A Gas Chromatograph/Resonant Electron Capture−TOF Mass Spectrometer for Four Dimensions of Negative Ion Analytical Information

ARTICLE *in* ANALYTICAL CHEMISTRY · JUNE 2004

Impact Factor: 5.64 · DOI: 10.1021/ac030324g · Source: PubMed

8 AUTHORS, INCLUDING:

Valery G Voinov
Oregon State University
34 PUBLICATIONS **374** CITATIONS
SEE PROFILE

Yury V Vasil'ev
Oregon State University
35 PUBLICATIONS **566** CITATIONS
SEE PROFILE

Jeff Morré
Oregon State University
36 PUBLICATIONS **416** CITATIONS
SEE PROFILE

Anal. Chem. **2004,** *76,* 2951−2957

A Gas Chromatograph/Resonant Electron Capture-TOF Mass Spectrometer for Four Dimensions of Negative Ion Analytical Information

V. G. Voinov,[†,‡] Y. V. Vasil'ev,[†,§] H. Ji,[†] B. Figard,[†] J. Morré,[†] T. F. Egan,[⊥] D. F. Barofsky,[†] and M. L. Deinzer*[,†]

Department of Chemistry and Environmental Health Sciences Center, Oregon State University, Corvallis, Oregon 97331, Pacific Institute of Bioorganic Chemistry, Vladivostok, Russia, Department of Physics, Bashkir State Agricultural University, Ufa, Russia, and Ionwerks Inc., 2472 Bolsover, Suite 255, Houston, Texas 77005

A prototype gas chromatograph (GC) electron monochromator (EM) reflectron time-of-flight (TOF) mass spectrometer has been constructed and demonstrated to simultaneously record four-dimensional resonant electron capture (REC) mass spectra (*m*/*z*, ion-intensity, electron-energy, and retention time) of electron-capturing compounds in real time. Specifically, complete REC mass spectra of all of the components in a mixture of perfluorocarboxylic acids and in a sample of pentafluorobenzyl alcohol were recorded in the GC mode. For each compound, the data enable one to distinguish different electronic states of the molecular ion and different possible decomposition pathways for each state. This new instrument can be used to obtain analytical information unrecognizable by any other mass spectrometric technique from the isomeric species of a variety of electron-capturing structures.

In contrast to the vast majority of mass spectrometric techniques, resonant electron capture mass spectrometry (REC MS) exhibits both the features of typical mass spectrometry and those of spectroscopic methods, since it deals with mode-selective species of negative ions with precisely tunable and measurable internal energies. The latter is based upon the resonant nature of negative ion formation via gas-phase electron−molecule reactions, cross sections of which represent more or less pronounced peaks as functions of electron energy. Each polyatomic molecule is characterized by its own electronic structure, and this becomes the basis for REC MS as a method for distinguishing between corresponding negative ions. Each ion originates from an intermediate state called a resonance; each resonance is, in turn, associated with particular electronic and vibrational states. Thus, the signal intensities for the ion peaks vary depending on the energies of the captured electrons. REC MS is especially effective and useful for distinguishing among isomeric species with close spatial structures but with different electronic energy levels.

Negative ions have obvious advantages over their positively charged counterparts, for which determining the internal energies is often a major issue. Unfortunately, dissociative electron capture leading to the formation of negative fragment ions is characterized by cross sections that vary over more than 10 orders of magnitudes from being virtually unmeasurable, that is, 10^{-23} cm^2 (as in the case of CH_3Cl[1]) to larger than 10^{-13} cm^2 (as in the case of CCl_4[2]). This is in stark contrast with the formation of positive ions generated via electron impact ionization in which cross sections typically have magnitudes of $\sim 10^{-16}$ cm^2. Historically, the broad range of cross sections in REC MS has presented a major challenge in obtaining useful analytical information, because accumulation of the total three-dimensional mass spectrum, that is, ion intensity (I), electron energy (E_e), and mass-to-charge ratio (m/z) of all negative fragment ions with low formation cross sections was so time-consuming. Indeed, when using a sector or a quadrupole instrument, either of which normally requires effective yield curves for negative ions to be recorded separately, the accumulated time for the total mass spectrum can take up to several days.

Recently, the present authors reported[3] that a time-of-flight (TOF) mass spectrometer fitted with a trochoidal electron monochromator (TEM) for generating a monoenergetic electron beam and equipped with a modern fast data acquisition system can decrease the acquisition time for three-dimensional REC mass spectra of a compound to just 1 s. It was proposed in that report that this speed would be sufficient to record effluents from a capillary gas chromatography (GC) column in real time. The present work was undertaken to determine if the unique spectroscopic features of REC could, indeed, be exploited for real time analysis of complex mixtures of chemical compounds that are indistinguishable by any other forms of GC/MS. Although a complete REC spectrum can in principle be obtained on a GC/quadrupole system[4] or a sector instrument,[5] the acquisition speed of these types of mass spectrometers is insufficient to conduct GC/REC MS experiments in real time. In this paper, a novel four-

† Oregon State University.
‡ Pacific Institute of Bioorganic Chemistry.
§ Bashkir State Agricultural University.
⊥ Ionwerks Inc.

(1) (a) Fabrikant, I. I. In *Dissociative Recombination. Theory, Experiment, And applications*; Rowe, B. R., Mitchell, J. A., Canosa, A., Eds.; Plenum Press: New York, 1993, pp 195−203. (b) Pearl, D. M.; Burrow, P. D.; Fabrikant, I. I.; Gallup, G. A. *J. Chem. Phys.* **1995**, *102*, 2737−2743. (c) Wilde, R. S.; Gallup, G. A.; Fabrikant, I. I. *J. Phys. B: At. Mol. Opt. Phys.* **2000**, *33*, 5479−5492.
(2) Dunning, F. B. *J. Phys. Chem.* **1987**, *91*, 2244−2249.
(3) Voinov, V. G.; Vasil'ev, Y. V.; Morré, J.; Barofsky, D. F.; Deinzer, M. L.; Gonin, M.; Egan, T. F.; Führer, K. *Anal. Chem.* **2003**, *75*, 3001−3009.
(4) Laramée, J. A.; and Deinzer, M. A. *Anal. Chem.* **1994**, *66*, 719−724.

10.1021/ac030324g CCC: $27.50
Published on Web 04/21/2004

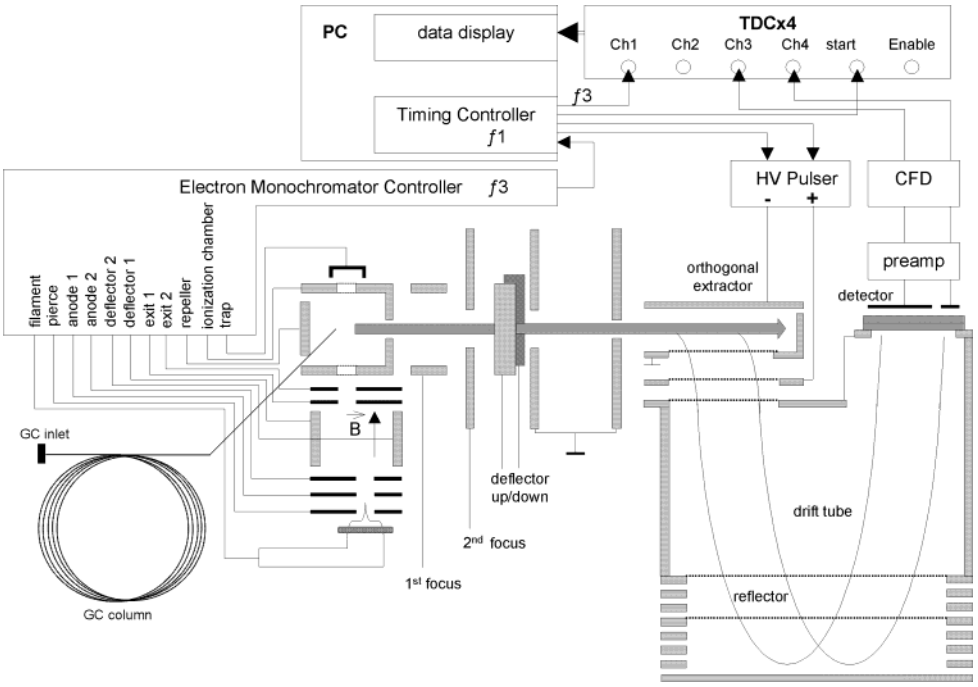


Figure 1. Schematic diagram of the GC/EM-TOF mass spectrometer, including TOF electronics.

dimensional MS technique that uses the EM-rTOF mass spectrometer described earlier[3] is demonstrated. Specifically, the three dimensions, I, E_e, and m/z, plus GC retention time, t, are recorded concurrently to greatly enhance analytical specificity.

EXPERIMENTAL SECTION

Materials. Pentafluorobenzyl alcohol (PFBA) (98%), the perfluorocarboxylic acids $C_7F_{15}COOH$, $C_8F_{17}COOH$, $C_9F_{19}COOH$, and $C_{10}F_{21}COOH$ (98%), and a mixture of *cis*- and *trans*-dibromoethylenes (97%) were purchased from Aldrich Chem. Co. (Milwaukee, WI). No purification was performed on any samples. HPLC grade methanol and hexane were purchased from Fisher Scientific, Fair Lawn, NJ. Spectroquality carbon tetrachloride (CCl_4) was purchased from Matheson (U.S.A.). PFBA and pentadecafluorooctanoic acid ($C_7F_{15}COOH$) were used as test samples for the chromatographic introduction of single compounds. A solution containing 0.3 mg/mL of each of the four perfluorocarboxylic acids was prepared to test the chromatographic introduction of a mixture of compounds.

Instrumentation. The instrument (Figure 1) consists of a Hewlett-Packard 5890 gas chromatograph coupled to a custom-built electron monochromator/time-of-flight mass spectrometer. Details of the mass spectrometer's design and operation were recently published[3]. Briefly, the EM-TOF instrument was built on the platform of a JEOL JMS-DX300 mass spectrometer. A trochoidal electron monochromator was introduced into its ion source, and the original EB analyzer was replaced with a compact, orthogonal extraction, time-of-flight analyzer. The monochromator, which was purchased from JEOL USA Inc., utilizes a design developed in the authors' laboratory.[6] The controller of this unit is designed so that it can be operated either in a static mode, whereby the electron energy is kept constant at some selected value, or in a dynamic mode, whereby the electron energy is linearly ramped within some preset energy range between the limits −1.70 and 25 eV. The TOF analyzer was custom-built by Ionwerks (Houston, TX). The external dimensions of its aluminum housing are 211 × 142 × 64 mm. A two stage ion reflector with a rectangular cross section is integral to the analyzer's design and gives the ions an effective flight path of ∼0.45 m. Ions with flight times of up to ∼12.5 μs ($m/z \sim 300$) can be orthogonally extracted into the analyzer at a frequency of 80 kHz while maintaining a mass resolving power, $m/\Delta m$, of ∼1000.

A time-to-digital (TDC) converter with four stop channels (Ionwerks, Houston, TX) was used to measure ion flight times. Data generated in the GC/MS experiment is transferred from this device, which can export data in a list mode, as a continuous stream of data events to the on-line computer and stored there in binary format as a data list. Specifically, the following signals (Figure 1) are recorded as events: (1) energy ramp start (Ch1), (2) TOF extraction (start), and (3) ion arrival (Ch3 and Ch4). In other words, every TOF extraction is stored as an individual m/z record corresponding to a specific time, which is the elution time in the case of a GC experiment, and a specific electron energy. All chromatographic, energy, and mass spectrometric data were reconstructed from this list using data-processing software supplied by Ionwerks.

Operating Conditions. PFBA and the perfluorocarboxylic acids (PFCs) were individually dissolved in methanol to a concentration of 1 mg/mL. Samples (0.5 μL) were introduced into the electron capture ion source by splitless injection through a SE-54 30 m × 0.25 mm capillary gas chromatography column. The injector temperature was held at 250 °C. The GC column was heated from 40 to 240 °C at a rate of 20 °C/min. The helium carrier gas flow rate was set at 5 mL/min in the case of pentadecafluorooctanoic acid ($C_7F_{15}COOH$). The column temperature programs were 10 °C/min and 2.5 mL/min, respectively,

(5) Voinov, V. G.; El'kin, Yu. N. *Instrum. Exp. Tech.* **1997**, *40*, 233−235.

(6) Laramée, J. A.; Kocher, C. A.; Deinzer, M. L. *Anal. Chem.*. **1992**, *64*, 2316−2322.

for the mixture of PFC's and for the PFBA. The mixture of carbon tetrachloride and *cis*- and *trans*-dibromoethylenes was dissolved in hexane to a volume ratio 1:10:100 (CCl_4 was used for calibration of energy and mass scale). The mixture (0.5 μL) was introduced into the ion source by splitless injection through a DB-624 30 m × 0.25 mm capillary gas chromatography column. The injector temperature was held at 150 °C. The GC column was heated from 30 to 150 °C at a rate of 4 °C/min, and the helium carrier gas flow rate was set at 3 mL/min.

The electron monochromator was adjusted to provide a 15-nA electron beam with an energy spread of 150−180 meV. The energy of the electrons entering the ion source was repeatedly ramped at a frequency of 11.1 Hz (ramping period, 90 ms) from 0 to 1.2 eV for the mixture of PFCs and from −1.7 to 13.3 eV for all the other samples. A potential of −24 V was applied to the ionization chamber. Ions from the 24-eV beam were orthogonally extracted into the TOF drift tube with 0.25-μs, 600-V pulses. At an extraction frequency or pulse rate of 60 kHz and an acceleration voltage of 2 kV, the TOF analyzer has an upper m/z limit of 550 and a mass-resolving power of ∼1000. The resolution of the TDC was set at 625 ps. In the prototype instrument's current configuration, independent clocks asynchronously time the heating rate of the gas chromatograph, the scanning rate of the ionizing electron energy, and the acquisition rate of ions. Consequently, initiation of mass spectrometric recording must be manually synchronized with the starting time of the gas chromatographic heating gradient.

RESULTS

Perfluorocarboxylic Acids. The total ion gas chromatogram of perfluorooctanoic acid (PFOA) exhibits a minor peak at ∼1.7 min and a major peak at ∼1.8 min (Figure 2A). Any one of the several energy-integrated mass spectra recorded within the chromatographic elution-profile of the major peak (e.g., Figure 2B) contains the molecular anion of PFOA at m/z 413 and five signals for negative ions at m/z 394 (base peak), 350, 331, 231, and 181. The ionization efficiency curves for these six negative ions have energy maximums of ∼0.4, ∼0.1, ∼0.6, ∼1.0, ∼1.1, and ∼1.2 eV, respectively (Figure 2C).

GC/MS data generated from the test mixture of four commercially available perfluoroalkyl carboxylic acids, $C_7F_{15}COOH$ (PFOA, M_r = 414), $C_8F_{17}COOH$ (M_r = 464), $C_9F_{19}COOH$ (M_r = 514), and $C_{10}F_{21}COOH$ (M_r = 564), were also recorded (Figure 3). In addition to the four primary compounds, the total ion chromatogram (Figure 3A) reveals the presence of minor compounds in the mixture. All of the chromatographically separated compounds exhibit the same mass spectrometric signature (Figure 3B and C) as described for PFOA (Figure 2B). The principal ion peaks correspond to $[M - H]^-$, $[M - HF]^{-\bullet}$, $[M - HF - CO_2]^{-\bullet}$, F^-, and the series of fragments $[M - CO_2\text{-}HF_2 - (CF_2)_n]^-$, in which the alkyl's chain-length n falls between 0 and 7.

Pentafluorobenzyl Alcohol. The total ion chromatogram of PFBA (Figure 4A) was recorded by scanning the electron energy from −1 to 10 eV. Two peaks are clearly evident in the chromatogram. The REC spectrum of the more intense component (no. 2) exhibits major ion peaks at m/z 168, 167, and 148 and minor peaks at m/z 196, 181, 178, 159, and 129 (data not shown). The REC spectrum of the smaller GC peak 1 contains three strong ion signals at m/z 168, 167, and 148 and a barely detectable signal at m/z 129 (data not shown). The ionization efficiency curves for

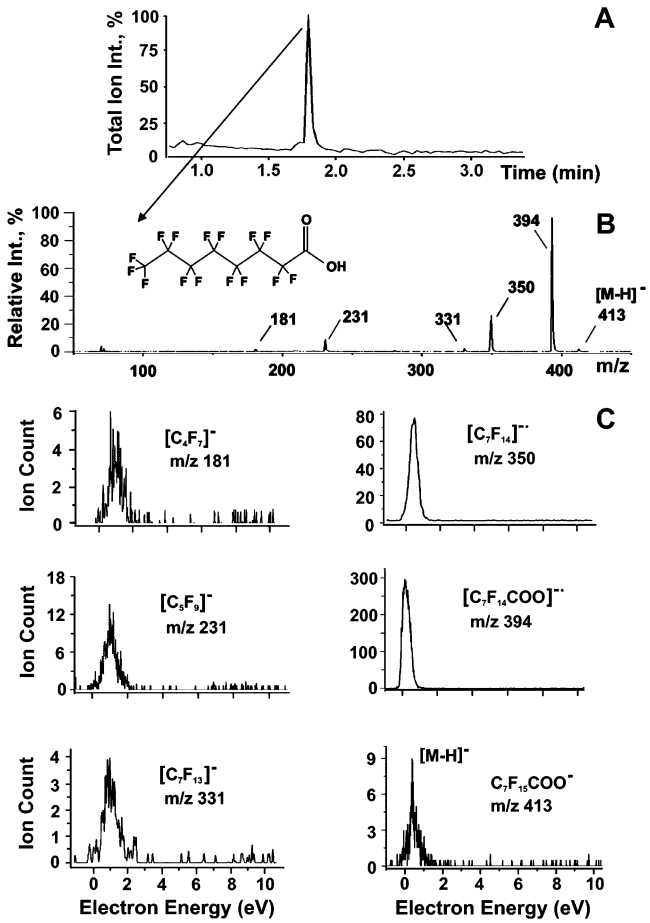


Figure 2. (A) Total ion current GC chromatogram for perfluorooctanoic acid (PFOA, $C_7F_{15}COOH$), (B) energy-integrated REC mass spectrum recorded at ∼1.8 min, and (C) effective yield curves for six diagnostic negative ions.

the formation of $C_6F_4^{-\bullet}$ at m/z 148 from GC peaks 1 (Figure 4B) and 2 (Figure 4C) have resonances around 1 eV. Peak 1, however, appears to have another resonance at ∼0.5 eV.

Dibromoethylenes. The commercially available mixture of *cis*- and *trans*-dibromoethylenes was well-separated by the DB-624 capillary gas chromatography column (Figure 5A). The two isomers clearly have different mass spectra (Figure 5B and C) and effective yield curves for ^{79}Br (Figure 5D and E). The relative intensity of $[M - Br]^-$ (m/z 105, 107) is much larger in the case of the trans isomer, but the yield of Br_2^- is stronger in the case of the cis isomer. The ion peaks at m/z 146 and 127 (almost imperceptible in the two spectra) correspond, respectively, to SF_6^- and SF_5^- from SF_6, which together with CCl_4 was included in the mixture to calibrate the energy and mass scales.

DISCUSSION

The EM-TOF mass spectrometer has several features that make it ideally suited for interfacing to a gas chromatograph. Unlike a conventional CI source operated in the negative ion mode, an EM ion source requires no reagent gas to generate thermal electrons; the carrier gas from the gas chromatograph, usually helium, is not ionized in an EM ion source and, thus, can serve to stabilize the molecular radical anions produced by REC. Consequently, the problems of irreproducibility and spurious ion production from ion molecule reactions that attend the use of reagent gases in electron capture negative ion mass spectrometry

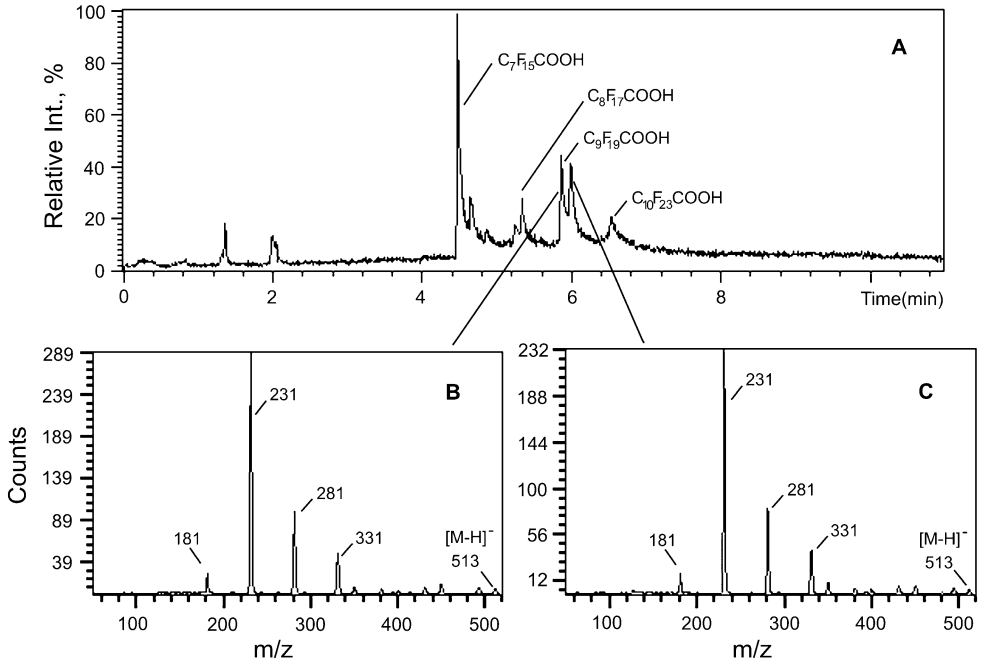


Figure 3. (A) Total ion current GC chromatogram of PFC mixture and (B and C) mass spectra of GC peaks corresponding to two homologues of $C_9F_{19}COOH$.

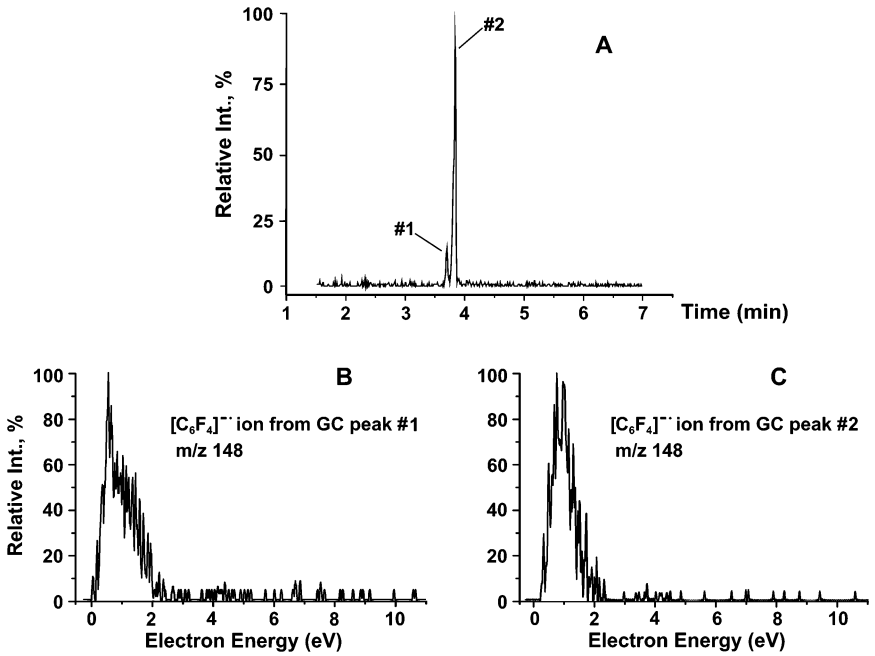


Figure 4. (A) Total ion current GC chromatogram of PFBA and ionization efficiency curves for $C_6F_4^{-\bullet}$ from peaks 1 (B) and 2 (C).

are avoided. The REC mass spectra recorded in this study (Figures 2B; 3B,C; and 5B,C) are clearly free of any extraneous mass peaks. Finally, the TOF analyzer's sensitivity and exceptional acquisition speed make it possible to record complete REC mass spectra of compounds as they elute from the GC. Typically with EM/quadrupole and EM/magnetic sector mass spectrometers, from several hours to several days is required to record a compound's complete resonance electron capture spectrum, that is, the effective yield versus electron energy curves of all the negative ions resulting from the compound. In stark contrast with this circumstance, three-dimensional negative ion electron capture spectra are recorded in an interval on the order of just 1 s with the EM-TOF mass spectrometer.

With the addition of a gas chromatograph, four dimensions of analytical information are recorded concurrently: (1) GC retention time, (2) resonance electron energy, (3) ion mass-to-charge ratio (m/z), and (4) ion intensity. Over the course of the entire chromatographic elution interval, the energy of the ionizing electrons is ramped repeatedly between −1.7 and +13.3 eV at 11.1 Hz, that is, every 90 ms, and the ions being produced by electron capture are orthogonally extracted into the TOF analyzer at a frequency of 60 kHz, that is, every 17 μs (Figure 6). Therefore, when the system is operating on-line, the software receives 60 000 m/z acquisitions every second from the TDC and stores them in memory. The TDC inserts an extra signal into this train of data every 90 ms to flag the start of each electron-energy scan. By

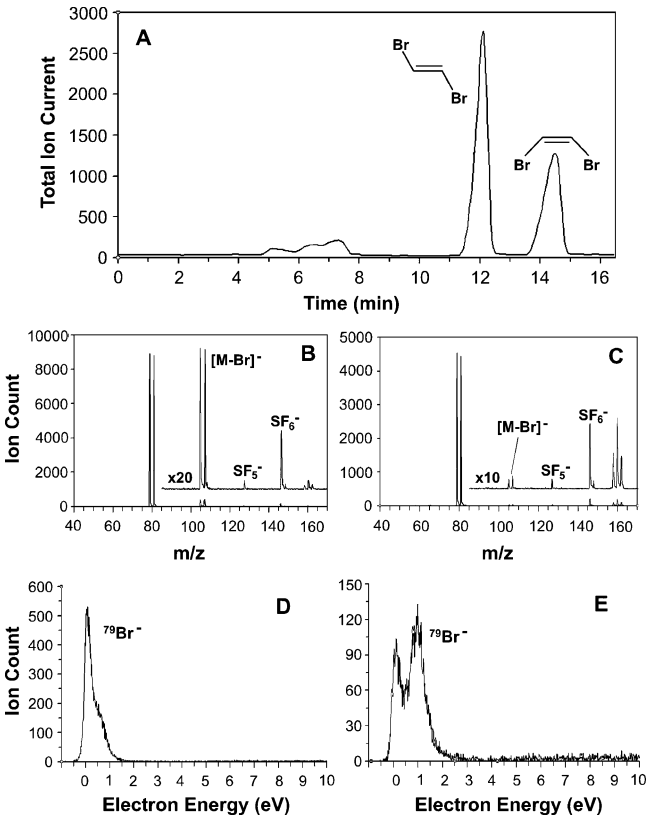


Figure 5. (A) Total ion current GC chromatogram, mass spectra of GC peaks corresponding to (B) *trans*- and (C) *cis*-dibromoethylenes, and effective yield curves of $^{79}Br^-$ from (D) *trans*- and (E) *cis*-dibromoethylenes.

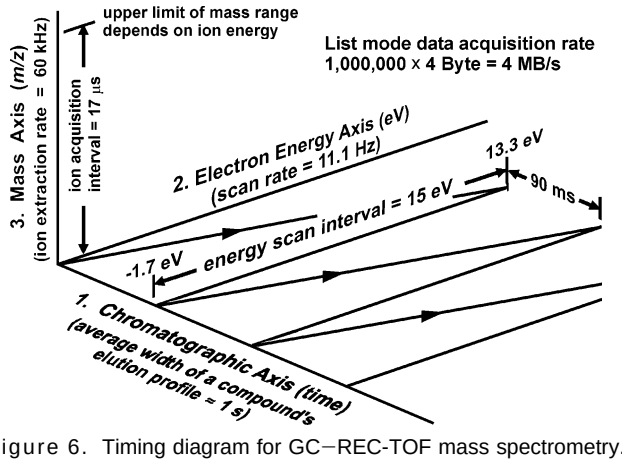


Figure 6. Timing diagram for GC−REC-TOF mass spectrometry.

this means, the software can use the positions of a particular energy flag and ion-acquisition in the data train to associate the m/z and intensity information contained in that segment of the recording with a specific electron energy and GC elution time, respectively. This data-acquisition scheme makes it possible, in turn, to process the enormous amount of data required to refresh the system's display monitor once every second and to use almost any data processing software, for example Microcal Origin,[7] Transform,[8] or custom programs, such as the Ionwerks software, employed in this work.

(7) *Microcal Origin Version 5.0*; Microcal Software, Inc.: One Roundhouse Plaza, Northampton, MA 01060.

(8) *Transform Version 3.4*; Fortner Software LLC, 100 Carpenter Drive Sterling, VA 20164.

As a general rule, fragment ions that are formed in the energy range 0−1 eV are presumed to originate from shape resonances associated with low-lying, normally unoccupied, molecular orbitals. According to molecular orbital theory, these fragment ions are formed by resonant capture of electrons into unoccupied molecular orbitals to generate a set of transient $M^{-\bullet}$ states that decay unimolecularly via different fragmentation channels. The ionization efficiency curves of PFOA, which show that very good definition and sensitivity can be achieved, even when the electron energy is ramped over a range of 15 eV at 11.1 Hz, that is, every 90 ms (Figure 2C), are typical in this regard. They indicate that several distinct transient $M^{-\bullet}$ resonance states exist for this particular compound.

Specifically, one PFOA state originates from electron capture (∼0.4 eV) into a low-lying orbital located on the carboxyl moiety and leads to the formation of a transient $M^{-\bullet}$ that eliminates the carboxyl hydrogen atom (Scheme 1) through a predissociation process to form a stable carboxylate anion $[M - H]^-$.[9−11] A second low-energy $M^{-\bullet}$ state (∼0.1 eV) is characterized by concerted elimination of HF to form a radical anion at m/z 394, probably through the formation of variously sized stable, lactonide ions (Scheme 1). The position from which the fluorine atom is eliminated determines the size of the cyclic structure. The elimination of fluorine atoms from different positions on PFOA's carbon chain is supported by investigations with deuterium-labeled carboxylic acids under resonance electron capture conditions;[12] these experiments have shown that hydrogen atoms are eliminated from all positions on the chain, but that elimination from the C2, C3, and C4 atoms is preferred. The ion at m/z 350, which corresponds to $(C_7F_{14})^{-\bullet}$, is formally equivalent to the ion at m/z 394, less CO_2. However, this ion peaks at a resonance energy of ∼0.6 eV, and consequently, a separate pathway through a unique $M^{-\bullet}$ (Scheme 1) may give rise to this ion. A resonance or family of resonances around 1.0 eV decay into an ion at m/z 331, which is formally equivalent to $[M - F_2 - CO_2H]^-$. A homologous series of ions, each 50 mass units (i.e., one CF_2 group) lighter than the previous one, may be represented as $(C_nF_{2n-1})^-$ (Scheme 1). All of these ions could arise from similar but individual resonance states, or since the electron energy resolution in the present study may not be sufficient to distinguish between states that differ by no more than ±0.1 eV, they could all arise from the same state (∼1.1 eV) through different metastable decomposition pathways. Finally, F^-, which has a wide effective yield curve peaked at ∼8 eV (data not shown), originates from a yet another high-energy state, possibly a σ^* shape or a core-excited Feshbach resonance.

The unexpected appearance of a small, slightly earlier, chromatographic peak (∼1.7 min) produced by an impurity compound in the PFOA sample (Figure 2A) provided an excellent opportunity to demonstrate the analytical power of the new GC/EM-TOF instrument. Various multidimensional plots of the PFOA data (Figure 7) illustrate this point. The plot of GC elution time versus m/z over the range m/z 330−400 (Figure 7A) definitely shows

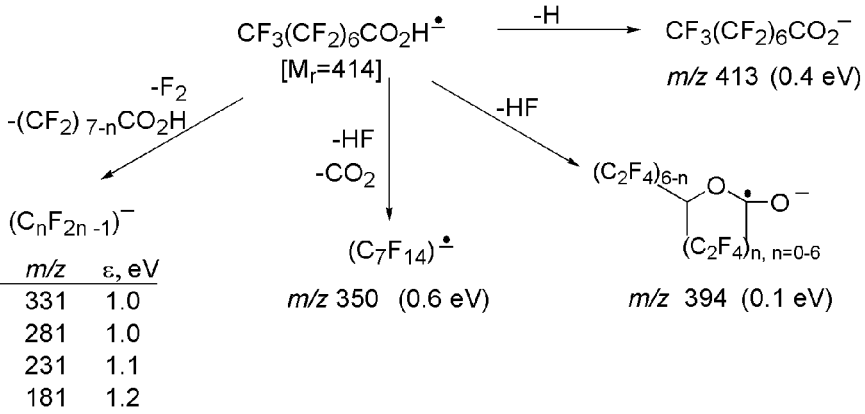
(9) Voinov, V. G.; Petrachenko, N. E.; Dorofeyev, V. E.; Nakamatsu, H.; Mukoyama, T. *Int. J. Mass Spectrom. Ion Processes* **1994**, *137*, 31−42.

(10) Vasil'ev, Y. V.; Muftakhov, M. V.; Tuimedov, G. M.; Khatymov, R. V.; Abzalimov, R. R.; Mazunov, V. A.; Drewello, T. *Int. J. Mass Spectrom.* **2001**, *205*, 119−135.

(11) Muftakhov, M. V.; Vasil'ev, Y. V.; Mazunov, V. A. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 1104−1108.

(12) Voinov, V. G.; Van den Heuvel, H.; Claeys, M. *J. Mass Spectrom.* **2002**, *37*, 313−321.

Scheme 1



n	*m/z*	ε, eV
7	331	1.0
6	281	1.0
5	231	1.1
4	181	1.2

that both PFOA and the impurity produce common ions at *m*/*z* 394, 350, and 331. The relative intensities of these mass peaks can be visualized more clearly in the 3-dimensional presentation of these same data (Figure 7B). The plots of electron energy versus mass-to-charge (*m*/*z*) and versus GC elution time (Figure 7C and D, respectively) distinctly indicate that the fragment ions produced by the impurity and the corresponding ions produced by PFOA are associated with the same resonances. Specifically, the most intense ion signal for both compounds occurs at *m*/*z* 394, with a maximum yield at ~0.1 eV; the second most intense ion-signal occurs at *m*/*z* 350, with a maximum at ~0.6 eV; and the least intense signal occurs at *m*/*z* 331, with a maximum yield at ~1.0 eV. These data show that the main resonances for the impurity fall within the same 0−1 eV range and have essentially the same distribution as the PFOA resonances. The high noise level (in green) is due to the low signal threshold used. All of the features of PFOA's REC data can be perceived in a single 4-dimensional plot (Figure 7E). Collectively, these data suggest that the impurity is a homologue, for example, a branched isomer, of PFOA.

The fact that all the resonances of the PFCs occur between 0 and 1.2 eV (excluding the low-intensity F^- formation) allows the efficiency and specificity of analysis to be increased by restricting scanning of the electron energy to just that particular energy range. The gas chromatogram of the mixture of perfluoroalkyl carboxylic acids (Figure 3A) was produced without optimizing the type of column, temperature program, or any other chromatographic conditions. Furthermore, the acids were not converted to their alkyl esters, but were injected as received from the supplier. Although these nonoptimal conditions caused extensive peak tailing, all four compounds did produce prominent, well-resolved peaks (peaks labeled $C_7F_{15}COOH$, $C_8F_{17}COOH$, $C_9F_{19}COOH$, and $C_{11}F_{23}COOH$ in Figure 3A) in the chromatogram. Moreover, the chromatogram reveals that more than four components are present. It is well-known that branched isomers form during the synthesis of the perfluorocarboxylic acids via electrochemical fluorination.[13] The absence of visible differences in the REC spectra of the different species, with regard to both ion mass (see, for instance, the spectra for $C_9F_{19}COOH$ acid, Figure 3B and C) and resonance energy, is consistent with a mixture of linear and branched homologues of the perfluoroalkyl acids.

PFBA is a derivatizing reagent used to transform carboxylic acids into an electron capturing form, namely, pentafluorobenzyl ethers.[14,15] In contrast to free fatty acids or their methyl esters, PFBA ethers increase sensitivity in conventional negative ion mass

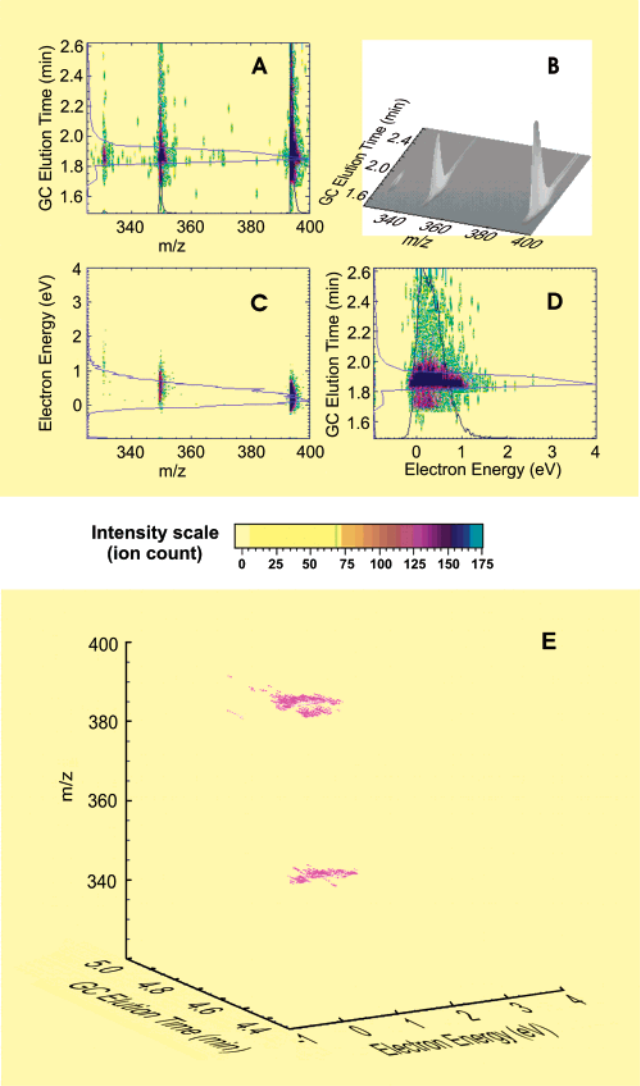


Figure 7. REC data for perfluorooctanoic acid ($C_7F_{15}COOH$) presented in (A, C, and D) 2-dimensional, (B) 3-dimensional, and (E) 4-dimensional plots. The two-dimensional graphs also show ion intensity plotted as a function of GC elution time (A, D) and electron energy (C, D) for the three ions with masses *m*/*z* 331, 350, and 394. The green areas are due to background ion counts.

(13) Geigy, J. P.; Kannan, K. *Environ. Sci. Technol.* **2002**, *36*, 147A−152A.

spectrometry by several orders of magnitude[16,17] because the added PFB moiety has such a high electron affinity. The sample of PFBA analyzed in this study was found to contain two components (Figure 4A). The resonances recorded for the component corresponding to the more abundant peak 2 in the chromatogram (data not shown) unambiguously assign this compound to PFBA. One interesting feature of the PFBA spectrum is the presence of signals at m/z 196, 168, and 148 that correspond, respectively, to the uneven-electron ions $[M - 2H]^{-\bullet}$, $C_6F_5H^{-\bullet}$, and $C_6F_4^{-\bullet}$. The origin of these three long-lived species deserves more detailed investigation in some future study. The REC spectrum of the less abundant GC peak 1 practically coincides with that of the more abundant compound, that is, GC peak 2. The only difference between the ionization efficiency of these two compounds appears in the curves corresponding to the formation of $C_6F_4^{-\bullet}$ at m/z 148 (Figure 4B, C); the GC peak 1 curve (Figure 4B) exhibits a narrow but discernible peak that is absent from the GC no. 2 curve. On the basis of this observation, it is likely that GC peaks 1 and 2 correspond to rotational isomers of PFBA, one without and another with an intramolecular hydrogen bond between the alcoholic hydrogen and one of the *ortho*-fluorines.

Cis- and *trans*-dibromoethylenes are available from Aldrich only as a mixture. This fact was exploited here to provide another test of the GC/EM-TOF-MS's powerful ability to distinguish and identify isomers. From the mass spectra (Figure 5B and C) and the effective yield curves of $^{79}Br^-$ (Figure 5D and E), it is clear that the electronic structures of the isomers are quite different. The difference lies not only in the energies of the resonances that decay into Br^- but also in the symmetries of their respective structures, since the relative yields of the ions vary dramatically as a function of energy. At first glance, one is tempted to rationalize the cis isomer's relatively large yield of Br_2^- (Figure 5C) on the basis that its geometry better enables the bromine atoms to approach each other before fragmentation than does the trans isomer's. Data from very recent experiments with the chlorine analogues to the dibromoethylenes indicate that the scenario might be much more complex and interesting; an extensive discussion of these newest results is beyond the scope of the present paper but it will appear elsewhere soon.

CONCLUSION

As demonstrated by the results presented here, the new GC/EM-TOF-MS goes a long way toward providing the characteristics identified as important in new methodology for analysis of environmental compounds. First, selectivity is improved by an added analytical dimension, and since complete sets of 4-dimensional data are recorded in a single experiment, efficiency is also vastly improved; i.e., the time of analysis is greatly reduced. In those cases in which compounds are not chromatographically resolved, compound-specific resonant electron energies could be used to discriminate between them by setting the monoenergetic electron beam at a predetermined energy.[18] Second, reliable or reproducible negative ion mass spectral data, which are difficult to obtain using a reagent gas in a CI ion source, are readily produced with an EM ion source. Lack of reproducibility has been one of the chief impediments to using negative ion mass spectrometry in environmental studies. Third, a GC/EM-TOF-MS system produces REC data that enables one to correlate the electronic states of a compound's different transient molecular ions with various possible decomposition pathways. This aspect of the technology emphasizes one of its most compelling scientific advantages over conventional negative ion mass spectrometry; namely, when REC is used in conjunction with high-level ab initio computational methods, it yields information on the mechanism of negative ion formation, something that is not generally possible with standard negative ion mass spectrometry.

Electron-capturing chemicals are frequently associated with major environmental health problems not only because of the potential negative health effects they produce, but often and sometimes more importantly because of their persistence in the environment. These compounds mainly include highly active electron sinks, such as chlorinated aromatics and other halogenated hydrocarbons, nitro compounds, polyaromatic hydrocarbons, and organophosphates. PFOA is an excellent case in point. This compound, which does not biodegrade under aerobic or anaerobic conditions, has been detected in blood plasma of nonoccupationally exposed humans,[19] and quite recently, it was discovered in various tissues of animals from less densely populated regions of the world where there are no local commercial, municipal, or industrial sources of fluorinated alkyl substances.[20,21] The REC mass spectra of PFOA and the other three perfluorocarboxylic acids presented in this paper are apparently the first ever to be reported. The results obtained with these compounds demonstrate both the quality and the utility of data generated by a GC/EM/-TOF-MS system.

As a final note, the range of application for GC/EM-TOF-MS can be extended to the vast family of compounds containing functional groups that can be derivatized with electrophores. Fatty acids, which are typical structural components of bacterial lipopolysaccharides; telltale long-chain fatty alcohols from mycobacterial infections, including tuberculosis; and small amino acid neurotransmitters are just a few examples for which it should be possible to use this instrument's power to great advantage in discriminating between compounds.

(14) Elkin, Yu. N.; Voinov, V. G.; Vysotskiy, M. V.; Svetashev, V. I. *Bioorg. Khim.* **1985**, *11*, 674−676.

(15) Elkin, Yu. N.; Voinov, V. G.; Vysotskiy, M. V.; Svetashev, V. I. *Z. Anal. Khim.* **1987**, *42*, 2232−2235.

(16) Hunt, D. F.; Crow, F. W. *Anal. Chem.* **1978**, *50*, 1781−1784.

(17) Hayashi, T.; Naruse, H.; Iida, Y.; Daishima, S. *Mass Spectrosc.* **1983**, *31*, 289−295.

(18) Voinov, V. G.; Elkin, Yu. N.; Kuznetsova, T. A.; Mal'tsev, I. I.; Mikhailov, V. V.; Sasunkevich, V. A. *J. Chromatogr.* **1991**, *586*, 360−362.

(19) Kissa, E. *Fluorinated surfactants and repellants*; Marcel Dekker, Inc.: New York, 2001.

(20) Hansen, K. J.; Clemen, L. A.; Ellefson, M. E.; Andjohnson, H. O. *Environ. Sci. Technol.* **2001**, *35*, 766−770.

(21) Giesy, J. P.; Kannan, K. *Environ. Sci. Technol.* **2001**, *35*, 1339−1342.

ACKNOWLEDGMENT

This project was supported directly by Grants from the National Institutes of Health, ES09536 and ES10338, and indirectly by the National Institute of Environmental Health Science, Environmental Health Sciences Center Grant ES00210.

Received for review September 9, 2003. Accepted March 15, 2004.

AC030324G