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Comparison of comprehensive two-dimensional gas chromatography and gas chromatography – mass spectrometry for the characterization of complex hydrocarbon mixtures

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Abstract

In this paper, we compare the current separation power of comprehensive two-dimensional gas chromatography (GC×GC) with the potential separation power of GC–mass spectrometry (GC–MS) systems. Using simulated data, we may envisage a GC–MS contour plot, that can be compared with a GC×GC chromatogram. Real examples are used to demonstrate the current potential of the two techniques in the field of hydrocarbon analysis. As a separation technique for complex hydrocarbon mixtures, GC×GC is currently about as powerful as GC–MS is potentially powerful. GC–MS has not reached its potential separation power in this area, because a universal, soft ionization method does not exist. The greatest advantage of GC×GC is, however, its potential for quantitative analysis. Because flame-ionisation detection can be used, quantitative analysis by GC×GC is much more robust, reliable and reproducible.

Keywords: Gas chromatography; Comprehensive two-dimensional gas chromatography; Gas chromatography–mass spectrometry; Hydrocarbons; Alkanes; Alkenes

1. Introduction

Mixtures of hydrocarbons, such as those resulting from oil-refining processes, are extremely complex. They almost invariably contain very large numbers [1] of different components in all or most of the following classes.

1. Saturated hydrocarbons (together known as alkanes or paraffins, and consisting of *n*-alkanes and branched alkanes; the latter are also called isoalkanes)
2. Cyclic alkanes (known as naphthenes and consisting of mono-, di- and multicyclic structures with various degrees of substitution)
3. Aromatics (consisting of mono-, di- and multiring structures with various degrees of substitution)
4. Components containing heteroatoms, such as sulphur, nitrogen, or oxygen. The first is easily the most abundant and it is present in several

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component classes (sulphides, disulphides, mercaptanes, thiophenes)
5. Unsaturated hydrocarbons (known as alkenes or olefins, possibly divided into *n*-alkenes, iso-alkenes, cyclic alkenes, etc.)
6. Combined structures (components, that cannot be classified in one of the above classes, containing, for example, both aromatic and naphthenic rings).

Unsaturated hydrocarbons do not occur in natural oils, but they are formed in substantial amounts in thermal and catalytic cracking processes.

Various characterizations of hydrocarbons may be needed for different purposes. A number of physical characterizations, such as density, cloud point, flash point, etc., are routinely performed, but these are not within the scope of this paper. Chromatography first becomes relevant when it can be used to replace physical measurements. For example, gas chromatography (GC) is a convenient, rapid, precise, and accurate alternative to distillation for measuring the boiling-point range of hydrocarbon mixtures. This routine application of GC is known as simulated distillation.

A second application of chromatography involves the separation of hydrocarbon mixtures into some of the classes and subclasses listed above. Normal-phase liquid chromatography (NPLC) and supercritical-fluid chromatography (SFC) are often used for this purpose. When a specific class of components needs to be determined, but preparative fractionation is not required, specific detectors are sometimes an option. In particular sulphur-specific detectors are useful in this context. Photoionization detection (PID) can be of some use for the selective detection of aromatics. NMR can sometimes be used for group-type analyses, for example to determine the number of aromatic carbon atoms or the presence of double bonds, but the kind of data provided cannot be converted to mass or volume percentages. Mass spectrometry (MS) is also an option for detecting classes of hydrocarbon mixtures, as will be discussed below. Fourier transform infrared (FT-IR) spectroscopy is of limited interest for complex hydrocarbons, either as an off-line instrument or as a GC detector, because of the limited chromatographic resolution and, consequently, the poor quantitation. FT-IR would in principle be a fantastic detector for GC×GC, either in an on-line or off-line (deposition) mode. FT-IR can be used to distinguish between different isomers. No efforts in this direction have been published to date.

A third area for the application of chromatography concerns the determination of specific components in hydrocarbon mixtures. These may be specific hydrocarbons, such as benzene, whose concentration in fuels is bound to maximum values in products, such as gasoline. Toluene, ethylbenzene and xylenes are also commonly determined in fuels. Together with benzene they constitute the BTEX group. Also, added components may need to be analysed individually. A good example is methyl *tert*.-butyl ether (MTBE), which is often added to gasolines to improve octane ratings. GC is typically used for these analysis. For MTBE oxygen-selective flame-ionization detection (O-FID) may be used. Two-dimensional GC (GC–GC) is a fundamentally attractive, but rather complicated technique. A narrow fraction from the chromatogram, containing the specific peak of interest, is transferred to a second, different column, for a more extensive separation. This so-called heart-cut technique can be applied to one component or a few (similar) ones, but when the number of analytes increases it soon becomes impractical. GC–MS is a good alternative. The concentrations of the analytes may be determined using either selected-ion monitoring (SIM) or deconvolution techniques. For these types of applications analyte standards are likely to be available for calibration. However, like GC–GC, GC–MS is still largely confined to Research and Development laboratories. It is too complicated and too expensive to be used for simple routine analysis in refinery laboratories.

The fourth and final area where chromatographic techniques are employed for separating hydrocarbon mixtures involves the determination of the composition of the mixture in substantial detail. Such comprehensive analyses are the subject of the present paper. We may define the objective of comprehensive analysis as identifying all components present in the sample and determining their concentrations. In practice, such a comprehensive analysis is only possible so far for straight-run hydrocarbon mixtures in the gasoline range. The number of possible

components is restricted both by the limited boiling range and by the absence of cracker products, such as alkenes. The detailed hydrocarbon analysis (DHA) method involves long high-resolution GC columns. A one-dimensional chromatogram takes several hours to record.

If a truly comprehensive analysis of a variety of hydrocarbon mixtures were possible, it would encompass all other types of analyses as subsets. All analytical questions that cannot be solved by any of the earlier types of analysis may be solved. The correlation of chromatographic data with physical properties (such as in simulated distillation) is the area where the benefits of more-detailed analysis are least obvious. However, even such measurements may only improve if more-detailed chemical information is obtained.

Comprehensive two-dimensional gas chromatography (GC×GC) [2–4] comes close to providing a truly comprehensive separation. In this technique, which was pioneered by the late John Phillips, two GC columns are connected in series. The entire sample that is injected into the first column also passes through the second column and into the detector — hence the adjective comprehensive [5,6]. Before entering the second-dimension column, the effluent from the first-dimension column is thermally modulated. Thermal modulation serves two purposes, i.e. to 'digitise' the first-dimension chromatogram and to focus the sample material in a series of sharp, equidistant chemical pulses (i.e. each tiny, concentrated fraction from the first chromatogram). Two different modulation principles are currently being investigated. The system we use is based on a moving heating element or 'sweeper' [4,7]. The alternative system, developed by Kinghorn and Marriott, is a moving cold-trap modulator [8,9]. The chemical pulses created by the thermal modulator serve as injections onto the second column. The dimensions of the latter are such as to allow a very fast analysis. Each pulse is very rapidly separated on the second-dimension column and the result is a huge stack of very fast chromatograms. This is usually depicted as a contour plot, with the retention on the first column indicated on one axis and the retention on the second column on the other.

We have previously suggested that GC×GC provides a more comprehensive analysis of hydrocarbon mixtures than GC–MS [10]. However, this claim has never been substantiated. This paper concerns the first comparison of GC×GC and GC–MS for this specific application area.

2. Experimental

The GC×GC system used consisted of an HP6890 gas chromatograph (Hewlett-Packard, Wilmington, DE, USA) configured with a flame-ionization detector, an Optic 1 programmed temperature vapouriser (PTV) injector (AI, Cambridge, UK), and a second-generation thermal-modulation assembly (Zoex, Lincoln, NE, USA) as described in Ref. [7]. This modulation assembly contains the rotating 'sweeper' thermal modulator and a cassette system, which allows independent temperature programming of the second-dimension column. This latter, novel feature of the instrument has only been used in combination with one of the column sets used in this study (set 3 in Table 1). Three different column combinations and corresponding sets of modulation conditions have been used. These are summarized in Table 1.

The GC–MS system used consisted of an HP5890 gas chromatograph (Hewlett-Packard) and an HP5989B mass spectrometer. The GC was equipped with a CIS 3 PTV injector (Gerstel, Mülheim an der Ruhr, Germany). The GC and MS conditions used are summarized in Table 2.

3. Results and discussion

3.1. Separations in GC×GC

Two successive chromatographic separations underlie a GC×GC plot, such as the ones schematically depicted in Fig. 1. Fig. 1a shows a schematic separation of a fictitious sample containing a limited number of saturated hydrocarbons, whereas alkenes, cyclic alkanes and monoaromatic compounds are also thought to be present in the schematic separation shown as Fig. 1b. Real samples are much more

Table 1
GC×GC experimental conditions

	1st column	2nd column	Modulation capillary
Set 1			
Length (m)	10	0.5	0.09
Diameter (mm)	0.25	0.10	0.10
Stationary phase	DB-1[a]	OV-1701[b]	SE-54[c]
Film thickness (μm)	0.25	0.14	3
Temperature program	30°C+5 min+2°C/min→200°C		
Carrier gas: helium, column head pressure: 100 kPa Injected sample: 0.1 μl at a split ratio of 1:125 Modulation conditions: Sweeper-slot temperature: 100°C above oven temperature, sweeper speed: 0.25 sweeps/s, 1-s delay at the end of the modulation capillary, one sweep every 4 s			
Set 2			
Length (m)	10	2.5	0.09
Diameter (mm)	0.25	0.10	0.10
Stationary phase	DB-1[a]	BPX50[d]	SE-54[c]
Film thickness (μm)	0.25	0.05	3
Temperature program	30°C+5 min+2°C/min→200°C		
Carrier gas: helium, column head pressure: 150 kPa Injected sample: 0.1 μl at a split ratio of 1:125 Modulation conditions: Sweeper-slot temperature: 100°C above oven temperature, sweeper speed: 0.25 sweeps/s, 1-s delay at the end of the modulation capillary, one sweep every 4 s			
Set 3			
Length (m)	10	0.7	0.07
Diameter (mm)	0.25	0.10	0.10
Stationary phase	DB-1[a]	BPX50[d]	SE-54[c]
Film thickness (μm)	0.25	0.10	3
Temperature program	30°C+5 min 2°C/min→200°C	55°C+5 min 2°C/min→225°C	
Carrier gas: helium, column head pressure: 100 kPa Injected sample: 0.1 μl at a split ratio of 1:125 Modulation conditions: Sweeper-slot temperature: 100°C above oven temperature, sweeper speed: 0.25 sweeps/s, 1-s delay at the end of the modulation capillary, one sweep every 7.5 s			

[a] DB-1 (J&W Scientific, Folsom, CA, USA), a dimethylpolysiloxane.
[b] OV-1701 (Quadrex, New Haven, CT, USA), a (14%) cyanopropylphenyl (86%)–dimethylpoysiloxane.
[c] SE-54 (Quadrex) a (5% phenyl)(1% vinyl)-methylpolysiloxane.
[d] BPX50 (SGE, Ringwood, Australia), a 50% phenyl(equiv.)-polysilphenylene–siloxane.

complicated in terms of the numbers and diversity of different components. However, Fig. 1 can be used to explain some of the observations in real chromatograms.

The first dimension in both figures is a temperature-programmed, high-resolution gas chromatogram. It is convenient to use temperature-programmed retention indices as units on this scale. Retention in GC is inversely proportional to the product of the pure-component vapour pressure (p_i^o) and the activity coefficient of the analyte in the stationary phase at infinite dilution (γ_i^∞). For isocratic elution the net retention time $t'_{R,i}$ of component i is proportional to the retention factor k_i:

$$t'_{R,i} \propto k_i \propto \frac{1}{p_i^o \gamma_i^\infty} \quad (1)$$

For temperature-programmed analysis, the relevant

Table 2
GC–MS experimental conditions

GC conditions	
Column	DB-5MS
Length (m)	30
Diameter (mm)	0.25
Stationary phase	DB-5MS (J&W, Folsom, CA, USA), a 5% phenyl(equiv.)-methylpolysiloxane
Film thickness (μm)	0.25
Temperature program	40°C + 1 min + 3°C/min → 250°C
Carrier gas	Helium Column head pressure: 65 kPa.
Injected sample	1 μl at a split ratio of 1:300.
MS conditions	
EI	70 eV
Source temperature	200°C
Scan range	20–400 u
Scan speed (s/spectrum)	1

parameter is the retention factor at the time (temperature) of elution ($k_{e,i}$):

$$k_{e,i} \propto \frac{1}{p_i^o(T_e)\gamma_i^\infty(T_e)} \quad (2)$$

In principle, all kinds of stationary phases can be used in the first dimension of a GC×GC separation, but there are some good reasons to use a non-polar phase, one being to minimize the effect of the activity coefficient in the first dimension. Ideally, in the absence of molecular interactions (and entropic effects), all analytes will have an activity coefficient of unity. This situation is approached when using a completely non-polar stationary phase. In addition, a linear temperature program is used. This results in roughly equal retention factors at the moment of elution (i.e. equal $k_{e,i}$ values). With all activity factors also approximately equal, this implies that all solutes are eluted from the first-dimension column with approximately equal vapour pressures [$p_i^o(T_e)$, see Eq. (2)]. Because each component has its own vapour pressure vs. temperature relationship, this determines the elution temperature (T_e), which in turn determines the retention time.

The boiling points of alkanes decrease with increasing branching. For example, *n*-octane has a boiling point of 125.7°C, 2-methylheptane has a boiling point of 117.6°C, 2,3-dimethylhexane has a boiling point of 113°C and 2,2,4-trimethylpentane (isooctane) has a boiling point of 99.2°C, close to that of *n*-heptane (98.4°C). Thus, the normal alkane stands out to the right in a series. To the left of it appear the branched alkanes, roughly (but not always exactly) they elute earlier as the degree of branching increases. Note that there are many more branched alkanes than the number of peaks (dots) in Fig. 1. Note also that highly branched C_{n+1} alkanes may elute before (or together with) the linear C_n alkanes. This causes errors when the ratio of normal and branched alkanes is determined based on conventional one-dimensional GC methods.

The second dimension separation is very fast and therefore takes place under essentially isothermal conditions. Using a non-polar first-dimension column, as explained above, all components have the same $p_i^o(T_e)$ values, so that separations are essentially determined by the values of γ_i^∞, i.e. by molecular interactions between the analytes and the stationary phase. In GC, these are usually described by the word polarity. Thus, GC×GC allows virtually orthogonal separation mechanisms [11,12] in the two dimensions, i.e. analyte volatility and analyte polarity.

Increased branching apparently also leads to a reduced polarity, because branched alkanes elute

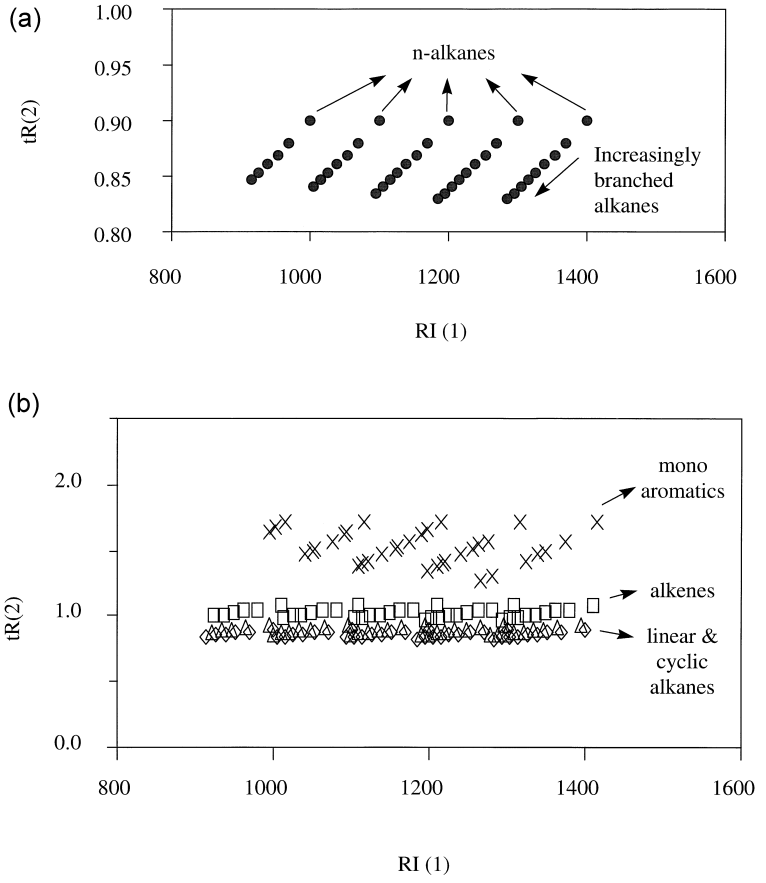

Fig. 1. Schematic representations of GC×GC separations (a) separation of normal and branched alkanes; (b) separation of alkanes, alkenes, cyclic alkanes and monoaromatics.

somewhat earlier from the second column than the linear homologues (same carbon number). This is plausible, because branched homologues are more compact, causing a smaller area across which molecular interactions occur. With retention in both dimensions decreasing as the degree of branching increases, we find the *n*-alkanes positioned at the top of what we call a 'roof tile', obviously at the round numbers (1000, 1100, etc.; see Fig. 1a). Of course, polarity is affected much more by chemical structure than by molecular area. As a result, broad classes of components, such as the alkanes, cyclic alkanes, alkenes and aromatics appear in horizontal bands in a GC×GC chromatogram (see Fig. 1b).

Similar roof tiles are found in the bands for the other classes. The roof tiles get steeper when the retention in the second dimension gets larger. This may be simply due to the basic resolution equation. This equation expresses chromatographic resolution ($R_{s,21}$) in terms of selectivity (the ratio of retention factors of two analytes 1 and 2, $\alpha_{21} = k_2/k_1$), retention (k_{12}, the average retention factor, $k_{12} = (k_1 + k_2)/2$) and column efficiency (number of theoretical plates, N):

$$R_{s,21} = \frac{\alpha_{21} - 1}{\alpha_{21} + 1} \cdot \frac{k_{12}}{1 + k_{12}} \cdot \frac{\sqrt{N}}{2}$$

This equation predicts zero resolution at $k_{12} = 0$ and increased resolution at increased retention values.

The occurrence of roof tiles in GC×GC chromatograms greatly aids in the interpretation and it is essential for separating highly branched alkanes with $n+1$ carbon atoms from linear or marginally branched alkanes with n carbon atoms (see Fig. 1).

There are two equivalent explanations for the occurrence of the roof-tile effect.

1. Branched components have lower activity coefficients (γ_i^∞ values) than the corresponding linear components on the first-dimension column, so that their vapour pressures at the temperature of elution from the first column are higher [Eq.(2), with $k_{e,i} \approx$ constant], causing them to elute earlier from the second-dimension column;
2. Branched components have higher activity coefficients (γ_i^∞ values) — and thus shorter retention times (Eq. (1)) — than the corresponding linear components on the second-dimension column.

The roof-tile effect gives rise to a good separation of the normal and branched members of a series. Consequently, a good quantitation of all the individual peaks is possible. Although the resolution between unbranched and minimally branched (one methyl substituent) members is better than the resolution between subsequent groups of members (e.g. between methyl-branched members and dimethyl-branched members), the intensity profile along a roof tile provides a very good impression of the degree of branching present.

If different classes of components are present in a mixture of hydrocarbons, the separation becomes clearly more difficult, as illustrated in Fig. 1b. In this schematic diagram, the bands for alkenes and for monoaromatics are completely separated from all other bands. However, the bands for alkanes and cyclic alkanes strongly overlap. A real GC×GC chromatogram that demonstrates this kind of separation is shown as Fig. 2. If we use a different set of columns, we are quite capable of separating the band representing the cyclic alkanes from that of the alkanes, but in that case we cannot separate the former from the alkenes, as illustrated in Fig. 3.

If the separation by GC×GC is a complete success, i.e. all different classes are separated into different bands, then adding an MS step may provide

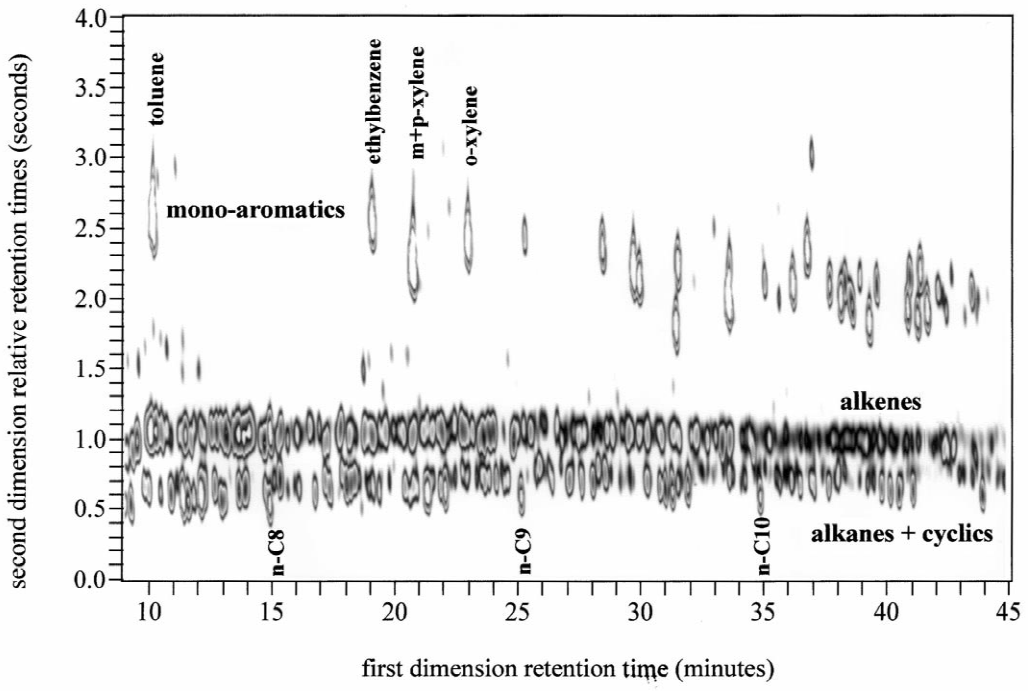

Fig. 2. Typical GC×GC chromatogram of a (cracked) gasoline developed using the conditions of set 1 (see Table 1).

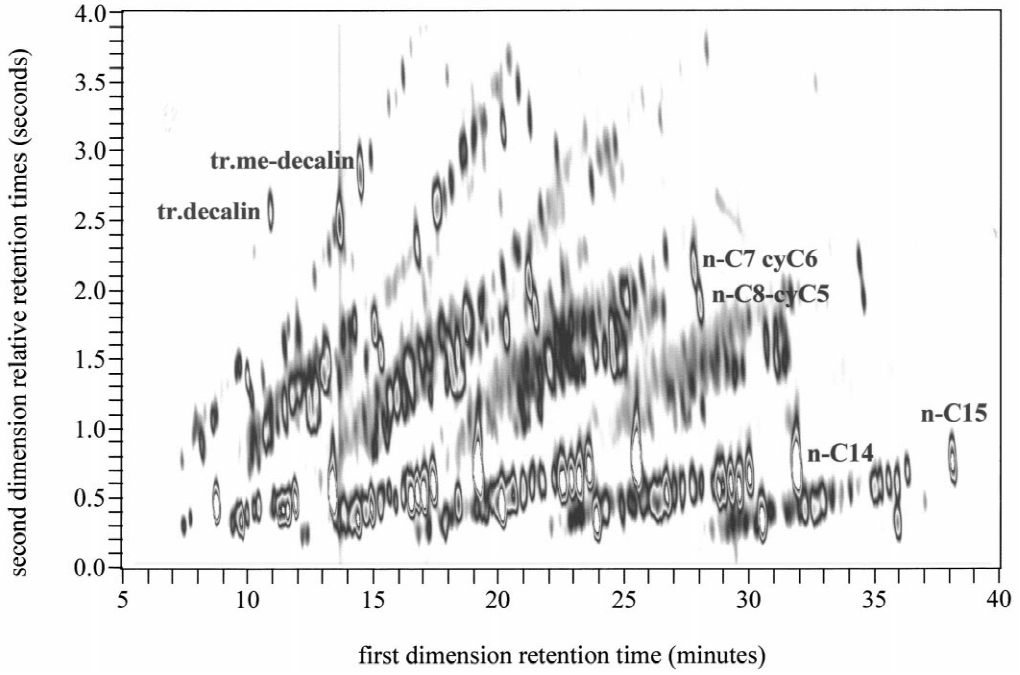

Fig. 3. Typical GC×GC chromatogram of a non-aromatic hydrocarbon solvent developed using the conditions of set 2 (see Table 1).

little new information. This point has not yet been reached. At present, we can either use GC×GC to separate alkanes and cyclic alkanes on the one hand from alkenes on the other, or we can separate alkanes on the one hand from cyclic alkanes and alkenes on the other. We have not yet created a set of columns that allows us to separate alkanes, alkenes, and cyclic alkanes in three different bands. In principle, it should be possible to separate all three classes by a three-dimensional separation (GC×GC×GC). An alternative three-stage separation technique would be GC×GC–MS. Both of these techniques face practical obstacles, but neither is thought to be fundamentally difficult. GC×GC×GC is a much more attractive option for quantitative analysis than GC×GC–MS.

In many cases (straight-run fractions that have not undergone cracking; products from hydrocracking or hydrotreating units; synthetic hydrocarbon fuels) not all possible component classes are present in a sample. In many other cases, the analytical question does not require all possible classes to be separated. Therefore, GC×GC is already an immensely useful separation technique within our type of industry.

Although we have not yet achieved complete separation of all possible classes of components and although the assignment of the peaks in a GC×GC chromatogram will be a horrendous task, GC×GC does allow very many detailed interpretations. These are based on rules underlying the observed order in the GC×GC chromatograms, such as those discussed above, and on the injection of reference materials. GC×GC patterns show an increased complexity as the number of carbon atoms in a group increases, but there is an underlying regularity, reminiscent of fractals. It should be possible to build a rigorous understanding of the patterns observed in GC×GC starting from the relatively few combinations possible for small members in a series and adding, for example, methyl groups at all possible positions. In this way GC×GC provides an intriguing challenge to computational scientists and chemometricians.

In order to obtain more information directly from

GC×GC chromatograms, coupling to informative (spectroscopic or spectrometric) detectors may be considered. Because of the high speed of elution of peaks from the second-dimension column, MS is the only reasonable choice. Time-of-flight (TOF) instruments appear most attractive, but a study has recently been published in which the GC×GC separation is performed sufficiently slowly to allow a more conventional quadrupole MS to be used [13]. If spectra are obtained with a high frequency, so that a complete characterization of the sample is obtained, it is better to speak of GC×MS (comprehensive CG–MS) than of GC–MS in the terminology of this paper. However, we will use the conventional GC–MS and GC×GC–MS abbreviations to avoid confusion. A large advantage of GC×GC–MS in comparison with GC–MS is that the preceeding separation is very much better. This allows a relatively easy interpretation of the results, even when electron-impact (EI) ionization is used, which yields highly informative spectra with substantial fragmentation. Disadvantages are the enormous amounts of data generated, but more importantly the weakness of MS in distinguishing between different isomers in a homologous series.

The greatest strength of GC×GC in comparison with GC–MS is the ease of quantification. This comparison is between flame-ionization detection (FID) and MS as quantitative detection methods. In this comparison we will not discuss discrimination from the injector. Such effects will be the same for both systems, but, more importantly, they will not occur with on-column or PTV injection. The latter type of injector is used in all the experiments described in this paper. Quantitative GC is much more difficult when conventional (hot) split injections are used.

FID is highly sensitive (1 pg carbon/s) and linear over at least six orders of magnitude. MS is even more sensitive in the SIM mode (typically 10–100-fold, depending on the analyte), but it is somewhat less sensitive in the full-scan mode (about 5 pg carbon/s). The linearity observed for MS detection is much less than that of FID, causing the dynamic range to be rather modest. This makes it difficult to quantify components of greatly varying concentrations (as are invariably present in complex hydrocarbon mixtures) in a single chromatogram. In contrast, the response of FID to large numbers of compounds is very similar and highly constant. If the response of FID is set to unity for an arbitrary *n*-alkane, then the relative responses for most hydrocarbons are very close to unity. Only components containing heteroatoms, such as oxygenates, show a markedly different response. Among hydrocarbons, unsubstituted polyaromatic hydrocarbons deviate most from the nominal response. Their response factor may be 20% higher (i.e. their sensitivity may be 20% lower) than that of *n*-alkanes. However, the vast majority of hydrocarbons show response factors that are constant within about 5%. Thus, a very good idea of the quantitative composition of a hydrocarbon mixture can be obtained without any calibration (normalized-area method). To improve this initial estimate, we can use response factors per component class, rather than for each individual component. This is a realistic way to calibrate, and the results will typically not be biased by more than a few percent. Although the response of the FID may be somewhat affected by the flows of gases (hydrogen, air or oxygen, and carrier gas), by the exact configuration of the detector (e.g. size, shape and position of the electrodes) and by its condition (e.g. cleanness of the electrodes), the relative response between different components and classes of components is highly constant. Thus, FID is the best known detector for quantitative purposes.

3.2. Separations in GC–MS

The simplest way to look at GC–MS is to imagine an ionization technique, that exclusively yields molecular ions (either at the exact molecular mass of the components, or with a fixed mass added or subtracted). Fig. 4 schematically illustrates the result of a GC–MS separation obtained with an extremely soft ionization technique that yields no fragmentation of the molecular ions. The components with different numbers of carbon atoms are very clearly separated. GC–MS obviously does not need a roof-tile effect to realize this kind of separation. The separation of the various components with a given number of carbon atoms within a class is completely determined by the separation achieved in the GC step. Unfortunately, this is also true for the separation between the alkenes and the cyclic alkanes. A distinction between

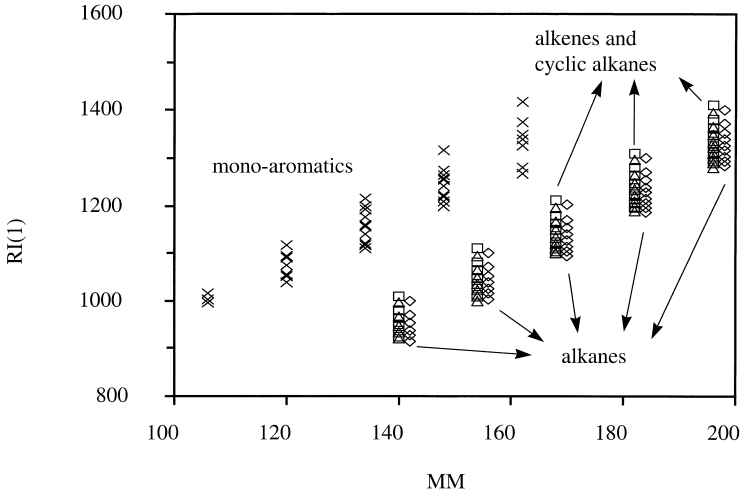

Fig. 4. Schematic representation of an imaginary GC–MS separation using a very soft ionization technique, so that only molecular ions are obtained.

these two classes (both with the molecular formula C_nH_{2n}) cannot be made on the basis of molecular ions. To create a better separation between the two classes in Fig. 4, a much greater degree of separation would have to be obtained on the GC column. This may be feasible by using specific interactions (e.g. adding a silver-loaded column to selectively retain unsaturated components), but in doing so the chromatographic integrity (widths and shapes of the peaks) will be jeopardized to a significant extent.

Yet, the separation shown in Fig. 4 is very attractive in its simplicity. The closest way to approach the separation of Fig. 4 for the GC–MS analysis of a mixture of hydrocarbons is to use nitrous oxide chemical ionization (NOCI) [14]. NOCI-MS is quite universal. It can be used successfully for the highly non-polar types of components in hydrocarbon mixtures. The greatest problem associated with the technique is the quantitation. Response factors are quite different for different components, as well as for different instruments. Even the long-term stability of the response for a given component on a given instrument may be an issue. The use of GC–NOCI-MS for quantitative analysis is documented in the literature [14], as is the use of GC× GC for the same purpose [15]. Considering the huge numbers of components present in typical hydrocarbon mixtures (see Figs. 2 and 3), the calibration of NOCI–MS systems is a horrendous task. As a result, the application of the technique is limited to only a few laboratories worldwide.

Because there are no chemical ionization techniques that are sufficiently universal and sufficiently reproducible to produce separations such as that illustrated in Fig. 4, EI ionization is most commonly applied for the GC–MS analysis of hydrocarbon mixtures. EI is universal and quite repeatable. This implies that a high response is obtained for almost all components and that this response is reasonably constant during a certain period of time on a given instrument. However, different components and different instruments yield substantially different response factors. Also, after retuning the spectrometer, a new calibration must be performed.

EI ionization yields highly informative, fragmented spectra. Thus, the result of a GC–MS analysis of a hydrocarbon mixture yields a very much more complex picture than the one shown in Fig. 4.

The high degree of fragmentation obtained in EI-MS spectra allows identification of many different components using knowledge of fragmentation patterns or — more and more commonly — computer-based searching and identification techniques. When two components overlap in a gas chromatogram, they may be deconvoluted using the MS data. GC–

MS has been advocated as an alternative to GC–FID for the so-called detailed hydrocarbon analysis (DHA) of fuels in the gasoline range [16]. These are relatively low-boiling fractions, the boiling range of which corresponds with alkanes containing 5–9 carbon atoms. Because there are relatively few components in this range, complete separation and identification of all of these is routinely attempted using very long (100 m), very efficient GC columns with long analysis times (90–120 min). Using GC–MS, the interpretation of the results (peak assignment) becomes much more reliable than using retention times only. The main problem associated with the application of GC–MS in this area again involves the calibration of the instrument. The response will vary for different analytes. A limited number of analytes have been selected that are representative for the entire (gasoline) mixture, reducing the required effort. Although GC–MS seems a reasonable alternative to GC–FID for the DHA of gasoline type mixtures, our personal experiences with the quantitative results obtained using this method are rather disappointing.

Fig. 5 illustrates the variability of the response encountered in the GC–MS analysis of a gasoline type sample. In this figure the experimental response factors are indicated for a number of standard alkanes (P), alkenes (O), cyclic alkanes (N), and aromatics (A). Over the range studied, the response factors vary by more than a factor of three. Also, the shape and position of the calibration curves for the different classes change dramatically every time the mass spectrometer has been tuned. Indeed, Fig. 5 is rather flattering in that it represents one of the more uniform and smooth calibration plots we have seen.

When applying GC–MS, similar to that described in Ref. [16], to the analysis of a catalytically cracked (and, therefore, alkene-containing) gasoline, we found that most alkenic components that eluted before benzene could be recognized as such. However, of the alkenic components eluting after toluene only 50% were labeled alkenes.

Clearly, the way forward for DHA is to achieve a much better separation in a shorter time, while maintaining FID as the best quantitative detection principle. This strongly suggests the use of GC×GC for DHA analysis. GC×GC is so far most easily applicable in the middle distillate range. However, we are currently working on an expansion of the technique towards more volatile fractions, encompassing the gasoline range.

In the middle-distillates range, where GC×GC yields excellent separations of most classes of components (see Figs. 2 and 3) GC–EI-MS may also be readily applied. Figs. 6 and 7 show some representative experimental results. Fig. 6 concerns GC–MS analysis using a (favorable) high-resolution column, while Fig. 7 shows a high-resolution GC×GC chromatogram.

Fig. 6a shows a total-ion-current (TIC) chromatogram, which is the universal detection mode of the MS. From this chromatogram the *n*-alkanes can be readily identified, as they dominate the chromatogram. This is often, but not always the case in oil fractions. It is not obvious to assign carbon numbers to the individual peaks at first glance. Of course, the mass-spectral data do provide this information. From the GC×GC plot we can draw quite a few conclusions at first sight. Two strong bands appear at the bottom of the chromatograms. The lowest band represents the alkanes, because the column set used (no. 3 in Table 1) is similar (same stationary phases) as the one used to record Fig. 3 (no. 2 in Table 1). The second band represents the cyclic alkanes and possibly alkenes. The patterns of the aromatic components are most easily recognized. At the top of the picture, naphthalene and the dimethylnaphthalenes are readily discerned. At the bottom left toluene, the xylenes and ethylbenzene are immediately identified. Subsequent assignments (disubstituted naphthalenes, trisubstituted benzenes, and so on) follow. Also, the horizontal axis is readily calibrated, based for example on the retention index of naphthalene on the non-polar column (about 1150).

The GC–MS data require a deeper look. One way to do so is to select a specific ion. This is useful for identifying all components in the class of aromatics, as all aromatic components yield some specific fragments (e.g. masses 78, 92, 106, 120, etc. are indicative of monoaromatics). Fig. 6b shows a selected-ion chromatogram for mass 92. The first and largest peak in this chromatogram represents toluene. All the other components yielding the same fragment are also believed to be aromatics. Fig. 6c shows a similar chromatogram, but now a mass of 120 has been selected. The first group of peaks represent the

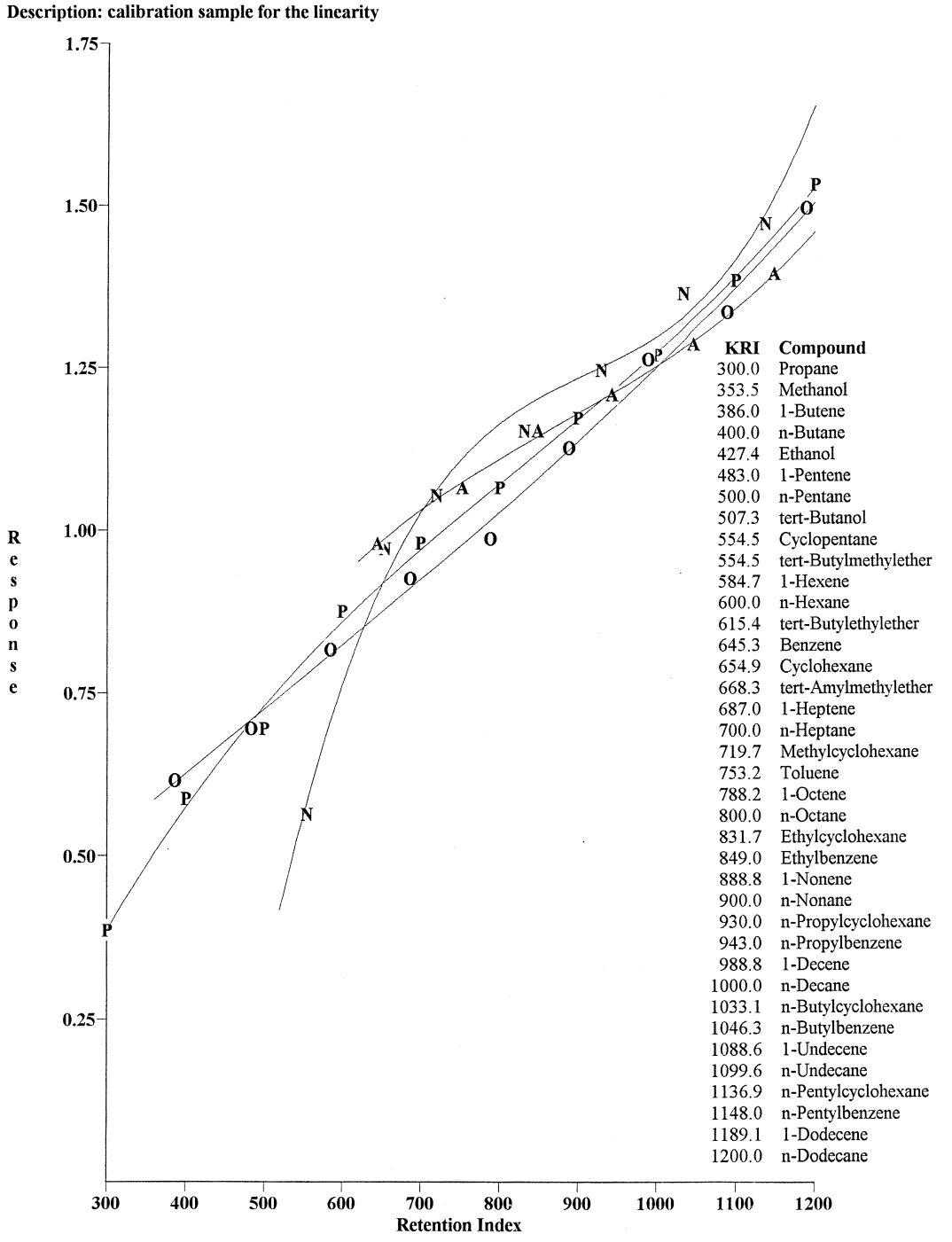

Fig. 5. Example of a calibration plot for the quantitative analysis of gasoline samples by (EI+) GC–MS. Based on a number of standard materials, calibration curves are obtained for alkanes (P), alkenes (O), cyclic alkanes (N) and aromatics (A).

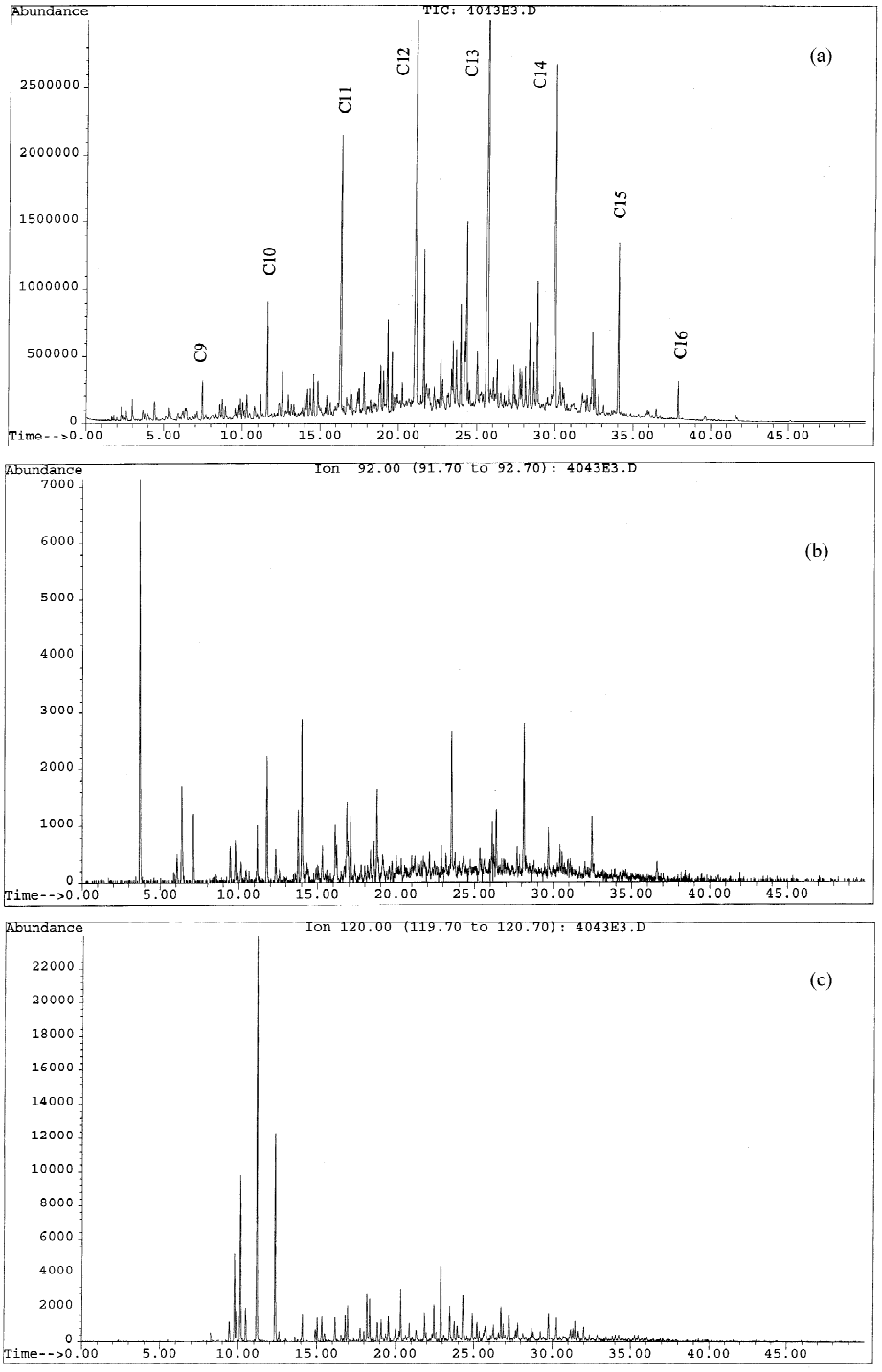

Fig. 6. (a–f) (EI+) GC–MS analysis of a kerosene sample: (a) total-ion-current (TIC) chromatogram; (b) ion trace 92; (c) ion trace 120; (d) ion trace 128; (e) ion trace 142; (f) ion trace 156; time scale in min. (g) EI+ spectrum at retention time 3.661 min. (h) :EI+ spectrum at retention time 14.015 min.

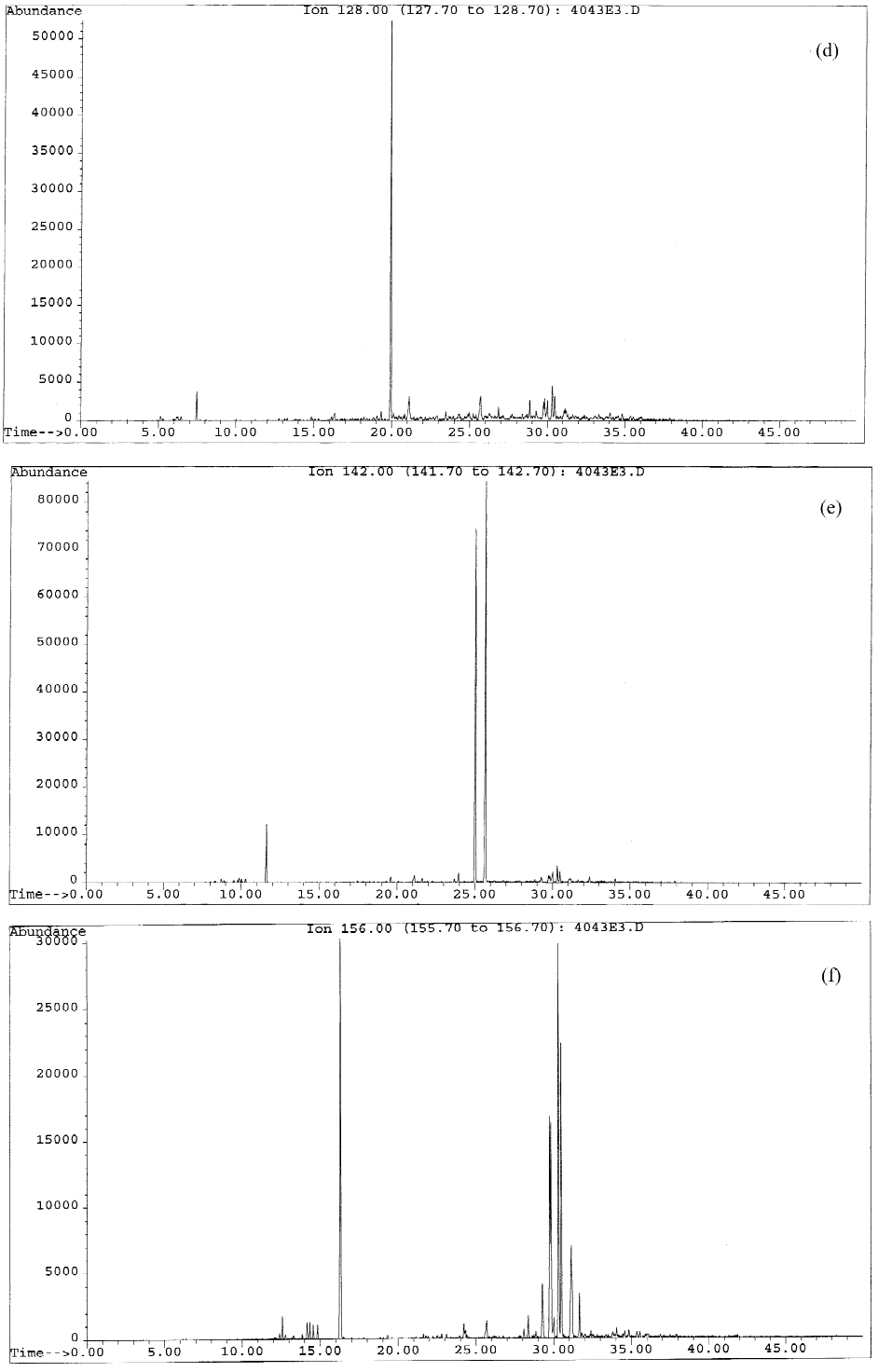

Fig. 6. (*continued*).

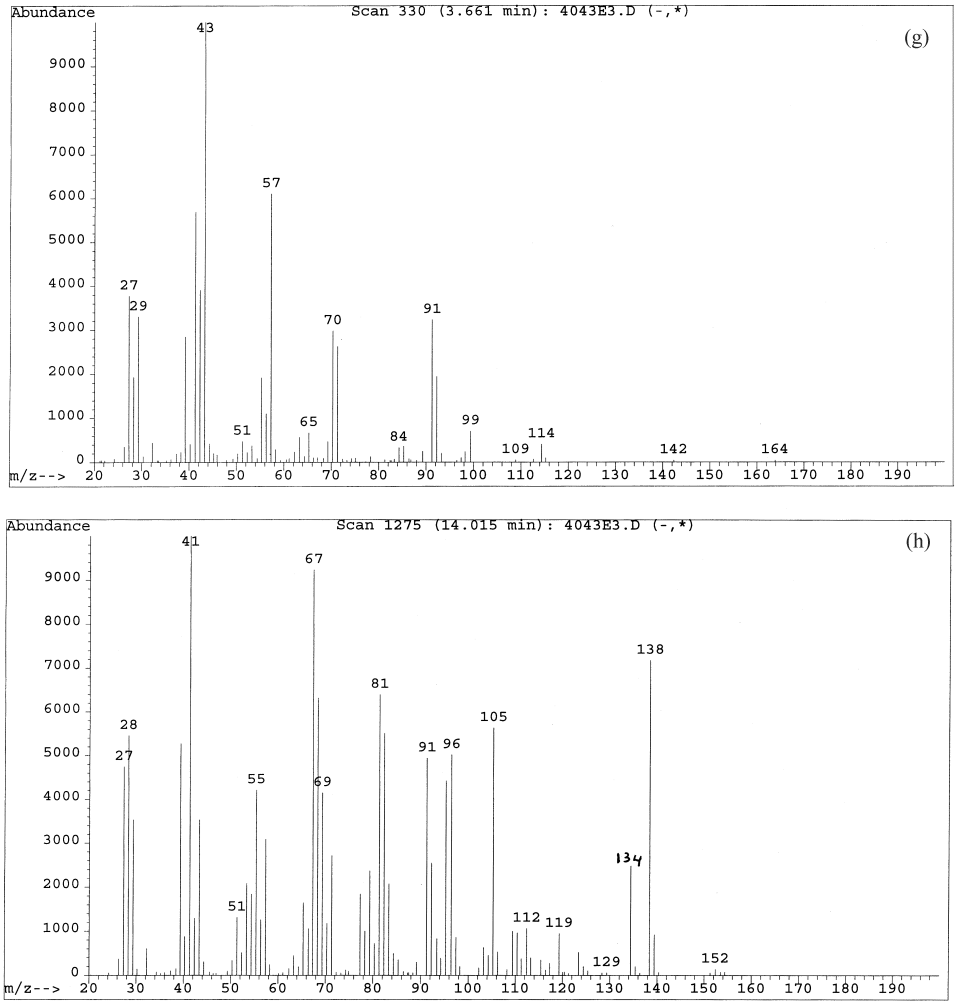

Fig. 6. (*continued*).

C3-substituted benzenes (trimethyl benzenes, ethylmethyl benzenes and propylbenzenes). This procedure allows us to locate the aromatic solutes in the chromatogram. Note that the relative intensities of the individual peaks are very different in Figs. 6b and c, due to large differences in the fragmentation patterns of individual analytes. Fig. 6d shows the chromatogram for mass 128, from which the peak of naphthalene can be easily identified. This may again be used to calibrate the retention scale, assigning *n*-dodecane to the large peak at $t_R \approx 20$ min in Fig. 6a. Likewise, the two possible methylnaphthalenes are dominant in the chromatogram at mass 142 (Fig. 6e), while Fig. 6f (mass 156) reveals the position of the C2-substituted naphthalenes. Note that the conclusions we have drawn from this set of chromatograms are quite similar to those we drew from Fig. 7 at first sight. The interpretation of GC–MS data in terms of analyte classes is more complicated for non-aromatic solutes. Although individual components can be located using selected ions, it is not possible to identify fragments that are indicative of the entire class.

The analysis of GC–MS data becomes really difficult when we focus on mass spectra obtained at a given retention time. Fig. 6g shows the mass spectrum obtained at 3.66 min, i.e. at the top of the toluene peak. While mass 91 is indicative of toluene,

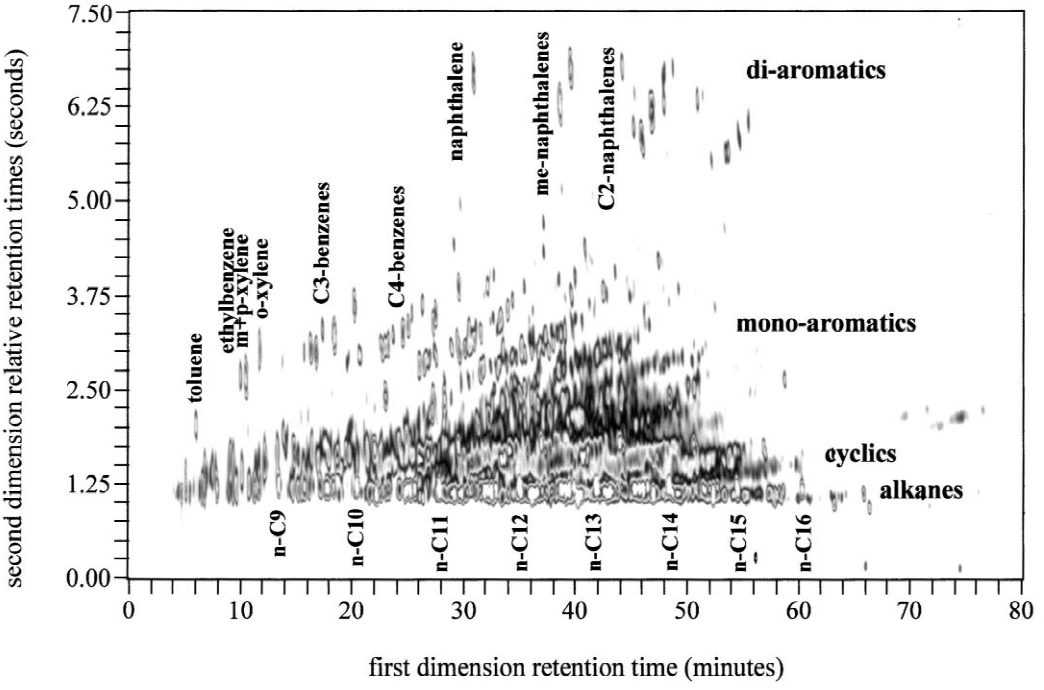

Fig. 7. GC×GC chromatogram of the same kerosene as in Fig. 6, obtained using the conditions of set 3 (see Experimental).

traces of (branched) octane (mass 114) and cyclic or alkenic C_8 materials (mass 112) can also be found in the spectrum. The higher the retention times, the more difficult it becomes to interpret the mass spectra. For example, all kinds of fragments from all kinds of components (aromatic, saturated, and cyclic or unsaturated) appear to contribute to the spectrum shown as Fig. 6h, obtained at a retention time of 14 min. The complexity of these spectra can be understood by inspecting Fig. 7. In this figure, the toluene peak can be found around a retention time of 5 min and if we draw a line down to the horizontal axis, only marginal overlap is suggested with other peaks. On the other hand, at a retention time of about 20 min (corresponding to 14 min in Fig. 6a and thus to Fig. 6h) a number of peaks are already seen to overlap in the GC×GC chromatogram. When moving further to the right in Fig. 7, it is clear that the number of coeluting components increases rapidly. Thus, mass spectra obtained at retention times higher than the 14 min of Fig. 6h will show a rapidly increasing complexity and their interpretation becomes immensely difficult. In this range, GC×GC still yields a good deal of information from a simple visual inspection of the chromatogram (Fig. 7).

4. Conclusions

In Table 3, the separation power of GC×GC and the separation potential of GC–MS are compared for complex mixtures of hydrocarbons. In order to reach the full potential of the latter technique, we either need an ideal (universal, no fragmentation) ionization technique, or we need perfect software to distill the essential information from a very complex data set (obtained, for example, by using electron-impact ionization).

Under these assumptions, the separation potential of GC–MS is greater than the separation power of GC×GC. However, the separation potential of GC×GC×GC is very much greater than either. In the

Table 3
Separation power of GC×GC (in current practice) and GC–MS (assuming the availability of an ideal soft-ionization technique or perfect deconvolution software). // indicates complete separation; / partial separation; + overlap; n_C = number of carbon atoms

GC×GC (in practice)	GC–MS (in principle)
Class level	
Alkanes//alkenes + cyclics//aromatics or alkanes + cyclics//alkenes//aromatics	Alkanes//alkenes + cyclics[a]//aromatics
Subclass level	
Monoring//diring//triring// . . . etc. Cyclopentanes//cyclohexanes// . . . etc.	Monoring//diring//triring// . . . etc.
Cluster level (given class, different n_C)	
Separation thanks to roof-tile effect	Ample separation
Isomer level (given class, given n_C)	
Linear isomers//methyl branched/ . . . /multiple branches (decreasing separation between successive groups)	Linear isomers//methyl branched/ . . . /multiple branches (decreasing separation between successive groups)[b]

[a] GC separation between these classes may be maximized for best results.
[b] Separation of isomers is entirely due to GC dimension and is, therefore, somewhat better in GC×GC than in GC–MS.

field of hydrocarbons, it may be much easier to realize GC×GC×GC than to realize the full potential of GC–MS.

GC×GC provides unique separations of subclasses. For example, the subclass of cyclopentanes can be separated from that of cyclohexanes [12]. We know of no other means to separate, for example, *n*-hexylcyclopentane from *n*-pentylcyclohexane.

At the isomer level, the separation is completely determined by the GC separation. This is better in GC×GC than in GC–MS, because of the added dimension (roof-tile effect).

In summary, as a separation technique for complex hydrocarbon mixtures, GC×GC is currently almost as powerful (at the class level) or more powerful (at the more-detailed levels) than GC–MS is ever likely to become. In addition, GC×GC has great advantage due to its potential for quantitative analysis. Because FID can be used, GC×GC is much more robust, reliable and reproducible.

Given the above conclusions, it is remarkable that GC×GC has yet to achieve broad acceptance as a very powerful new analytical technique. Indeed, GC×GC would benefit dramatically from an expansion of its user base. One reason for the slow proliferation of GC×GC may be a need for much better (more automated, more user-friendly) integration and quantitation software than is currently available. Another, non-technical reason may be the conservative nature of the industry.

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