

# Simultaneous Real-Time CI-MS and GC-EI-MS Analysis using the EC-TOF

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Standard analytical methods for the determination of volatile organic compounds (VOCs) include sampling in sorption tubes, followed by desorption, gas chromatographic separation and identification by mass spectrometry using electron ionization. These methods are well established and have multiple advantages, including separation of isomeric species, ease of identification, and quantitation of compounds. This chemical specificity is crucial for many applications, since subtle changes in composition can significantly affect the characteristic of a sample, such as the flavor of a beverage or the effectiveness of a drug.

Although these methods are well established and provide certain advantages for VOC analysis, they do not provide real-time or on-line data and are limited to certain classes of VOCs. The VOCs that can be measured depend on choice of trap, GC column, and detector. This makes them non-ideal solutions for some important compounds and locations in which fast, continuous measurements are required due to fast composition

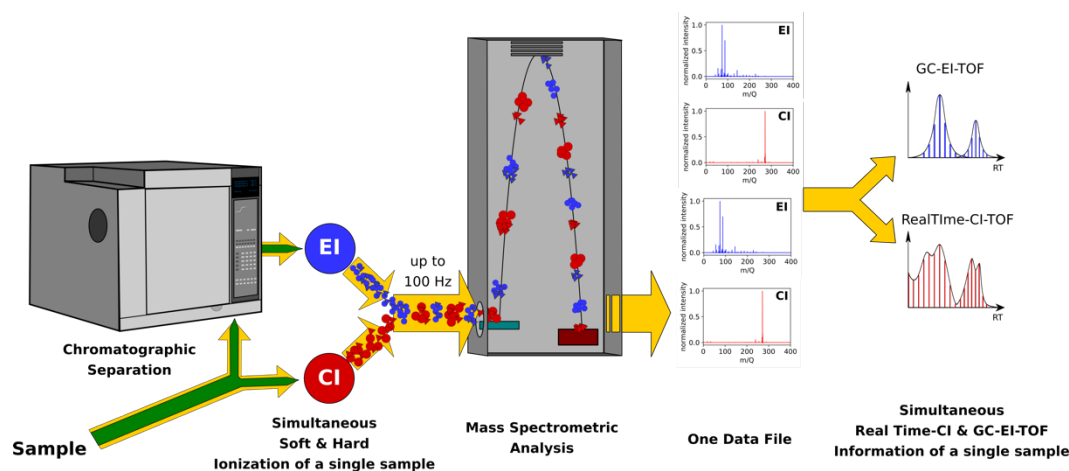
changes or where high throughput is a key factor.

The EC-TOF combines both types of measurement: real-time CI-MS data captures fast processes, while the GC-EI-TOF provides chemical information in high detail. The EC-TOF technology allows both measurements to happen simultaneously within one single instrument.

## Instrumental Set Up

The EC-TOF simultaneously operates a 70 eV electron ionization (EI) source and a medium- or high-pressure chemical ionization (CI) source on the same time-of-flight (TOF) mass analyzer.

Because the ion optical switching is extremely fast (up to 100 Hz), both types of ions are quasi simultaneously detected. Both the EI and CI measurements are stored within the same data file but can be analyzed separately. This greatly simplifies data alignment and analysis workflows. By coupling the CI source directly to the experiment, and simultaneously performing a GC-MS measurement (with or without a pre-concentration step) with the EI source, it is possible to observe fast processes and



**Figure 1.** Principle of operation of the EC-TOF for simultaneous real time CI-MS and GC-MS measurements

changes in concentration in real time via the CI-MS without compromising the GC-EI-MS information required for more detailed analysis of the sample. Various choices of CI sources and reagent ions offer high flexibility and the best fitting setup for your individual analysis.

### Experimental Set Up and Analysis

As a proof-of-concept experiment, a VOC-rich, complex sample with many isomers was created by burning pine needles with gradually increasing temperature and capturing the resulting smoke. The smoke was sampled directly into the chemical ionization source using an ambient inlet, and into the GC using a gas syringe.

Figure 2 shows a time series of several VOCs, measured in real time with the direct-sampling CI-MS. The specific ionization chemistry used, proton transfer reaction with  $\text{H}_3\text{O}^+$  reagent ions, is a soft ionization technique that results in little fragmentation. Generally, only the parent molecule of each VOC is

detected, which means that the observed ions can be interpreted as the molecular ion. Where isomers exist, their sum is measured.

The composition of the smoke changes rapidly as the temperature increases. From left to right, the appearance of various groups of VOCs indicate the start of pyrolysis, low-temperature pyrolysis reactions, high-temperature pyrolysis reactions, and finally sustained smoke emission.

The real-time data from the CI-MS reveals the exact timing of the different reactions. In this experiment, we have chosen a time interval during the high-temperature pyrolysis (indicated by furfural, blue line) for collecting the gas for the GC measurement. The decrease in the CI-MS signal at this point is caused by the removal of some of the sample with the gas syringe, and could be avoided using a split inlet setup.

In Figure 2, the detected signal from monoterpenes is highlighted in red. Many monoterpene isomers exist in smoke, and the isomer composition

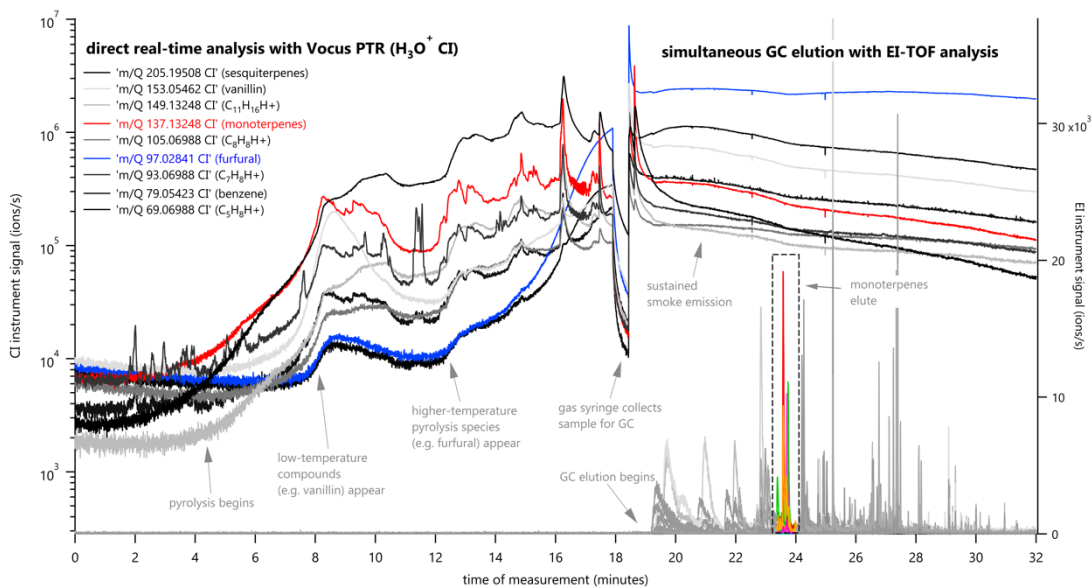


Figure 2. Time series of simultaneous real-time CI and GC-EI measurements.

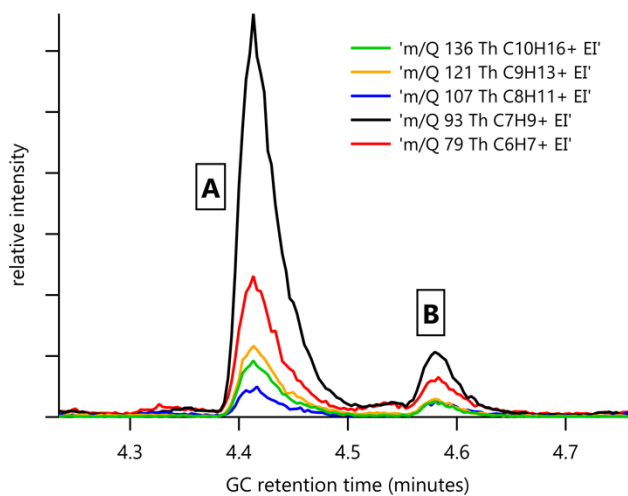


Figure 3. Section of GC chromatograph showing monoterpene elution.

may change over time. The chemical ionization measures only the sum of all monoterpene isomers, but the exact isomer composition can be determined using the GC capability of the instrument. Figure 2 also shows the GC measurement in the lower right part of the figure.

The same TOF mass analyzer is used for both the GC-EI-MS measurement, and the continuing direct real-time CI-MS measurement. Therefore, only one mass analyzer is required for two distinct measurements, and the real-time measurement is not interrupted by the GC elution.

The section of the chromatograph where monoterpenes are expected to elute is highlighted in color in Figure 2. Figure 3 shows a zoomed-in view of this region of the chromatograph. Relevant high-resolution EI ions are shown. Two monoterpene isomers are seen in this region of the chromatograph. Using the EI fragmentation pattern, the two monoterpenes shown here can be identified as camphene (A) and  $\beta$ -pinene (B).

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