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ORIGINAL PAPER

Better screening of non-target pollutants in complex samples using advanced chromatographic and mass spectrometric techniques

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Abstract

The number of priority and emerging contaminants nowadays exceeds several thousands. As a consequence, it is a daunting task to monitor thousands of compounds using classical gas chromatography–mass spectrometry (GC–MS). Preliminary non-targeted screening is thus usually performed to identify the most relevant contaminants. Here we analyzed complex environmental samples of snow, rain water and cloud water from the Arctic, France, Chile, and Russia by two-dimensional gas chromatography (GC × GC) with ionization methods including electron ionization (EI), positive chemical ionization (PCI), and electron capture negative ionization (ECNI) modes, combined with high-resolution mass spectrometry. This approach combines the separation capacity of GC × GC, detailed EI mass spectral libraries, the softness of PCI, and the selectivity of ECNI. Switching between ionization modes without any hardware change allowed to increase the information capacity and reliability of analysis. The structural elucidation becomes easier and more reliable due to the detection of molecular ions in PCI and ECNI modes with corresponding extensive fragmentation in EI, while the ECNI mode improves about 100 times the detection limits for environmentally relevant halogenated and nitro compounds. Overall, a notable enhancement of the analytical capabilities for both targeted and non-targeted purposes is achieved.

Keywords Mass spectrometry · GC–HRMS · Environmental analysis · Chemical ionization · Non-targeted analysis · Electron capture negative ionization

Introduction

Mass spectrometry is the most sensitive and comprehensive analytical technique used in environmental analysis (Lebedev 2013). The majority of the analytes of environmental interest are volatile or semi-volatile compounds; therefore, gas chromatography–mass spectrometry (GC–MS) is the most widely used mass spectrometry-based technique in environmental studies (Lebedev 2012; Dsikowitzky and Schwarzbauer 2014; Heim et al. 2004; Novaković et al. 2012). It is well known that performing comprehensive environmental analysis is a challenging task. The number of known priority pollutants and emerging contaminants of environmental concern is currently exceeded several thousand (US EPA Part 423; US EPA Part 401). This list grows every day as new pollutants enter the environment (NORMAN List of Emerging Substances; Richardson and Kimura 2020; Tijani et al. 2016). This expanding list can also include their metabolites and degradation products, as well as reaction products occurring due to exposure to water, soil, atmosphere, and sunlight. In some cases, these products may even be more toxic than their parent compounds. Therefore, it becomes more and more challenging to conduct comprehensive screening for known and emerging environmental contaminants using traditional, well-established GC–MS methods (Hites and Jobst 2018; la Farré et al. 2008; Greca et al. 2014).

In our opinion, the best approach for a comprehensive environmental analysis would include the following steps. First, the most relevant contaminants for the site of interest (a factory, river, lake, town, region, etc.) should be identified

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via non-targeted screening in order to assess the current environmental situation over there (Sinikova et al. 2003; Polyakova et al. 2012). Then, the list of the detected and identified compounds should be carefully reviewed by experts in chemistry, biology, and toxicology in order to create a list of local priority pollutants based on their environmental hazard, abundance, toxicity, persistency, physical–chemical properties, relevant properties of their degradation and transformation products, etc. The third step involves the creation of a comprehensive monitoring program covering the site of interest for the local priority pollutants. Appropriate sample collection techniques, quantification of the listed pollutants and application of geotagging-based information systems for data processing will all result in establishing the sources of the environmental pollutants and can be followed by proposals of policies to address those sources. And finally, these local priority pollutants should then be regularly monitored to assess the environmental trends and the needs for reviewing efficiency of the corresponding environmental policies. The non-targeted screening should be repeated periodically to reveal new contaminants.

The very first step of the described approach starts with the analysis of environmental samples containing thousands of natural and anthropogenic analytes with their concentrations ranging in several orders of magnitude. It is practically impossible to develop ideal chromatographic methods providing efficient separation of all compounds in such a sample. Multiple cases of very close coelution of the chromatographic peaks or their overlapping should be expected in such complex data. Therefore, deconvoluted mass spectra of the individual compounds in complex samples should not be expected to be always ideal and library-like. Thus, even the best analytical tool for environmental analysis, such as GC–MS, faces multiple challenges when it deals with the tasks of that complexity and often struggles to produce reliable identification of unknowns during screening of environmental samples (Lebedev et al. 2018a, b; Giri et al. 2019; Lorentz et al. 2017; Portolés et al. 2011). That is why the number of publications dealing with non-targeted analysis is more than 100-fold less than that of those related to the targeted analysis. New approaches for environmental non-targeted screening, which can provide better chromatographic separation, enhanced mass spectra accuracy, and complementary data, such as various ionization techniques, should be proposed for improved reliability of identification of unknowns in the complex environmental samples and their quantification.

Fortunately, recent instrumentation and cheminformatics advances significantly expanded the analytical capabilities of the modern GC–MS instrumentation. For example, GC coupled with high-resolution mass spectrometry (GC–HRMS) can provide high mass accuracy spectra defining elemental composition of the analytes, and it becomes an efficient tool for structural elucidation of unknowns (Mazur et al. 2017; Lebedev et al. 2013). Coupling mass spectrometry (either high resolution or low resolution) with comprehensive two-dimensional gas chromatography (GC × GC) has enhanced separation efficiency and peak capacity (de Vos et al. 2011; Alam and Harrison 2016; Lorentz et al. 2017; Kates et al. 2020; Röhler et al. 2020). Various ionization methods applied to the same set of samples provide complementary information for reliable analytes assignment (Portolés et al. 2011; Portolés et al. 2014). Application of such advanced analytical instrumentation in environmental screening could drastically increase the analysis throughput, improve accuracy of the analytes assignment, improve sensitivity of analysis, quantitative accuracies, and precision, and ultimately provide the environmental scientists with comprehensive and reliable information.

Here, we demonstrate capabilities of such advanced approach, namely a combination of HRMS, GC × GC, and various ionization methods [electron ionization (EI), positive chemical ionization (PCI), and electron capture negative ionization (ECNI)] using examples from our work on non-targeted analysis with environmental samples from the Arctic, France, Chile, and Russia.

Experimental

Sampling and sample preparation

The analyzed samples were in the form of snow, rain water, and cloud water. Snow samples were collected in Moscow (Russia) at various sites on February 10, 2018 (Mazur et al. 2018a). The snow samples from the Russian Arctic were collected at the Novaya Zemlya Archipelago in the summer of 2016 (Lebedev et al. 2018a). The rain samples were collected in Moscow in April–May 2017 (Polyakova et al. 2018) and in Valparaiso (Chile) in the period of 2003–2012 (Lebedev et al. 2018c). Samples of cloud water were collected at the top of the Puy de Dôme Mountain (France) in the spring of 2015 (Lebedev et al. 2018b).

All snow samples were melted, and sample preparation of all water samples was carried out according to US EPA Method 8270. Triplicate extraction at pH 11 and pH 2 with dichloromethane (10–60 ml) was followed by drying over sodium sulfate. Concentrated (0.5 ml) basic and acidic dichloromethane extracts were mixed before the injection. Perdeuterated polycyclic aromatic hydrocarbons (PAHs) (SV Internal Standards, Restek, USA) were used as the internal standards. Details of sample preparation procedure could be found elsewhere (Lebedev et al.; 2018a; Mazur et al. 2017).

GC × GC–MS analysis

The samples were analyzed using a modified Pegasus® GC-HRT+ 4D high-resolution time-of-flight mass spectrometer (LECO Corporation, Saint Joseph, MI, USA) providing resolving power up to 50,000 for m/z 219 at FWHH and mass accuracy below 1 ppm.

The GC × GC setup was as follows: The LECO-made thermal modulator (quad-jet liquid nitrogen cooled) and a separate secondary column oven were installed inside gas chromatograph oven (Agilent 7890A with 7650 autosampler). The system was controlled by a prototype version of the ChromaTOF® brand software (LECO Corporation), also used for spectra collection and qualitative and quantitative data processing. All samples were analyzed using 1D GC and GC × GC chromatographic modes for data comparison purposes under conditions described in (Lebedev et al. 2018a, b). The reagent gas used in PCI and ECNI modes was methane. All 1D GC runs were performed using same column set and conditions as in GC × GC runs, except that the modulator jets were off. To make sure that all samples were analyzed at the best sensitivity, we used the programmed temperate vaporization (PTV) injector with the following settings: inlet solvent vent time—6 s, inlet solvent vent flow—100 ml/min, inlet solvent vent pressure—5 psi, inlet purge time—120 s, and inlet purge flow—20 ml/min. The PTV temperature settings were: start at 50 °C (hold 0.1 min), ramp at 500 °C/min up to 350 °C, and hold for 2 min. Injected samples volumes are 5 µl.

Results and discussion

Accurate mass measurements

Earlier, we demonstrated the benefits of accurate mass measurements (Lebedev 2013; Mazur et al. 2017; Lebedev et al. 2013) in environmental studies, including targeted and non-targeted analysis as well a workflow for manual structural elucidation. Thus, it was shown (Lebedev et al. 2013) that 25% of the analytes assignments using just NIST library matches (Polyakova et al. 2012) were corrected when accurate mass information was implemented. “Distorted” (due to coelution and/or low abundance of analytes) mass spectra of certain analytes detected in complex environmental samples may be quite different from their “ideal” library spectra. As a result, the correct compound may be very low in the hit list as their similarity library match scores can be very poor. The use of elemental composition information as a library match hit list filter always moves correct compounds to the higher positions in the hit list (Lebedev et al. 2013).

GC × GC–HRMS

When dealing with complex environmental samples, GC × GC plays a crucial role in obtaining quality results (Muscalu and Gorecki 2018; Kates et al. 2020). In our earlier papers, we have shown examples of GC × GC advantages in the case of coelution of two furan derivatives found in the cloud water samples (Lebedev et al. 2018b) and the case of five closely coeluting compounds of different origins in the Arctic snow samples (Lebedev et al. 2018a). Without the power of enhanced separation by GC × GC, the results in those and many other cases would have been erroneous. Also implementation of retention indices along the secondary column using deuterated PAHs was shown to be very useful in identification of compounds from the same homolog family, e.g., alkanes, fatty acids, etc. (Mazur et al. 2018b).

Complimentary soft ionization techniques

A well-known shortcoming of the classic EI mass spectra is low abundance or even absence of molecular ion peaks for various classes of organic compounds, first of all aliphatics (Samokhin and Revelsky 2012). The absence of molecular ions in the mass spectrum always leaves some doubts in the identification accuracy no matter how high the matching score of the library search result. Therefore, complementary soft ionization data, i.e., data with molecular species of any kind present in mass spectra, are very helpful in confirmation of the analytes assignment. Chemical ionization (CI) (Munson and Field 1966) is one of such soft ionization techniques widely used in the variety of GC–MS applications (Flamini et al. 2007; Kim et al. 2008; Zhang et al. 2011). More soft ionization techniques were introduced later on, including field ionization (Beckey 1977), glow discharge ionization (Carazzatoa and Bertrand 1994), photoionization (Syage et al. 2000), cold EI (Amirav et al. 2008), etc., to assist in elucidation of the unknown compounds and for confirmation of the analytes assignments. Thus, it is obviously beneficial to obtain complementary mass spectra for environmental samples of interest using the same chromatographic conditions and, ideally, on the same instrument without any hardware changes between switching ionization techniques to avoid any variations in analysis conditions, intentional or not. In our research, we were using GC × GC–HRMS in EI, PCI, or ECNI modes without any hardware changes. The retention times of the analytes collected in all three modes of ionization are exactly the same (Fig. 1S), which simplifies information linking between the data to assist in analytes assignment confirmation. Following are several examples of the results obtained.

Positive chemical ionization mode

Fatty acids From the environmental chemist's point of view, fatty acids are not as important compounds as, for example, PAH or halogenated compounds. However, fatty acids of natural or anthropogenic origin are very often present in the environmental samples as the products of oxidation of hydrocarbons, of hydrolysis of fats, etc. EI analysis usually allows easy fatty acids detecting (Fig. 2S) based on their characteristic fragments ($C_2H_4O_2^+$, m/z 60.02058 and $C_3H_5O_2^+$, m/z 73.02841); however, molecular ions of fatty acids are very often absent in EI mass spectra. That could result in false species assignment unless it is corrected or confirmed by running standards or by PCI data as it is illustrated in Figs. 1 and 3S. In the shown example, the EI data, after peak deconvolution, library search, and retention index matching, suggest that the best library hit for the detected analyte assignment is heptanoic acid (Fig. 3S). However, PCI data show (Fig. 1) that mass spectrum of the analyte with the same retention index of 1001 includes the protonated molecule of m/z 117.0910, corresponding to the chemical formula of hexanoic acid ($C_6H_{12}O_2$) with mass accuracy – 0.12 ppm.

Thus, the PCI data corrected the initial false EI data assignment, and in a similar manner, we were able to verify the assignments for all detected fatty acids in our sample based on their molecular formulae (Fig. 4S).

Phthalates Phthalates are an important class of organic pollutants widely present in any environmental object. Identification of phthalates using GC–MS with EI sources sometimes becomes rather challenging, as during ionization, the molecular ion is almost completely fragmented and the base peak of phthalates mass spectrum is $C_8H_5O_3^+$ ion of m/z 149.0233 (Fig. 5S). Elucidation of the carbon backbone in the ester groups using just EI data sometimes becomes completely impossible without additional data (standards, RI). On the contrary, chemical ionization by providing molecular ions allows reliable determination of individual species of phthalates. An ion of m/z 149.0233 is the base peak in EI spectra for the majority of phthalates (Fig. 5S). However, this characteristic fragment is also formed during PCI, making extracted ion chromatograms of m/z 149.0234 in EI and PCI data look very similar (Fig. 6S). Therefore, the EI data could provide primary information for detection of phthalates, while PCI mass spectra of the peaks with the same retention times contain complementary information, including ions of protonated molecules, adducts, and some other fragment ions important for structural elucidation. Moreover, the rules of fragmentation of even-electron ions in PCI similarly to odd-electron ions in EI mode are well studied (Tureček and McLafferty 1993). Therefore, PCI mass spectra make reliable structural elucidations possible.

Thus, Fig. 2 shows EI mass spectrum of an unknown phthalate. According to the fragmentation pattern, one can conclude that this compound contains one butyl group based on characteristic ions of m/z 205 and 223. However, the second alkyl group remains hidden. Fortunately, its PCI spectrum (Fig. 2, bottom) contains a protonated molecule peak of m/z 335.2217–$C_{20}H_{31}O_4^+$, which suggests that the unknown phthalate is butyloctylphthalate.

Moreover, the presence of m/z 177 ion allows establishing the absence of branching at the α and β atoms of the both aliphatic chains. It forms due to consecutive losses

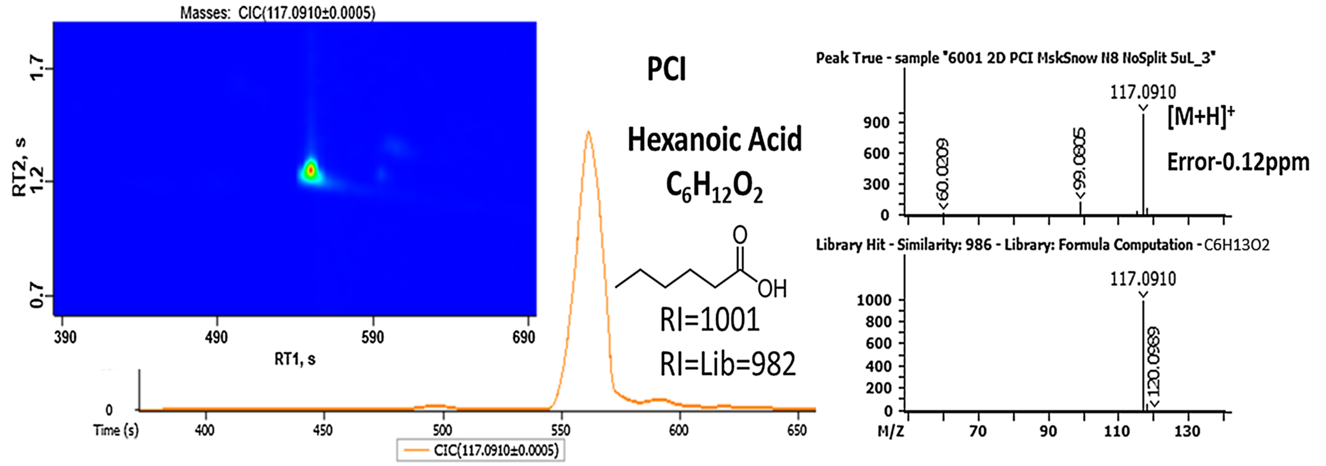
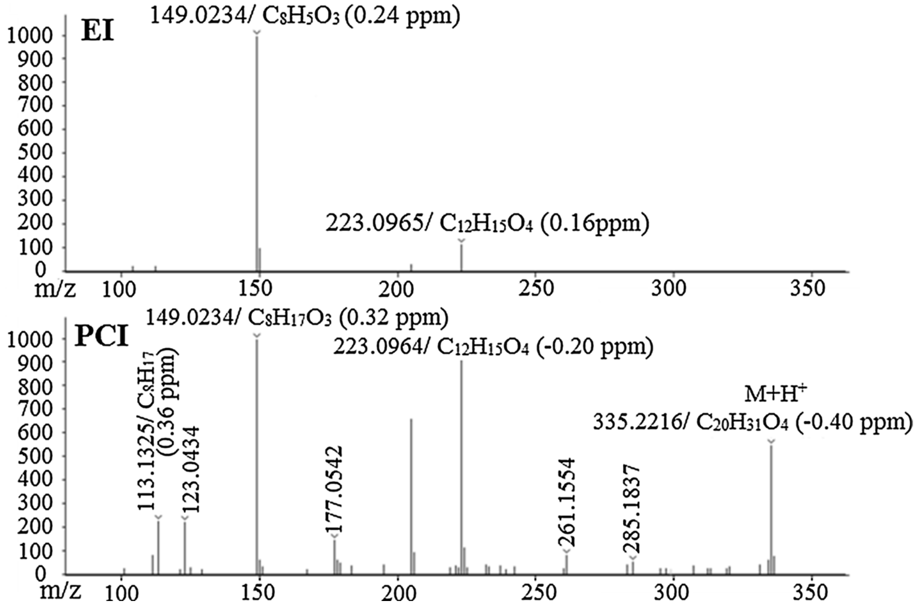


Fig. 1 Extracted ion chromatogram (EIC) and contour plot (upper left corner) of the fatty acid protonated ion m/z 117.0910 (hexanoic acid) from the Moscow snow samples, analyzed with dual chamber source in positive chemical ionization (PCI) mode. The PCI signal precisely identifies unknown fatty acid by means of HRMS with PCI mode

Fig. 2 Electron ionization (EI) (top) and positive chemical ionization (PCI) (bottom) mass spectrum of an unknown phthalate. PCI mass spectrum provides complementary set of ions significantly simplifying identification of unknown phthalate



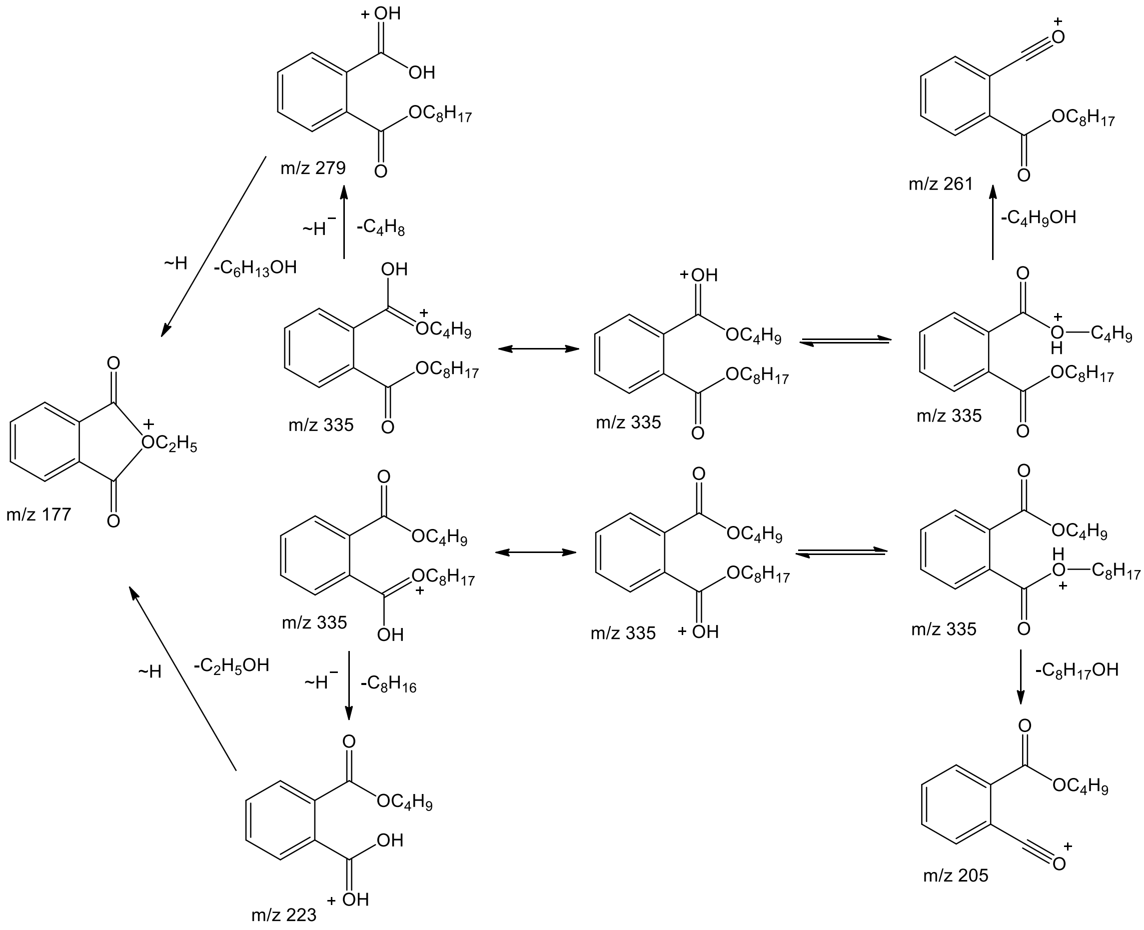


Fig. 3 Fragmentation pathway of an unknown phthalate under PCI conditions revealing its structure

of octene and ethanol or butene and hexanol molecules (Fig. 3) from the MH^+. All processes follow the standard rules of fragmentation of even-electron ions (Tureček and McLafferty 1993).

Electron capture negative ionization mode

Halogenated and nitro containing compounds ECNI mode allows detecting analytes with high-electron affinity present in the environmental samples at the trace level. Most halogenated compounds in ECNI mode produce strong peaks of the corresponding halogens, and that signal is used for detecting halogenated analytes. Figure 4 shows eight EIC plots of a Moscow snow sample analyzed in EI and ECNI modes: $^{35}Cl^-$ isotope ion with m/z 34.9694 and m/z 34.9683 for $^{35}Cl^+$; $^{79}Br^-$ m/z 78.9189 and m/z 78.9178 for $^{79}Br^+$; m/z 126.9050 for I^- and m/z 126.9039 for I^+; m/z 45.9924 for NO_2^+; and m/z 45.9935 for NO_2^-, correspondingly.

Higher sensitivity of chlorinated and brominated compounds in ECNI analysis mode allows for reliable detection of such environmentally relevant compounds as polybromodiphenyl ethers and polychlorinated biphenyls (PCBs) (Figs. 7S–12S). Operating ECNI mode allows reaching 100 times higher sensitivity than in EI mode for identification of some PCBs (Fig. 9S). Moreover, many PCBs were not detected at all when using the EI mode, but confidently detected using ECNI mode of analysis (Figs. 10S–12S).

Nitro-group-containing compounds represent an important class of chemicals of environmental concern. Unfortunately, their detection limits in EI mode are much worse than that of a majority of priority pollutants, and as the result, these hazardous compounds often remain undetected. Figure 4d shows the EIC plots of the characteristic for

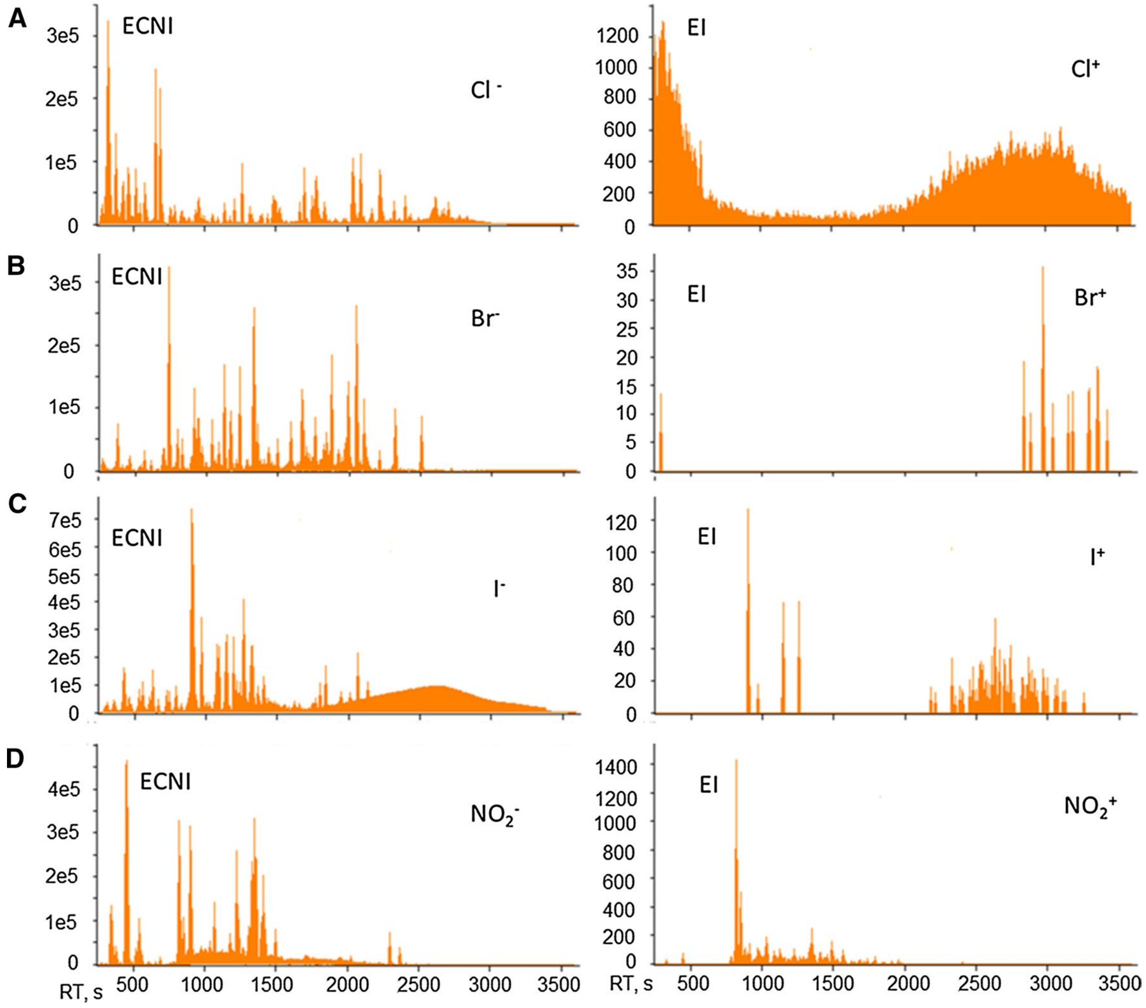


Fig. 4 Extracted ion chromatograms of a Moscow snow sample analyzed in electron ionization (EI) and electron capture chemical ionization (ECNI) mode based on the characteristic ions of $^{35}Cl^-$ and $^{35}Cl^+$ (**a**); $^{79}Br^-$ and $^{79}Br^+$ (**b**); I^- and I^+ (**c**); NO_2^- and NO_2^+(**d**). The given plots demonstrate significant difference in sensitivity of halogenated and nitro-group-containing compounds when ECNI is used. Pay attention to the *y*-scale.

nitro-group-containing compounds ions NO_2^+ (m/z 45.9924) and NO_2^- (m/z 45.9935) in the Moscow snow samples in EI and ECNI modes. For the latter mass chromatogram, the corresponding signals are 1000 times higher.

Figure 13S demonstrates the difference in sensitivity for dinitrobenzene isomers analyzed in EI and ECNI modes. EIC plots of the base peaks in the mass spectra of dinitrobenzenes acquired in EI mode ($C_6H_4N_2O_4^{+\cdot}$, m/z 168.0166) show only a few weak, poorly detectable peaks. However, the EIC plot of the base peak obtained in ECNI mode ($C_6H_4N_2O_4^{-\cdot}$, m/z 168.0177) shows all three isomeric dinitrobenzenes with very high intensities, thus allowing their reliable quantification. The difference in sensitivity is similarly pronounced for dinitrotoluenes ($C_7H_6N_2O_4$). Signals of the base peaks (Fig. 14S) in ECNI mode (molecular ion $C_7H_6N_2O_4^{-\cdot}$, m/z 182.0333) are by two orders of magnitude higher than that of the base peaks signals in EI mode (fragment ion $C_7H_5N_2O_3^+$, m/z 165.0295).

Another good example of enhanced ECNI sensitivity is detection of 4-nitrophenol in Moscow snow samples. The ECNI signal is 100 times higher (Fig. 15S) than the related signal in EI mode. Just one peak of dinitrophenols was detected at trace levels in EI mode (Fig. 16S). In ECNI mode, four isomers were detected with intensities hundred times higher, allowing automatic detection and quantification.

Conclusion

Employment of a nontarget analysis workflow for screening environmental samples by GC × GC–HRMS in several ionization modes significantly improves reliability of the data and expands the dynamic range and the coverage of analysis. The GC × GC mode increases separation capacity and reduces the number of completely overlapped peaks of coeluting compounds, creating more favorable conditions for successful peak deconvolution and identification. HRMS generates high mass accuracy full mass range spectra making analyte assignments more reliable. Switching between ionization modes (EI, PCI, and ECNI) without any hardware change simplifies alignment of chromatograms collected in the different ionization modes. Linking the EI and PCI results allows for compounds confirmation and verification. The ECNI data show significant improvements in sensitivity for high-electron affinity compounds, and its selectivity allows highlighting the presence of the halogenated and nitro compounds in the samples, which are usually the classes of major concern in environmental analysis. Overall, the combination of all these advanced features in a single analysis will enhance the analytical capabilities in the modern environmental studies both for targeted and non-targeted purposes.

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Compliance with ethical standards

Conflict of interest Authors declare no conflicts of interest.

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