Journal of Chromatography A, 1216 (2009) 2288–2301

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Multiresidue analysis of pollutants as their trimethylsilyl derivatives, by gas chromatography–mass spectrometry

Á. Sebők, A. Vasanits-Zsigrai, A. Helenkár, Gy. Záray, I. Molnár-Perl*

Institute of Chemistry Department of Analytical Chemistry, L. Eötvös University, P.O. Box 32, H-1518, Budapest 112, Hungary

ARTICLE INFO

Article history:
Received 14 October 2008
Received in revised form 16 January 2009
Accepted 19 January 2009
Available online 23 January 2009

Keywords:
Multiresidue analysis
Wastewater
Danube River
Sixty-three pollutants
GC–MS
Trimethylsilylation
Oximation
Selective fragment ion

ABSTRACT

This paper reports a multiresidue analysis procedure which permits the identification and quantification of sixty-three water-soluble pollutants. Subsequent to their solid-phase extraction (SPE) enrichment, analyses of species have been carried out from one solution, by a single injection, as their trimethylsilyl-oxime ether/ester derivatives, by gas chromatography–mass spectrometry, within 31 min. Based on our optimized extraction, derivatization and mass fragmentation studies separation have been performed in the total ion current mode, identification and quantification of compounds have been carried out on the basis of their selective fragment ions. Including various pharmaceuticals, benzoic acid, its substituted species, different aromatic carboxylic acids, cholic acids, unsaturated and saturated fatty acids, aliphatic dicarboxylic acids, as well as synthetic pollutants of various origins (2,4-di-*tert*-butylphenol, different phthalates). Standard compounds were added to 500 mL effluent wastewater samples, at three concentrations (1–5 μg/L, 5–10 μg/L and 10–20 μg/L). Recoveries, using the Waters Oasis cartridges performing extractions at pH 2, pH 4 and pH 7 proved to be the optimum at pH 4 (average recoveries (94.5%), except for cholesterol (10%), paracetamol (18%) and 2,5-dihydroxybenzoic acid (25%). Carbamazepine could be recovered at pH 7, only. Responses, obtained with derivatized standards proved to be linear in the range of 4–80 μg/L levels. Limit of quantitation values varied between 0.92 ng/L (4-hydroxyphenylacetic acid) and 600 ng/L (dehydrocholic acid) concentrations. One of the most important messages of this work is the confirmation of the origin of blank values. It was shown that contaminants, mainly 2,4-di-*tert*-butylphenol, different phthalates and fatty acids, are sourced both from the reagents and mainly from the SPE procedure, independent on the cartridge applied. Reproducibilities, characterized with the relative standard deviations (RSDs) of measurements, varied between 0.71% and 10%, with an average of 4.38% RSD. The practical utility of the method was shown by the identification and quantification of the pollutant contents of Hungarian influent and effluent wastewaters (for six consecutive months and that of the Danube River for 2 months).

1. Introduction

In order to identify and quantify several functional group containing compounds, simultaneously – like in case of pharmaceuticals, personal care products and their metabolites, synthetic compounds of various origin, caffeine, etc. (further on: pollutants), present in waste, in river and in drinking waters – gas chromatographic–mass spectrometric (GC–MS) analysis as their trimethylsilyl derivatives was found as a preferred technique [1–12]. In this term, also authors of the present paper are convinced, (due to self experiences [13–19]), that in the cases of any matrices consisting of several functional group containing organics, GC–MS of the derivatized constituents is the best selection.

After a literature overview [20–43], the question arises: what is meant by the terminus technicus “multiresidue analysis”? Papers declaring to report a “multiresidue” analysis procedure, are containing basically different suggestions. Independent on the chromatographic methods applied, {GC [20–28], liquid chromatography (LC) [29–42], or capillary electrophoresis (CE) [29], including also two review papers [43,44]}, two main types of multiresidue proposals can be distinguished.

1.1. *Methods suitable to determine pesticides, only*

Solid-phase extraction (SPE)–GC–MS [20,22] were described for the identification and quantification of five antifouling agents in marine and costal water [20] and for 24 pesticides

---

* Corresponding author.
E-mail address: perlne@chem.elte.hu (I. Molnár-Perl).

0021-9673/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2009.01.056

from source and drinking water samples [22]. SPE–GC–electron-capture/nitrogen–phosphorus detection (ECD/NPD) was proposed for the analysis of 24 common pesticides of different polarities, contaminants in red vines [21].

Solid-phase microextraction (SPME)–GC–ECD/thermionic specific detection (TSD) [23], or SPME–GC–MS/flame ionization detection (FID) [24], or (SPME)–GC–μECD methods were described for the analyses of 17 pesticides in ground and drinking waters [23], 23 priority pesticides in river water [24] and 35 pesticides in bovine milk [28].

Also as multiresidue methods were declared [32,33,35,37], the identification/quantification of different number of pesticides measured by various techniques: 22 compounds were determined by SPE–LC–UV-diode-array detection (DAD) and/or SPE–atmospheric pressure chemical ionization (APCI) MS [32], 12 compounds [33], 4 compounds [35] and 7 compounds [37] were measured by SPE–LC–electrospray ionization (ESI) MS [33,35] and by SPE–HPLC–UV/MS [37], respectively.

1.2. Methods, suitable to determine organics of different origin, belonging to various groups of environmental pollutants, including pesticides

These types of proposals are, in point of fact, the multiresidue ones. In the understanding of this paper's authors, if the analysis can be performed from a single injection resulting in the analysis of various types of pollutants, this procedure might be indicated as a 'really multiresidue' process. These papers apply both GC [25–27,38] and LC [29–31,34,36,38–41] separations.

The method of stir bar sorptive extraction (SBSE) followed by GC–MS was applied with limited success [25–27].

The analytical method elaborated for the identification and quantification of 35 priority semivolatile pollutants in water samples was optimized [25] and validated [26]. As to the limit of quantitation (LOQ) values (0.1 and 36 ng/L), working in the MS full scan mode [25,26], this method can be regarded as an excellent one.

Multiresidue analysis of acidic and polar, in total of 46 water contaminants, was studied by means of SBSE–GC–MS, combined with large volume injection and in port silylation with *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA) [27]. The optimized method proved to be suitable for the determination of 37 pollutants: however, in fact, 15 have been determined, in strongly polluted, untreated wastewater, only.

Two methods were developed, in parallel, (SPE–HPLC–MS and SPE–CE–MS [29]), for the determination of 9 drug residues, present in river water samples. In spite of the fact that the detection limits of CE–MS (27–93 μg/L) proved to be significantly poorer in comparison to the HPLC–MS ones (4.8–19 ng/L), with both procedures, identically, 4 drug residues were measured. By means of CE–MS bezafibrate, naproxen, diclofenac and clofibric acid, while with HPLC–MS bezafibrate, carbamazepine, diclofenac and mefenamic acid were determined.

SPE–HPLC–ESI-MS/MS methods were developed [30,31] for the identification and quantification of various pharmaceuticals present in influent/effluent waste-, surface, ground and river water samples.

The method elaborated for the analysis of 13 pharmaceuticals of effluent and surface waters [30] provided relatively high limit of detection (LOD) values (10–50 ng/L); LOQ values were not given.

Similarly high LOD values (0.017–1.25 μg/L) were reported for the multiresidue SPE–LC–ESI-MS/MS method described for the determination of clofibric acid, bezafibrate, gemfibrosil, fenofibrate, atenolol, sotalol, metaprolol and betaxolol [31]. In addition to the good recovery values (all were above 60%), direct measured concentrations of contaminants were not given.

In general, it is known that ion suppression phenomena is the common drawback in LC–MS/MS analysis [31]. All these procedures are suffered of this limitation resulting in relatively high LOD values and decreased reproducibility of results.

Multiresidue procedures based on the use of SPE–LC–MS/MS [36–38], combined by SPE–GC–MS [36,38], or by SPE–HPLC–UV [37] were developed for the analysis of 27 pharmaceutically active compounds [36], for 5 pesticides, 1 herbicide and 1fungicide [37], and for 33 multiclass pollutants [38].

Due to the advantage of the high sensitivity of GC–MS [36], 27 contaminants (methylated and underivatized, together) have been measured: from two separate solutions, in the range of 0.01–7.97 ng/L concentrations, in the effluent samples of a sewage treatment plant (STP) of Sweden.

The method development for the identification and quantification of five pesticides, 1 herbicide and 1 fungicide from surface water, spiked with the model compounds [37] revealed recoveries above 60%, LOQ values were comparable by UV detection (48.3 ng/L) and by MS/MS detection (26.9 ng/L), respectively. Pollutants concentration proved to be at the threshold level of the method.

The analysis of 33 priority pollutants, present in the registration evaluation and authorization (REACH) system was the aim of the multiresidue method development implemented from the same SPE extract, by LC–MS/MS (25 pollutants) and by GC–MS (8 pollutants) [38]. In total 12 water samples were tested (5 influent, 2 effluents, 3 ground and 2 surface water samples) with both methods. In average, results revealed that all 8 GC–MS measured pollutants were found in the concentration range of 0.040–645 μg/L. Out of 25 compounds intended to determine by LC–MS, 12 were measured in the concentration range of 0.0022–13.2 μg/L.

Recent papers [39–42], came from the same laboratory, contain a continuously extended method development for the determination of basic/neutral pharmaceuticals and illicit drugs, applying subsequently to SPE (Oasis MCX) a new technique: ultra-high-pressure liquid chromatography–electrospray tandem mass spectrometry (UHPLC–MS/MS). As the first step [39,40], the analysis of 28 basic/neutral pharmaceuticals and illicit drugs [39], thereafter 25 multiple classes of acidic/neutral pharmaceuticals and personal care products [40] were described: in a single run, from surface water, applying electrospray ionization in the positive mode (ESI$^+$). As the second step, [41,42] the method has been extended, in order to be suitable for the analysis of 56 pharmaceuticals, personal care products and illicit drugs [41,42]. Analyses have been carried out from the same SPE extract, however in two runes, applying the ESI$^+$ (method 1) and the ESI$^-$ (method 2) modes, in parallel. The spectacular possibility of these four proposals [39–42] can be attributed to the advantages of using this new UHPLC–MS/MS technology providing significant advances in resolution, speed and sensitivity: due to the use of columns of 1 mm internal diameter, filled with 1.7 μm, bridged ethylsiloxane/silica hybride particle, operating at high pressures (up to 15,000 psi). As a result of these conditions the LOQ of the method ranged from the tenths of ng/L to tens of ng/L in surface water, and from single ng/L to a few hundreds of ng/L in the case of wastewater samples.

The goal of this paper was

(a) to present a literature overview on recent multiresidue proposals suitable for the analysis of water-soluble pollutants,

(b) to perform a GC–MS derivatization and mass fragmentation pattern study in order to identify and quantify as many pollutants as possible, expected in waste and in river waters: ready to react with silylating agents, or measurable without derivatization, from a single solution by one injection, simultaneously.