

Simultaneous Electron Ionization & Chemical Ionization with the EC-TOF for GC-MS

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In this white paper we present the principle of operation of the EC-TOF mass spectrometer for GC-MS analysis with simultaneous 70 eV electron ionization and chemical ionization. Basic instrument specifications and performance are presented through standard GC-MS measurements.

Introduction

70 eV electron ionization (EI) is the most common ionization technique for gas chromatography-mass spectrometry (GC-MS). EI is highly reproducible and fragmentation data are available for a large number of compounds in mass spectral databases, making EI the most stable and reliable ionization technique for probing compound structure. However, information about the molecular ion is often lost with EI because the large excess energy of the ionization process leads to strong analyte fragmentation [1]. Because of this fragmentation, identification probabilities are compromised.

For accurate compound identification, it is critical to record the masses of the molecular analyte and its fragments, especially when identification using EI fails due to insufficient library data and standard materials [2]. Softer ionization techniques are required to ensure the generation of this information. One very effective and highly flexible soft ionization technique is chemical ionization (CI) at elevated pressure [3]. Sum formulas of compounds can be determined using accurate, high-resolution CI-MS measurements. Chemical ionization under controlled conditions and via understood mechanisms additionally yields information about physico-chemical properties, e.g., proton affinity (PA).

Determination of both the sum formula and physico-chemical properties is required in non-target screening applications where a high certainty of the identification or other generated information for statistical approaches is essential [4]. Generation

of this dual information is complicated with typical GC-MS setups. Multiple GC runs are commonly required, leading to complex data alignment issues due to instrumental performance shifts and long analysis times.

To overcome these challenges, TOFWERK has developed a unique time-of-flight mass spectrometer that enables simultaneous detection of EI and CI information within a single GC run.

EC-TOF Principle of Operation

Dual Ionization with the EC-TOF mass spectrometer enables simultaneous acquisition of both hard (70 eV EI) and

soft (CI) ionization chemical information without addition of analysis time. In this way, analyte structural and molecular information is generated within a single GC run.

System Performance

To demonstrate basic system performance 1 ng on column of a common alkane standard mixture (C₇-C₃₀) was used for a general GC-MS analysis.

For the chromatographic separation a common Agilent 7890A GC (Agilent technologies, Santa Clara, CA, USA)

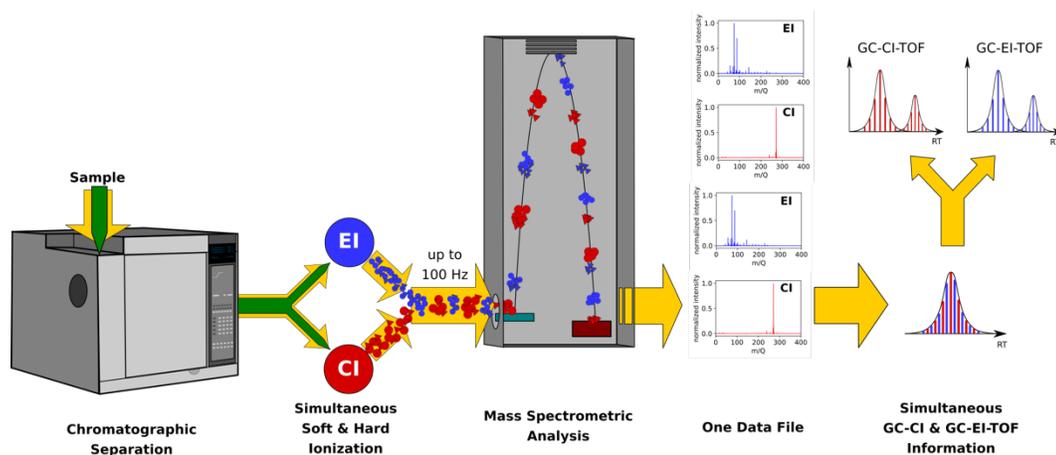


Figure 1. Principle of operation schematic. After the common GC (or GCxGC) -separation the effluent is split (1:1) and subsequently delivered to the EI and the CI source simultaneously. The continuously running ionization sources generate ions via EI and CI processes of the sample in parallel. The generated ions are guided on separate pathways towards the TOF analyzer via ion optical devices. On their path an ion optical switching leads to alternating introduction of EI or CI ions into the TOF analyzer for detection. In this way CI and EI mass spectra are generated in alternation. Due to the high-switching frequency (up to 100 Hz) even narrow GCxGC peaks are scanned with both ion information and quasi-simultaneous GC-CI-TOF and GC-EI-TOF information is acquired. All information is stored within one data file and can be analyzed separately or in combination.

equipped with a liquid injection inlet and a Rxi-5ms column (30 m, 0.25 mm ID, 0.25 μm , Restek, Bellefonte, PA, USA) was coupled to the mass spectrometer. After the separation the effluent was split in two parts (1:1) and each part was transferred via its own heated transfer line to the corresponding ionization source. The EI process took place at an energy of 70 eV. The novel medium pressure chemical ionization HRP source using N_2H^+ as the reagent was used for the generation of molecular ion information of the alkanes.

After the chromatographic separation the ionization of the analytes

simultaneously took place via a standard 70 eV EI process (black traces) and a medium pressure proton transfer reaction process using nitrogen (N_2H^+) as reactant gas (colored traces). The top diagram shows the overall chromatogram with a head-to-tail picture of the EI-extracted ion chromatograms (EIC) (black) and the CI EICs (colored). The middle part of Figure 2 depicts three separate zoom-ins into the chromatographic peaks of the C_{16} -, C_{20} - and C_{24} -compounds. The corresponding mass spectra of these three compounds with the detected CI (colored) and EI (black) information (head-to-tail) are shown in the bottom part of the figure.

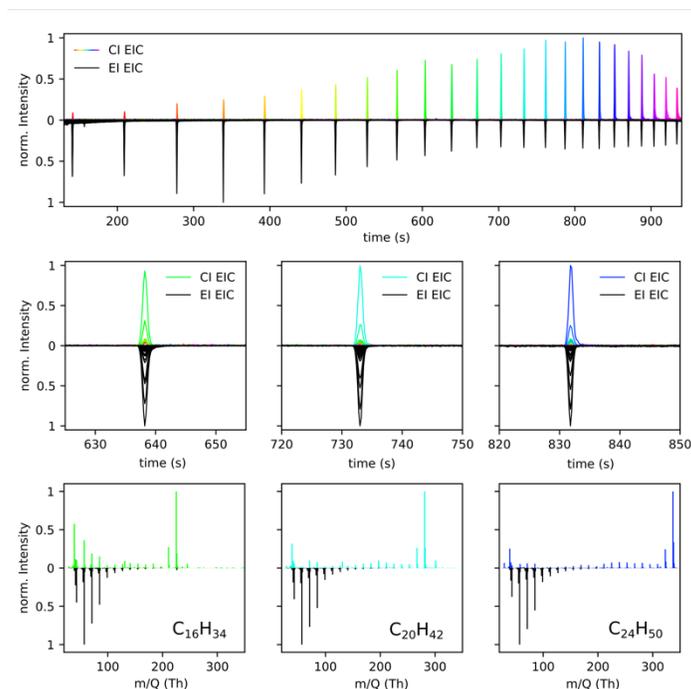


Figure 2. Data from a 1 ng on column C7-C30 alkane standard-mix generated with the EC-TOF for GC-MS analysis. Black traces cover EI EIC information, colored traces cover CI EIC information of the quasi-molecular ion signals. Top: Overall chromatogram, middle: zoom-in-chromatogram to C_{16} -, C_{20} - and C_{24} -compound peaks, Bottom: Corresponding EI & CI mass spectra of C_{16} -, C_{20} - and C_{24} -compounds.

While the overall chromatogram depicts the performance stability and the ionization efficiencies over the whole GC run for each alkane species, the zoom-in chromatograms demonstrate the great alignment of the CI and the EI data as well as the perfect chromatographic symmetry between the two ionization sources.

CI mass spectra are mainly dominated by the molecular ion information. Even for small alkanes, commonly difficult to measure using various CI methods, quasi molecular ion signals are observed using N_2H^+ as reagent ions. The high mass resolution and accurate mass analysis allowed a sum formula calculation with relative mass errors < 3 ppm. The EI mass spectra were used for common library searches. NIST library searches resulted in match factors > 800 for all compounds. Even with high match factors NIST probabilities are rather low due to very similar fragmentation patterns of various larger alkanes. The molecular ion information from CI in combination with the EI library searches, identifies each alkane with high certainty.

Summary

Within this white paper we present the principle of operation of the EC-TOF for GC-MS analysis and demonstrate the basic performance of the system on a simple alkane standard mixture measurement. Multiple

advantages of dual ionization GC-HRTOFMS with simultaneous EI and CI are highlighted.

Advantages of dual ionization EC-TOF for GC-MS:

Increased identification certainty – Simultaneous generation of molecular and structural information

Utilization of existing data bases for library searches – 70 eV EI usage for structural information generation

High flexibility within the molecular ion information generation – newly developed HRP CI source offers a broad range of selectivity and high sensitivities

Perfect synchronization and data alignment of EI and CI data – single GC run to acquire soft and hard ionization information, no risk of chromatographic or mass spectrometric performance shifts between different GC runs

All data stored in one data file – data can be analyzed separately or in combination

Reduced analysis time – only one single GC run to acquire soft and hard ionization data, no instrument down times

No risk of sample composition changes – only one single GC run to acquire soft and hard ionization information

Simplified workflow usage – only one data file for all information

EC-TOF Specifications

| | |
|-----------------------------|--|
| Mass Range: | 1-5000 Th; Extendable to 6000 Th |
| Relative Mass Accuracy: | < 5 ppm |
| Mass Resolving Power: | 4500 Th/Th (model R), 10000 Th/Th (model 2R) |
| Ion Source Switching Speed: | up to 100 Hz |
| Linear Dynamic Range: | > 4.5 orders of magnitude |
| LOD (CI): | < 500 fg on column benzophenone (CI only mode) |
| LOD (EI): | < 10 fg on column OFN (EI only mode) |
| EI Energy: | adjustable up to 70 eV |

Reagent ions for GC-CI-MS: N_2H^+ (N_2), C_4H_9^+ (iso-Butane), H_3O^+ (water), NH_4^+ (Ammonia), $\text{C}_2\text{H}_5\text{OH}_2^+$ (Ethanol), ...

- Full compatibility to Vocus ion sources
- Coupling to diverse common GC systems possible
- CI source maintenance without venting the system

References

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