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# CS<sub>2</sub> Charge Exchange as a Low-Energy Ionization Technique for Hydrocarbon Characterization

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CS<sub>2</sub><sup>++</sup> ions formed under low-energy electron ionization conditions readily undergo charge-exchange reactions with hydrocarbons having ionization potential less than 9.5 eV. CS<sub>2</sub> charge exchange (CS<sub>2</sub>/CE) has many advantages over low-voltage electron-impact ionization (LV/EI) in the characterization of hydrocarbons. Small variations in electron beam energies do not affect the relative yields of the molecular ions. Higher sensitivities in CS<sub>2</sub>/CE over LV/EI facilitate high-resolution accurate mass measurements. Uniform sensitivities over a wide range of compound types eliminate the need for calibration compounds for the quantitative determination of the components in a hydrocarbon mixture.

## INTRODUCTION

Since its introduction by Field and Hastings in 1956,<sup>1</sup> low-voltage electron-impact ionization (LV/EI) has been commonly used in the petroleum industry for compound type analysis of aromatic hydrocarbons in fossil fuels. In this technique, the electron energy is generally set around 10 eV so that aromatic hydrocarbons, which have ionization potentials below 9.5 eV, can be selectively ionized with minimum fragmentation, leaving saturated hydrocarbons largely un-ionized. This technique, when combined with either high-<sup>2-5</sup> or low-<sup>6-11</sup> resolution mass spectrometry, provides quantitative measurements of molecular ions, which yield the compound type distribution as well as the carbon number distribution within each compound type (or homologous series) of a hydrocarbon mixture. We have recently applied LV/EI high-resolution MS coupled with HPLC for the characterization of mixtures of heavy hydrocarbons.<sup>12,13</sup>

There are, however, several disadvantages associated with the LV/EI technique. The sensitivity of the mass spectrometer is relatively low because of low electron density and small ionization cross sections under LV/EI conditions. The

effective electron energy is sensitive to ion source conditions, especially the space charge and cleanliness of the ion source. Small changes in electron beam energy can cause large variations in ion yield. In other words, in LV/EI conditions the ionization efficiency curve has a steep slope.

Other ionization techniques have also been used for hydrocarbon characterization. Field ionization and field desorption (FI/FD) have been gaining popularity in recent years<sup>14-21</sup> because of their unique features, such as uniform sensitivity across a broad range of compound types, applicability to both saturated and aromatic hydrocarbons, and the ability to measure less volatile hydrocarbons. FI has been used for volatile organics while FD has become the method of choice for the characterization of heavy hydrocarbons. However, with FI/FD the mass spectrometer can only be operated at low resolution and cannot at present be coupled with a liquid chromatograph for on-line liquid chromatography/mass spectrometric (LC/MS) analysis of heavy complex hydrocarbon mixtures. To characterize heavy hydrocarbons using FDMS, tedious preparative liquid chromatographic separations are usually required.

Chemical ionization (CI), such as proton transfer and charge exchange, has also been explored for hydrocarbon analysis.<sup>22-27</sup> Munson and co-workers<sup>28</sup> recently suggested the use of the benzene charge-exchange reaction for aromatic hydrocarbon analysis, which yields uniform molar sensitivity for various hydrocarbon compounds. This method was also applied to differentiate between paraffins and olefins: paraffins in general do not react with benzene ions by charge transfer whereas olefins do. However, the rather low volatility of benzene makes it difficult to introduce enough benzene vapor into a combined EI/CI source or a CI source for a moving belt interface, which has a finite opening to allow the belt moving into the ion source, to produce a stable stream of benzene ions, resulting in low sample ion yields. A specially designed

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or dedicated CI source with a heated reagent gas transfer line to effectively introduce benzene vapor into the ion source would be needed for the application of this technique.

Another reagent gas with an ionization potential similar to benzene's is  $\text{CS}_2$ , which has been used as a reagent gas for charge-exchange mass spectrometric studies.<sup>29</sup>  $\text{CS}_2$  does not contain hydrogen so that proton transfer from  $\text{CS}_2^{*+}$  is impossible. In addition, the  $\text{CS}_2^{*+}$  ion is not a good electrophile to form an adduct ion with an organic molecule. Therefore, charge exchange is the predominant process for  $\text{CS}_2^{*+}$  to interact with organic molecules with ionization potentials less than 9.5 eV, yielding simplified spectra of almost exclusively molecular ions. We have recently evaluated  $\text{CS}_2$  charge exchange ( $\text{CS}_2/\text{CE}$ ) as a low-energy ionization technique for hydrocarbon characterization. The fact that the boiling point of  $\text{CS}_2$  is only 46 °C, 36 °C lower than that of benzene, facilitates charge-exchange experiments using a combined EI/CI source or a CI source for a moving belt interface without any modification.

## EXPERIMENTAL SECTION

The comparison between  $\text{CS}_2$  charge exchange and low-voltage EI ionization techniques was carried out using a VG-70 VSE double-focusing mass spectrometer which is coupled with a Hewlett-Packard 5890 gas chromatograph (GC) and a Varian 5560 ternary liquid chromatograph (LC) via a moving belt interface. GC/MS was used for the studies of relative sensitivities of polynuclear aromatic hydrocarbons and alkylbenzenes. In GC/MS, a 25-m  $\times$  0.25-mm-internal diameter fused silica capillary column coated with 0.25- $\mu\text{m}$  HP-1 methyl silicone stationary phase was used. The column temperature was programmed to rise from 100 to 300 °C at 10 °C/min. Helium was used as a carrier gas.

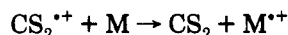
In the LC/MS experiments, a petroleum fraction boiling between 650 and 1050 °F was selected to compare the sensitivities of  $\text{CS}_2/\text{CE}$  and LV/EI ionization techniques. The LC/MS conditions have been described previously.<sup>12</sup> In brief, the petroleum fraction was separated by HPLC into elution regions of saturates, monoaromatics, diaromatics, triaromatics, tetraaromatics, and polars. The LC eluants were continuously transported into the ion source of the VG-70 VSE double-focusing mass spectrometer using a moving belt interface. The resolution of the mass spectrometer was set at 10 000. The nose heater current of the moving belt interface was set at 2.4 A with an estimated temperature of 300 °C.

To set up LV/EI conditions, xylene was used as a reference compound to set the electron beam energy and tune the mass spectrometer. The electron beam voltage was adjusted until the ratio of the intensities of the  $m/z$  (mass-to-charge) 106 molecular ion to the  $m/z$  91 fragment ion of xylene was greater than 50:1. This ratio matches the largest achievable ratio in  $\text{CS}_2/\text{CE}$ . For  $\text{CS}_2/\text{CE}$  experiments,  $\text{CS}_2$  was introduced into the ion source of the VG-70 VSE mass spectrometer via a standard chemical ionization (CI) reagent gas inlet. Since there was no pressure measuring device in the ion source, the source pressure is adjusted until the source chamber gauge read  $2 \times 10^{-5}$  Torr. The actual pressure inside the ion source is estimated to be in the range 0.1–0.5 Torr.

$\text{CS}_2$  was purchased from EM Science with a purity of 99.9%. Xylene from J. T. Baker Chemical Co. Polynuclear aromatic hydrocarbons and alkylbenzenes were purchased from Aldrich.

## RESULTS AND DISCUSSION

In low-voltage electron-impact ionization, molecular ions are formed with a distribution of internal energies. In contrast, in  $\text{CS}_2$  charge exchange the internal energy of the molecular ion is well defined and equal to the difference between the recombination energy (RE) of  $\text{CS}_2^{*+}$  cation and the ionization potential (IP) of the sample molecule.<sup>30</sup>



$$\Delta E = \text{RE}(\text{CS}_2^{*+}) - \text{IP}(\text{M})$$

However, almost all of the  $\text{CS}_2$  charge-exchange experiments reported in the literature used  $\text{CS}_2^{*+}$  ions formed by high-energy ionization processes, such as by reaction with  $\text{N}_2^{*+}$  or by direct bombardment with 70-eV electrons.<sup>29</sup> Under these high-energy (and high pressure for chemical ionization) conditions, fragment and cluster ions, such as  $\text{S}_2^{*+}$  and  $(\text{CS}_2)\text{S}^+$  with different recombination energies, are also produced.  $\text{CS}_2^{*+}$  itself may also be electronically and/or vibrationally excited. Thus, the charge-exchange process is not limited to  $\text{CS}_2^{*+}$  ions in the ground state. Hence, to exclude these other ionic species and higher energy states of  $\text{CS}_2^{*+}$ , it is desirable to ionize  $\text{CS}_2$  using a low-energy electron beam. Table I lists the relative abundances of these species for electron beam energies of 70 and 10 eV. The multiple ionic species formed at 70 eV can result in complicated charge-exchange spectra. At 10 eV, essentially all of the ionic species formed are  $\text{CS}_2^{*+}$  ions.

To establish optimal LV/EI conditions, xylene is commonly used as a reference compound. To illustrate the dependence of the degree of fragmentation on electron energy, the relative abundances of the molecular ion ( $m/z$  106) and two fragment ions ( $m/z$  91 and 15) of xylene are plotted versus nominal electron beam energy in Figure 1. To minimize fragmentation the nominal electron energy is usually set below 10 eV, which is accompanied by a significant loss in ion yield, as shown in Figure 2. Chemical ionization (CI) generally has higher sensitivity than electron-impact ionization (EI) considering the rate constant in CI and ionization cross sections in EI.<sup>29</sup> For this reason  $\text{CS}_2/\text{CE}$  is expected to provide higher sensitivity than LV/EI; this expectation is borne out in Figure 2 over an electron energy range of 9–16 eV. Specifically, in the range of 9–10 eV which is commonly used in LV/EI,  $\text{CS}_2/\text{CE}$  is about 50 times more sensitive.

Because of this improvement in MS sensitivity (i.e., signal-to-noise ratio) we realize an increase in mass measurement precision. An example is shown in Table II which lists measured mass defects of four ions,  $\text{C}_{33}\text{H}_{50}$  (MW 446.391),  $\text{C}_{33}\text{H}_{52}$  (MW 448.407),  $\text{C}_{31}\text{H}_{46}\text{S}$  (MW 450.332), and  $\text{C}_{31}\text{H}_{48}\text{S}$  (MW 452.348), by  $\text{CS}_2/\text{CE}$  and LV/EI. Averaged over 10 consecutive scans, both techniques yield similar results in mass measurement accuracy (1–2 millimass units (mmu) from the actual masses). However, the increased sensitivity of the mass measurement in  $\text{CS}_2/\text{CE}$  allows this technique to be more precise than LV/EI with the same number of scans: 1 versus 3 mmu. With this high precision fewer scans are needed in  $\text{CS}_2/\text{CE}$  for accurate mass measurement, which is an important feature for components in low abundance (weak peaks) and for samples with limited quantities.

The dependence of the peak intensity ratio,  $m/z$  91 to  $m/z$  106, on nominal electron beam energy in  $\text{CS}_2/\text{CE}$  and LV/EI is illustrated in Figure 3. In LV/EI this ratio increases rapidly from 1% to 65% as the electron beam energy increases from 9 to 16 eV. In contrast, it increases very slowly from 1% and maximizes at around 7% in  $\text{CS}_2/\text{CE}$ .

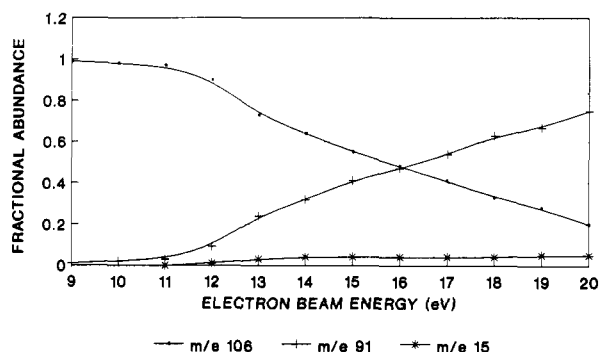
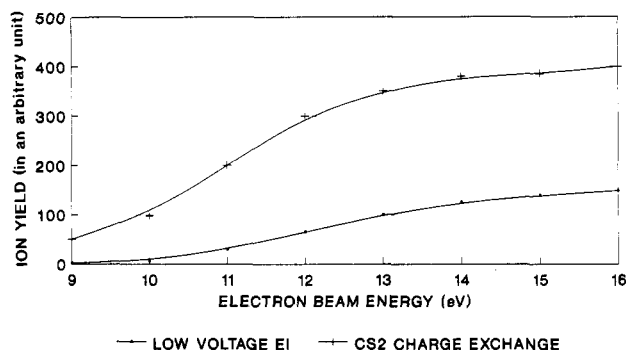
To achieve a desirable condition for either LV/EI or  $\text{CS}_2/\text{CE}$ , i.e., maximum sensitivity with minimum fragmentation, the electron beam energy is reduced to around 10 eV so that the ratio of the  $m/z$  106 ion to the  $m/z$  91 ion is greater than 50:1. This ratio is much less sensitive to the electron beam energy in  $\text{CS}_2/\text{CE}$  than in LV/EI, thereby greatly simplifying the tuning procedure and improving reproducibility.

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**Table I. Mass Spectral Data of CS<sub>2</sub> Charge-Exchange Gas Ionized by an Electron Beam at 70 and 10 eV**

<i>m/z</i> <sup>a</sup>	ionic species	fractional abundance	
		70 eV	10 eV
32	S <sup>+</sup>	0.83	
44	CS <sup>+</sup>	0.54	
64	S <sub>2</sub> <sup>+</sup>	11.64	
76	CS <sub>2</sub> <sup>+</sup>	79.34	99.01
96	S <sub>3</sub> <sup>+</sup>	0.89	
108	(CS <sub>2</sub> )S <sup>+</sup>	2.03	
152	(CS <sub>2</sub> ) <sub>2</sub> <sup>+</sup>	1.06	0.99
160	S <sub>5</sub> <sup>+</sup>	2.82	
192	S <sub>6</sub> <sup>+</sup>	0.85	
sum		100	100

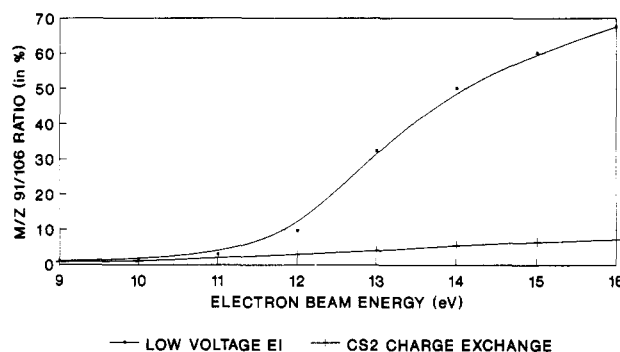
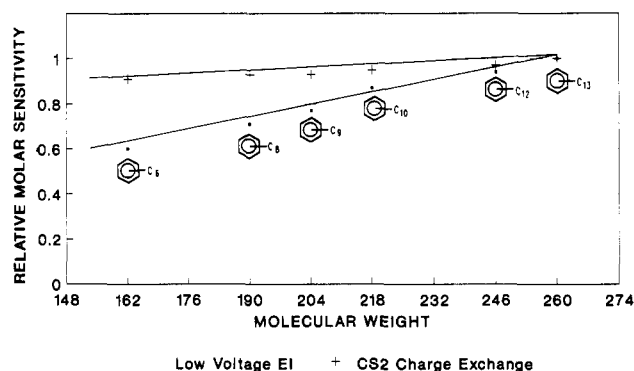
<sup>a</sup> *m/z* of the lightest isotopic peak.**Figure 1.** Relative abundances of xylene molecular and fragment ions as a function of electron beam energy in LV/EI.**Figure 2.** Ion yield of the xylene molecular ion (*m/z* 106) as a function of electron beam energy in LV/EI and CS<sub>2</sub>/CE.

One of the difficulties of using LV/EI for the quantification of components in hydrocarbon mixtures is the scarcity of alkylated aromatic and hydroaromatic model compounds for sensitivity calibration. This calibration is important because the ionization cross section in EI strongly depends on the polarity and structure of the molecules. This difficulty can be alleviated to some extent by using CS<sub>2</sub>/CE ionization. The relative molar sensitivities of alkylbenzenes (a compound series with various lengths of alkyl substituents) and polynuclear aromatic hydrocarbons (PAH's, core structures with different degrees of aromaticity) in CS<sub>2</sub>/CE and LV/EI, at a source temperature of 280 °C, are shown in Figures 4 and 5. Clearly, the relative sensitivity in CS<sub>2</sub>/CE is largely independent of molecular structure as in benzene charge-exchange ionization.<sup>28</sup> In LV/EI, on the other hand, relative molar sensitivities are strongly dependent on molecular weight and molecular structure.<sup>4,6,7</sup>

It is often reported in the literature that the temperature of the ion source be kept below 200 °C even for quantitative analysis of rather high-boiling hydrocarbon mixtures.<sup>1,23,24,27,28</sup> This could have been due to the consideration of fragmen-

**Table II. Mass Defects of Four Ions at Nominal Masses of 446, 448, 450, and 452 Measured by CS<sub>2</sub>/CE and LV/EI**

	scan no.	nominal mass			
		446	448	450	452
CS <sub>2</sub> /CE	1	0.392	0.406	0.339	0.348
	2	0.390	0.406	0.334	0.348
	3	0.392	0.405	0.334	0.348
	4	0.391	0.405	0.333	0.348
	5	0.392	0.408	0.334	0.347
	6	0.393	0.405	0.334	0.350
	7	0.392	0.405	0.333	0.348
	8	0.395	0.408	0.334	0.350
	9	0.392	0.408	0.332	0.349
	10	0.394	0.407	0.335	0.350
	mean	0.392	0.406	0.334	0.349
	std dev	0.001	0.001	0.002	0.001
LV/EI	1	0.390	0.402	0.335	0.345
	2	0.393	0.407	0.333	0.349
	3	0.392	0.408	0.332	0.350
	4	0.392	0.409	0.335	0.347
	5	0.388	0.407	0.330	0.343
	6	0.390	0.404	0.326	0.346
	7	0.394	0.403	0.335	0.349
	8	0.397	0.403	0.334	0.349
	9	0.398	0.407	0.337	0.346
	10	0.396	0.406	0.335	0.344
	mean	0.393	0.408	0.333	0.347
	std dev	0.003	0.004	0.003	0.002
actual mass defect		0.391	0.407	0.332	0.348

**Figure 3.** The intensity ratio of the *m/z* 91 to *m/z* 106 ion of xylene as a function of electron beam energy in LV/EI and CS<sub>2</sub>/CE.**Figure 4.** Relative molar sensitivity of alkylbenzenes as a function of molecular weight in LV/EI and CS<sub>2</sub>/CE.

tation of molecular ions caused by excess thermal energy at higher source temperatures. Figure 6 shows the dependence of the relative sensitivity of PAH's in CS<sub>2</sub>/CE on the source temperature. At a source temperature of 280 °C the molar sensitivities of all PAH's are almost equal. However, the sensitivities of heavy PAH's decrease rapidly as the source block temperature decreases from 280 to 150 °C. Similar phenomena were also observed in other ionization techniques; thus, one may conclude that this loss in sensitivity for heavier

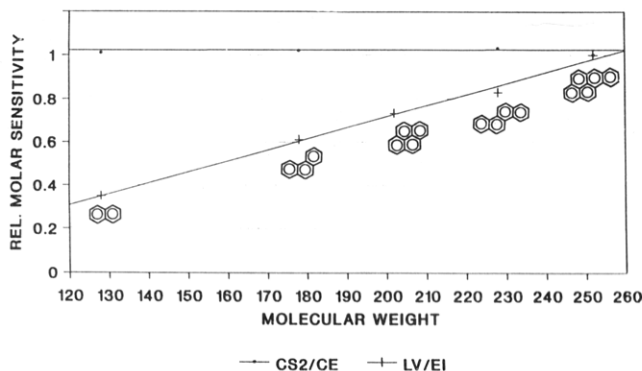


Figure 5. Relative molar sensitivity of polynuclear aromatic hydrocarbons as a function of molecular weight in LV/EI and CS<sub>2</sub>/CE.

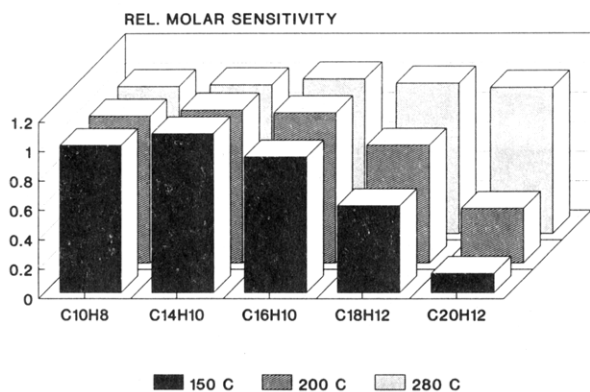


Figure 6. Relative molar sensitivity of polynuclear aromatic hydrocarbons in CS<sub>2</sub>/CE as a function of ion source temperature.

PAH's is mainly due to their condensation in a cold source. For a good result in quantification, therefore, a preferred ion source temperature would be above 280 °C.

LC can be easily combined with LV/EI and CS<sub>2</sub>/CE MS via a moving belt interface. The characterization of heavy hydrocarbons by LC/MS under LV/EI conditions has been discussed previously.<sup>12,13</sup> The relative amounts of sample in the various LC elution regions as measured by HPLC using an evaporative mass detector (EMD), LC/MS with LV/EI and LC/MS with CS<sub>2</sub>/CE, are shown in Figure 7. The results by EMD is expressed as weight % after sensitivity correction, whereas those by LC/MS are percentages of total ionization without sensitivity corrections. CS<sub>2</sub>/CE shows much better agreement with EMD than does LV/EI because of its uniform sensitivities for all aromatic compound types. Using EMD results as a reference, the tendency of overestimating 2+ring aromatics and underestimating 1-ring aromatics by LV/EI is evident. This result is consistent with the fact that LV/EI sensitivity increases with the number of aromatic rings as shown in Figure 5.

Despite the rather large differences in overall sensitivities, the distributions of compound types *within* each LC elution region as determined by LV/EI and CS<sub>2</sub>/CE show only small differences. The compound type distributions of monoaromatic hydrocarbons and diaromatic thiophenes of a petroleum distillate as determined by LV/EI and CS<sub>2</sub>/CE are shown in Figures 8 and 9. In Figure 8 the C<sub>n</sub>H<sub>2n-6</sub> series are alkylbenzenes, the C<sub>n</sub>H<sub>2n-8</sub> series are mononaphthenobenzenes, the C<sub>n</sub>H<sub>2n-10</sub> are dinaphthenobenzenes, etc. It can be observed in this figure that LV/EI relative sensitivities of hydroaromatic hydrocarbons (C<sub>n</sub>H<sub>2n+z</sub> with  $z < -6$ ) decrease with the number of naphthene rings attached to the aromatic core. For benzothiophenes (C<sub>n</sub>H<sub>2n-10</sub>S) and naphthenobenzothiophenes (C<sub>n</sub>H<sub>2n+z</sub>S with  $z < -10$ ) shown in Figure 9, the relative sensitivities are almost identical regardless of the number of naphthene rings.

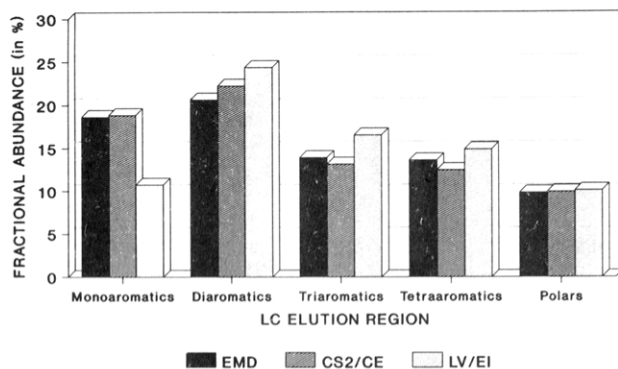


Figure 7. Distribution of aromatic hydrocarbons determined by EMD, CS<sub>2</sub>/CE, and LV/EI.

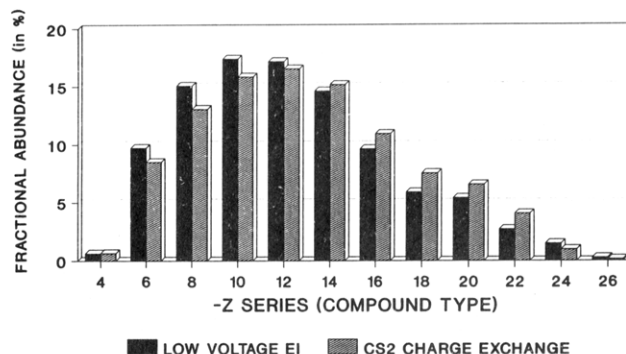


Figure 8. Distribution of hydrocarbon types in monoaromatic LC region determined by LV/EI and CS<sub>2</sub>/CE.

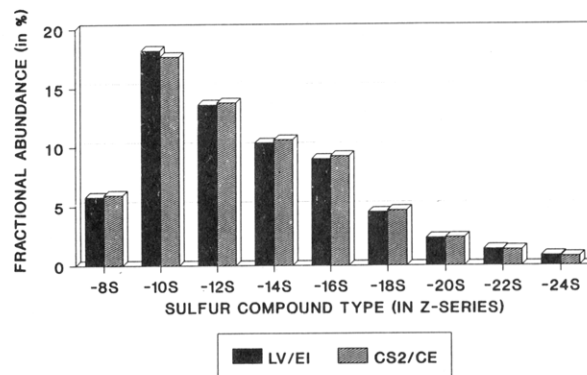


Figure 9. Distribution of sulfur compound types in diaromatic LC region determined by LV/EI and CS<sub>2</sub>/CE.

The carbon number distributions of each compound series determined by LV/EI and CS<sub>2</sub>/CE in general show very good agreement. An example is shown in Figure 10 for dinaphthenobenzenes (C<sub>n</sub>H<sub>2n-10</sub> series in monoaromatic LC elution region). Both techniques yield a carbon number distribution centered around C<sub>34</sub> with a full width at half height of about 12 carbons.

## CONCLUSIONS

Charge exchange using CS<sub>2</sub> as a reagent gas (CS<sub>2</sub>/CE) has been evaluated and compared with a traditional low-voltage electron-impact ionization (LV/EI) technique for the characterization of hydrocarbons. It would be desirable to obtain primary CS<sub>2</sub><sup>•+</sup> ion using a low-energy electron beam. The optimal ionization conditions for CS<sub>2</sub>/CE are much easier to obtain than LV/EI because ionization of the molecules depend on the well-defined recombination energy of the CS<sub>2</sub><sup>•+</sup> ions rather than the energy settings of the electron beam. Thus, small variations in electron beam energy do not affect the relative sensitivity significantly. In addition, CS<sub>2</sub>/CE is found

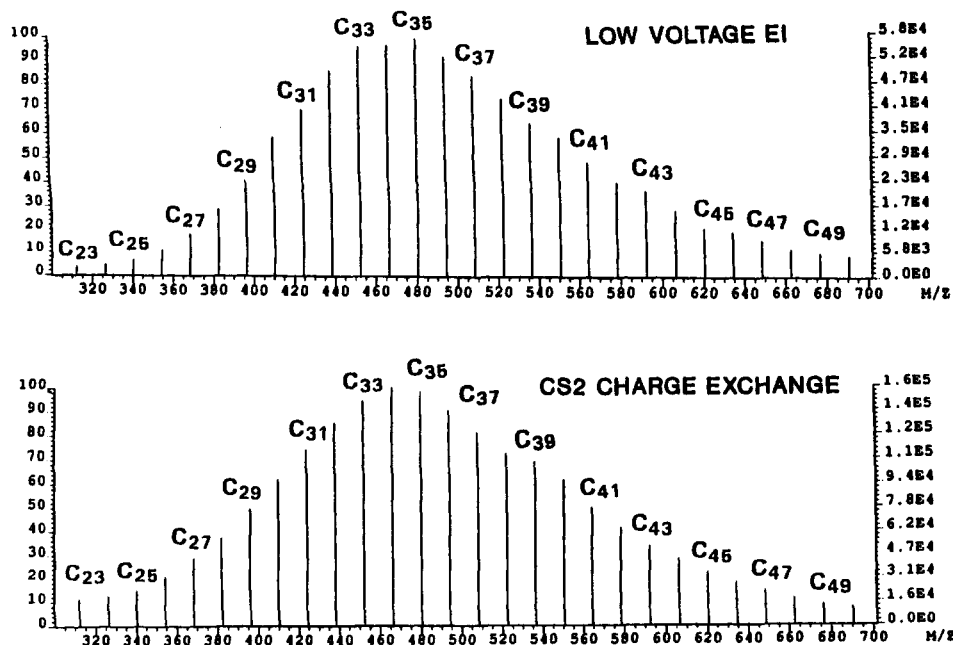


Figure 10. Carbon number distribution of dinaphthenobenzenes determined by LV/EI and CS<sub>2</sub>/CE.

to be much more sensitive than LV/EI and therefore it provides a better mass measurement precision than LV/EI. This feature is particular useful when high resolution mass spectrometry is used for accurate mass measurements. Furthermore, CS<sub>2</sub>/CE also provides more uniform molar sensitivity for the quantitative measurements of hydrocarbon molecules with different aromatic structures than LV/EI. Thus, it eliminates the necessities of obtaining a wide range of alkylated aromatic and hydroaromatic hydrocarbons for the calibration of their relative molar sensitivities for quan-

titation. Therefore, for the characterization of complex hydrocarbon mixtures CS<sub>2</sub>/CE is recommended over LV/EI.

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