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Use of electron ionization and atmospheric pressure chemical ionization in gas chromatography coupled to time-of-flight mass spectrometry for screening and identification of organic pollutants in waters

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ABSTRACT

A new approach has been developed for multiclass screening of organic contaminants in water based on the use of gas chromatography coupled to hybrid quadrupole high-resolution time-of-flight mass spectrometry with atmospheric pressure chemical ionization (GC–(APCI)QTOF MS). The soft ionization promoted by the APCI source allows effective and wide-scope screening based on the investigation of the molecular ion and/or protonated molecule. This is in contrast to electron ionization (EI) where ionization typically results in extensive fragmentation, and diagnostic ions and/or spectra need to be known a priori to facilitate detection of the analytes in the raw data. Around 170 organic contaminants from different chemical families were initially investigated by both approaches, i.e. GC-(EI)TOF and GC-(APCI)QTOF, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and a notable number of pesticides and relevant metabolites. The new GC–(APCI)QTOF MS approach easily allowed widening the number of compounds investigated (85 additional compounds), with more pesticides, personal care products (UV filters, musks), polychloronaphthalenes (PCNs), antimicrobials, insect repellents, etc., most of them considered as emerging contaminants. Both GC-(EI)TOF and GC-(APCI)QTOF methodologies have been applied, evaluating their potential for a wide-scope screening in the environmental field.

1. Introduction

A relevant applied field of modern analytical chemistry is water analysis, where many different anthropogenic pollutants may be present in samples, typically at low concentrations. Even at sub-μg/L levels they can cause hazardous effects on living organisms and aquatic ecosystems. Multi-analyte methodologies must be developed and applied in monitoring programs to provide a broad and realistic knowledge about water pollution in a rapid, sensitive and selective way. It is also crucial that the scope of these methodologies can be easily updated and extended, as new "emerging contaminants" are continuously being reported and are a matter of concern [1,2].

Combination of chromatography with mass spectrometry (MS) is nowadays the method of choice to investigate the presence of organic pollutants in water. Both gas chromatography (GC) and liquid chromatography (LC) are required to cover the entire range of contaminants of interest, from non-polar/volatile compounds to polar/non-volatile ones [3]. Until now, most analytical methods employed in routine analytical environmental monitoring are focused on the accurate quantification of a restricted number of target compounds, commonly taken from priority lists of contaminants [4,5]. For this purpose selected ion monitoring (single stage MS) or multiple reaction monitoring (tandem MS) is often performed, which involves acquisition of a priori selected target analytes. Consequently, any other potentially harmful compounds that might be present in the samples are not detected. This is an important drawback, given the high number of pollutants, their varying occurrence in time, and difficulties in setting priorities in monitoring programs.

In the last decade, high-resolution time-of-flight (TOF) mass analyzers have been investigated as an alternative to triple quadrupole MS/MS. Using TOF MS it is feasible to obtain sensitive full scan data while an elevated resolving power and mass accuracy

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provides the required selectivity [6–8]. This facilitates widening the number of analytes that can be detected in a single run, with the additional advantage that data can be re-examined to search for other compounds that were not yet of interest at the time of analysis, without the need of additional analysis. In the past years, TOF MS and hybrid quadrupole-TOF MS (QTOF MS) have been successfully applied for screening purposes in combination with GC or LC in different applied fields, like environmental analysis, food safety or toxicology [9–12].

In GC–MS, electron ionization (EI) has been the most widely used ionization source with various types of mass analyzers, including high resolution TOF-MS. Various applications of quantitative and qualitative determination of residues and contaminants have been described [6,13–15]. In EI-MS a rather strong fragmentation of the molecule typically occurs during ionization. As a result, the most diagnostic ion, the molecular ion, is often lost and similar spectra may be obtained for analogues of certain analyte classes. Therefore, for detection and identification, reference spectra of target analytes are required and in addition retention times to distinguish between structural analogues are essential. In EI-high resolution/accurate mass MS, which has high potential for elucidation of unknowns, the absence of a molecular ion is a serious drawback.

When using soft ionization modes, such as chemical ionization (CI), field ionization (FI), supersonic molecular beam (SMB) or atmospheric pressure chemical ionization (APCI) [14,16–18] the (quasi)molecular ion is often present. This facilitates large-scope screening approaches based on the investigation of the (abundant) molecular ion and/or protonated molecule. Especially the APCI interface is a very promising option because it is more generic than CI and enables coupling of GC with a range of high-end mass spectrometers (MS/MS, TOF, QTOF) initially developed for LC–MS, thereby providing highly sensitive and selective detection. The possibilities of GC–(APCI)MS were recently reported in the field of pesticide residue analysis in food [19].

In this paper we have applied both existing GC–(EI)TOF MS and the now available GC–(APCI)QTOF MS instrumentation for screening and identification/elucidation of organic contaminants and transformation products (TPs) in water samples. A method for the detection and identification of 250 organic contaminants has been developed based on GC–(APCI)QTOF MS with the simultaneous acquisition of low and high collision energy spectra (MS^E mode). Screening is based on the presence of molecular ion and/or protonated molecule in the low energy function and subsequent information available in the high energy function is used in order to confirm/reject the suspect identity reducing the number of false positives. Critical parameters have been carefully studied and optimized in order to widen the number of organic contaminants included in the method. This paper aims to investigate and describe the GC–(APCI)QTOF MS approach, and to compare its possibilities with the existing GC–(EI)TOF MS methodology in terms of capabilities for wide-scope screening. It is not the objective of this article to perform a detailed comparison of analytical characteristics, such as sensitivity or mass accuracy, because the mass analyzers belong to different generations.

2. Experimental

2.1. Reagents

Reference standards of pesticides, PCBs (Mix 3, 100 μg/mL in cyclohexane; Mix 41, 10 μg/mL in cyclohexane) and PAHs (Mix 9, 100 μg/mL) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). PBDE standard mixture "Lake Michigan Study", containing BDE 28, 47, 66, 85, 99, 100, 138, 153 and 154 (50 μg/mL in isooctane) and two individual standards of BDE 71 and 183 (50 μg/mL in isooctane) were purchased from Chiron (Trondheim, Norway). For confirmation purposes, musks standards were purchased from LGC Standards (Barcelona, Spain), and UV filters and insect repellents from Sigma Aldrich (Madrid, Spain). Stock solutions (around 500 μg/mL) were prepared by dissolving solid reference standards in acetone and stored in a freezer at −20 °C. Working solutions were prepared by diluting stock solutions in acetone for sample fortification and diluting in hexane for injection in the chromatographic system.

Acetone (residue analysis), ethyl acetate, dichloromethane (DCM), methanol and hexane (ultra-trace quality) were purchased from Scharlab (Barcelona, Spain). HPLC-grade water was obtained by purifying demineralised water in a Milli-Q Gradient A10 (Millipore, Bedford, MA, USA). 500 mg Bond Elut C18 cartridges (Varian, Harbour City, CA, USA) and 60 mg Oasis HLB cartridges (Milford, MA, USA) were used for solid-phase extraction.

2.2. Samples

Seven groundwater samples were collected from highly vulnerable aquifers within agricultural areas. All samples were collected in high-density polyethylene bottles and stored in the dark at a temperature below −18 °C until analysis.

100 mL of centrifuged water sample were gravity filtered through a 60 mg OASIS HLB cartridge previously conditioned using 3 mL methanol and 3 mL water avoiding dryness. The cartridge was air-dried, using vacuum for 30 min, and then eluted with 5 mL methanol. An aliquot of 2.5 mL was evaporated under a gentle nitrogen stream at 35 °C to a volume of 1 mL. Then 1 mL of ethyl acetate was added and evaporated to 100 μL. The final extract obtained was injected into the GC–(EI)TOF MS and GC–(APCI)QTOF MS systems.

2.3. Instrumentation

2.3.1. GC–(EI)TOF MS

GC instrumentation consisted on an Agilent 6890 N GC system (Palo Alto, CA, USA), equipped with an Agilent 7683 autosampler, coupled to a time-of-flight mass spectrometer, GCT (Waters Corporation, Manchester, UK), operating in electron ionization (EI) mode. The GC separation was performed using a fused silica HP-5MS capillary column of 30 m × 0.25 mm i.d. and a film thickness of 0.25 μm (J&W Scientific, Folson, CA, USA). The oven temperature was programmed as follows: 90 °C (1 min); 5 °C/min to 300 °C (2 min). Splitless injections of 1 μL sample extract were carried out at 280 °C. Helium was used as carrier gas at 1 mL/min.

The interface and source temperatures were both set to 250 °C and a solvent delay of 3 min was selected. TOF MS was operated at 1 spectrum/s acquiring the mass range m/z 50–650 and using a multi-channel plate voltage of 2800 V. TOF-MS resolution was about 8500 (FWHM) at m/z 614. Heptacosa, used for the daily mass calibration as well as lock mass, was injected via syringe in the reference reservoir at 30 °C. The m/z ion monitored was 218.9856. The application manager TargetLynx, a module of MassLynx software, was used to process data obtained from standards and samples in the analysis of target compounds. The application manager ChromaLynx XS in non-target mode, also a module of MassLynx software, was used to investigate the presence of non-target compounds in samples. Library searching was performed using the commercial NIST library.

2.3.2. GC–(APCI)QTOF MS

An Agilent 7890N gas chromatograph (Palo Alto, CA, USA) equipped with an Agilent 7683 autosampler was coupled to a quadrupole time-of-flight mass spectrometer, Xevo G2 QTOF (Waters Corporation, Manchester, UK), operating in APCI mode. The GC separation was performed using a fused silica DB-5MS capillary