



Determination of tributyltin in whole water matrices under the European Water Framework Directive



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ABSTRACT

Monitoring of water quality is important to control water pollution. Contamination of the aquatic system has a large effect on human health and the environment. Under the European Water Framework Directive (WFD) 2000/60/EC and the related directive on environmental quality standards (EQS) in the field of water policy 2008/105/EC, the need for sensitive reference methods was highlighted. Since tributyltin (TBT) is one of the WFD listed priority substances a method was developed which is capable to qualify and quantify the pollutant at the required low WFD EQS of 0.2 ng L^{-1} in whole water bodies, i.e. in non-filtered water samples with dissolved organic carbon and suspended particulate matter. Therefore special attention was paid on the interaction of TBT with the suspended particulate matter and humic substances to obtain a complete representation of the pollution in surface waters. Different water samples were investigated varying the content of organic dissolved and suspended matter. Quantification was performed using species-specific isotope dilution (SSID) and gas chromatography with inductively coupled plasma mass spectrometry (GC-ICP-MS). Different sample treatment strategies were evaluated and compared. The process of internal standard addition was investigated and optimized, hence the equilibrium between internal standards and matrix is of primary importance to perform accurate SSID. Samples spiked at EQS level were analyzed with a recovery between 95 and 105 %. Additionally real surface water samples were investigated and the TBT concentration for the whole water body was determined and compared with conventional routine analysis method.

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1. Introduction

With the implementation of the European Water Framework Directive (WFD) 2000/60/EC and the related directives 2008/105/EC and 2013/39/EU new and challenging demands on analytical methods for environmental water analysis are faced. In those directives a list of pollutants, present in European surface waters, was introduced. All listed substances, if occurring in toxicological relevant concentrations, show high hazardous potential for the water environment. Environmental quality standards (EQS) and limits of quantification (LOQ) for 33 priority substances and eight other pollutants were specified. For several substances the defined limits are below the LOQ of established analytical methods [1,2].

WFD claims the analysis of whole water bodies. The analysis of surface waters must be performed without previous filtration, which is typically done in water analysis. Therefore not only the dissolved contaminants need to be quantified but also the contaminants associated to suspended solids and colloids, which are present in surface waters.

Sensitive and reliable reference methods to quantify some of the WFD listed priority substances were developed and validated within the Joint Research Project ENV08 "Traceable measurements for monitoring critical pollutants under the European Water Framework Directive 2000/60/EC" of the European Metrology Research Programme (EMRP). Tributyltin (TBT) was one of the addressed priority substances due to the lack of a standardized analytical method meeting WFD requirements. The EQS level for TBT is 0.2 ng L^{-1} (TBT as cation). WFD claims the analysis of whole water bodies. The analysis of surface waters must be performed without previous filtration, which is typically done in water analysis. Therefore not only the dissolved contaminants need to be quantified but also the con-

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taminants associated to suspended solids and colloids, which are present in surface waters. This is quite low compared to other pollutants and the performances of routine analytical methods. The LOQ defined by the Directive 2009/90/EC specifying the technical requirements for the method, is even more challenging. An LOQ lower than or equal to 30% of the EQS and a measurement uncertainty equal or lower than 50% at the EQS must be achieved. An overview of WFD challenges and requirements and the EMRP project scope are discussed elsewhere [2].

The low EQS for TBT is based on its high toxicity on the aquatic environment [1,3]. TBT effectuates disorders in growth, development and reproduction of many marine species [4]. The pollutant affects the function of mitochondria, triggers DNA damage and the imposex phenomena on mollusks [5,6]. Even at sub ppt contamination level acute and chronic impairments on marine organisms are observed [7]. Polluted waters and marine organisms provide a potential source of TBT uptake for mammals and humans. It is assumed that TBT causes endocrine system imbalance of mammals specifically humans and rodents [7]. Acute poisoning by TBT causes dyspnea, cardiac failure and brain hemorrhage. Chronic uptake leads to a damage of the immune system and a dysfunction of the immune cell functions [5,6]. TBT is introduced to the environment by an anthropogenic pathway. Before prohibiting its use in the EU in 2003 it was mainly used as antifouling paints for ships [8]. Although the applications as biocides and for PVC stabilization were popular, the input in the environment is declining due to legislative regulation [3,9].

Despite the decreasing TBT contamination through industrial pathways the pollutant will still be present in water, sludge and soil for indefinable time. Especially due to its high adsorption affinity to organic matter it is persistent in the environment [6]. TBT is released continuously into the aquatic ecosystems for the next decades from sediments, which constitute natural sinks [5]. Interactions between TBT and organic matter have a major impact on stability, transformation and analysis of the analyte especially the extraction behavior. Organic matter in surface waters consists of humic substances and dissolved organic matter (DOM). Another important compartment of surface waters is suspended particulate matter (SPM). TBT is not only present in the water phase, but also adsorbed on DOM and SPM due to its high affinity and accumulation potential towards solids and colloids present in water [1,3].

TBT quantification in water samples is well described and reviewed [2,6]. Many different extraction and analytical techniques are discussed and reported [10,11]. But the low EQS and LOQ values and the whole water body exacerbate the development of a robust analytical method for TBT quantification. Analytical methods quantifying TBT not only dissolved in water but also associated with DOM and SPM are not described yet. Up to now, only dissolved or adsorbed TBT was analyzed independently, due to the lack of a method for quantification of TBT in the whole water body. For the analysis of complex matrices like waste or coastal waters a filtration step might be applied to separate the water phase from humic substances or SPM. In this case the residue and the filtrate should be analyzed independently. The analysis of TBT at EQS level using different extraction techniques combined either with GC-MS/MS or GC-ICP-MS is reported in literature. For example Rodríguez-Cea et al. and Alasonati et al. used liquid-liquid extraction (LLE) or solid phase extraction (SPE) and isotope dilution analysis (IDA) to detect and quantify TBT in water samples [12,13]. Some novel adsorbent techniques like dispersive liquid-liquid microextraction (DLLME) described by Birjandi et al. [14] and stir bar sorptive extraction (SBSE) shown by Devos et al. [9], enable quantification of TBT at EQS. But in all approaches reported the LOQ of the method was only determined instrumentally in simple water matrix like mineral water and ultrapure water. Those simple water matrices are samples with a low content of DOM and without SPM. In the reported

recovery experiments water samples containing higher amounts of DOM and SPM were used, but TBT was added in solution. The association with SPM was not be taken into account. In general influences of humic acid and SPM were neglected or only single compartments of the water body were investigated.

The method developed in this work is capable to quantify TBT in complex water samples at sub ng L^{-1} and particularly at EQS level for the first time. Different sample treatment methods were evaluated to quantify TBT in whole water matrices containing SPM and humic acid fractions.

Quantification was performed using species-specific isotope dilution mass spectrometry (SS-IDMS). This technique allows the correction of matrix effects, which are often present in complex surface waters. Non-quantitative derivatization and extraction steps are also compensated [15]. Different strategies for the application of the internal isotopically labeled ^{119}TBT -standard are evaluated here. Optimization of measurement and quantification procedure and instrumentation characteristics are discussed elsewhere [16].

Different water matrices were investigated to evaluate the robustness of the method. A model water containing mineral water, humic acid and TBT contaminated SPM material was used to prepare reproducible whole water samples mimicking complex real water samples. The preparation and characterization of the model water, stability and homogeneity studies are described by Elordui-Zapatarietxe et al. [17,18]. The applicability on real water samples was investigated by spiking water samples with TBT and evaluating the TBT recovery by SSID-GC-ICP-MS. TBT recoveries as a function of the concentration of humic acid and SPM were investigated and discussed.

2. Experimental

2.1. Chemicals and standards

Tributyltin chloride (TBT, 96%), nitric acid (HNO_3 , 68–70%) and ammonium hydroxide solution (30%) were obtained from Sigma-Aldrich (Taufkirchen, Germany). Methanol (MeOH) and n-hexane were purchased from LGC Standards (Wesel, Germany). Sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium sulfate (Na_2SO_4), sodium acetate (NaAc), hydrochloric acid (HCl, 32%) and L-(+) tartaric acid were obtained from Merck KGaA (Darmstadt, Germany). Acetic acid (HOAc) was purchased from Chemsolute (Rennigen, Germany). Sodium acetate buffer solutions (0.1 M, 1 M) were prepared by dissolving NaAc in ultrapure water and adjusting to pH 5 with HOAc. The 0.1 M buffer solution was prepared by diluting with ultrapure water. The ethylation reagent sodium tetraethylborate (NaBET_4) was purchased as a 10% solution in tetrahydrofuran from Merseburger Spezialchemikalien (Schkopau, Germany). A 1% (v/v) solution was prepared daily by diluting with ultrapure water. Commercially available ethylated tributyltin (EtTBT, Chiron AS (Trondheim, Norway)) was used as the measurement mass bias control and for GC-ICP-MS method optimization. Dilutions were prepared in n-hexane. The ^{119}Sn -enriched butyltin mix was purchased from ISC Science (Oviedo, Spain). Standards and dilutions of the native and ^{119}Sn enriched tins were prepared in 3:1 (v/v) HOAc/MeOH mixtures. Working solutions for spiking were prepared daily with mineral water. All solutions were stored in the dark at -18°C . Bottled natural mineral water was purchased in 1 L glass bottles from a local supplier.

2.2. Sample preparation – suspended particulate matter and humic acid

Until now there is no certified reference material for organotin in water on the market. For reproducible conditions during method

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