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Synthesis and evaluation of molecularly imprinted polymers for organotin compounds: a screening method for tributyltin detection in seawater

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This paper is dedicated to the memory of Dr. Juan C. del Amo, a victim of the terrorist attack on Madrid on 11 March.

Abstract

The environmental impact of some organotin compounds (OTC) has given particulate importance to analytical studies. This paper reports the first attempt to apply the emerging molecular imprinting technology to this field. Several imprinted polymers have been synthesised by the non-covalent free radical approach using sodium methacrylate (NaMA) or 4-vinylpyridine (4-VP) as monomers in the presence of TBT as template molecule in three different polymerisation media (toluene, acetonitrile and methanol/water). The ability of the polymers synthesised to retain and distinguish TBT from its degradation products has been evaluated and optimized. The results clearly showed the presence of cavities within the polymeric matrix allowing specific recognition of TBT. Cross-reactivity from other Sn species (monobutyltin (MBT), dibutyltin (DBT) and inorganic Sn) has also been evaluated. Rapid and direct differentiation of TBT from its main degradation products in seawater was achieved. The analytical characteristics included linearity (0.05–50 $\mu g\,l^{-1}$), a pre-concentration factor of 150, and a quantification limit of 0.04 $\mu g\,l^{-1}$ for 1 l.

Keywords: Molecular imprinting technology; Organotin compounds; Seawater analysis

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1. Introduction

Environmental contamination problems coming from the extensive industrial release of organotin compounds (OTC) have been well known for more than 50 years now. The first large scale application of these compounds was in the plastics industry, particularly the production of PVC. Additionally, their biocidal properties discovered in the late 1970s spread their use as fungicides, wood preservatives and anti-fouling paints (mainly containing tributyltin (TBT)) [1]. Due to their widespread use, considerable amounts of OTC have entered various ecosystems. So far, attention has mainly been given to TBT pollution in water and sediments because of its highly toxic effects at very low concentrations [2,3]. As a consequence, TBT was included in the European Union pollutant list (EU, Directive 76/464) [4]. Strict legislative restrictions have also been applied in many Western countries during the last 10 years (mainly in shipyards) in order to reduce accumulation of these compounds in the affected areas [5]. Despite all these efforts, recent studies have shown that OTC are still being released into the aquatic environment from various sources, especially in the southeast Asian region, e.g.

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Thailand [6]. Thus, these substances still represent a risk for aquatic and terrestrial ecosystems.

As a consequence, analytical methods are needed to control the effectiveness of the legal provisions and to monitor the distribution and fate of OTC in the marine environment. Most existing methods are based on the use of chromatography coupled to sensitive detectors after derivatization [7–9]. One critical step of any proposed method is the extraction procedure. In general, liquid–liquid extraction methods have been grouped according to the polarity of the solvent employed and the use of acidic media and/or complexing agents such as tropolone [7]. Some attempts using enzymatic hydrolysis have also been made for biotic samples [10]. Regarding liquid samples, the use of solid-phase extraction (SPE) has become a promising alternative to the tedious traditional liquid–liquid extraction due to the incorporation of direct sampling which is fast, simple and less hazardous. Recent works have been published based on the use of chemically modified silica fibres and/or C_{18} cartridges coupled to chromatography [11–15]. In the last few years, molecularly imprinted polymers (MIPs) have been recognized as useful materials in SPE procedures as well as in other analytical chemistry fields (i.e. stationary phases for HPLC and CE, binding assays, sensors) [16–18]. MIPs are synthetic polymers obtained by polymerising a monomer with a cross-linker around a template (analyte) molecule. At present, the imprinting of organic molecules (e.g. pharmaceuticals, pesticides, steroids, phenylureas, etc.) is a well established technology allowing the development of highly selective molecularly imprinted solid-phase extraction (MISPE) methods [19–22]. Ionic Imprinting Technology, when an ion or metal is the targeted molecule that will act as template, is based on the same principle. Some efforts have been made in this field [23–26] as well as for organosulphur [27], organophosphosphates [28] and organosilanes [29] compounds. However, no references have been found for organometallic like organotin compounds.

The main purpose of the work reported here is to evaluate several MIPs synthesised for organotin compound recognition. This was done by preparing TBT-imprinted polymers using a simple MISPE process. Experimental conditions were optimized for optimum analyte recognition and for high capacity retention in order to distinguish TBT from its main degradation compounds (MBT and DBT). The method has been then applied to seawater analysis.

2. Experimental

2.1. Instrumentation

A Varian Vac Elut-20 solid-phase extraction system with glass cartridge and polyethylene frits supplied by J.T. Baker (Deventer, Holland) was used for pre-concentration and elution of the samples.

A Perkin-Elmer Model 5000 atomic absorption spectrometer with deuterium background correction equipped with a HGA-400 graphite furnace and an AS 70 auto sampler was used for the determination of tin compounds. A Sn-electrodeless discharge lamp (EDL) with the power supply operating at 310 mA, wavelength 286.3 nm, and spectral bandwidth 0.7 nm were used. Pyrolytically coated graphite-furnace tubes treated first with wolframium, then with zirconium and finally with iridium were used [30]. A volume of 20 μl either with the AS 70 autosampler or manually was injected.

A gas chromatograph GC-FPD HP-5890-Series II equipped with a SPL-1 column (15 m × 0.53 mm) was used to detect the different OTC fractions obtained from the polymers. The chromatography was employed in the present work for species confirmation purposes.

2.2. Reagents

Analytical grade chemicals were used for all studies. TBT (>97%), DBT (>97%), MBT (>95%) were obtained from Sigma–Aldrich Quimica S.A. (Madrid, Spain). The organotin stock solutions containing 100 mg l^{-1} of tin were prepared in methanol and stored at −20 °C in the dark. Working solutions were prepared daily in water or methanol. Sodium methacrylate (NaMA), 4-vinylpyridine (VP), ethylene glycol dimethacrylate (EGDMA), and azobisisobutyronitrile (AIBN) were obtained from Sigma–Aldrich Quimica S.A. (Madrid, Spain). Purified water was obtained from a Element Milli-Q water system purchased from Millipore Iberica S.A. (Madrid, Spain).

Organic solvents were of HPLC grade from SDS (Barcelona, Spain). Hydrochloric and acetic acids were supplied by Merck (Darmstad, Germany) and Panreac Química S.A. (Madrid, Spain), respectively.

Seawater from Algeciras harbour (Spain) with an intense shipping activity was analysed for the content of different organotin compounds. No sample treatment was needed apart from filtering through 0.45 μm to eliminate the particulate content before the MISPE procedure (see below).

2.3. Procedures

2.3.1. Preparation of TBT-imprinted polymers (MIP)

The template molecule (TBT, 150 mg) was mixed with the monomer (NaMA or 4-VP, 200 mg) in a 15 ml glass assay tube and left in contact for prearrangement for 5 min. Thus, the cross-linker (EGDMA, 2 g), the initiator (AIBN, 10 mg) and 5 ml of porogen (3:1 methanol:water, acetonitrile or toluene) were added. Then the glass tube was sealed and bulk polymerisation was carried out in a water bath at 65 °C for 24 h [31]. The polymers obtained were ground and sieved at <100 μm particle size and the template was removed by Soxhlet extraction for 8 h with 0.1 M HCl in MeOH (methacryate-based polymers) or with 1:1 methanol:NH_3 (vinylpyridine-based polymers). Finally, polymers were air-