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Qualitative nontarget analysis of landfill leachate using gas chromatography time-of-flight mass spectrometry

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ABSTRACT

Nontarget analysis means that a sample is analysed without preselection of the studied analytes. While target analysis attempts to determine whether certain selected compounds are present in the sample, nontarget analysis is performed to explore what unknown compounds can be found. We developed a nontarget method using a landfill leachate sample as a complex test sample. The method was based on the use of a gas chromatograph–time-of-flight mass spectrometer (GC–TOF–MS) for final analysis and a deconvolution computer application for data processing. This nontarget analysis method was tested and validated by applying it to a landfill leachate sample spiked with 11 organic pollutants that were treated as unknowns. Sensitivity was found to be the most critical parameter affecting the success of nontarget analysis. The limit of identification (LOI) was 2500 ng L⁻¹ for four of the 11 compounds, 500 ng L⁻¹ for three compounds and 100 ng L⁻¹ for one compound. Three compounds were not detected in any of the spiked samples. A six-stage identification process was developed based on the spiking experiments. The process was based on the forward fit value of the library hit, the number of deconvoluted ions and the accurate mass scoring of the measured ions. The process was applied to an unspiked leachate water sample. Altogether, 44 compounds were tentatively identified in the sample. Elemental compositions of 36 components were additionally determined for which an unequivocal compound identification could not be given. Nontarget analysis with GC–TOF–MS is a promising method for the qualitative analysis of complex water samples. However, we conclude that the computer application for nontarget analysis needs improvement to decrease the amount of manual work needed in the identification process.

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1. Introduction

The increased global use of chemicals has caused an emerging concern among scientists and policymakers concerning resultant environmental pollution [1]. The number of chemicals used worldwide is steadily increasing, and novel compounds are continuously being synthesized. As a result, trace levels of organic compounds are found in all spheres of the environment. The emerging contaminants are structurally diverse and heterogeneous group of chemical compounds which are currently not covered by existing regulations or legislation, have not been widely studied and are believed to pose a threat to ecosystems [2]. Richardson [3] and Wille et al. [4] recently published high-quality reviews about the current status of the analysis of emerging contaminants in the environment. Some of the emerging contaminants are used in domestic households as the ingredients of common consumer products. Municipal solid waste and wastewater therefore provide a possible route for emerging contaminants to enter into the environment [5–10]. Stormwater in

urban areas additionally forms a little-studied route for chemicals into the water system [11–13].

The most common GC–MS approach in use is still electron ionization (EI) and quadrupole analyser in selected ion monitoring (SIM) mode. A higher sensitivity may alternatively be gained with chemical ionization (CI) for some analytes, producing intensive adduct of molecular ion [14,15]. Environmental scientists have recently shown also an increased interest in GC tandem MS [16–19]. With these techniques, the target ions are determined before the analysis and during the data acquisition all other ions are excluded. Thus other instrumentation in which full spectrum data are collected and used to identify sample components are needed for the nontarget analysis instead of quadrupole mass spectrometers.

All ions with a mass-to-charge ratio (m/z) within the defined mass range eluting from the column and ionizing in the ionization chamber are measured in full spectrum techniques. These techniques allow the application of post-target and nontarget analysis [20]. One additional advantage of the comprehensive datasets produced in these analyses is the enablement of retrospective sample reanalysis, even a long time after data acquisition [21,22]. Modern gas chromatography–time-of-flight (GC–TOF) MS instruments are well suited for these purposes, as they provide high mass

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accuracy (typically below 5 ppm) and mass resolution (> 7000 full width at half maximum height (FWHM)) combined with high full-spectrum sensitivity and speed. High mass resolution enables the use of narrow-window extracted ion chromatograms (nw-XIC) of 20–50 mDa, which efficiently reduces background noise and enhances the signal-to-noise ratio of the analyte. In nontarget analysis using GC-TOF-MS, the peaks of previously unknown components in the sample chromatogram are extracted from the full spectrum data, using special deconvolution software that detects and combines ions arising from the same component without any previous information about the compound. The formed spectrum is then searched against the spectral library, and component identification is confirmed by comparing the measured accurate masses of molecular and fragment ions with the corresponding exact masses of the library hit compound. Applicability of GC-TOF-MS for the nontarget analysis of complex sample matrices like human breast adipose tissue [23] and honeybee samples [24] has recently been reported. More information on the analytical strategies using GC-TOF-MS can be found in an extensive review of Hernández et al. [25].

Emphasis of the previously published research using GC-TOF-MS has so far focused on the post-target analysis of different contaminants in environmental samples. Identification has been based on the utilisation of the nw-XICs, and ion ratios of the selected masses corresponding to the analytes of interest are extracted from the complete dataset [26–29]. Recently, Portolés et al. [26] reported a qualitative wide-scope post-target screening method in which approximately 150 contaminants were examined from water samples with GC-TOF-MS. The potential of nontarget screening has briefly been demonstrated in some previous papers [26,28,29], but so far only a few applications concentrating purely on nontarget analysis of aquatic samples using GC-TOF-MS have been reported [30,31].

The need for nontarget methods in environmental analysis is indisputable. However, their use is still very limited as they are considered very laborious and ineffective. Additionally, the high mass resolution instrumentation required for nontarget screening is uncommon. Spectra produced by GC-(EI)-MS contain more information for nontarget screening because of the natural fragmentation in EI compared to the LC-MS data. Availability of extensive commercial spectral libraries additionally facilitates identification. The main objective of our study was to develop a systematic procedure for the qualitative nontarget analysis of emerging contaminants in a complex liquid environmental sample, using a GC-TOF-MS instrument and deconvolution software. Furthermore, our other goals were to estimate identification reliability and explore the possible limitations of nontarget analysis. A landfill leachate sample was selected as the complex matrix for method development. Generic liquid-liquid extraction (LLE) was used without optimization for any particular group of compounds. Identification of the sample components through nontarget analyses was tested and validated, using a leachate sample spiked with a mixture of 11 semi-volatile organic compounds. Finally, the nontarget method was applied for the analysis of a real unspiked sample. In addition to the analysis itself, the performance and features of the deconvolution application were evaluated and some improvement proposals are presented.

2. Materials and methods

2.1. Reagents and reference standards

The method 526 calibration mixture of the Environmental Protection Agency (EPA), containing acetochlor (CAS 34256-82-1),

cyanazine (CAS 21725-46-2), diazinon (CAS 333-41-5), 2,4-dichlorophenol (CAS 120-83-2), 1,2-diphenylhydrazine (CAS 122-66-7), disulfoton (CAS 298-04-4), fonofos (CAS 944-22-9), nitrobenzene (CAS 98-95-3), prometon (CAS 1610-18-0), terbufos (CAS 13071-79-9) and 2,4,6-trichlorophenol (CAS 88-06-2) in ethyl acetate at a concentration of $200 \mu\text{g mL}^{-1}$ was purchased from Ultra Scientific (North Kingstown, RI, USA). Working and spiking solutions of the EPA-mixture were prepared in ethyl acetate and methanol using volumetric dilution. Triethyl phosphate and tris(1-chloro-2-propyl)phosphate were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Dichloromethane (DCM) and *n*-hexane for organic residue analysis were purchased from Mallinckrodt Baker B.V. (Deventer, Holland). LC-MS-grade methanol (MeOH) and anhydrous granular sodium sulphate $\geq 99\%$ was purchased from Sigma-Aldrich (Munich, Germany). SupraSolv[®]-grade ethyl acetate was purchased from Merck KGaA (Darmstadt, Germany). Ultrapure water was produced by PURE-LAB Ultra from ELGA Process Water (Marlow, UK).

2.2. Sampling and sample preparation

The landfill leachate samples were collected as grab samples from a reservoir at an active municipal landfill in the City of Lahti, Southern Finland. In physical appearance the leachate was a strong-smelling and black turbid liquid. Samples were stored in the dark in 2.5-L amber glass bottles at 4°C before analysis. Prior to extraction, the water samples were filtered with $1.6\text{-}\mu\text{m}$ GF-A and $0.7\text{-}\mu\text{m}$ GF-F fibreglass filters from Whatman (Maidstone, Kent, UK). The samples were concentrated using LLE. The laboratory blanks of ultrapure water were processed in parallel. An aliquot of 100 mL leachate sample was first extracted with 50 mL of *n*-hexane and then with 50 mL of DCM. After LLE the extracts were concentrated to about 5 mL in a rotary evaporator and transferred into glass tubes. Approx. 1 g of anhydrous sodium sulphate (dried in a muffle furnace at 400°C for 3 h) was added to the solution, which was left to stand overnight. The sample was decanted and concentrated under a gentle nitrogen flow at 35°C to a final sample volume of 500 μL .

2.3. Instrumentation and analytical conditions

Leachate sample analyses were performed using a gas chromatograph orthogonal-acceleration time-of-flight mass spectrometer GCT Premier (Micromass[®] MS Technologies, Manchester, UK) equipped with a GC Pal injection system (CTC Analytics, Zwingen, Switzerland). Separation of the sample compounds was carried out using a ZB-5MSi column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) from Phenomenex (Torrance, CA, USA) with a deactivated guard column ($2\text{ m} \times 0.25\text{ mm}$) from Phenomenex. Helium was used as the carrier gas in a constant flow mode of 1.0 mL min^{-1} . The samples were injected, using the splitless injection technique with an injection volume of $1.0\text{ }\mu\text{L}$. The purge valve was opened after an injection time of 1 minute. The inlet temperature was 280°C . For the DCM extract, the oven temperature program was set as follows: 30°C (hold 1 min), to 320°C at an increase of $10^\circ\text{C min}^{-1}$ and hold for 8 min. For the *n*-hexane extract, the oven temperature program was as follows: 50°C (hold 1 min), to 320°C at an increase of $10^\circ\text{C min}^{-1}$ and hold for 8 min. The temperature of the transfer line into the mass spectrometer was 300°C . The TOF-MS was operated in EI mode at 70 eV. The source temperature was 200°C and the detector voltage 2600 V. The resolution of the instrument was > 7000 FWHM. The acquisition rate was 0.09 s per scan with an interscan delay of 0.01 s between scans. The measured mass range (m/z) was 50–550 in centroid mode. A solvent delay period of 5 min was used at the beginning of the analytical run. The accuracy of mass measurements is improved in GCT Premier by using a fixed lock mass ion, which is automatically applied to correct for any possible

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