



Non-target screening of organic contaminants in marine salts by gas chromatography coupled to high-resolution time-of-flight mass spectrometry

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ARTICLE INFO

Article history:

Received 15 December 2010

Received in revised form 18 April 2011

Accepted 20 April 2011

Available online 19 May 2011

Keywords:

Marine salt

Saltworks

Gas chromatography

Mass spectrometry

Non-target screening

Organic contaminants

ABSTRACT

Gas chromatography coupled to time-of-flight mass spectrometry (GC–TOF MS) has been applied to characterize the organic pollution pattern of marine salt samples collected in saltworks from the Spanish Mediterranean coast. After dissolving the samples in water, a solid-phase extraction was applied reaching with a 250-preconcentration factor. The screening methodology allowed the detection of sample components without any kind of pre-selection of target pollutants. The identity of components detected was established by accurate mass measurements and comparison of experimental full-acquisition spectra with theoretical MS libraries. Several organic pollutants were identified in the samples, like plasticizers – potentially toxic to humans – and fragrances – included within the group of pharmaceuticals and personal care products –, among others. Our results indicate that these contaminants can be found in the marine salt after the crystallization process. GC–TOF MS is a powerful technique for wide-scope screening of (semi)volatile, low-polar organic contaminants, able to investigate the presence of a large number of compounds. Searching of contaminants is not restricted to a target list of compounds. Therefore, unexpected contaminants can be discovered in an efficient way, with better sensitivity and selectivity than other conventional analytical techniques, and making use of the powerful qualitative information provided by full-spectrum acquisition at accurate mass.

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1. Introduction

Marine salt is obtained by evaporation of sea water due to the combined effect of wind blow and sunlight heat in the solar saltworks. Salt pans are located near the sea, becoming peculiar environments inhabited by wildlife species associated with high salinity conditions. Concern has arisen as consequence of the vulnerability of these environments to anthropogenic pollution. Run-off from farms and industries may contain high concentrations of pesticides and industrial sub-products and reach these vulnerable coastal locations, with a deleterious impact on the briny aquatic systems [1]. This fact can also affect to the quality of the marine salt produced. Several authors have reported the presence of contaminants in coastal sea and saline waters, such as pesticides [2], halocarbons, aliphatic and aromatic hydrocarbons and ketones [3]. Badoil and Benanou [4] have detected phenols, phosphates and other volatile and semi-volatile compounds in waste landfill leachates, which reach coastal waters.

Contaminants produced by anthropogenic activities are transported by rivers and water flows from wastewater treatment plants and are frequently deposited on coastal locations like salt marshes or river estuaries and deltas. Several authors have detected a variety of contaminants in these vulnerable areas [5,6]. The marine salts obtained from salt pans can contain the contaminants present in sea water, provided that they remain after the concentration and crystallization processes. As a consequence, monitoring the presence of organic contaminants in marine salts seems necessary to have a realistic knowledge of their quality, since they are widely used for feeding purposes in human and animal nutrition and also for aquaculture activities, such as the artemia growth. Bath salts could also constitute possible routes of human exposure to the potentially toxic compounds found in the sea salts.

Hyphenation of gas chromatography (GC) with mass spectrometry (MS) is the most widely used and accepted technique for determination of volatile and semivolatile compounds of low-medium polarity in aquatic ecosystems, particularly in surface coastal water and marine environments. Different MS analyzers have been applied for this purpose, from single quadrupole to ion-trap or triple quadrupole, although the two later allow working under tandem MS mode [2,3,7,8]. Recently, Silva et al. [3] reported a methodology based on head space solid phase microextraction and GC–quadrupole mass spectrometry for the analysis of volatile

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compounds in marine salt, able to detect 40 volatile compounds belonging to different chemical groups.

The wide majority of methods reported until now in the environmental field are focused on a limited list of target contaminants. Even in the case that target pollutants investigated belong to priority lists, target methods do not allow the wide-scope screening required to investigate a large number of compounds that might be present in the samples. In most target methods, other non-selected contaminants would not be detected due to the specific-analyte information acquired. Although conventional MS analyzers can also work under scan mode, their capability to detect organic contaminants at low levels in complex-matrix samples is rather limited due to their low sensitivity and selectivity and their nominal mass measurements.

The recent emergence of modern high-resolution time-of-flight (TOF) analyzers opens new perspectives to develop wide-scope screening methodologies. GC–TOF MS offers interesting features for this purpose, as it combines high full-spectrum sensitivity and elevated mass resolution making feasible the accurate mass measurements of the molecular and/or fragments ions of any GC-amenable compound present in the sample. This technique allows searching organic contaminants in a post-target (i.e. searching for selected compounds after MS acquisition) and also in a non-target way (i.e. searching for unknowns, without any kind of compound pre-selection) [9]. GC–TOF MS has been successfully applied for screening, identification and elucidation of organic pollutants in environmental water and biological samples [9,10], and also for confirmation of pollutants in highly complex matrix like wastewater [11].

The limited dynamic range of GC–TOF MS instruments reduces their potential for quantitative analysis. For this reason, in the present study, GC–TOF MS has been used for qualitative purposes because of its high sensitivity in full spectrum acquisition complemented with mass accuracy.

In this work, we have applied GC–TOF MS for the rapid and wide-scope screening of organic pollutants in sea water and in marine salts obtained from solar saltworks and from a pristine sea shore salt marsh sited along the Spanish Western Mediterranean coast. The identity of the sample components detected in a non-target way was established by means of exact mass measurements and by comparison with theoretical spectral libraries. In addition, the organophosphate esters (OPEs) identified were confirmed by injecting reference standards.

2. Materials and methods

2.1. Sampling points

Marine salt samples from four solar saltworks sited in the Spanish Mediterranean shore (see Fig. 1) were collected directly from the crystallized salt stock in saltpans (samples 3 and 5) or purchased from the producers (samples 1 and 4). A seawater sample was also collected from the sea shore in front of a pristine salt marsh located in Torre la Sal, neighbouring a natural protected area (Natural Park of Ribera de Cabanes, Spain), sited close to the city of Castellon (sampling point 2). Sampling point 1 is a solar saltwork sited in the Alfaques bay, south of the Ebro River delta. This river receives domestic and industrial wastewater from numerous minor settlements along its way. Discharges into the Ebro River vary at different locations, showing an increase downstream, probably due to inputs from the tributaries or natural recharge of the stream, and finally it flows into the Mediterranean sea after crossing through the Ebro Delta [12]. Sampling point 3 is a solar saltwork located in the vicinity of an important fishing and middle trade harbour, surrounded by a highly urbanized area. Sampling points 4 and 5 are

solar saltworks sited in high valuable natural areas but neighbouring important summer touristic areas. All samples were stored at -20°C until analysis.

2.2. Reagents

HPLC-grade water was obtained from a MilliQ water purification system (Millipore Ltd., Bedford, MA, USA). Acetone, ethyl acetate, dichloromethane (DCM) and *n*-hexane (ultra trace quality) used in solid-phase extraction (SPE) experiments were purchased from Scharlab (Barcelona, Spain). Bond Elut cartridges C_{18} (500 mg) (Varian, Harbor City, CA, USA) were used for SPE. Triphenyl phosphate (TPhP) and 2-ethylhexyl diphenyl phosphate (EHDPP) reference standards were purchased from TCI Europe (Zwijndrecht, Belgium). Tri-*n*-butyl phosphate (TBP) and Tris(1-chloro-2-propyl) phosphate (TCPP) reference standards were purchased from Sigma–Aldrich (Madrid, Spain).

2.3. GC–TOF MS instrumentation

GC system (Agilent 6890N; Agilent, Palo Alto, USA) equipped with an autosampler (Agilent 7683) was coupled to a time-of-flight mass spectrometer (GCT, Waters Corporation, Manchester, UK), operating in electron ionization (EI). GC separation was performed using a fused silica HP-5MS capillary column with a length of 30 m, an internal diameter of 0.25 mm and a film thickness of 0.25 μm (J&W Scientific, Folson, CA, USA). The injector temperature was set to 280°C . Splitless injections of 1 μL samples were carried out. Helium (99.999%; Carburros Metálicos, Valencia, Spain) was used as carrier gas at a flow rate of 1 mL/min. The interface and source temperature were set to 250°C and a solvent delay of 4 min was selected.

The oven program in GC–TOF MS analysis was programmed as follows: 90°C (1 min); $5^{\circ}\text{C}/\text{min}$ to 300°C (2 min). The TOF MS operated at 1 spectrum/s, acquisition rate over the mass range m/z 50–650, using a multichannel plate voltage of 2850 V. TOF-MS resolution was approximately 7000 (FWHM). Heptacosane standard, used for the daily mass calibration and as lock mass, was injected via syringe in the reference reservoir at 30°C for this purpose; the m/z ion monitored was 218.9856. The application manager ChromaLynx and TargetLynx was used to process the qualitative data obtained from standards and from sample analysis. Library search was performed using the NIST 02 Mass Spectral Library (www.nist.gov).

2.4. Recommended analytical procedure

The recommended procedure is based on a generic sampling extraction procedure previously applied for the determination of around 50 compounds, including organochlorine and organophosphorus insecticides, herbicides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, brominated diphenyl ethers, octyl/nonyl phenols and pentachlorobenzene with some modifications [8]. Briefly, 62.5 g of salt was diluted with water to a final volume of 250 mL and filtered. The filtered solution was passed through the C_{18} SPE cartridge, previously conditioned by passing 6 mL methanol, 6 mL ethyl acetate:DCM (50:50), 6 mL methanol and 6 mL water avoiding dryness. After loading the sample (250 mL), the cartridges were washed with 3 mL water and dried by passing air under vacuum for at least 15 min. The elution was performed by passing 5 mL ethyl acetate:DCM (50:50). The extract collected was evaporated under a gentle nitrogen stream at 40°C and redissolved in 0.25 mL of *n*-hexane. The overall procedure also involved a method blank to test that no contamination was introduced in the extracts along the analysis.

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