m, prec. Sorbitol on Chromosorb WHP 80/100	Glass beads, $-196\,^\circ$C, 400–600 cm^3	FID	Chromatographic (Sorbitol precolumn)
D (third)	Siemens Sichromat II	ASTEC Gas Pro GSC, 0.32 mm dia., 60 m	Glass beads, $-196\,^\circ$C, 400–600 cm^3	FID	None
L (second)	Carlo Erba Megair VOC Analyser	Al$_2$O$_3$/Na$_2$SO$_4$, 0.32 mm dia., 50 m or WAX CV20M, 0.32 mm dia., 50 m	Tenax GR, $-150\,^\circ$C, 30 cm^3	FID	None
F (second, third)	Varian 3600 X	CP-Sil 5CB, 0.25 mm dia., 50 m and Gas Pro GSC, 0.32 mm dia., 15 m	Carbopack BHT, $-120\,^\circ$C, 400 cm^3	FID + MS (third)	Cold trap, $-30\,^\circ$C
F (second)	Chrompack CP 9000	Al$_2$O$_3$/Na$_2$SO$_4$, 0.53 mm dia., 50 m	Carbotrap, $-25\,^\circ$C, 400 cm^3	FID	Mg(ClO$_4$)$_2$ + NaOH
N (second, third)	Chrompack VOC-Air	Al$_2$O$_3$/KCl, 0.32 mm dia., 50 m	Carbosieve + Carbotrap + Carbotap C, $-30\,^\circ$C, 500 cm^3	FID	NaOH
I (second, third)	Carlo Erba 4160	Al$_2$O$_3$/Na$_2$SO$_4$, 0.53 mm dia., 50 m	Carbopack B, $-150\,^\circ$C, 250 cm^3	FID	None
H (second)	Carlo Erba 5300 Mega	Al$_2$O$_3$/Na$_2$SO$_4$, 0.53 mm dia., 50 m	Tenax, $-150\,^\circ$C, 450 cm^3	FID	Ascarite + K$_2$CO$_3$ + NaOH
R (third)	Hewlett-Packard 5890	Al$_2$O$_3$/KCl, 0.53 mm dia., 50 m	Glass beads, liq. argon, 60 cm^3	FID	Nafion
T (second, third)	Fisons Trace Gas Anal.	CP-Sil 5, 0.53 mm dia., 50 m and RTX-volatiles Restek, 0.53 mm dia., 30 m	TenaxGR, $-150\,^\circ$C, 200 cm^3 (second) Carbopack B, $-150\,^\circ$C, 200 cm^3 (third)	FID	None
Q (second, third)	Chrompack CP 9001	Al$_2$O$_3$/KCl, 0.32 mm dia., 25 m	Carbosieve + Carbotrap + Carbotap C, $-21\,^\circ$C, 1800 cm^3	FID	Nafion
C (second, third)	Varian 3400 CX	Al$_2$O$_3$/KCl, 0.53 mm dia., 50 m	Hayesep D, $-44\,^\circ$C, 200 cm^3	FID	Nafion
P (second, third)	Chrompack CP 9000	Al$_2$O$_3$/Na$_2$SO$_4$, 0.32 mm dia., 50 m	Glass beads, $-196\,^\circ$C, 400 cm^3	FID	K$_2$CO$_3$ + NaOH
A (second, third)	Chrompack CP 9000	Al$_2$O$_3$/Na$_2$SO$_4$, 0.32 mm dia., 50 m	Glass beads, liq. Argon, 200 cm^3	FID	K$_2$CO$_3$ + NaOH
M (second)	Chrompack VOC-Air	Al$_2$O$_3$/KCl, 0.32 mm dia., 50 m	Poraplot Q, $-130\,^\circ$C, 100 cm^3	FID	None
K (second)	AI Cambridge GC94	Al$_2$O$_3$/Na$_2$SO$_4$, 0.53 mm dia., 50 m	Carbosieve + Carbotrap + Carbotrap C, $-25\,^\circ$C, 800 cm^3	FID	Cold trap + K$_2$CO$_3$
K (third)	AI Cambridge GC94	Al$_2$O$_3$/Na$_2$SO$_4$, 0.53 mm dia., 50 m	Carbosieve SIII, $-40\,^\circ$C, 500 cm^3	FID	Cold trap + K$_2$CO$_3$
G (second)	Fisons 8000	CP Sil 5 CB, 0.32 mm dia., 50 m	Silica cold trap, $-150\,^\circ$C, 2000 cm^3	FID	None
G (third)	Chrompack CP 9002 + Perkin Elmer ATD 400	CP Sil 5 CB, 0.32 mm dia., 50 m	Carbotrap + Carbosieve SIII, $-10\,^\circ$C, 2000 cm^3	FID	None
B (third)	Varian 3600 CX	Al$_2$O$_3$/KCl, 0.53 mm dia., 50 m	Glass beads, $-186\,^\circ$C, 400–500 cm^3	FID	Nafion
B (third)	Varian 3400 CX	BPX-5, 0.22 mm dia., 50 m	Carbopack C + Cabopack B, 40 $^\circ$C, 300–800 cm^3	FID (+MS)	None
E (third)	Hewlett-Packard 5890	HP Al$_2$O$_3$/"M", 0.32 mm dia., 50 m	Glass beads, $-196\,^\circ$C, 60–80 cm^3	FID	K$_2$CO$_3$ + NaOH

mixture. The data were collected and analysed by NPL which served as the referee.

For the present study, the areas of the chromatographic peaks for both test and calibration mixtures were divided by the gravimetric concentrations in ppbC to obtain a carbon response factor (CRF) per atom in area counts/ppbC. To enable a comparison among laboratories, the carbon atom response factors were normalised by the carbon atom response factor for butane to provide an effective carbon atom response (ECR)$_i$ for the i-th hydrocarbon of:

$$ECR_i \ (\text{rel. to butane}) = \frac{(\text{area}_{\text{comp }i}/\text{ppbC}_{\text{comp }i})}{(\text{area}_{\text{butane}}/\text{ppbC}_{\text{butane}})} \qquad (1)$$

The normalised effective carbon atom responses of each laboratory for the calibration and test mixtures were averaged, and the average was used for a further statistical evaluation. An alternative normalisation using the carbon atom response factor averaged over all compounds provided almost identical results and is, therefore, not discussed here.

For comparison with data in the literature it is useful to note that our definition of ECR$_i$ by Eq. (1) corresponds to the value 1/(relative molar C response factor), where the relative molar response factor, $F_i(R\text{-molar})$ was defined by Scanlon

and Willis [19] as:

$$F_i(R\text{-molar}) = \frac{(\text{area}_{\text{refer}}/\text{mol}_{\text{refer}})}{(\text{area}_{\text{compd }i}/\text{mol}_{\text{comp }i})} \qquad (2)$$

Scanlon and Willis [19] also provide transformation formulas into mass related response factors frequently used in the literature.

3. Results and discussion

The difference between the carbon atom response of a particular hydrocarbon derived by each laboratory from two independent measurements, one of the test and one of the standard mixtures, were usually below 5%, indicating the level to which each laboratory was capable of reproducible measurements. The averages of the ECRs for each individual hydrocarbon for each laboratory were then averaged across all laboratories for each intercomparison measurement. These are presented in Fig. 2 for the second intercomparison and in Fig. 3 for the third intercomparison.

Despite the good reproducibility achieved by individual laboratories for individual compounds, the ECRs shown in Figs. 2 and 3 sometimes differ considerably when com-
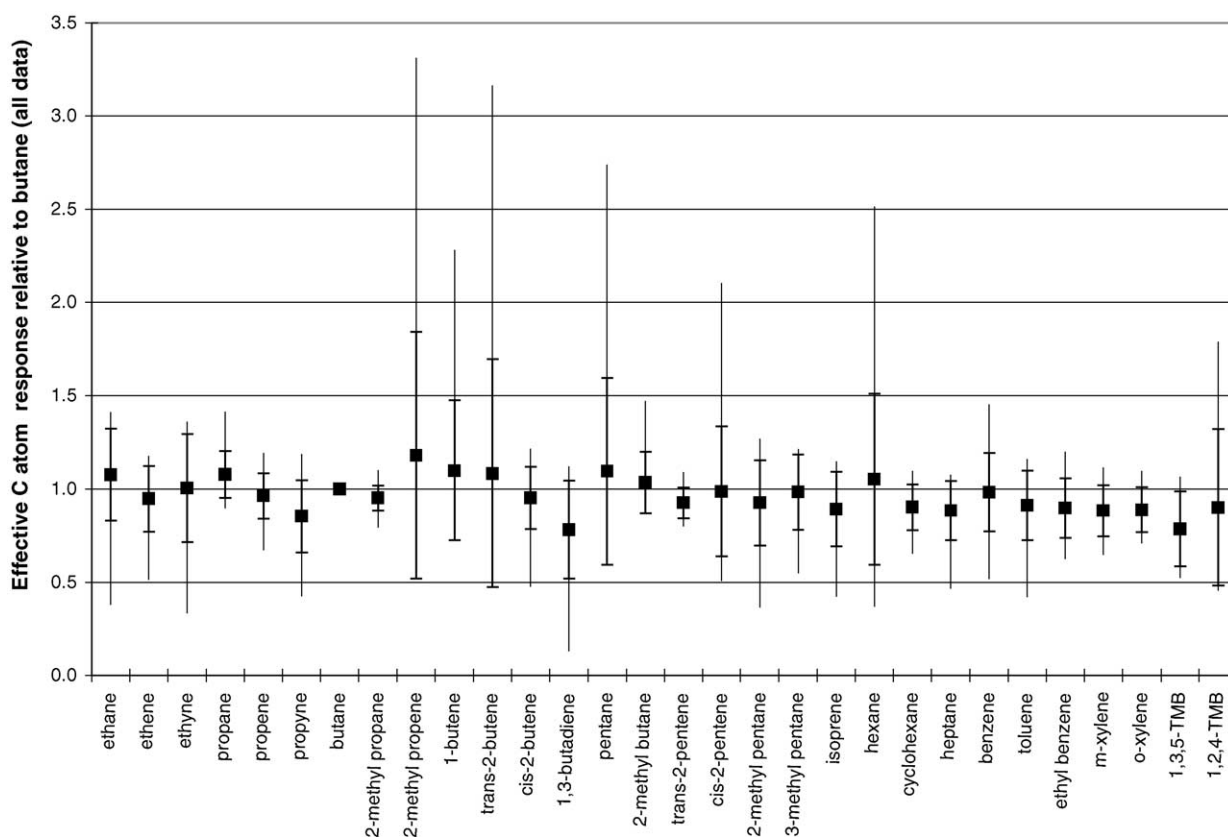

Fig. 2. Effective carbon number response factors of NMHCs relative to butane as measured by 14 laboratories during the second AMOHA intercomparison. The long lines indicate maximum and minimum values and the shorter vertical lines indicated by small horizontal lines show standard deviations. TMB stands for trimethyl benzenes.
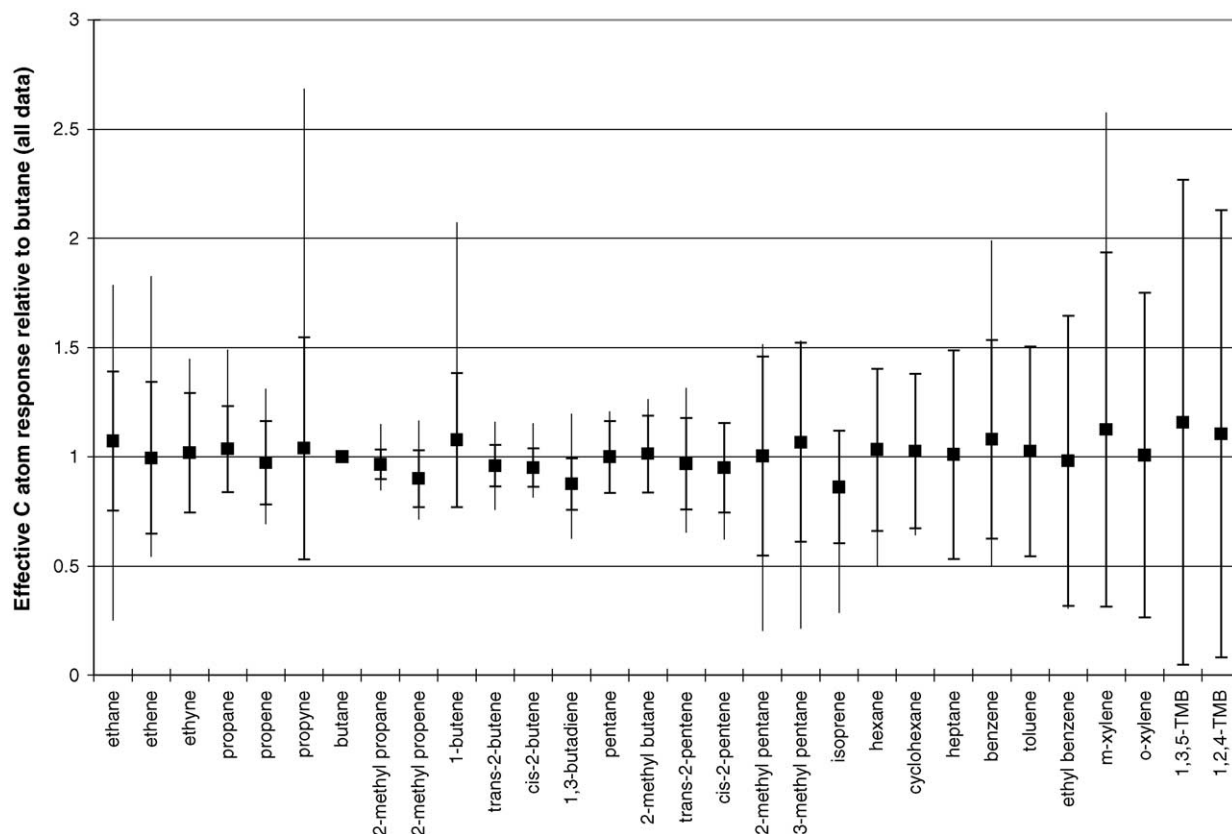
Fig. 3. Effective carbon atom response factors of NMHCs relative to butane as measured by 14 laboratories during the third AMOHA intercomparison. The long lines indicate maximum and minimum values and the shorter vertical lines indicated by small horizontal lines show standard deviations. TMB stands for trimethyl benzenes.

pared between laboratories. This is probably due to two main causes. The first is that the participating laboratories used a variety of different GC systems (Table 2), and thus there could well be actual loss of hydrocarbons to different degrees in the preconcentration and cryofocusing stages, in the desorption processes plus variations in the efficiency of chromatogram peak area measurement due to problems such as inadequate peak separation and incorrect baseline drawing. The second cause is that different FID constructions and operating conditions probably lead to deviations from strict carbon number linearity for the FID itself. The deviations of $(ECR)_i$ from the ideal value of 1 exceeded 200% in six cases for the second intercomparison and three cases for the third intercomparison. Such extreme results were considered to be outliers and each set of data was thus checked using a Nalimov test for outliers [22]. For the second intercomparison 86 outliers were identified in the total of 390 measurements of individual compounds and for the third intercomparison 118 values out of a total 414 measurements were outliers. As a result about 25% of all measurements of individual compounds were excluded. A discussion with the participants [18] revealed that the outliers were mostly caused by incidents such as overheating of the adsorbent in a pre-concentration trap, breakthrough of the most volatile compounds in a pre-concentration trap and contamination due to relatively high hydrocarbon concentrations

in the ambient air of a laboratory. Mis-identification of a particular compound and a co-elution or insufficient separation of individual NMHCs also contributed to the scatter.

Sets of data without outliers are displayed in Figs. 4 and 5, and here the ECR values deviate by less than 50% from unity, with the exception of 1,3,5- and 1,2,4-trimethylbenzenes in the third intercomparison. The ECRs displayed in Figs. 4 and 5 show a consistent pattern despite the fact that a few laboratories which participated in the second did not take part in third intercomparison and vice versa, that the third intercomparison was carried out 1 year later and that some of the laboratories had updated their equipment during this year. Common features of the second and third intercomparisons are as follows:

1. The average ECRs of C_3–C_4 alkanes and alkenes (except 1,3-butadiene) were nearly all smaller than that of butane, but by an amount less than 10%. The ECR values of different laboratories for each hydrocarbon varied within a narrow range of usually less than 10%. This is consistent with reports in literature [12,16].
2. The average ECR for ethene was close to unity in both intercomparisons, while the ECR for ethane was about 6% higher in both intercomparisons. Although the difference was statistically not significant, a thermodegradation of
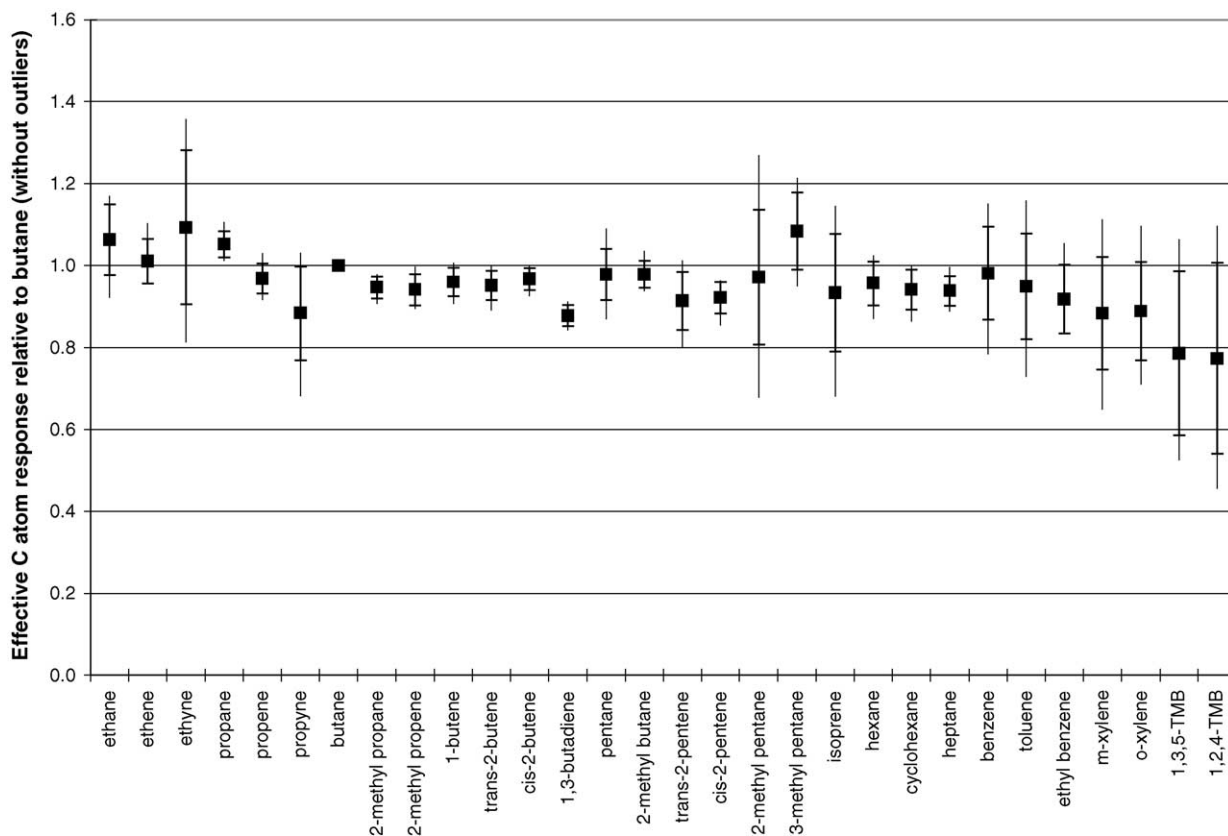
Fig. 4. Effective carbon atom response factors from the second AMOHA intercomparison, as in Fig. 2 after elimination of outliers by Nalimov test [22].

higher compounds may contributed to higher ECR values of lighter compounds. The interlaboratory variations of ECRs for ethane and ethene were substantially larger than those of C_3–C_4 alkanes and alkenes. These effects are probably due to the difficulties experienced by some laboratories in achieving a reproducible and quantitative preconcentration for these most volatile analytes. Breakthrough of material in the preconcentration trap due to the use of an insufficiently low preconcentration temperature was identified as a reason in some laboratories [18]. However, such breakthrough should have caused a reduction in the amount of C_2 compounds reaching the FID and thus should have reduced the ECR to a value below unity (since, by contrast, the butane reference material should have been well retained by the trap). A value above unity is thus unexpected on this basis.

3. There was a large scatter of relative ECR values between the laboratories for both ethyne and propyne. The ethyne ECR showed an average deviation of +9% from unity in the second intercomparison (although none in the third intercomparison), which is in agreement with the known anomalous FID behaviour of ethyne [15]. In addition, the carbon atom response factor for ethyne is known to depend strongly on the operating conditions of the FID, and thus accurate ethyne measurements require specific calibration by ethyne [20]. To our knowledge no information is available on propyne, but the ECR of

propyne presented here indicates also the need of specific calibration.

4. The average ECR for 1,3-butadiene was, in view of its small interlaboratory variation, clearly significantly lower than unity, by −13% in both intercomparisons. The average ECR of another diene, isoprene, was −7% and −9% low in the second and third intercomparisons, respectively, but due to its high interlaboratory variation (as indicated by uncertainty bars in Figs. 4 and 5) these differences are not very accurate and statistically significant difference was found only in the third intercomparison. A negative difference of ECR for isoprene is in agreement with experimental results by Apel et al. [16]. The negative deviations of both 1,3-butadiene and isoprene observed here are also consistent with the systematically reduced ECRs of alkenes as reported by Sternberg et al. [7] and Ackman [10].

5. An interesting feature of Figs. 4 and 5 is that almost all of the aliphatic hydrocarbons from C_3 upwards have ECR values that are less than unity, in both of the intercomparisons. This is most unlikely to be due to chance and is more likely to be due to an inadequate calibration by a single calibrant, here a frequently used butane. If so this highlights the dangers of relying on a single calibrant, since if the determination of this is not achieved with sufficient accuracy, for whatever reason, then the concentrations of all of the other hydrocarbons will be similarly affected.
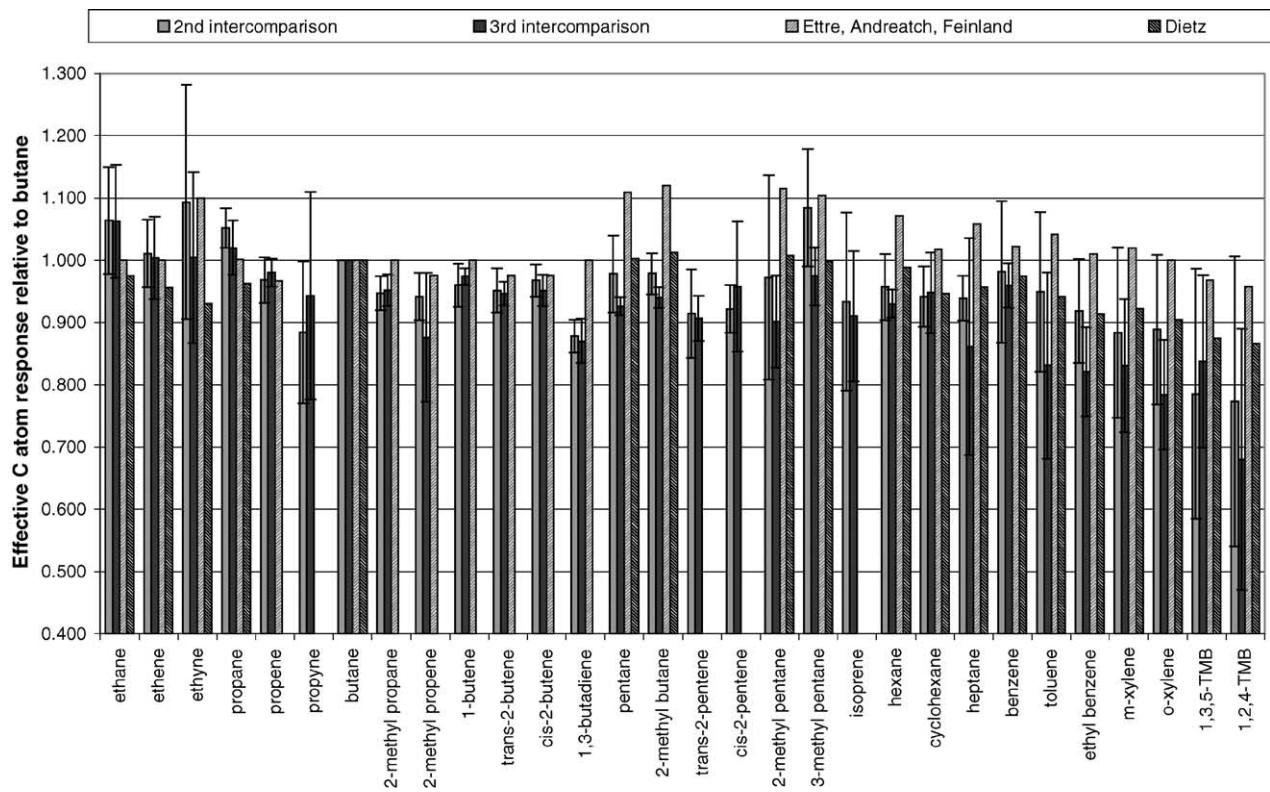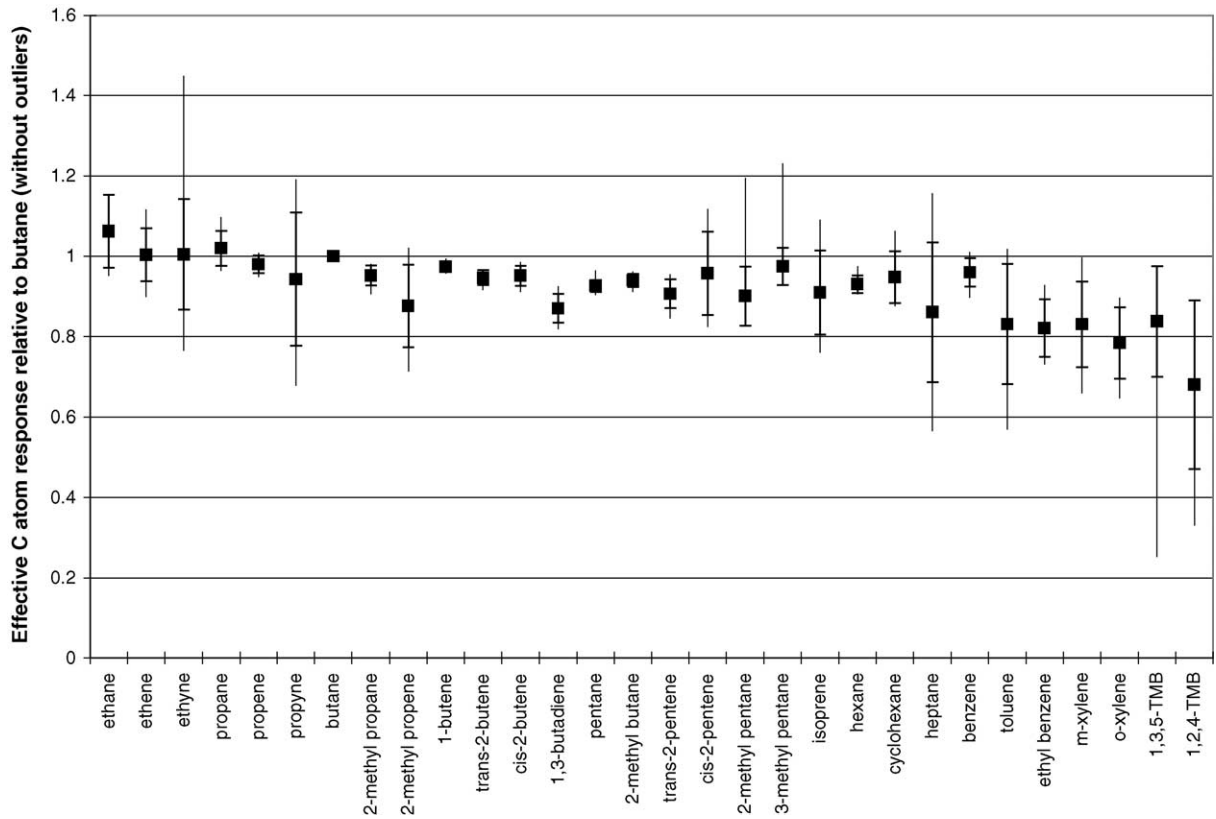
Table 3
Concentrations of gravimetrically prepared gas mixtures used in second and third AMOHA intercomparisons

Hydrocarbon	Second intercomparison		Third intercomparison	
	Calibration (ppb)	Test (ppb)	Calibration (ppb)	Test (ppb)
Ethane	7.87	8.20	5.75	5.65
Ethene	12.33	4.28	9.00	3.47
Ethyne	10.28	9.09	7.50	7.22
Propane	2.98	3.64	2.18	3.43
Propene	7.77	4.11	5.67	4.79
Propyne	3.35	2.53	2.44	0.98
n-Butane	3.00	1.90	2.20	1.48
2-Methyl propane	3.48	1.21	2.54	2.16
2-Methyl propene	3.30	4.05	2.41	1.56
1-Butene	3.86	4.02	2.81	4.28
trans-2-Butene	2.58	1.36	1.88	1.84
cis-2-Butene	2.76	2.70	2.01	3.34
1,3-Butadiene	6.17	5.46	4.50	4.38
n-Pentane	3.07	1.12	2.24	2.62
2-Methyl butane	1.37	1.40	1.00	6.70
trans-2-Pentene	4.69	4.68	3.42	7.76
cis-2-Pentene	1.79	2.41	1.30	4.20
2-Methyl pentane	3.69	1.79	2.69	1.89
3-Methyl pentane	4.22	2.78	3.08	4.11
Isoprene	2.13	2.93	1.56	5.98
n-Hexane	2.05	3.15	1.50	3.79
Cyclohexane	3.87	4.77	2.82	1.85
n-Heptane	3.21	2.43	2.35	4.79
Benzene	3.97	5.40	2.90	3.64
Methyl benzene	3.74	4.17	2.73	5.37
Ethyl benzene	2.06	1.71	1.50	3.35
1,3-/1,4-Dimethyl benzene	1.62	2.12	1.18	2.84
1,2-Dimethyl benzene	1.16	1.40	0.85	1.50
1,3,5-Trimehyl benzene	1.07	1.25	0.78	0.89
1,2,4-Trimethyl benzene	1.31	1.07	0.96	1.13

6. The ECRs for aromatic compounds show generally higher interlaboratory variation than for any other compound class except alkynes. The deviations of the average ECRs from unity were systematically negative and generally increased with increasing carbon number, i.e. with decreasing boiling points. The average ECRs for all of the aromatic compounds were lower in the third than in the second intercomparison. This can be explained by the use of a needle valve in the second intercomparison and a pressure regulator in the third intercomparisons. The pressure regulator with a substantially larger internal surface area is likely to cause higher losses of the aromatic compounds by adsorption. Besides adsorption losses, a non complete flash desorption can contribute to negative ECN deviations. It is also quite likely that the FID response is appreciably different for some or most of the aromatics as compared to the alkanes and that this varies appreciably from one FID and its supply gas composition to another. However, it is not possible to quantify this here due to the variations in the efficiency of the GC process already noted.

The ECRs obtained in the second and third AMOHA intercomparisons are compared with those reported by Ettre [8] and Dietz [12] in Fig. 6. The relative molar responses given by Ettre [8] for alkanes, cyclohexane and aromatic compounds were combined with the alkene relative molar responses published by Andreatch and Feinland [23] and converted to ECRs using the relative molar response for butane. The weight relative sensitivity data given by Dietz [12] were converted into ECRs using a relative weight sensitivity of 1.03 for butane. The aforementioned works do not provide any information about the uncertainty of the reported responses but the second value of 1.09 for butane reported by Dietz [12] suggests an uncertainty of about 5%. Comparison of values given by Dietz [12] with those of Ettre [8] and Andreatch and Feinland [23] in Fig. 6 indicates that the uncertainties of the molar responses might be even larger.

In view of the mentioned uncertainties, Fig. 6 shows generally a reasonable agreement of results for alkanes, alkenes, and alkynes as obtained by various European laboratories. The carbon atom responses for aromatic compounds found by Dietz [12], Ettre [8] and Andreatch and Feinland [23] tend to decrease with increasing carbon number. Our measurements show similar but more strongly pronounced behaviour. Although insignificant for some of the individual compounds due to the large standard deviations, this general trend points again to losses of higher boiling aromatic compounds by many of the participating laboratories.

It is important to note that the values removed by the outlier test represent either blunders or analytical problems of a specific laboratory for a specific compound. Several difficulties/errors such as insufficient resolution, coelution, wrong identification, quenching of FID response by coeluted CO_2 were identified during AMOHA workshops attended by the participants after each intercomparison. The above characterisation of the use of carbon atom response based on the data set without outliers (Figs. 4 and 5) thus provides a substantially better picture than the data sets provided by the laboratories. By contrast, the possible errors from indiscriminate use of constant carbon atom response in monitoring of NMHCs in ambient air are displayed in Figs. 2 and 3.

Fig. 5. Effective carbon atom response factors from the third AMOHA intercomparison, as in Fig. 3 after elimination of outliers by Nalimov test [22].

Fig. 6. Comparison of the effective carbon atom responses relative to butane measured in the second and third AMOHA intercomparisons with those published by Ettre [8], Andreatch and Feinland [23], and Dietz [12].

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4. Conclusions

Analyses of synthetic, gravimetrically prepared gaseous mixtures of 30 NMHCs by 14 European laboratories show clearly that in the routine monitoring of NMHCs in air the effective carbon atom response of a GC system cannot be a priori assumed to be constant for all components. Deviations from a constant carbon atom response were found to be mostly due to the various necessary chromatographic processes involved in the monitoring of NMHCs in air, and particularly to preconcentration, cryofocusing and chromatographic separation of the individual NMHCs. The deviations of ethyne, propyne, 1,3-butadiene and isoprene seem to be systematically negative and to be in part directly due to variations in the efficiency with which they are detected by an FID. Such efficiency probably varies from one FID system to another, but this is not easy to establish clearly in view of the concurrent chromatographic variations already noted.

The frequent failure of the assumption of constant carbon atom response has two consequences for accurate monitoring of NMHCs in air. It is obvious that substance-specific calibration based on the use of high quality multicomponent gas standard mixtures is necessary if accuracy better than 10% is required. Due to the anomalous responses of FIDs to ethyne and possibly propyne, which are strongly dependent on FID operating conditions, substance-specific calibration is always required for ethyne and probably also for propyne if errors in excess of 10% are intolerable.

The use of constant carbon atom response and calibration based on one- or two-component calibration gas mixtures is still preferred by many laboratories because of the relatively high costs of multicomponent calibration NMHC gas mixtures. This study, however, shows that this approach for the AMOHA intercomparisons would have led to serious errors for some compounds in nearly all of the participating laboratories. To avoid these errors, characterisation of the entire analytical system by a high quality certified multicomponent gas mixture is necessary. It enables the diagnosis of analytical errors in a particular GC–FID system. It also allows the possibility of working with a simple calibration mixture, by applying correction factors for individual substances, if the repeated use of a multicomponent standard mixture is too costly for routine monitoring. In this case, however, a regular check of the analytical performance of the GC–FID system using a multicomponent calibration mixture is then most important.

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