Improved Analysis of Environmental Samples Using Soft Ionization and Novel GCxGC-HR-TOFMS

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Overview

A novel ion source for use in GCxGC-HRTOFMS based on the Folded Flight Path® (FFP®) mass analyzer is being developed. Its capabilities as applied to analysis of complex environmental samples are presented.

Introduction

Current demand for faster, more accurate analysis of complex environmental samples can be addressed through improvements in analytical instrumentation. Comprehensive two-dimensional gas chromatography (GCxGC) reduces data complexity by enhancing separation capacity. GC-HRMS instruments exhibit increased selectivity and allow reducing spectral library match lists by excluding elemental formulae ruled out by corresponding exact masses. Various soft ionization methods are available for improving accuracy of analyte assignment and selectivity. They produce spectra with high abundance molecular or quasi-molecular ions, and simplify the compound characterization through formula searches of corresponding exact masses. This work focuses on the analysis of complex environmental samples using GCxGC-HRTOFMS, and a novel soft ionization source operating in positive and negative ion polarities.

Ion Source

A prototype of the novel ion source for use in our GCxGC-HRTOFMS was developed. In addition to the positive ion polarity CI, it has capabilities to operate in the EI and the negative ion polarity CI ionization modes. The multimode ionization sources are well known, but typically, when using CI source in EI mode, the sensitivity is limited compared to the dedicated EI source. The chromatographic peak shapes are also not ideal in those "combined" sources, especially when performing comprehensive GCxGC analysis, which requires producing of very narrow (~50 ms) chromatographic peaks. With our novel ion source we are attempting to overcome deficiencies of the typical multimode sources, and make multi-ionization mode operation part of the normal analytical workflow for analysis on GCxGC-HRTOFMS instruments with minimum compromises in their performance.
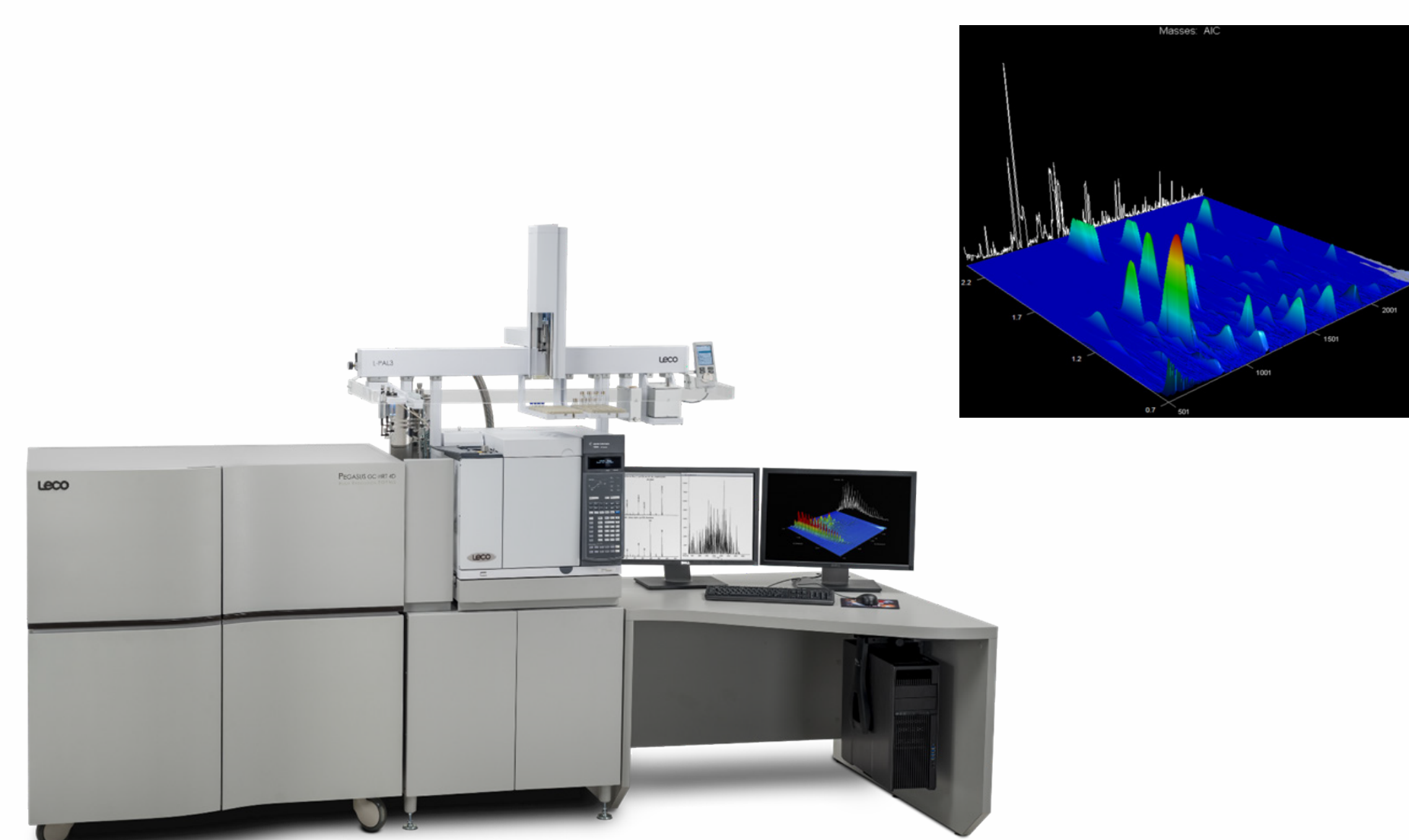
LECO Pegasus® GC-HRT+ 4D

Methods

The GCxGC system is comprised of the Agilent 7890B GC equipped with the LECO quad-jet liquid nitrogen-cooled thermal modulator. Two-dimensional gas chromatography (GCxGC) separations were carried out with an Rxi-5SilMS 30 m x 0.25 mm x 0.25 mm as the primary column, and an Rxi-17SilMS 1 m x 0.25 mm x 0.25 mm (Restek, Bellefonte, PA), as the secondary column. The GC oven program was as follows: a 2 min isothermal hold at 50 ºC, and then ramping at 5 ºC/min to 300 ºC, followed by an 8 min isothermal hold. The secondary oven was set to a temperature 15 ºC higher than that of the primary oven. The modulator temperature was offset by 15 ºC higher than the secondary oven, and the modulation period was set to 5 s. The helium flow rate was set to 1 ml/min. The high resolution mass spectrometer was a LECO Pegasus GC-HRT+ research prototype with Encoded Frequent Pushing® (EFP®) capabilities. The data acquisition rate was 200 full spectra/s, in order to match sampling speed requirements for GCxGC peaks (~50 ms). The environmental samples are the snow samples collected in the city of Moscow (Russia), provided by Prof. A. Lebedev (Lomonosov Moscow State University) and prepared in his lab according to the EPA Method 8270 (liquid-liquid extraction). The data were collected in GC and GCxGC runs using all three ion source ionization modes: EI, positive, and negative polarity CI.
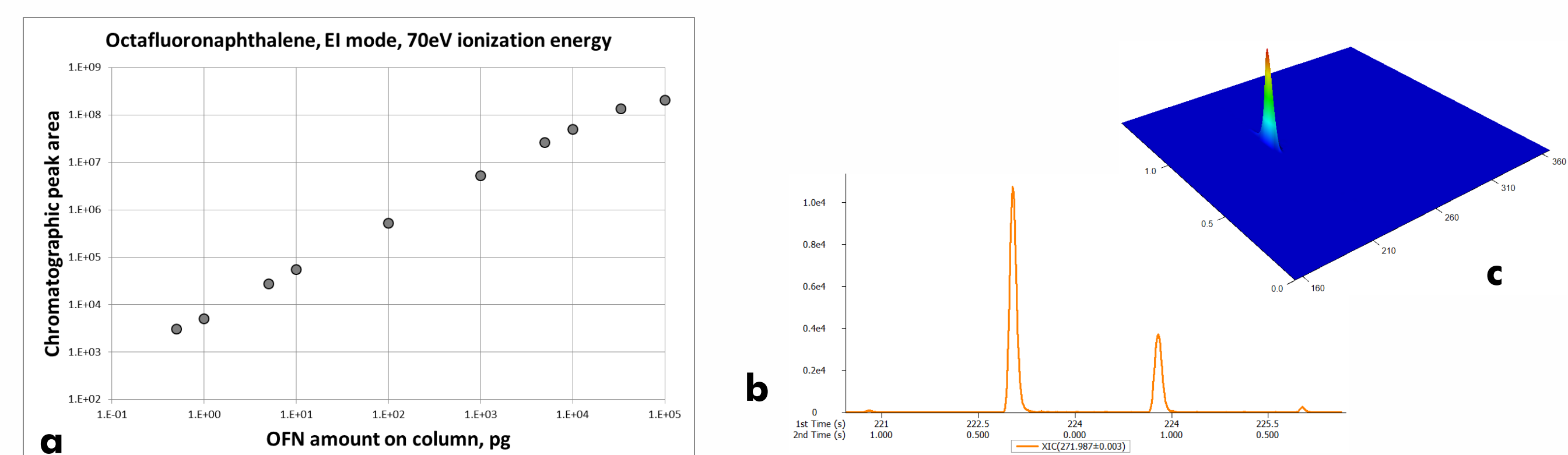

Figure 1. The source performance in the EI mode, positive ion polarity; (a) Octafluoronaphthalene (OFN) 1D dynamic range; (b) 2D GC chromatographic peaks; and (c) 2D GC surface plot, 100 pg OFN on column (middle of the dynamic range).
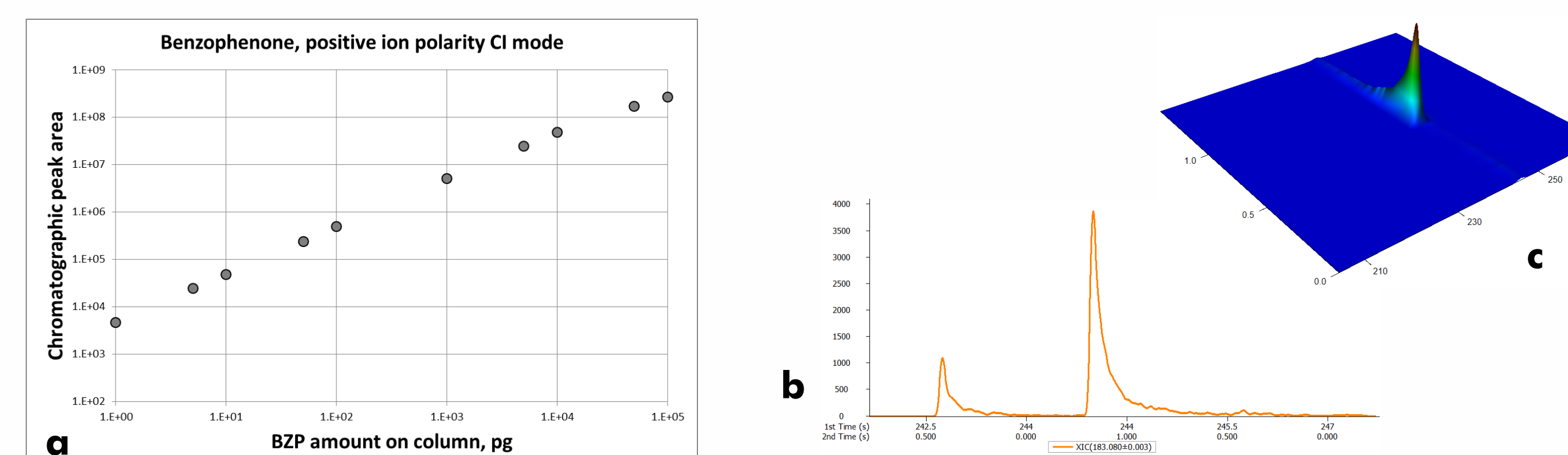

Figure 2. The source performance in the CI mode, positive ion polarity; (a) Benzophenone (BZP) 1D dynamic range; (b) 2D GC chromatographic peaks; and (c) 2D GC surface plot, 50 pg BZP on column (middle of the dynamic range).
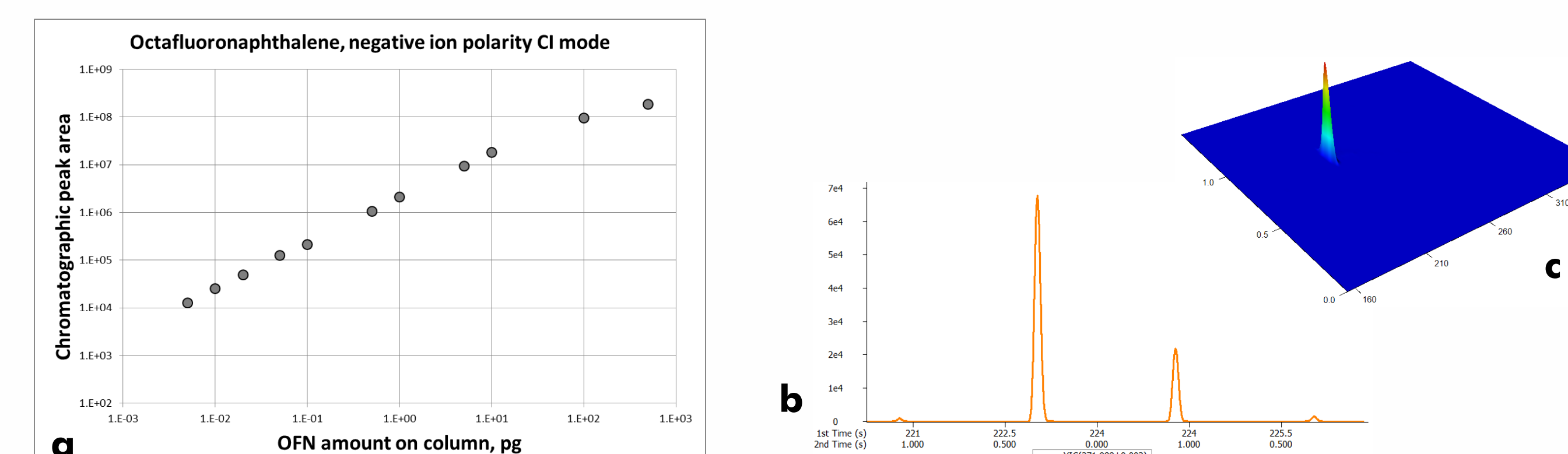

Figure 3. The source performance in the CI mode, negative ion polarity; (a) Octafluoronaphthalene (OFN) 1D dynamic range; (b) 2D GC chromatographic peaks; and (c) 2D GC surface plot, 500 fg OFN on column (middle of the dynamic range).
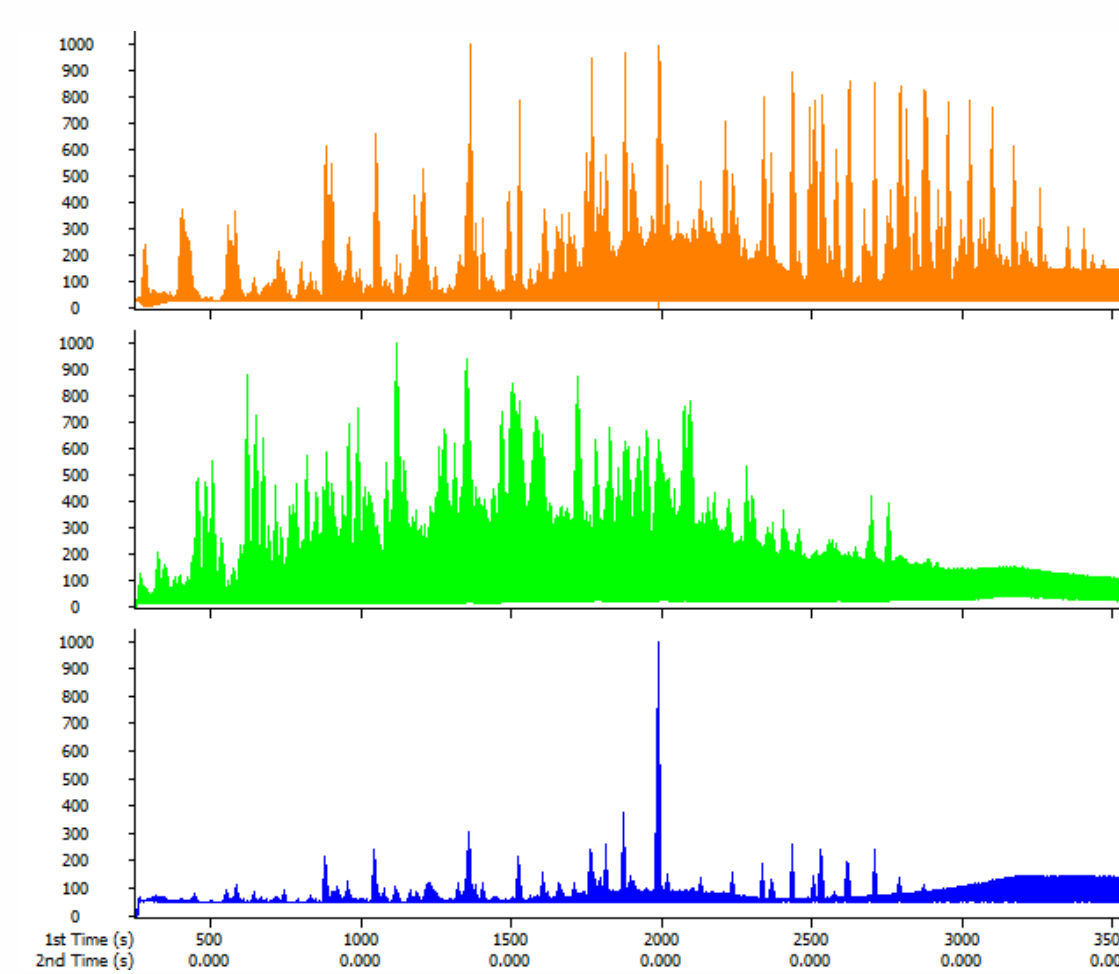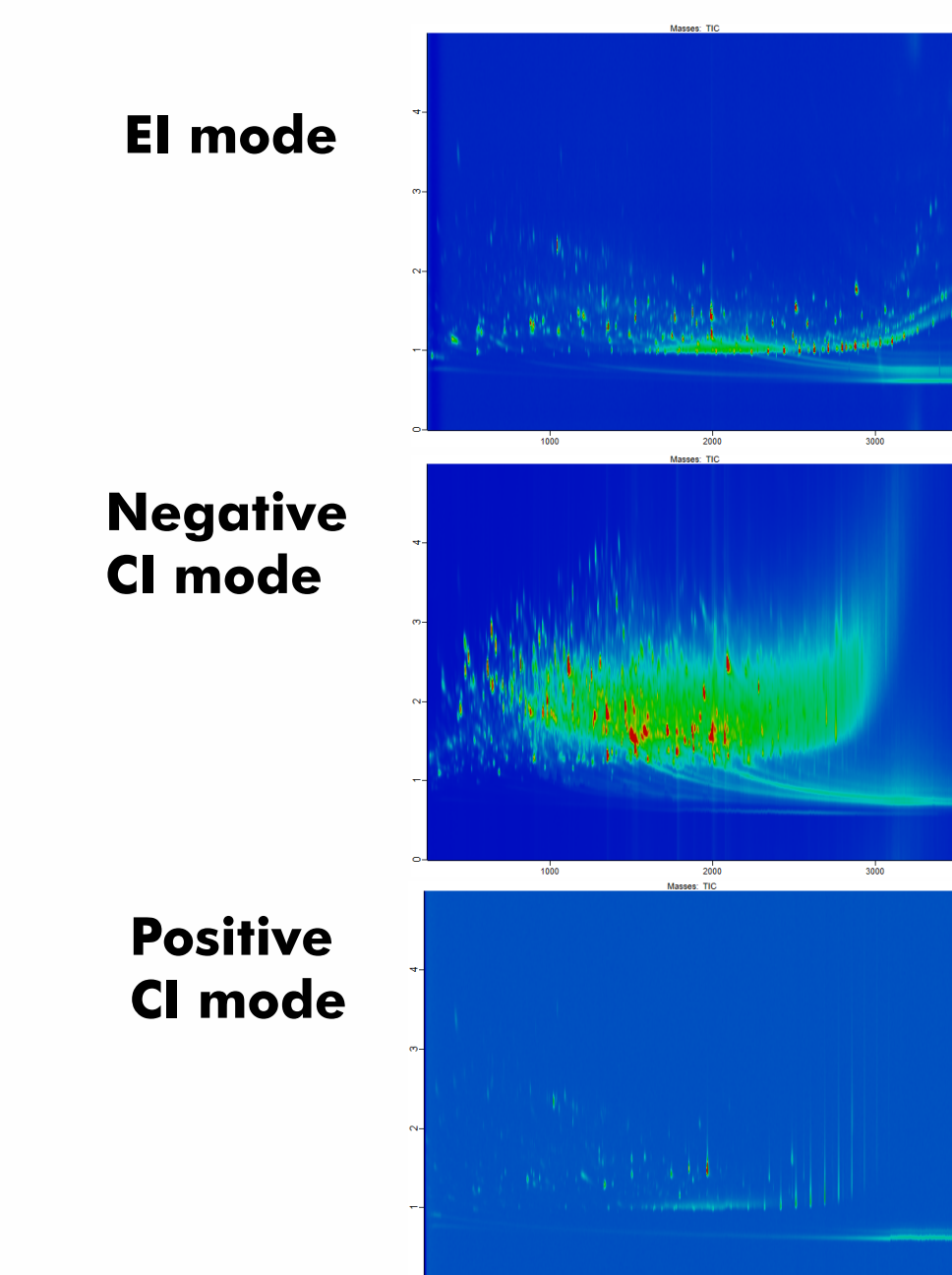

Figure 4. EI (top), negative (middle), and positive (bottom) CI mode TIC plots; 2D TIC contour plots below.

EI mode

Negative CI mode

Positive CI mode

Results and Discussion

The preliminary data has shown that in all three ionization modes the dynamic range was improved (Figures 1-3). The LOD in the negative ion polarity CI mode was in the low fg range for OFN. As usually observed for negative chemical ionization, the sensitivity in this mode varies widely depending on the chemical properties of the analyte. The 2D chromatographic peaks are about 0.08 sec wide in EI and CI. Thus, one can analyze the sample in all three modes within the same ion source, using the same chromatographic method, preserving retention times across all three modes of operation for improved analytes assignment. The samples used in this study contained thousands of analytes with the most peaks detected in the negative CI chromatograms (Figure 4). As expected, sensitivity for halogenated compounds was greatly enhanced in the negative CI mode, up to 200 times for PCBs (Penta-, Hepta- CB) (Figure 5 and 6). The positive ion polarity CI mode was especially helpful ionization mode for alkanes identification (Figure 7).
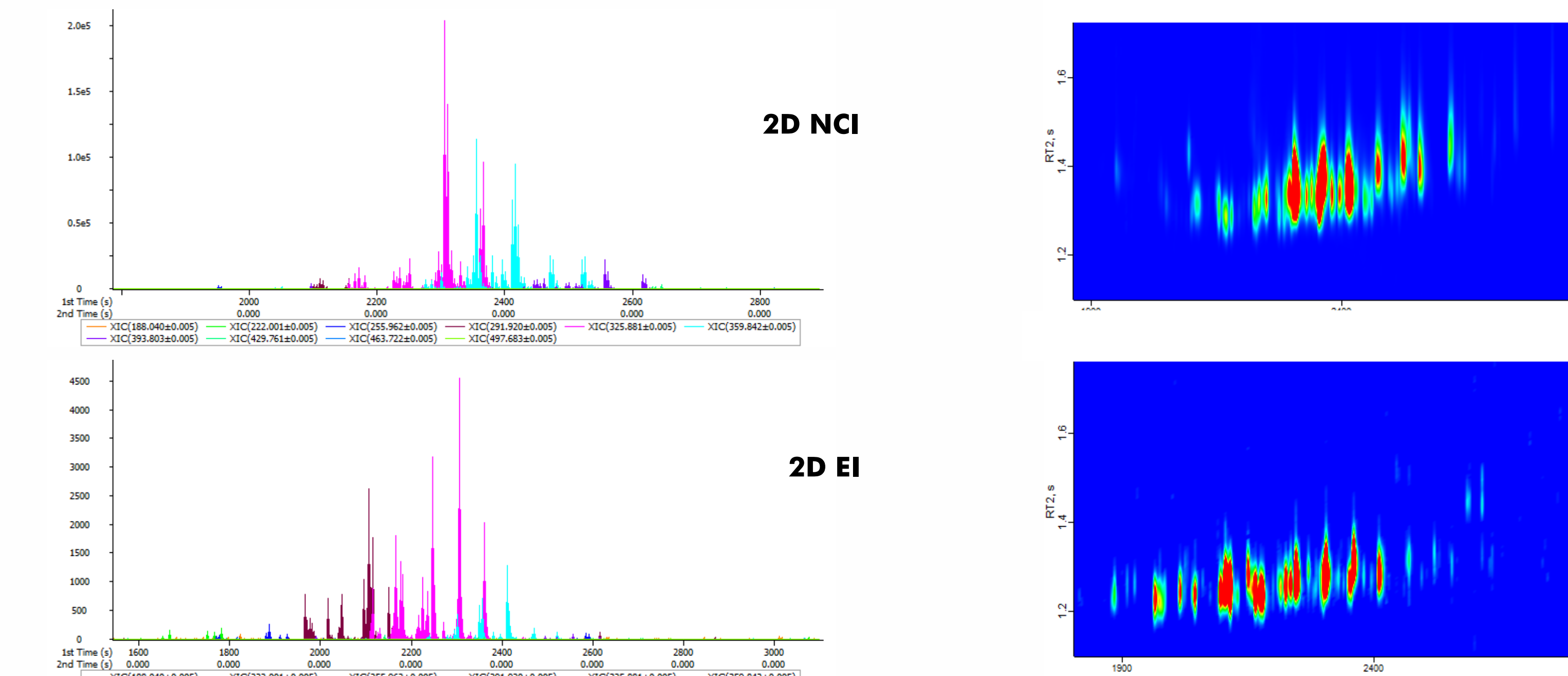

2D NCI

2D EI

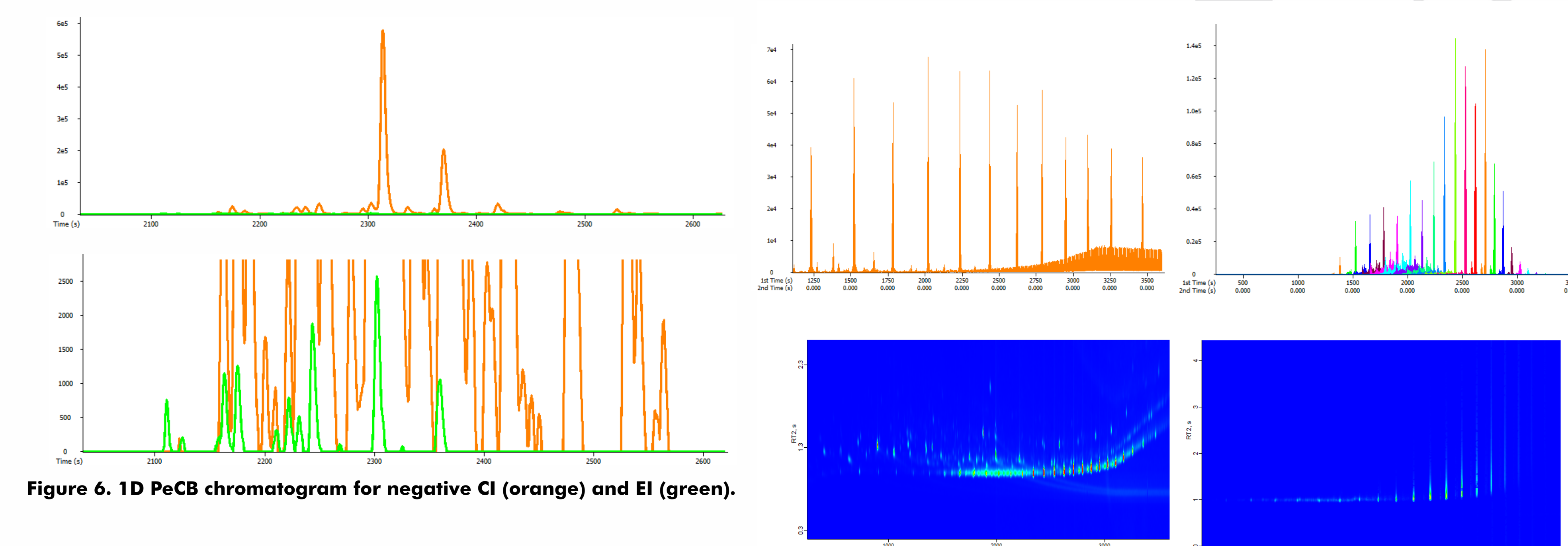**Figure 5. PCBs in negative CI (top) have 50X higher response for 2D compared to EI (bottom).**

Figure 6. 1D PeCB chromatogram for negative CI (orange) and EI (green).

Figure 7. Alkanes, C_{15}–C_{35} EI mode, m/z=57.0699 (left), Positive polarity CI, $(M-H)^+$ (right).

Conclusions

- The novel multimode ion source allows to analyze complex environmental samples in three ionization modes (EI, positive polarity CI, and negative polarity CI) with the GCxGC-HRTOFMS.

- With the use of the same chromatographic method and essentially the same source, the three modes of ionization provide complementary chemical information, further enhancing the analytical capabilities of the accurate mass, GCxGC-HRTOF system.

Acknowledgments

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