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Comparison of Low Voltage Electron Ionization and Field Ionization Mass Spectra of Coal-Derived Liquids from the Wilsonville Pilot Plant

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ABSTRACT

Low voltage electron ionization (LV-EI) and field ionization (FI) mass spectra of coal-derived liquids (CDLs) obtained from the Wilsonville coal liquefaction plant before and after hydrotreatment were compared. LV-EIMS (12 eV) analysis of Wilsonville CDLs before and after hydrotreatment produces spectral patterns very similar to those obtained by FIMS. This is especially true for the more highly aromatic hydrotreater feed samples, since the hydroaromatic compounds which dominate the hydrotreater product samples tend to fragment more under LV-EIMS conditions. Canonical variate analysis confirms that the mass spectral patterns produced by both techniques are highly correlated with the exception of the higher mass range (above m/z 300), which is severely under-represented in the LV-EIMS patterns, due to lower inlet temperatures and to mass discrimination effects in quadrupole MS systems. Furthermore, in spite of the highly complex nature of the original spectral profiles, use of multivariate statistical analysis techniques, such as factor analysis and canonical correlation analysis, enables “numerical extraction” of simplified spectral patterns, which can be tentatively interpreted in terms of chemical components or compound series.

INTRODUCTION

Direct mass spectrometry (MS) using soft ionization methods such as low voltage electron ionization (LV-EI) or field ionization (FI) has been established as one of the prime methods for characterizing coal-derived liquids (CDLs) [1–7]. Compared to FIMS, LV-EIMS causes more fragmentation. Even at electron energies as low as 12–14 eV, compound classes such as short chain alkanes tend to produce little or no molecular ion signal. Moreover, LV-EIMS ionization efficiencies show considerable preference for aromatic com-

pounds and other compounds with low ionization potentials [8–11]. Together with the remaining fragment ion intensities, the discrimination trend tends to complicate the direct use of LV-EIMS profiles for determining molecular weight distributions in complex mixtures. In addition, FIMS has been shown to give slightly more accurate quantitative results for hydrocarbon mixtures [12].

On the other hand, an important advantage of LV-EIMS over FIMS lies in the nearly universal availability of electron ionization sources on general purpose MS instruments. Furthermore, in properly designed electron ionization sources the sample can be introduced as a molecular beam with little contact between sample molecules and reactive surfaces inside the source prior to ionization, whereas ionization of polar molecules in FI sources is thought to occur primarily on the surface of the FI emitter [13]. This may cause memory effects when mixtures containing polar substances are being analyzed, unless special techniques are used to rejuvenate the emitter surface, e.g., by flash heating the emitter filament after each MS scan [14]. This approach, however, cannot be used with volcano-style FI sources as those commonly used in FIMS studies of coal-derived liquids [1–7, 13].

In view of the wide availability of small quadrupole mass spectrometers with LV-EI capabilities, it would be of great practical interest to fuels technologists to be able to follow the effects of various processing steps, e.g. hydrotreatment, by LV-EIMS, rather than FIMS techniques, which are available to only a handful of laboratories around the world. This consideration prompted us to compare LV-EIMS and FIMS data obtained on a series of CDLs from the Wilsonville coal liquefaction pilot plant before and after hydrotreatment. Since objective, quantitative comparison of complex data matrices obtained by two rather different analytical methods requires the use of sophisticated multivariate analysis techniques, we decided to use factor analysis (principal component analysis) based canonical correlation methods.

EXPERIMENTAL

Sample collection

The data presented here were obtained on eight CDL samples collected during run No. 244 of Illinois No. 6 coal (Burning Star Mine) while the pilot plant was operating in the ITSL (integrated two stage liquefaction) mode. The eight samples discussed in this paper represent a subset of a larger collection of samples collected during run 244, which has served as the basis for separate studies on the influence of process conditions on CDL composition [15] and on the integration of mass spectrometric data with conventional CDL characterization data [16]. The eight samples selected for the present study are identified in Table 1. For more detailed data on sample composition and process conditions the reader is referred to previous work [16].

TABLE 1

Sample identification

Sampling date	Hydrotreater feed sample no.	Hydrotreater product sample no.
7-06-83	1	11
7-24-83	5	15
8-07-83	6	16
9-08-83	10	20

Sample preparation

A portion (ca. 2 mg) of each CDL sample was aliquotted and immediately dissolved in 1 ml of a 1:1 mixture of benzene and methanol. Solutions were kept at -10°C prior to analysis.

Low voltage mass spectrometry

LV-EIMS analyses were carried out on an Extranuclear 5000-1 quadrupole MS system with Curie-point heating inlet. A detailed description of the system can be found elsewhere [17].

Operating conditions were as follows: inlet temperature ca. 200°C , maximum filament temperature 610°C , sample size $10\text{ }\mu\text{g}$, temperature-rise time 5.5–6 s, electron energy 12 and 20 eV, scanning rate 1000 a.m.u./s, mass range m/z 100–400 and total scanning time 2 min.

All spectra were recorded by computer and summed to obtain a single, time-integrated spectrum.

Field ionization mass spectrometry

FIMS data were obtained from SRI International using a volcano-style field ionization source and a magnetic sector mass spectrometer. A detailed description of the FIMS technique used can be found elsewhere [2,18].

Operational conditions were as follows: probe temperature was brought to -50°C , preventing loss of any volatiles. The temperature was subsequently raised in discrete temperature intervals to 450°C , keeping the total ion count rate constant (whenever the total ion count rate dropped below a preset level the temperature was raised to get the number of counts back up to 1000 cps), mass range m/z 100–800, scanning rate 17 a.m.u./s, number of scans 8 and total scanning time 5.46 min. All of the scans were added to obtain a single spectrum.

Data analysis

Data analysis was carried out using the SIGMA package [19] developed at the University of Utah. Prior to multivariate analysis, spectra were normalized with regard to ion intensity in order to correct for variations in sample size. However, in calculating total ion intensity values, peaks with unusually large variance contributions were excluded in order to minimize error propagation over the data set [20].

Multivariate analysis involved a combination of factor analysis and canonical correlation analysis [21].

Factor analysis describes the variance in the data set in independent linear combinations of the variables. The linear combinations (“factors”) obtained by factor analysis describe the total variance in the data set as effectively as possible. The first factor describes the maximum variance, the second orthogonal factor the maximum of the residual variance, and so on.

In order to transfer variable “loadings” (i.e. the correlation coefficients between the factor and each of the contributing variables) into a form comparable to the original mass spectra, the loadings are multiplied by the standard deviation of the corresponding mass variable. The values obtained are then represented in the form of a bar plot, the so-called “factor spectrum” [22]. Since factor loadings generally can have a positive or negative sign, the factor spectrum exhibits positive and negative intensities. The positive and negative parts of the spectrum can be interpreted individually.

Finally, canonical correlation was performed using the factor scores of both data sets. The basic objective of canonical correlation analysis is to establish the degree of correspondence between two or more data sets by calculating linear combinations of the variables in each data set in such a way that the correlations between each set of corresponding linear combinations are maximized. Multiple sets of linear combinations may be derived. Just as factor analysis selects a first factor that accounts for a maximum amount of variance in a given data set and then computes subsequent independent (“orthogonal”) factors, each of which account for as much as possible of the variance left unaccounted for by the previous factors, canonical correlation follows a similar procedure. The first pair of canonical variates is selected so as to have maximum correlation possible. A second pair of independent (“orthogonal”) canonical variates is then selected to account for the maximum remaining correlation between the two sets of variables, and so on.

RESULTS AND DISCUSSION

Typical field ionization mass spectra of Wilsonville CDLs are shown in Fig. 1. These spectra show the molecular weight distribution of both hydrotreater feed and hydrotreater product samples. Compared to the hydrotreater feed

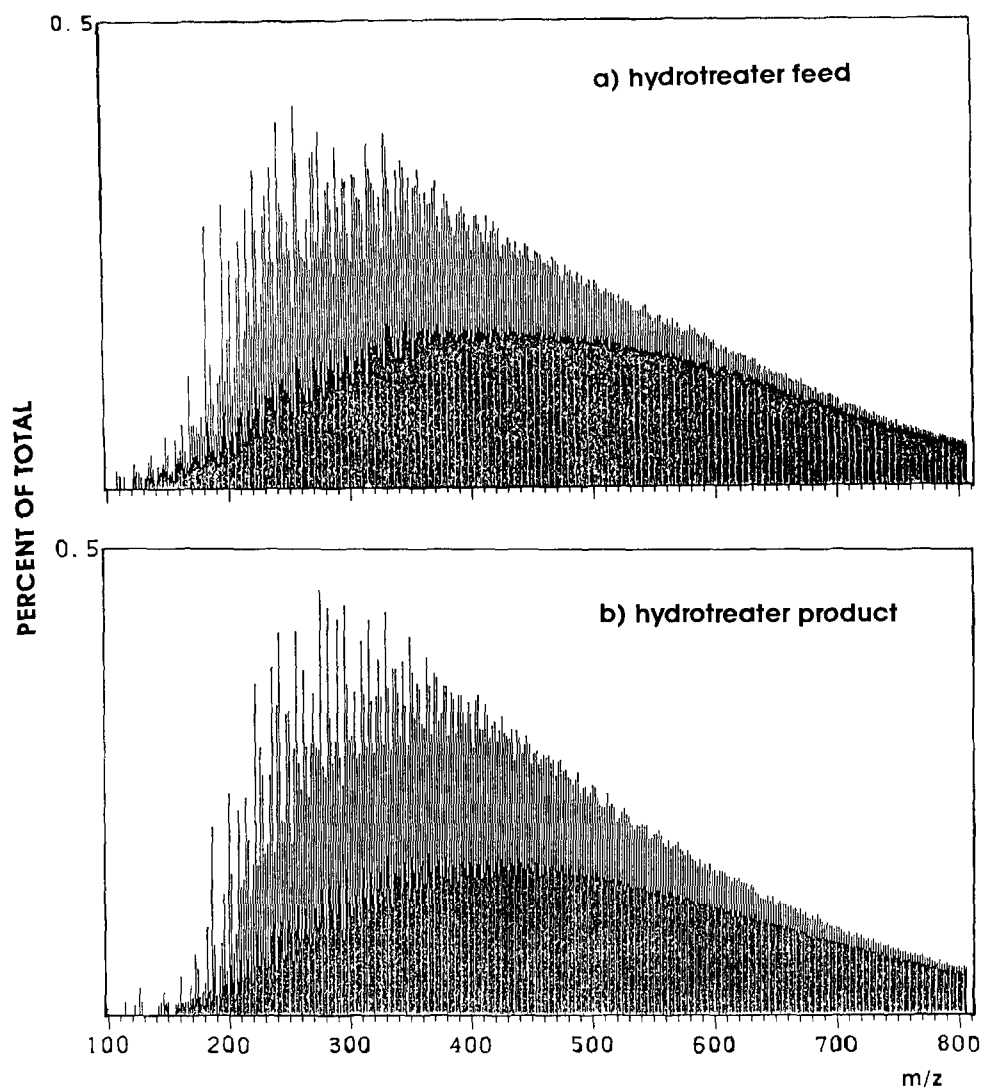


Fig. 1. Typical field ionization mass spectra of (a) hydrotreater feed (sample 5) and (b) hydrotreater product (sample 11).

profile (Fig. 1a), the average molecular weight of the hydrotreater product (Fig. 1b) has shifted slightly upwards, as might be expected. Both spectra are obviously very complex, in that signals can be found at every nominal mass. As a result, chemical interpretation of spectra of this type is not possible without the use of sample prefractionation methods (e.g., liquid chromatography),

multidimensional MS techniques (e.g., high resolution MS, GC-MS, MS-MS) or numerical deconvolution procedures.

The averaged spectra of hydrotreater feed and hydrotreater product obtained by different ionization methods are shown in Figs. 2 and 3 respectively. In order to enable direct comparison between the FIMS data and the LV-EIMS data, all mass peaks above m/z 400 were deleted from FIMS spectra because the higher masses in the LV-EIMS spectra appear to be under-represented. This may be caused by the lower inlet temperature (200°C) in contrast with the high final temperature (450°C) in FIMS, the unheated ion source (ambient temperature) and lower ion transmissivity, as well as the detection efficiency of quadrupole mass spectrometers for high mass ions. Profiles (a), (b) and (c) in Fig. 2 show the mass spectra of the hydrotreater feed under 20 eV and 12 eV LV-EIMS and under FIMS conditions, respectively. Similarly, profiles (a), (b) and (c) in Fig. 3 show the mass spectra of the hydrotreater product under 20 eV, 12 eV and FI conditions. Close inspection and peak by peak comparison of spectra (a), (b) and (c) in Fig. 2 (hydrotreater feed) and also spectra (b) and (c) in Fig. 3 (hydrotreater product) reveals a remarkable degree of similarity between the detailed peak patterns of FI spectra and low voltage (12 eV) EI spectra, especially in the case of the hydrotreater feed samples. To facilitate visual comparison, a selected region (m/z 220–300) of these spectra was replotted on a different scale in Fig. 4. The high degree of similarity was somewhat of a surprise in view of the major differences in sample evaporation, ionization and mass separation conditions, but was felt to be encouraging with regard to the prospects for a more detailed comparison by means of numerical techniques. The somewhat better match of the EI and FI hydrotreater feed patterns is thought to be due to the lower fragmentation tendency of aromatic molecular ions at 12 eV compared to their hydroaromatic counterparts. Increasing the set value of the electron energy to 20 eV [see Figs 2(a) and 3(a)] largely destroys the similarity, due to increased fragmentation of molecular ions.

As mentioned above, the extreme complexity of the LV-EIMS and FIMS spectra makes it difficult to draw conclusions about the chemical composition and/or trends, e.g., the hydrotreatment effect, which might be present in the data set. Therefore, computerized data analysis techniques were employed. Unfortunately, sophisticated data reduction methods such as factor analysis cannot be readily applied to mass spectral patterns containing many hundreds of mass variables, due to the size limitations of data files which can be handled by existing multivariate statistical analysis programs for microcomputers. For example, in SPSS (Statistical Package for the Social Sciences) the number of variables is usually limited to 100. However, a program developed in our lab (SIGMA) can handle a data matrix of up to 30,000 entries. Since there were only eight spectra in each data set, the FIMS spectra were easily accommodated.

Initially, the LV-EIMS and FIMS data were subjected to factor analysis

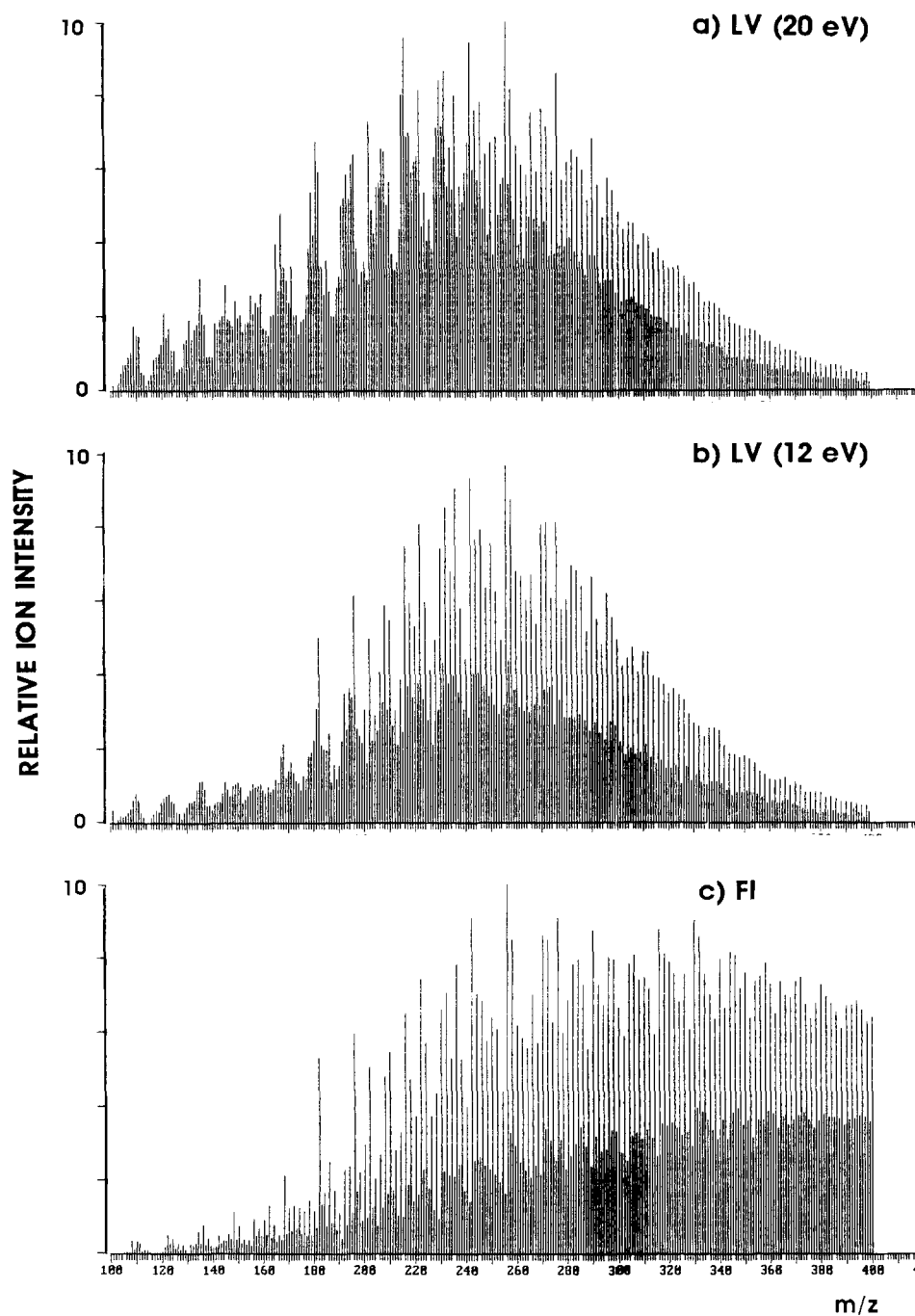


Fig. 2. Average mass spectra of hydrotreater feed at (a) 20 eV EI, (b) 12 eV EI, and (c) FI conditions (samples 5–10).

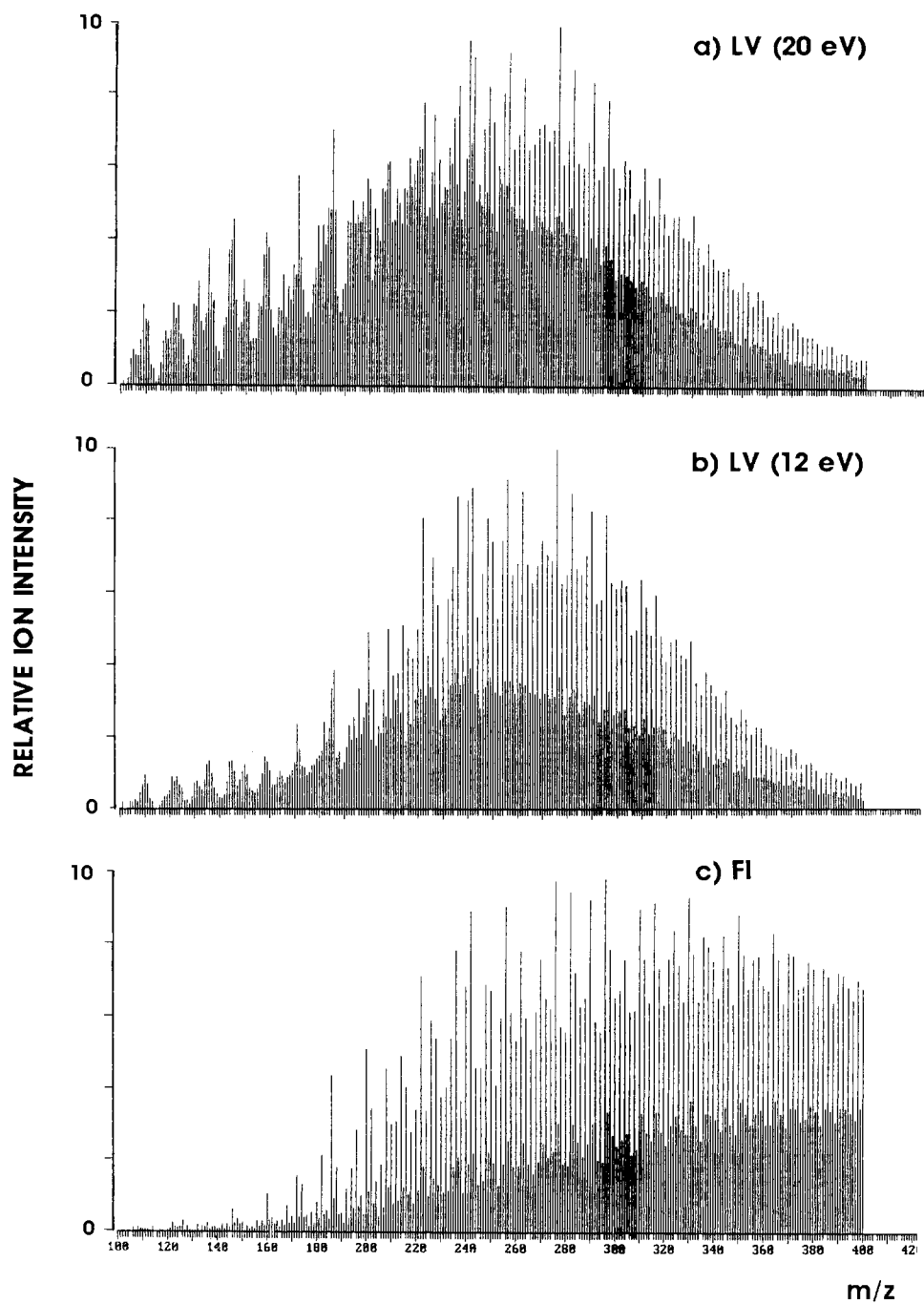


Fig. 3. Averaged mass spectra of hydrotreater product at (a) 20 eV, (b) 12 eV, and (c) FI conditions (samples 11-20).

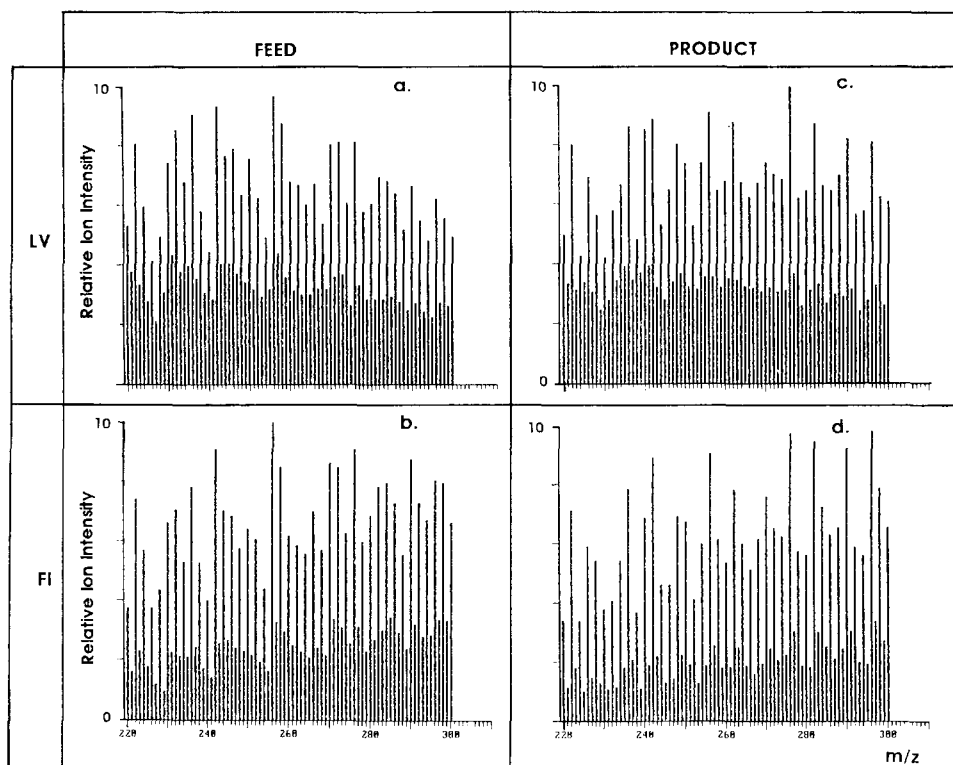


Fig. 4. Selected short mass ranges of hydrotreater feed (samples 5–10) (a and b) and hydrotreater product (samples 11–20) (c and d) under 12 eV EI (spectra a and c) and FIMS (spectra b and d) in wide bar form for better visual comparison.

TABLE 2

Factor analysis of LV-EIMS data

Factor	Eigenvalue	Total variance (%)	Cumulative variance (%)
1	96.6	64.4	64.6
2	24.1	16.0	80.4
3	10.2	6.8	87.2
4	6.8	4.6	91.8
5	4.4	2.9	94.7
6	4.2	2.8	97.3
7	3.7	2.5	100.0

separately. Factor analysis results are given in Tables 2 and 3. From the LV-EIMS (12 eV) data, a total of seven factors with eigenvalues higher than 1 was obtained when taking 150 mass variables with highest variance. The score plot

TABLE 3

Factor analysis of FIMS data

Factor	Eigenvalue	Total variance (%)	Cumulative variance (%)
1	116.9	78.3	78.3
2	19.3	12.9	91.2
3	7.7	5.2	96.4
4	2.3	1.6	98.0
5	1.7	1.1	99.1
6	1.3	0.9	100.0

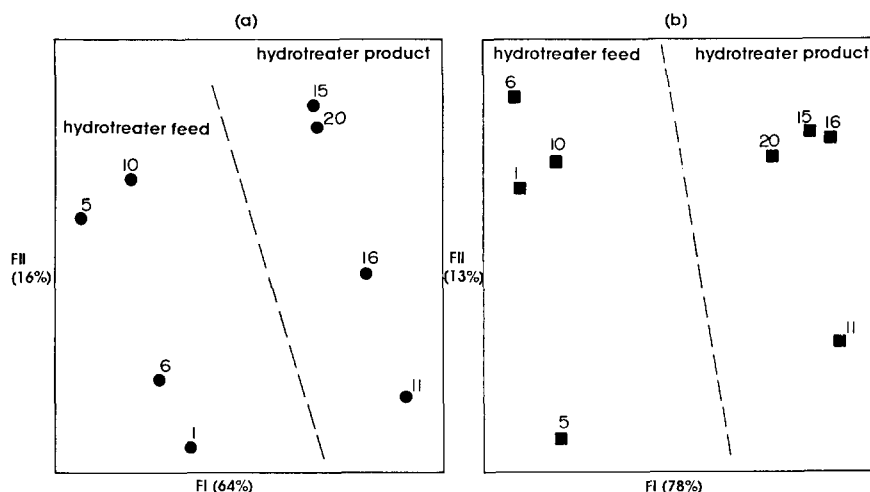


Fig. 5. Factor scores plot of (a) LV-EIMS and (b) FIMS in the factor I and factor II space.

of the first two factors is shown in Fig. 5(a). Factor I with 64% of total variance reveals the effect of hydrotreatment, whereas factor II shows a weak correlation with sample number (i.e. run time). The remaining five factors did not show any obvious trend. In view of the limited number of samples analyzed, caution should be exercised in the assignment and interpretation of any trends. However, in a separate study of up to 20 samples by means of LV-EIMS (12 eV) and factor analysis techniques, the two major trends, namely the “hydrotreatment effect” and “time-temperature effect”, were also observed [15].

The score plot of the first two factors from the FIMS data is shown in Fig. 5(b). In this data set factor I, with 78% of total variance, also reveals the hydrotreatment effect. The other factors do not show any clear trend.

In order to determine the degree of correspondence (“overlap”) between the LV-EIMS and FIMS data, canonical correlation analysis was performed by

using the first three factor scores from each data set. The results of the canonical correlation analysis are given in Table 4. Two significant canonical variates (CVI and CVII) with correlation coefficients of 0.99 and 0.98 respectively were obtained. The score plots of both data sets in CVI and CVII subspace are shown in Fig. 6. The corresponding data points from both data sets are connected; the shorter the distance the higher the correlation, and vice versa. Obviously, canonical variate I represents the same hydrotreatment effect which had already been observed separately in each data set.

Mass variables loading most strongly on the first canonical variate function for both data sets are shown in Fig. 7. The positive part of the "numerically

TABLE 4

Canonical correlation analysis of LV-EIMS and FIMS data

Canonical variable	Eigenvalue	Canonical corr. coeff.	Relative variance (%)	
			LV-EIMS	FIMS
I	0.99	0.99	56.4	74.0
II	0.97	0.98	12.8	12.4
III	0.72	0.85	12.6	7.5
Total var.			81.9	93.9

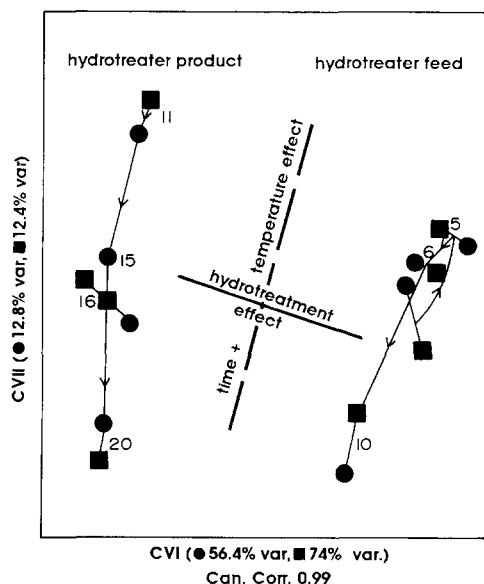


Fig. 6. Canonical scores plot of LV-EIMS (●) and FIMS (■) in the common subspace of both data sets.

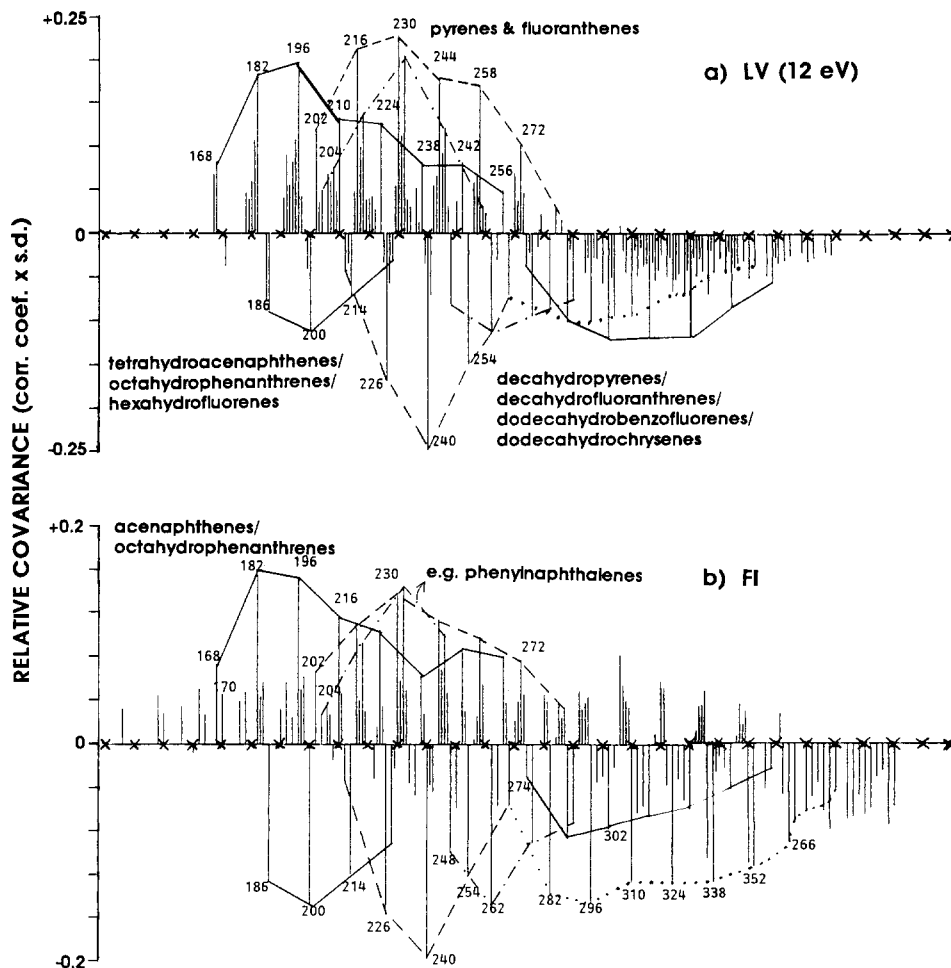


Fig. 7. Numerically extracted spectra along CVI for both data sets under (a) 12 eV EI and (b) FI conditions.

extracted" low voltage spectrum [Fig. 7(a)] shows abundant mass peaks at m/z 168, 182, 196, 210, 224, 238, 252 and 266 (tentatively identified as acenaphthenes and tetrahydrophenanthrenes [22]) in addition to EI signal series at m/z 178, 192 and 206 (phenanthrenes and/or anthracenes [23,24]) and prominent ion series at m/z 202, 216, 230, 244, 258, 272 and 286 (pyrenes and/or fluoranthrenes [23,24]). Another prominent signal series at m/z 204, 218, 232, 246 and 260 may represent phenylanththalenes. The negative part of the numerically extracted spectrum in Fig. 7(a) shows signal series with a definite hydroaromatic character; e.g. at m/z 186, 200, 214 and 228 (tentatively identified as octahydrophenanthrenes and/or octahydroanthracenes and hexahy-

drofluorenes, with possible contributions from tetrahydroacenaphthenes) and 212, 226, 240 and 254 (tentatively identified as decahydropyrenes and/or decahydrofluoranthenes with possible contributions from dodecahydrobenzofluorenes and dodecahydrochrysenes [25]). Finally, a signal series at m/z 248, 262, 276 and 290 may well represent alkyl substituted hexahydrochrysenes. At higher masses, it becomes more and more difficult to assign chemical structures which can be confirmed by GC-MS analysis.

The numerically extracted CVI spectrum of the FIMS data set is shown in Fig. 7(b). Compared to the CVI spectrum of the LV-MS data in Figure 7(a), most of the same ion series are present. The main differences between Figs. 7(a) and 7(b) are caused by the presence of higher MW homologous series in the FI spectrum. These differences have already been discussed.

Although the second canonical variate function (CVII) shows a high correlation (correlation coefficient 0.98) between the EI and FI data sets, no clear trend is observed in this direction (see Fig. 6). The larger data set, consisting of 20 samples, previously analyzed suggests that the second major trend should reflect "time - temperature" related differences. Because of the limited number of samples analyzed, this second trend is apparently not so clearly observed here.

CONCLUSIONS

Visual as well as numerical comparisons between mass spectral patterns of Wilsonville CDL samples obtained by FIMS as well as LV-EIMS (12 eV) show a high degree of correspondence, especially between the more aromatic hydrotreater feed samples. More detailed inspection of the compositional differences between the samples by means of canonical correlation analysis reveals several series of very similar homologous molecular ions. However, due to lower inlet temperature as well as lower ion transmissivity of the quadrupole MS instrument used for the LV-EIMS experiments, higher molecular weight components (above m/z 400) were observed only in FIMS.

The results obtained indicate that it may well be possible to use more widely available EIMS instruments to obtain compositional information which thus far has been available only through FIMS, provided the mass spectrometric equipment used has similar ion transmissivity characteristics and inlet temperatures are kept sufficiently high.

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