

A Novel Gas Chromatograph/Resonant Electron Capture/TOF Mass Spectrometer

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Overview

Purpose

To build a mass spectrometer capable of recording ionization efficiency curves with good energy resolution (at least 100 meV) and enough speed to record the curves in the GC mode in real time.

Method

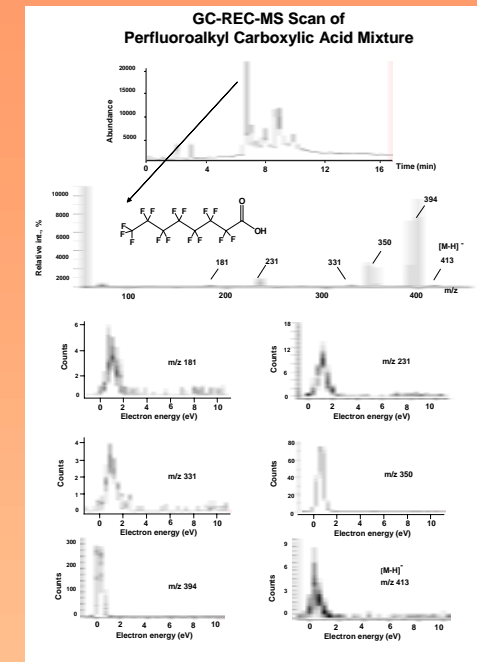
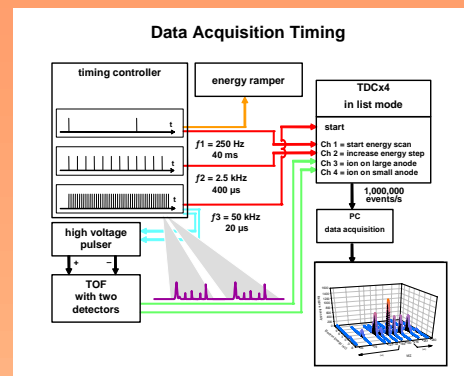
- Trochoidal monochromator for selecting electrons with specific energy;
- Monochromator controller that enables the electron energies to be scanned over the full range 0 -12 V in 40 ms;
- Orthogonal TOF analyzer with extraction frequency up to 80 kHz to record ions produced by resonance electron capture;
- Use of a list mode to record every TOF extraction to a file;
- The synchronization of TOF extractions with energy ramping.

Result

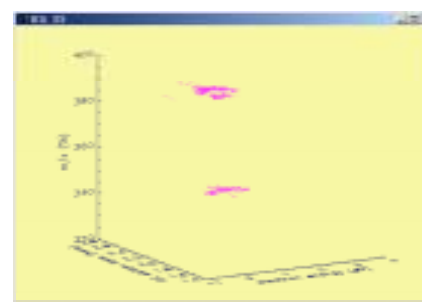
Four dimensional information of the target compounds was achieved with one GC run.

Experimental

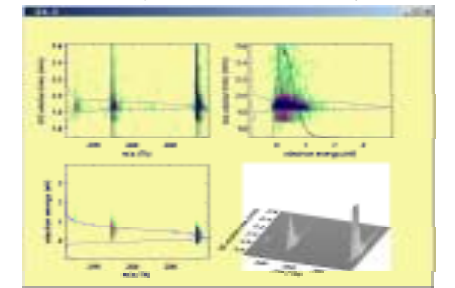
A Hewlett-Packard 5890 gas chromatograph was connected to a custom built trochoidal electron monochromator/time-of-flight mass spectrometer system. The perfluorocarboxylic acids $C_7F_{15}COOH$, $C_9F_{17}COOH$, $C_{11}F_{19}COOH$, and $C_{13}F_{21}COOH$ (98%, Aldrich Chem. Co) are representatives of a large family of fluoroalkyl substances. A mixture of these four compounds was used as a test sample. All acids were dissolved in methanol to a concentration of 1 mg/mL. Sample (0.5 μ L) was introduced into the electron capture ion source by splitless injection through a SE-54 30 m \times 0.25 mm id capillary gas chromatography column. The injector temperature was held at 210 $^{\circ}C$. The GC column was heated from 40 to 200 $^{\circ}C$ at 10 $^{\circ}C/min$. The flow rate of helium was 0.5 mL/min. The electron energy was ramped from -1.7 eV to 13.3 eV at a frequency of 90 Hz, and the energy spread of 15 nA electron beam was about 150-180 meV. Ions were extracted orthogonally into the analyzer at a frequency of 60 kHz. At this acquisition rate, the m/z -range is nominally 550, and a resolving power of a \sim 1000.



An Example of 4-D Presentation of Experimental Data



An Example of Data Presentation as Projections on Planes Time \times m/z , Time \times Energy and Energy \times m/z , and as 3 Dimensional Graph in Axes Time \times m/z \times Intensity



Conclusion

A prototype gas chromatography/resonant electron capture/time of flight mass spectrometer (GC-REC-TOF) has been constructed and demonstrated to record the effective-yield versus electron-energy curves for all negative ions of perfluoroalkyl carboxylic acids in a GC mode.

References

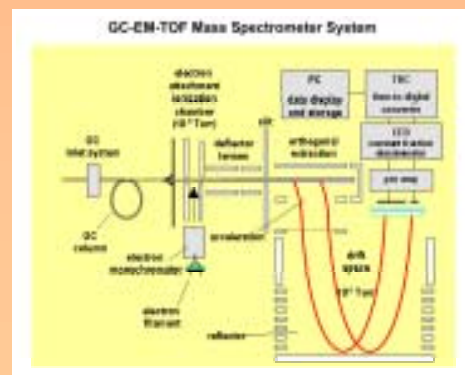
1. J.A.Laram e and M.L.Deinzer "Capillary Gas Chromatographic Introduction of Environmental Compounds into a Trochoidal Electron Monochromator/Mass Spectrometer", Analytical Chemistry 1994, v.66, No.5, pp.719-724.
2. V.G. Voinov, Y.V. Vasil'ev, J. Morr , D. F. Barofsky, M.L. Deinzer, M. Gonin, T. F. Egan, K. F hrer "A novel resonant electron capture TOF MS with trochoidal electron monochromator", Analytical Chemistry 2003, v.75, No.13 article ac030019v, in press.

Acknowledgement

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Introduction

Resonant electron capture (REC) MS provides three-dimensional electron capture spectra that reveal unique analytical information about compounds under investigation. In principle, the power of REC MS can be increased by using it in conjunction with gas chromatography (GC), but implementing such a system places stringent demands on the data acquisition system. The amount of data processed increases dramatically because four dimensions of analytical information are acquired (retention time \times electron energy \times m/z \times ion intensity) simultaneously. Although in principle a complete REC spectrum can be obtained on a GC/quadrupole system [1], the acquisition speed of such a system is insufficient to perform a GC-REC MS experiment in real time. Recently, we reported the construction and successful operation of an electron monochromator /orthogonal acceleration / reflectron / time-of-flight (EM-oa-TOF) mass spectrometer [2]. We have now succeeded in coupling this instrument to a GC and have used this novel prototype GC/EM-oa-TOF mass spectrometer to record four-dimensional spectra (i.e. retention time + effective yield versus electron energy curves for all negative ions produced from the analyte) in real time for a mixture of perfluoroalkyl carboxylic acids.



Results

As expected, the fast energy ramping speed and high ion extraction frequency allowed the full "4-dimensional" spectral information to be recorded. As an example, under the gas chromatogram the mass spectrum of pentadecafluorooctanoic acid $C_{15}F_{31}COOH$ is shown, which in this presentation is the projection of the full REC spectrum on the plane m/z \times intensity. The ionization efficiency curves shown are representative of all the observed ions and demonstrate the very good quality accessible in time scale used.

The analysis of mass spectra of all four of the carboxylic acids in the sample exhibits signals for $[M-H]^-$, $[M-HF]^-$, $[M-HF-CO_2]^-$, F^- , and the series of fragments $[M-CO_2HF_2-(CF_2)_n]^-$ with $n = 0$ to 7 (n depends on alkyl chain length). All fragment ions originate from a low energy resonance except for F^- , which is generated from another wide resonance at ca. 5 eV. The low energy resonances start at ca. 0.2 eV for $[M-H]^-$ and move to higher energies for each of the subsequent fragments.