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Identification of commercial and recreational vessels coated with banned organotin paint through screening of tin by portable XRF

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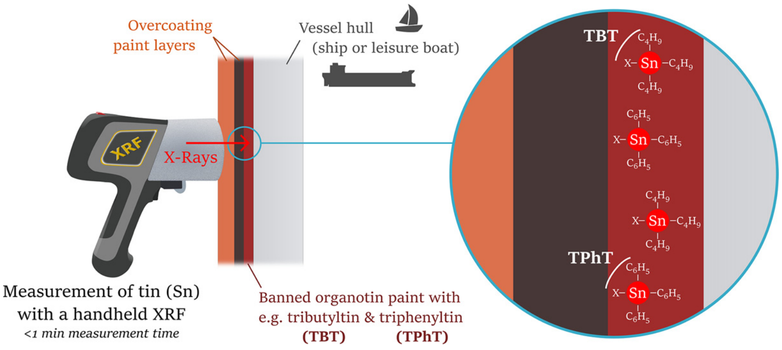
GRAPHICAL ABSTRACT



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ABSTRACT

The most effective biocide used historically in antifouling paints is tributyltin (TBT). However, due to its extreme toxicity to non-target organisms and its persistence in the environment, the use of TBT and other organotin compounds (OTCs) was restricted in EU on leisure boats and ships in 1989 and 2003, respectively. Nevertheless, studies worldwide still report TBT to be released from both ships and leisure boats. Here, we present a new application for a field portable X-ray fluorescence spectrometer (XRF) used for screening for organotin paint through measurements of tin (Sn) on leisure boats and ships. Measurements on ships built after the restrictions showed concentrations of up to 68 μg Sn/cm^2, likely due to impurities of inorganic Sn, as shown through chemical analysis of 21 organotin-free paints. A threshold value of 100 μg Sn/cm^2 is suggested, where exceedance indicates presence of OTCs. Screening with the XRF method showed 10% of the commercial vessels (n = 30) and 23–29% of leisure boats (n = 693, investigated in this and in a previous study) to hold concentrations exceeding 100 μg Sn/cm^2. The XRF technique presented here provides a useful tool for quick screening and identification of vessels holding banned organotin paint.

1. Introduction

Tributyltin (TBT) is one of the most toxic substances ever purposely introduced into the aquatic environment and was used as an active substance in antifouling paints starting in the 1960's [1]. However, due to their endocrine disruptive properties, long half-life and severe

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toxicity to aquatic organisms, TBT and other OTCs were prohibited from use on leisure boats and ships in the EU in 1989 and 2003, respectively [2]. Since 2008, a global ban exists through the enforcement of the Anti-Fouling Systems (AFS) convention [3]. Despite the global prohibition, recent studies have shown TBT still to be released in e.g. France [4], Sweden [5], the Southern Baltic Sea [6], Panama [7] and in various South American coastal areas [8–10]. In Sweden, environmental monitoring programs have shown TBT levels in sediment to frequently exceed the newly established sediment Environmental Quality Standard (EQS) (1.6 μg TBT/kg dw, normalized to 5% organic carbon), not only along the coasts but also at 10 out of 16 offshore monitoring stations [11]. A continued supply of TBT to the aquatic environment is suspected to occur mainly during maintenance work. For instance, wastewater produced from pressure hosing of leisure boats in Sweden has shown to contain as much as 14,000 ng TBT/L (median value 1600 ng/L, n = 15) [12]. For comparison, the annual EQS value in the EU is 0.2 ng TBT/L in seawater (Directive 2008/105/EC). TBT concentrations of 9000 and 990,000 ng/L have also been measured in the waste water from commercial ships at two dry docks in Gothenburg, Sweden, in 2007 [13].

In connection with the organotin ban for ships in 2003, a study was conducted in Japan using XRF technology to screen for OTCs on ship hulls through the measurement of Sn [14]. The method was however designed to only measure the concentration in the outmost paint layer on the hull, and as the instrument in the study was not of a handheld type, it also required collection of paint fragments onto abrasive paper prior to analysis. A method utilizing a handheld XRF enabling non-destructive and rapid (30 s) measurement of metals (including Sn) in antifouling paints on plastic boat hulls was recently developed [15]. However, the XRF only measures the total Sn concentration and does not provide any information regarding speciation, i.e. in which form the element is present. In a study by Lagerström et al. [16] paint samples from leisure boats were collected and chemically analyzed for total Sn and OTCs. A strong correlation was found between total Sn and the total amount of Sn present as OTCs, confirming that Sn can be used as an indicator for the presence of OTCs. The XRF method for plastic hulls has been used to screen for Sn on nearly 700 leisure boats located in by Swedish inland or coastal waters [17]. Approximately 10% of these had concentrations of Sn > 400 μg/cm^2 (roughly equivalent to the Sn content of a 20–40 μm layer of old TBT paint).

As ship hulls consist of steel, it is not possible to use the same calibration developed for plastic hulls. The aim of this study was therefore to develop a new XRF application to investigate the occurrence of organotin paint on vessels with steel hulls, i.e. mainly commercial ships, but also recreational boats. Another aim was to investigate background concentrations of Sn in various organotin-free antifouling paints, sealers and primers and to propose a threshold value for Sn, where exceedance indicates presence of OTCs.

2. Materials & methods

2.1. XRF instruments

Two handheld XRF instruments (Innov-X Delta-50) equipped with a 50 kV X-ray tube were used in this study. The instruments are appointed with a special mode (Empirical Mode) that enables the creation and storage of custom calibration curves in the instrument software. A calibration curve to quantify Sn in antifouling paint on a steel background could therefore be established by recording the intensity of the Sn Kα line (25.3 KeV), which is free from interferences of other elements [14].

2.2. Calibration for measurement on steel hulls

As the application of organotin paint on ships was restricted in 2003, it is assumed that if such paint layers are present on vessels, they have been overcoated with organotin-free antifouling paint. However, as both the amount and type of overlying paint will vary between vessels depending on each ship's unique maintenance history, it is impossible to make a calibration that will be representative for all types of overcoating scenarios. The standards were therefore made without applying any overlying paint. However, the influence of overlying paint layers on the measured Sn concentrations was investigated (see Section 2.3).

2.2.1. Preparation of standards

For the standards, 10 x 10 cm panels of the same steel type that is used for ship hulls (Normal Strength Steel, 6 mm) were used. The panels were coated with a commercial primer (PPG, Sigmaprime 200, 350 μm dry film thickness (DFT)), followed by a sealer (PPG, Sigmacover 555, 115 μm DFT). Five paints of different Sn concentrations (0, 0.5, 3, 8 and 14 wt %) were prepared through the addition of tin powder (99% purity, ≤10 μm) to a metal-free paint base (Hempel Underwater Primer). To obtain smooth homogenous paint films, the coatings were applied onto 75 μm plastic sheets of Mylar A © (Pütz GmbH + Co. Folien KG) using an automatic film applicator (TQC AB3120). To achieve a concentration gradient, varying wet film thicknesses (100–400 μm, yielding a maximum DFT of 88 μm) were used for each paint. Squares of approximately 1.5 cm^2 were cut from each film. Their weights and exact areas were then determined prior to mounting onto the prepared panels. Two parallel sets of 18 standards were prepared, one for each XRF instrument. Dry subsamples of the paints were analyzed by ALS Scandinavia AB for their total Sn concentration. The samples were digested by microwave with an acid mixture of HNO_3/HCl/HF according to ASTM D3683, followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis. Using the chemical analytical results (in μg/g), the weight (m) and area (A), the area concentration of Sn in μg/cm^2 was calculated according to the following equation:

$$Sn\ (\mu g/cm^2) = \frac{m\ (g) \times Sn\ (\mu g/g)}{A\ (cm^2)}$$

The area concentrations were found to range from 0 to roughly 4600 μg/cm^2.

2.2.2. Instrument calibration

Calibration curves were established on both instruments between the signal at the emission energy of the Sn Kα-peak (25.3 KeV) and the calculated area concentrations of the standards. Before calibration, the measurement precision was evaluated for different measurement times (10, 20, 30, 45, 60 and 90 s). There was no significant difference (ANOVA, $p > 0.05$) in average concentration (n = 8) between any of the measurement times and the precision was found to be low (≤2%) and equivalent for all measurement times from 20 to 60 s (data not shown). Therefore, 20 s was chosen as the analytical time.

Linear calibration curves were established on both instruments ($r^2 \geq 0.999$ for both instruments, see Fig. S1 of the Supporting Information). The limit of detection (LOD, calculated as three times the standard deviation of the blank), was determined to be 3.5 μg/cm^2. The performance of the instruments were evaluated by measuring all standards on both XRF instruments. The results were found to be comparable with an average difference (± 1 standard deviation) of 3 ± 5%.

2.3. Examination of parameters affecting measurement accuracy

2.3.1. Determination of critical thicknesses

Both the thickness and sample composition can affect the XRF analysis of metals in thin films. The penetration of the primary X-ray (from the instrument), as well as the returning secondary X-rays (from the sample to the detector) are subject to absorbance from the metals present in the sample [18]. The maximum depth in the sample from which the signal measured by the detector originates is referred to as the critical saturation depth (d_{thick}). Beyond this depth, all X-rays are