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Selective Quantitation of Organic Sulfur with the Precursor Scan Method of Neutralization–Reionization Mass Spectrometry

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Quantitation of organosulfur compounds in a hydrocarbon matrix was studied by the precursor scan method of neutralization–reionization mass spectrometry. The CHS^+ ion was used as a marker selectively to detect and quantify sulfur compounds dissolved in a synthetic hydrocarbon mixture. Precursor ion abundances showed a linear dependence on the organosulfur content in the 1–100% concentration range. Detection limits of 0.5% were achieved, which were limited by the instrument sensitivity. Isobaric interferences of ^{13}C isotopomers from hydrocarbons were negligible. Small interferences from oxygen- and nitrogen-containing additives are discussed. Several neutralization gases were examined to minimize interferences and to maximize the ion abundances. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Analysis of sulfur-containing petroleum products has been a major focus in the petroleum refining industry. Sulfur removal is important owing to the problems caused by poisoning of expensive catalysts and corrosion of production plant equipment in petroleum processing. In addition, anthropogenic sulfur emissions cause air pollution and the levels of these emissions are tightly regulated.[1] The determination of sulfur in heavy oils is important since the current refining methods include processes that convert large sulfur-containing organic molecules to hydrogen sulfide, thiols and sulfides, which must be removed before using the final petroleum product.[2,3] In the geological field, alkylthiophenes have been investigated as biomarkers for geological maturation.[4]

In mixture analysis by mass spectrometry, sulfur-containing ions overlap with hydrocarbon ions at the same nominal *m*/*z* values. The small difference between the mass of SH_4 and C_3 (0.003 37 u) mandates the use of high-resolution magnetic sector instruments to distinguish and characterize sulfur components in oil mixtures.[5] However, the acquisition and use of high-resolution mass spectrometers can be prohibitively expensive in some instances. Less costly instruments based on quadrupole mass analyzers therefore represent a desirable technology to be used for mixture analysis.

Gallegos[6] described a gas chromatographic/mass spectrometric method that was based on selected-ion monitoring of organosulfur compounds in naphtha. The sulfur-containing components were detected through the CHS^+ fragment ion, which was selected at mass resolution >2000 to eliminate isobaric interferences from $C_7H_6^{2+}$.[6] Detection limits at the low ppm level were demonstrated, although the sulfur components were identified by their retention times only.[6] Tandem mass spectrometry has also been used to distinguish sulfur compounds in hydrocarbon mixtures. McLafferty and Bockhoff[7] demonstrated the detection of 25 ppm of thiophene in gasoline using a double-focusing magnetic sector instrument and a combination of mass-analyzed ion kinetic energy spectrometry (MIKES) and collision-induced dissociation (CID). Morgan and Steel[8] distinguished sulfur-containing compounds in a hydrocarbon matrix by detecting the loss of the HS radical and H_2S by a V^2/E linked scan, and in a similar method Hunt and Shabanowitz[9] used a tandem quadrupole mass spectrometer. The linked scan methods were based on the detection of fragment ions that characterized the sulfide or thiol functional groups in the target molecule and hence depended critically on the particular fragmentations of the gas-phase ions.

In contrast to mass spectrometric techniques based on ion chemistry, neutralization–reionization mass spectrometry (NRMS)[10,11] provides the means for precursor, survivor and fragment ion monitoring which are based on unimolecular dissociations of neutral intermediates. The techniques of survivor ion mass spectrometry,[12,13] variable-time NRMS[14–16] and NR precursor scan[17] have been introduced recently. Product scans, such as used in MIKES/CID, tandem quadrupole mass spectrometry or NRMS are typical single-channel methods,[18] which are able to characterize one selected ion or neutral intermediate at a time. In contrast, survivor scan,[12,13] constant neutral-loss scan[18] and precursor scan methods achieve multi-channel monitoring in

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the MS-1 domain (Fig. 1) and are suitable for monitoring selected types of compounds in mixtures.[18]

In particular, the neutral precursor scan method[17] utilizes a marker fragment that characterizes a given functional group. The marker is produced from a mixture of ions by collisional neutralization and reionization, and hence it can be formed by neutral or ion dissociations or a combination of both. The marker species is a neutral molecule, which is eliminated following collisional neutralization or collision-induced ion dissociations and detected following collisional reionization. Stable neutral molecules that are eliminated by consecutive dissociations can also be utilized as functional group markers following reionization and ion detection. The relationships between the precursor scan and the other scan methods of NRMS are shown graphically in Fig. 1.

Precursor-scan neutralization–reionization mass spectrometry was used previously to detect organophosphorus compounds selectively in synthetic organic mixtures.[17] NRMS of organophosphates, phosphites and phosphonates produced stable PO^+ ions by reionization of $PO^•$ radicals that were produced by ion and neutral dissociations.

In the present work, we utilized the precursor scan technique for the selective monitoring of organosulfur compounds in a hydrocarbon matrix. The CHS^+ (*m*/*z* 45), $^{32}SH_3{}^+$ (*m*/*z* 35), $^{32}SH_2{}^{+•}$ (*m*/*z* 34), $^{32}SH^+$ (*m*/*z* 33) and $^{32}S^{+•}$ (*m*/*z* 32) ions are produced by dissociative ionization of many sulfur compounds[6,19–21] and could be used as suitable markers. In particular, $CHS^•$ is formed abundantly by NRMS of thiol, sulfide, disulfide and sulfur heterocycle ions,[15,22,23] so that CHS^+ obtained after collisional reionization can serve as a universal marker for compounds with sulfidic groups. The $CHS^•$ radical and CHS^+ ion are stable species, as documented by the thermochemistries of their lowest energy dissociations by loss of $H^•$ (the pertinent heats of formation in kJ mol^{-1} from Ref. 24 are as follows: $CHS^•$ 305, CS 267, $H^•$ 218, CHS^+ 1018, $CS^{+•}$ 1368, C 717, CH 596, $HS^•$ 551, S 277, $C^{+•}$ 1803, CH^+ 1622, HS^+ 839 and $S^{+•}$ 1275):

$$CHS^• \rightarrow CS + H^• \quad \Delta H_r = 180 \text{ kJ mol}^{-1} \tag{1}$$

$$CHS^+ \rightarrow CS^{+•} + H^• \quad \Delta H_r = 568 \text{ kJ mol}^{-1} \tag{2}$$

The other neutral and ionic dissociations to form C, CH, S, HS and their ionic analogues are highly endothermic[24] and should not occur extensively on NRMS. In addition, $CHS^•$ has a relatively low ionization energy of ~7.3 eV,[24] and can be expected to show a good reionization efficiency. The CHS^+ ion was therefore considered a prospective marker ion for distinguishing sulfidic organic compounds in hydrocarbon mixtures through precursor scan NRMS.

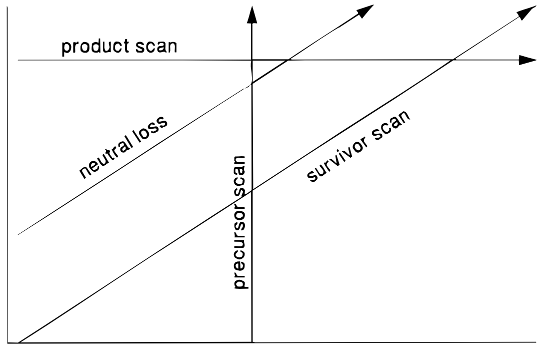

Figure 1. Scan lines in the precursor (MS-1) and product (MS-2) domains.

EXPERIMENTAL

A quadrupole acceleration–deceleration quadrupole (QADQ) mass spectrometer, described previously,[25] was used for precursor scan measurements. Briefly, the ions were formed in an electron impact ion source floated at ~80 V and transmitted without mass selection through a quadrupole mass filter (Q-1), which was operated in the r.f.-only mode and floated at 40–50 V. The ions were accelerated to 8170 eV by a special multielement lens and subsequently passed through a neutralization chamber that was floated at the acceleration potential. Trimethylamine (TMA) was used as neutralization gas that was introduced at a pressure such as to achieve 30% transmittance of the ion beam, unless noted otherwise. The fast beam of neutral intermediates was passed through a cylindrical lens floated at +250 V, which reflected the remaining ions. The neutrals passed through a 60-cm long drift region and entered a reionization cell, which was floated at a negative potential, which was scanned from 0 to −8170 V. Oxygen was introduced into the reionization cell at a pressure such as to achieve 30% transmittance of the precursor ion beam. The ions formed in the cell were decelerated, energy filtered and mass analyzed by a second quadrupole (Q-2) mass filter, which was tuned to achieve unit mass resolution. For precursor scans, Q-2 was set at the *m*/*z* ratio of the product ion with unit mass resolution, whereas the deceleration voltage was scanned from 0 to −8170 V.[17] The ions were detected with a Galileo 4880 channeltron multiplier, the electron currents were converted to voltage by a Keithley Model 428 inverting amplifier and the data were treated by a PC-based acquisition system.[26] Ten consecutive scans were typically acquired and averaged per spectrum. Precursor ion abundances in the spectra were obtained as integrated peak areas.

The neutral fragments at *m*/*z* values corresponding to m_{marker} have fractional kinetic energies, which depend on the precursor mass according to

$$\Delta T = T_{precursor}(m_{marker}/m_{precursor}) - T_{marker} \tag{3}$$

where is ΔT is the kinetic energy defect due to the two charge transfer collisions (15–20 eV).[27,28] Marker ions produced by dissociations in the ion source are detected at deceleration potentials (U_{dec}) close to the acceleration potential (U_{acc}), whereas marker neutrals produced from heavier precursors are detected following reionization at lower U_{dec}. The U_{dec} scan function is linear in ion kinetic energy [Eqn (3)], but non-linear in the precursor mass [Eqn (4)],[17] where *a* depends on the marker ion mass and precursor ion kinetic energy and *b* is an offset due to ΔT, which is minimized by calibrating the kinetic energy scale with the survivor ion of CS_2.

$$U_{dec} = T_{marker}/ze = a/m_{precursor} - b \quad (4)$$

The U_{dec} scale in the precursor-ion scans was transformed to a linear mass scale using a spreadsheet program. The precursor mass resolution in the precursor scan depends on the precursor and marker mass and the kinetic energy release in the fragmentation producing the neutral marker, as discussed previously.[17]

Chemicals were purchased from Aldrich or Baker and used without further purification. Mixture samples were prepared by serial dilution of sulfur-containing compounds in a base oil solution. The base oil was prepared by mixing equal volumes of benzene, cyclohexane, *n*-hexane, hex-1-ene, hexa-1,5-diene and cyclohexane. The liquid samples were injected into a heated glass reservoir at 100 °C and leaked into the ionization chamber through a fine metering valve to achieve pressures of 5.0×10^{-6} Torr (1 Torr = 133.3 Pa). The sample pressure was measured with a Bayard–Alpert ionization gauge which was mounted on the source diffusion pump intake. The sample pressure inside the ionization chamber was estimated to be 10^{-5} Torr.

RESULTS AND DISCUSSION

The precursor scan method comprises two collisional charge permutations performed with a mixture of gas-phase ions. The resulting spectrum depends on (i) the relative abundances of the precursor ions sampled for neutralization, (ii) the neutralization cross-sections and (iii) the kinetics of neutral and reionized-ion dissociations that yield the marker neutral or ion, respectively. The reionization cross-sections play a lesser role because the same marker species is detected from all precursors. With the tandem quadrupole instrument used, the precursor ion relative abundances depend on the ion transmission through the r.f.-only Q-1 quadrupole mass filter.[17] The ion transmissions depend on the precursor ion mass and kinetic energy and show periodicity for a given a.c. voltage amplitude and d.c. pole offset.[29] In the present measurements, the ion transmission was kept constant by tuning the Q-1 d.c. and r.f. parameters to obtain a constant standard spectrum. The [*m*/*z* 84]/[*m*/*z* 45] and [*m*/*z* 92]/[*m*/*z* 39] ratios in the electron impact spectra of thiophene and toluene, respectively, were used for tuning the Q-1 transmission.

Neutralization targets

The neutralization target gas was selected to optimize the neutralization efficiency while avoiding interferences. Table 1 shows that dimethyl disulfide exhibited a good neutralization efficiency for the molecular ion of thiophene. However, electron impact fragmentation of dimethyl disulfide produces CHS^+, which caused interferences at low levels of organosulfur analytes. Since relatively high partial pressures of several millitorr of the neutralization gas were used in the collision cell to achieve 70% attenuation of the analyte ion beam, it was difficult to prevent traces of the neutralization gas from penetrating into the ion source. Ionization of residual CH_3SSCH_3 produced background CHS^+, which gave rise to interference peaks at *m*/*z* 94 in the precursor spectra [Fig. 2(a) and (b)]. To remove this interference, trimethylamine (TMA) was used throughout the precursor scan measurements, which showed no background peaks in the precursor spectra of CHS^+ at *m*/*z* 45 [Fig. 2(c) and (d)]. The good neutralization efficiencies of CH_3SSCH_3 and TMA may be due to their vertical ionization energies ($IE_v = 8.96$ and 8.54 eV, respectively), which are close to that of thiophene (8.85 eV).[30] Neutralization targets with higher IE_v, such as cyclopropane (10.54 eV) and Xe (12.13 eV), showed progressively lower efficiencies (Table 1).

Table 1. Neutralization–reionization efficiencies of thiophene $C_4H_4S^{+\cdot}$ ion

Neutralization target[a]	Efficiency (%)[b]
Dimethyl disulfide	0.047
Trimethylamine	0.025
N,*N*-Dimethylaniline	0.020
Cyclopropane	0.014
Xenon	0.007

[a] At 70% precursor ion beam transmittance, reionization with O_2 at 70% ion transmittance.
[b] Relative to the sum of reionized ion abundances, $\%\Sigma I_{NR}$.

Neutralization–reionization spectra

The NR mass spectrum of thiophene [Fig. 3(b)] was similar to the conventional electron ionization spectrum.[19] Both spectra showed an abundant CHS^+ ion. CHS^+ was also formed by electron ionization and NR of butane-1-thiol, diethyl sulfide and dimethyl disulfide as shown for the former [Fig. 3(a)]. Hence CHS^+ appears to be a universal marker ion for monitoring various organosulfur compounds with sulfide and thiol groups. The NR spectrum of CHS^+ from thiophene showed an abundant survivor ion that amounted to 45% of the total reionized ion current ($\%\Sigma_{[NR]}$). The NR efficiency for CHS^+ ranged between 0.04 and 0.12% for 70–30% ion transmittance, which is at the high end of the typical NR efficiency range.[16,17,31,32] The NR spectra of CHS^+ from thiophene, butane-1-thiol, diethyl sulfide and dimethyl disulfide did not show any significant differences that would indicate the formation of isomeric structures, e.g. H—C=S and C=S—H. We assume that the marker ions had the H—CS^+ structure.

Precursor scans

The precursor scan of CHS^+ from thiophene [Fig. 4(a)] showed peaks due to NR of CHS^+ formed in the ion source (*m*/*z* 45) and a major peak due to dissociation of C_4H_4S and/or $C_4H_4S^{+\cdot}$ at *m*/*z* 84. The $C_2H_2S^{+\cdot}$ fragment at *m*/*z* 58 also yielded CHS^+ on NR. The loss of CH on neutralization–reionization is uncommon and may point to the cyclic thiirene structure for the $C_2H_2S^{+\cdot}$ precursor ion. For example, methyloxirene,

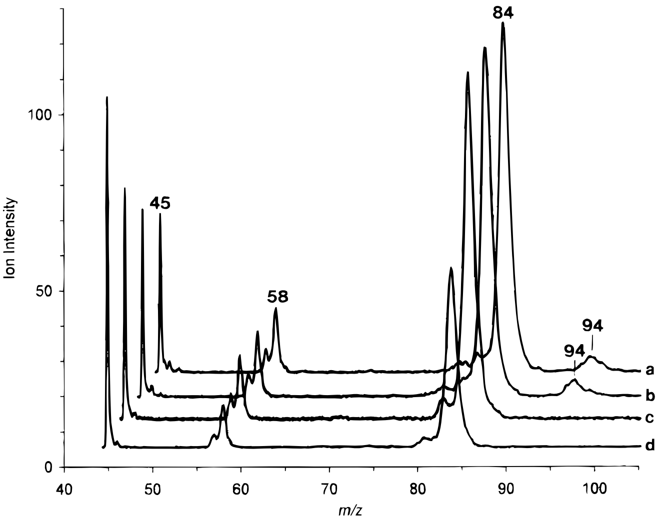

Figure 2. NR precursor scans of CHS^+ from thiophene with CH_3SSCH_3–O_2, 30% transmittance (a), 70% transmittance (b), TMA–O_2, 30% transmittance (c) and 70% transmittance (d).

but not the other C_3H_4O isomers, was found to eliminate CH upon NR.[33] Dimethyl disulfide formed CHS^+ from several precursor ions [Fig. 4(b)], e.g. the molecular ion at *m/z* 94, $[M - CH_3]^+$ at *m/z* 79, $[M - HS]^+$ at *m/z* 61 and the CH_xS^+ group at *m/z* 45–48. Likewise, diethyl sulfide [Fig. 4(c)] and butane-1-thiol [Fig. 4(d)] showed their molecular and fragment ions as precursors of CHS^+. The mechanisms for these CHS^+ formations from thiol and sulfide precursors have not been elucidated. It appeared, however, that CHS^+ was formed through multi-step dissociations with the possible intermediacy of CH_2SH^+. The latter ion forms CHS^+ abundantly upon NR.[22] By comparison with the electron ionization and conventional NR mass spectra, the CHS^+ precursor scans showed much simpler patterns. In particular, for butane-1-thiol and analogously for higher alkanethiols the hydrocarbon fragments are filtered out by the CHS^+ selective scans, which results in substantial simplification of the spectra. It may also be noted that the CHS^+ marker ion need not be a prominent fragment ion in the EI spectrum of the sulfur compound under study. For example, CHS^+ is a minor fragment ion in the EI spectra of butane-1-thiol and diethyl sulfide.[19] The facile detection of these sulfur compounds by CHS^+ precursor scans is made possible by the non-specific formation of $CHS^\cdot$ and CHS^+ upon neutralization–reionization of most sulfur-containing ions produced by electron impact.

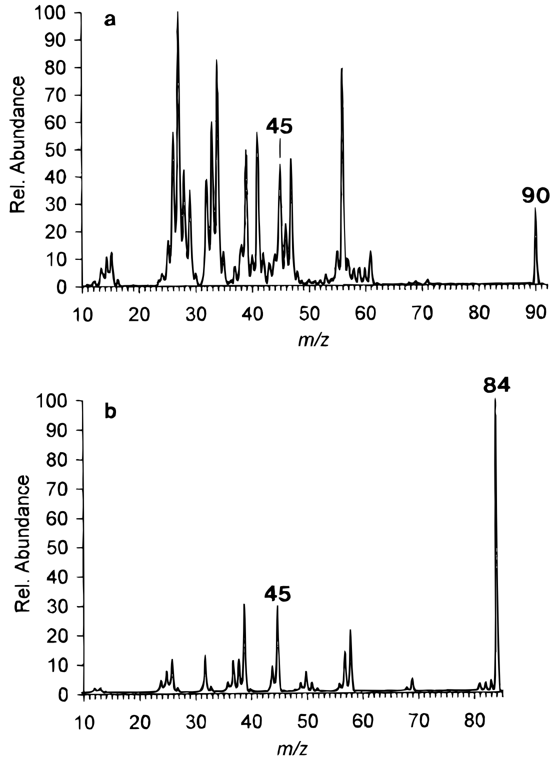

Figure 3. NR (TMA–O_2, 70% transmittance) mass spectra of (a) *m/z* 90 from butane-1-thiol and (b) *m/z* 84 from thiophene.

Quantitative analysis

The concentration dependence and limits of detection in the CHS^+ precursor scans were investigated for thiophene, butane-1-thiol, dimethyl disulfide and diethyl sulfide. One or two prominent precursor peaks were selected that were characteristic for the given organosulfur compound, and the integrated intensities were monitored as a function of the organosulfur concentration in the hydrocarbon matrix. Two concentration ranges were studied, e.g. 0–10% and 0–100% w/w. No internal standards were used in these measurements. Monitoring thiophene at the peak of the C_4H_4S precursor (apparent *m/z* 84) gave linear responses for both concentration ranges. The 0–10% range gave correlation coefficients $r^2 = 0.9354$–0.9981 ($n = 8$) from several runs. The day-to-day reproducibility in the absolute peak intensities (root mean square deviations) was about 30% and the reproducibility for runs taken on the same day was within 5%. Dimethyl disulfide was monitored at the peaks of CH_3S_2 (apparent *m/z* 79) and CH_3SSCH_3 (apparent *m/z* 94) with similar results. Linear responses were obtained for both concentration ranges. The CH_3S_2 channel gave $r^2 = 0.9966$ and 0.9947 ($n = 7$) for the 0–100% and 0–10% concentration ranges, respectively. The CH_3SSCH_3 channel gave $r^2 = 0.9871$ and 0.9950 ($n = 7$) for the 0–10% and

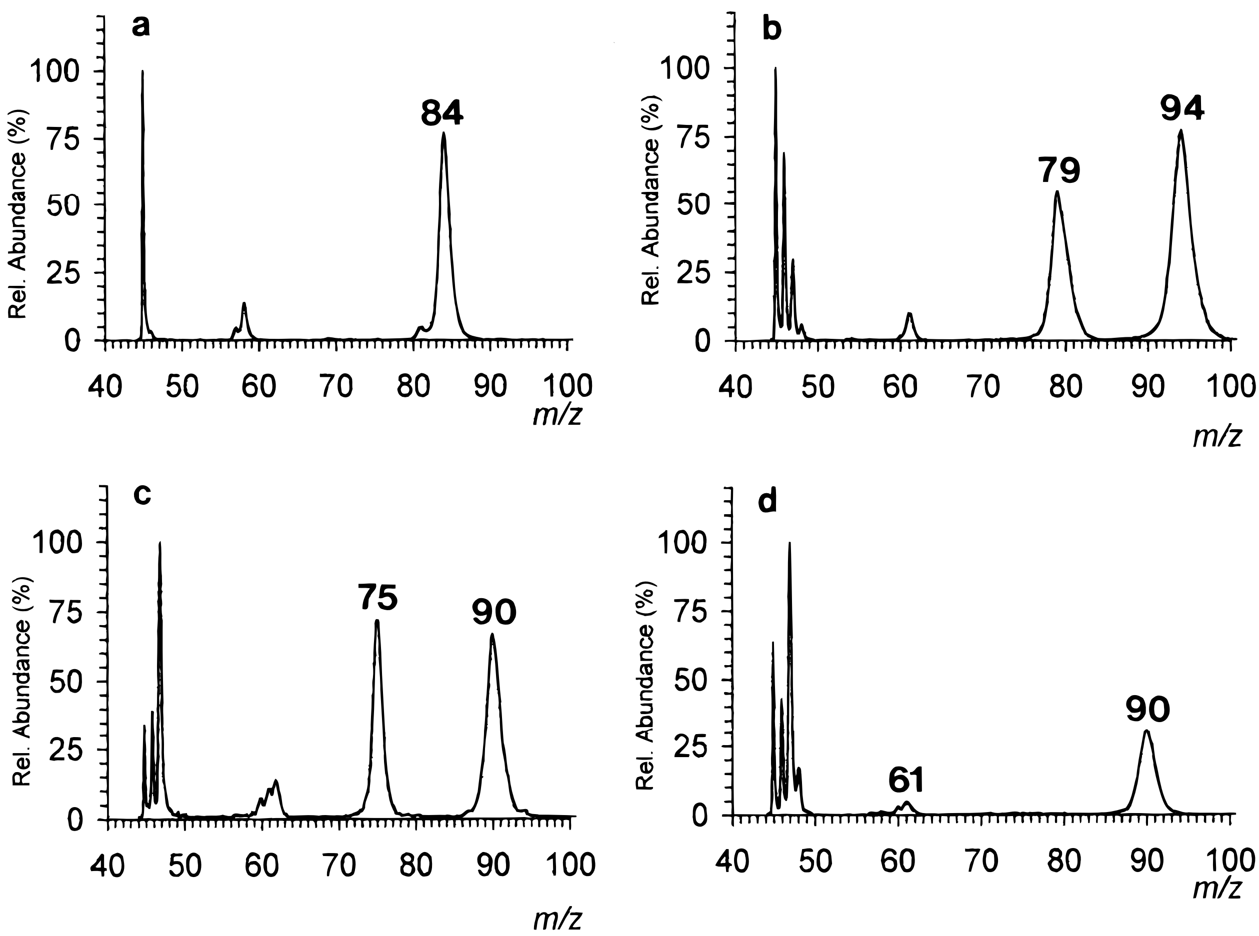

Figure 4. NR precursor scans (TMA–O_2, 30% transmittance) of CHS^+ from (a) thiophene, (b) dimethyl disulfide, (c) diethyl sulfide and (d) butane-1-thiol.

0–100% ranges, respectively. Diethyl sulfide was monitored at the precursor channels of $(C_2H_5)_2S$ (apparent *m/z* 90) and $C_2H_5SCH_2$ (apparent *m/z* 75) with comparable results. The *m/z* 75 channel gave $r^2 = 0.9989$ and 0.9936 for the 0–100% and 0–10% concentration ranges, respectively, whereas the *m/z* 90 channel gave $r^2 = 0.9990$ and 0.9776, respectively. The response to butane-1-thiol was monitored in the C_4H_9SH channel (apparent *m/z* 90), which gave a less sensitive response. The linearity was moderate, $r^2 = 0.9661$ in the 0–10% concentration range.

The detection limits were extrapolated from the concentration-dependent precursor scans for the organosulfur compounds under study, as shown for thiophene [Fig. 5(a)–(e)]. The precursor scan afforded detectable peaks at a signal-to-noise ratio $\geqslant 5$ down to 0.5% thiophene concentration [Fig. 5(d)] which represented the practical detection limit in these measurements. The background spectrum of the base oil [Fig. 5(e)] showed no interferences at the apparent *m/z* values corresponding to thiophene peaks, e.g. *m/z* 84 and 58. The relatively high detection limit was therefore due to the lack of ion signal from the analyte rather than the presence of chemical background. This suggested that improving the precursor ion currents, ion transmission and detection levels could result in substantially lower detection limits for thiophene in hydrocarbon matrices. Detection limits around 0.5% were also achieved for dimethyl disulfide and diethyl sulfide, which were due to the disappearance of ion currents whereas the base oil background was low. In contrast, the ion currents in the precursor scan of butane-1-thiol vanished at 1.5% concentration. The reason for this high detection limit stems from the broad precursor peak of C_4H_9SH at apparent *m/z* 90, which is more difficult to detect at low butane-1-thiol levels.

Interferences

Interferences at the marker ion *m/z* 45 can originate from several sources.[6] The hydrocarbon matrix which is present in large excess can interfere with $^{13}C_2CH_7$, which amounts to 0.025% of the usually abundant $C_3H_7{}^+$ ion. However, the blank spectrum of the matrix showed no detectable signal in the *m/z* 45 precursor scan [Fig. 5(e)]. This was due to the low abundance of the precursor ion, low relative abundance of survivor ion in the NR spectrum of $C_3H_7{}^+$ and its low NR efficiency, all of which make this species a poor marker for hydrocarbons. In addition, the intermediate $C_3H_7{}^{\bullet}$ radicals formed by neutralization of $C_3H_7{}^+$ fragment readily.[34] Nitrogen-containing compounds can similarly interfere at *m/z* 45 by the ^{13}C and ^{15}N isotope satellites of the ubiquitous $C_2H_6N^+$ fragment ion, which combined amount to 2.57% of the latter. However, NR

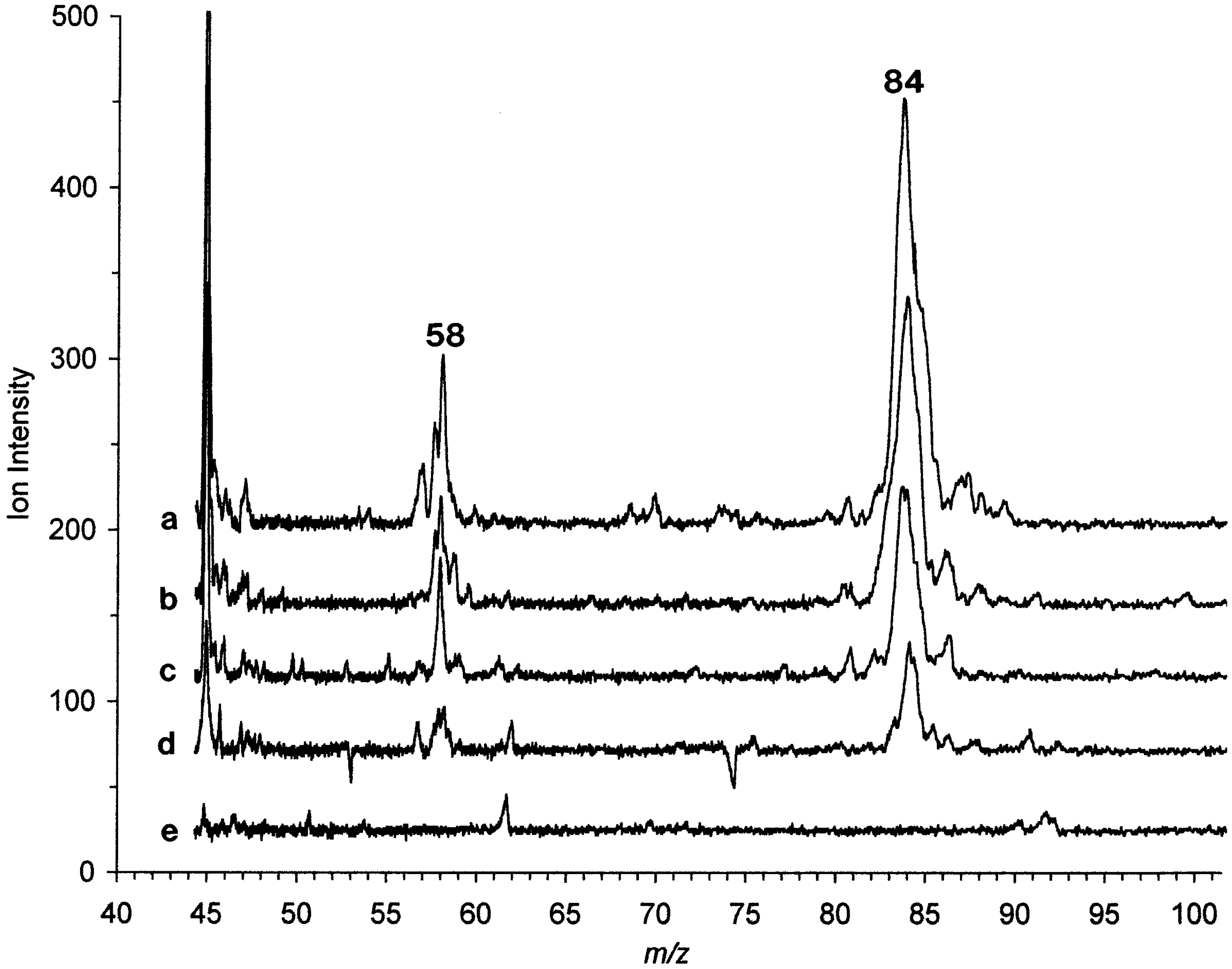

Figure 5. Detection limits in the NR precursor scan of CHS^+ from thiophene: (a) 2.1%; (b) 1.5%; (c) 1.0%; (d) 0.5%; (e) base oil background.

mass spectra of immonium ions show survivor ions[35] of low abundance, which should disfavor the interference by C_2H_6N isotopomers. In addition, the levels of nitrogen and sulfur compounds in petroleum are comparable. Hence the low-abundance C_2H_6N isotopomers should not represent a serious interference in precursor scans.

Oxygenated molecules, such as alcohols, ethers, carboxylic acids and esters appear in the petroleum process streams and may represent interferences in organosulfur monitoring.[36,37] Alcohols and ethers give rise to the non-specific $C_nH_{2n+1}O^+$ ion series,[21] including $C_2H_5O^+$, which coincides in mass with the CHS^+ marker ion. Precursor scans for three model oxygen compounds, methyl *tert*-butyl ether, propan-2-ol and tetrahydrofuran, gave only weak signals of $C_2H_5O^+$ precursors. In each case, the dominating peak corresponded to survivor $C_2H_5O^+$ at *m/z* 45. This observation was consistent with the standard NR spectra of the major ion species in the EI spectra of methyl *tert*-butyl ether, propan-2-ol and tetrahydrofuran (spectra not shown). For example, the NR spectrum of the $[M - CH_3]^+$ ion from methyl *tert*-butyl ether (*m/z* 73) gave a negligible (<0.1%) peak of $C_2H_5O^+$ at *m/z* 45. Likewise, the NR spectrum of the molecular ion of tetrahydrofuran gave no $C_2H_5O^+$. However, it is possible that higher alcohols may form $C_2H_5O^+$ by consecutive alkene eliminations from $C_nH_{2n+1}O^+$ ions, which would then appear as peaks in the precursor scans.

The $C_2H_5O^+$ ions from EI dissociations of methyl *tert*-butyl ether, propan-2-ol and tetrahydrofuran represented different isomers or isomeric mixtures, as revealed by their NR spectra. The NR spectrum of $C_2H_5O^+$ from propan-2-ol corresponded to $CH_3CH{=}OH^+$ [Fig. 6(a)], which differed from the NR spectrum of $CH_3OCH_2{}^+$ prepared from 1,2-dimethoxyethane [Fig. 6(b)]. The NR spectra of $CH_3CH{=}OH^+$ and another isomer, $CH_2{=}CHOH_2{}^+$, were reported previously by Polce *et al.*[38] The present NR spectrum of $CH_3CH{=}OH^+$ is in a reasonable agreement with the previously published spectrum that was obtained on a sector instrument.[38] The NR spectra of $C_2H_5O^+$ from methyl *tert*-butyl ether [Fig. 6(c)] and tetrahydrofuran [Fig. 6(d)] differed from the above standards in that they showed weak survivor ions and very abundant peaks of C^+ through $CH_3{}^+$. The structures of these weak ions were not studied further in detail. The facile dissociation may point to an unstable intermediate radical, such as that of *O*-protonated oxirane. However,

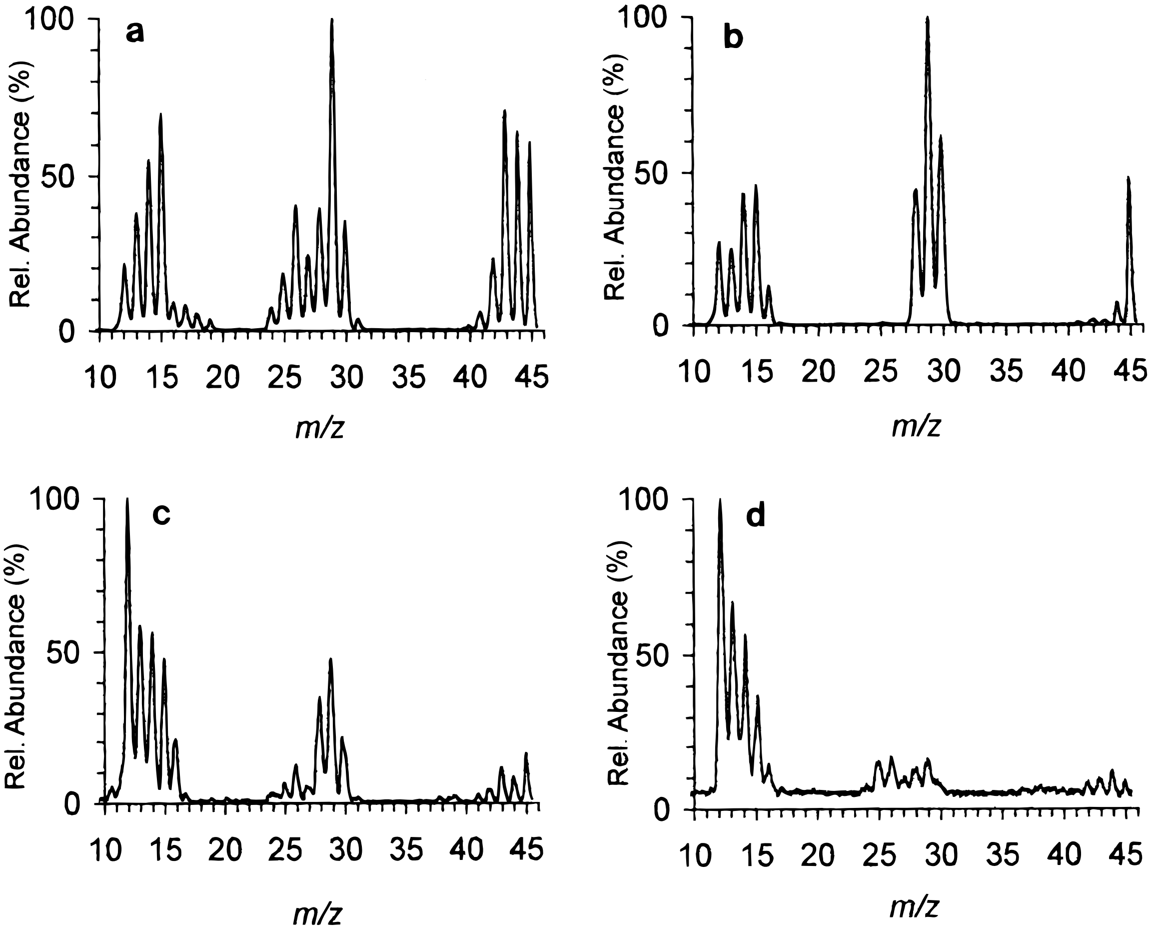

Figure 6. NR (TMA–O$_2$, 70% transmittance) mass spectra of $C_2H_5O^+$ ions from (a) propan-2-ol, (b) 1,2-dimethoxyethane, (c) methyl *tert*-butyl ether and (d) tetrahydrofuran.

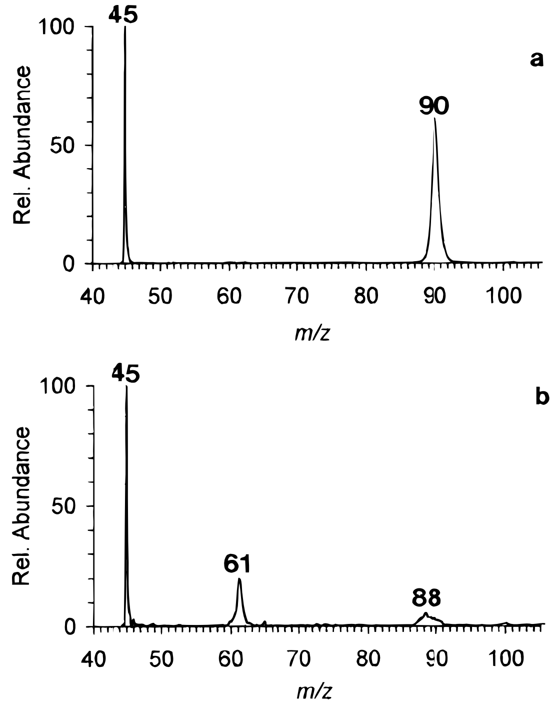

Figure 7. NR precursor scans (TMA–O$_2$, 30% transmittance) of *m/z* 45 from (a) 1,2-dimethoxyethane and (b) ethyl acetate.

the spectra also suggested that the $C_2H_5O^+$ ion from methyl *tert*-butyl ether contained contributions from $CH_3OCH_2^+$ (*m/z* 45, 30–28) and $CH_3CH{=}OH^+$ (*m/z* 44, 43) (Fig. 6).

Ethyl esters give rise to fragment ions at *m/z* 45.[19,21] The precursor scan of *m/z* 45 from ethyl acetate showed mostly the survivor ion at *m/z* 45, and weak peaks of $CH_3COOH_2^+$ at an apparent *m/z* 61 and of ethyl acetate molecular ion at an apparent *m/z* 88 [Fig. 7(b)]. These suggested that the *m/z* 45 ion was a mixture of $C_2H_5O^+$ and CO_2H^+. Owing to the low relative abundance of precursor peaks in these scans, esters do not appear to represent serious interference for monitoring organosulfur molecules. The possible interference from $C_2H_5O^+$-yielding ethers is illustrated by the NR precursor scan of 1,2-dimethoxyethane [Fig. 7(a)].

CONCLUSIONS

Neutralization–reionization precursor scans of CHS^+ were used for the selective monitoring of organosulfur compounds in hydrocarbon matrices. The precursor scans showed negligible interferences from hydrocarbons and nitrogen compounds and low interferences from alcohols, ethers and esters. Linear response was achieved over a broad concentration range without using an internal standard. With the present instrumentation, the precursor scan method gave relatively high detection limits that were due to low ion currents. Improvements in the ionization and ion transmission efficiency could lead to lower detection limits. The absence of interferences should make the precursor scan method suitable for the monitoring and speciation of organosulfur compounds at 1–10% levels in crude oil prior to desulfurization.

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REFERENCES

1. R. S. Hutte, in *Chromatography in Petroleum Industry*, p. 201. Elsevier, Amsterdam (1995).
2. M. R. Gray, *Upgrading Petroleum Residues and Heavy Oils*. Marcel Dekker, New York (1994).
3. K. H. Altgelt and M. M. Boduszynski, *Composition and Analysis of Heavy Petroleum Fractions*. Marcel Dekker, New York (1994).
4. M. P. Koopmans, J. S. Sinninghe Damste, M. D. Lewan and J. W. De Leeuw, *Org. Geochem.* **23**, 583 (1995).
5. J. E. Hunt, G. W. Haas, R. E. Winans and J. T. Miller, in *Proceedings of the 44th ASMS Conference on Mass Spectrometry and Applied Topics*, Portland, OR, 1996, Communication No. ThPE 125.
6. E. J. Gallegos, *Anal. Chem.* **47**, 1150 (1975).
7. F. W. McLafferty and F. M. Bockhoff, *Anal. Chem.* **50**, 69 (1978).
8. R. P. Morgan and G. Steel, *Adv. Mass Spectrom.* **8**, 1725 (1980).
9. D. F. Hunt and J. Shabanowitz, *Anal. Chem.* **54**, 574 (1982).
10. P. O. Danis, C. Wesdemiotis and F. W. McLafferty, *J. Am. Chem. Soc.* **105**, 7454 (1983).
11. P. C. Burgers, J. L. Holmes, A. A. Mommers and J. K. Terlouw, *Chem. Phys. Lett.* **102**, 1 (1983).
12. F. Tureček and M. Gu, *Org. Mass Spectrom.* **27**, 1335 (1992).
13. F. Tureček and M. Gu, *J. Mass Spectrom.* **30**, 144 (1995).
14. D. W. Kuhns, S. A. Shaffer, T. B. Tran and F. Tureček, *J. Phys. Chem.* **98**, 4845 (1994).
15. D. W. Kuhns and F. Tureček, *Org. Mass Spectrom.* **29**, 463 (1994).
16. M. Sadilek and F. Tureček, *J. Phys. Chem.* **100**, 224 (1996).
17. M. Gu and F. Tureček, *Org. Mass Spectrom.* **28**, 1135 (1993).
18. J. C. Schwartz, A. P. Wade, C. G. Enke and R. G. Cooks, *Anal. Chem.* **62**, 1809 (1990).
19. F. W. McLafferty and D. B. Stauffer, *The Wiley/NBS Registry of Mass Spectral Data*. Wiley, New York (1989).
20. Q. N. Porter, *Mass Spectrometry of Heterocyclic compounds*, 2nd edn. Wiley, New York (1985).
21. F. W. McLafferty and F. Tureček, *Interpretation of Mass Spectra*, 4th edn. University Science Books, Mill Valley, CA (1993).
22. F. Tureček, D. E. Drinkwater and F. W. McLafferty, *J. Am. Chem. Soc.* **111**, 7696 (1989).
23. F. Tureček, F. W. McLafferty, B. J. Smith and L. Radom, *Int. J. Mass Spectrom. Ion Processes* **101**, 283 (1990).
24. S. G. Lias, J. F. Liebman, J. L. Holmes, R. D. Levin and G. W. Mallard, *J. Phys. Chem. Ref. Data* **17**, Suppl. 1 (1988).
25. F. Tureček, M. Gu and S. A. Shaffer, *J. Am. Soc. Mass Spectrom.* **3**, 493 (1992).
26. D. E. Drinkwater, F. Tureček and F. W. McLafferty, *Org. Mass Spectrom.* **26**, 559 (1991).
27. J. Bordas-Nagy, J. L. Holmes and C. E. C. A. Hop, *Int. J. Mass Spectrom. Ion Processes* **94**, 189 (1989).
28. J. L. Holmes, *Mass Spectrom. Rev.* **8**, 513 (1989).
29. P. H. Dawson and J. E. Fulford, *Int. J. Mass Spectrom. Ion Phys.* **42**, 195 (1982).
30. S. G. Lias, J. F. Liebman, R. D. Levin and S. S. Kafafi, *NIST Standard Reference Database, Version 2.01*. NIST, Washington, DC (1994).
31. P. O. Danis, R. Feng and F. W. McLafferty, *Anal. Chem.* **58**, 348 (1986).
32. C. Wesdemiotis, R. Feng, E. R. Williams and F. W. McLafferty, *Org. Mass Spectrom.* **21**, 689 (1986).
33. F. Tureček, D. E. Drinkwater and F. W. McLafferty, *J. Am. Chem. Soc.* **113**, 5958 (1991).
34. W. Tsang, *J. Am. Chem. Soc.* **107**, 2872 (1985).
35. S. A. Shaffer, F. Tureček and R. L. Cerny, *J. Am. Chem. Soc.* **115**, 12117 (1994).
36. S. M. Lewis and F. Hatch, *Chemistry of Petrochemical Processes*, pp. 11–19. Gulf Publishing, Houston, TX (1994).
37. M. R. Gray, *Upgrading Petroleum Residues and Heavy Oils*, pp. 16–22. Marcel Dekker, New York (1994).
38. M. J. Polce, M. M. Cordero, C. Wesdemiotis and P. A. Bott, *Int. J. Mass Spectrom. Ion Processes* **113**, 35 (1992).