New analytical application for metal determination in antifouling paints

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ABSTRACT

Despite the ban of applying TBT coatings on leisure boats in the late 80s, recent studies show an ongoing spread of TBT from leisure boats, particularly during hull cleaning events. Therefore, countries in EU have adopted expensive measures to clean this wash water. A more cost-efficient measure is to focus directly on the source, i.e. identify leisure boats with high concentrations of TBT and prescribe boat owners to remove the paint. We have developed a new antifouling paint application for a handheld X-ray fluorescence (XRF) analyzer to be used for identifying boats with high area concentrations ($\mu g/cm^2$) of Sn (indication that the hull contains TBT paint residues). Copper and zinc are also included in the application since these metals are used in the vast majority of today's paints. A blind test with up to four layers of TBT-, copper- and zinc-based paints showed good correlation between XRF-measured area concentrations and chemically analyzed concentrations. Future usage of the applications involves identification of boat hulls in particular with high Sn concentrations and also with high Cu and Zn concentrations. This method has the potential to become a useful tool in regulatory management of existence and use of toxic elements on boat hulls.

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1. Introduction

Marine biofouling is a natural process in which microorganisms, plants and animals attach and accumulate on submerged surfaces and has been combated by maritime transporters the last 3000 years [1,2]. The adverse effects of biofouling are well-known and comprise higher frictional resistance, increased fuel consumption and hull maintenance costs. Since the mid-19th century the most common strategy to prevent biofouling is to coat the hull with antifouling paints containing various toxicants. Around 1950, organometallic paints (with e.g. tin, mercury and arsenic) were developed which later (early 1960s) gave rise to tributyltin (TBT)-based paints [1]. TBT-based paints became increasingly popular due to their efficiency in preventing biofouling, and as a result, they were estimated to cover around 70–80% of the world's fleet in 2004 [3]. About 20 years after the development of TBT-based paints, adverse effects were reported on several mollusc species. For example, populations of Pacific oysters were severely affected in France by a complete lack of reproduction [4], and the cause of this effect was traced back to TBT in the water [4–6]. Other

populations of mollusc species were also shown to be sensitive to extremely low TBT concentrations (< 10 ng/L) [7,8]. Due to the negative environmental impact, TBT was restricted for use on leisure boats (less than 25 m in length) in several countries in the late 1980s (e.g. EU Directive (89/677/EEC)), and since 2008 there is a global ban of TBT for all sizes of ships due to the adoption of the AFS-convention by the International Maritime Organization (IMO).

Even though TBT has been restricted for use on leisure boats in the EU for more than 20 years, several studies indicate that it is still being emitted to the aquatic environment [9,10]. In Sweden for example, the waste water produced during pressure water blasting of leisure boat hulls has been shown to contain TBT concentrations as high as 14,000 ng/L (median value 1600 ng/L, $n=15$) (own unpublished data). What is not known, though, is the quantity of TBT that is still present on leisure boats. This knowledge is of importance in order to adopt adequate measures to reduce or eliminate the emissions of TBT to the environment. This is particularly essential since the countries in the European Union are obligated under the EU Water Framework Directive (2000/60/EC) to implement necessary measures to cease emissions, discharges and losses of so-called "priority hazardous substances", which include TBT.

In most countries it is common practice to pressure hose leisure boats on hard standings close to the foreshore. The major part of biocides released during these cleaning events is in the form of paint particles that eventually can be incorporated in the sediment

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[9,11]. To prevent pollution of hazardous substances from cleaning activities, specific measures have been adopted in several countries. For example national guidelines have recently been adopted in Sweden requiring wash water from pressure hosing to be cleaned through treatment systems prior to being discharged to the water. However, the treatment systems' efficiency in removing organotin compounds is questionable since data suggest these systems to be inadequate in cleaning wash water (the average cleaning capacity of 13 treatment systems was 50% with respect to TBT, own unpublished data). Thus, a more effective measure would be to remove existing organotin-based paint directly from leisure boat hulls. This would in a much faster way get the dangerous TBT phased out, as the Water Framework Directive (WFD) requires.

To accurately determine the concentrations of organotin compounds on boat hulls, the total antifouling paint layer needs to be scraped off and analyzed by advanced chemical analytical techniques, such as inductively coupled plasma-sector field mass spectrometry (ICP-SFMS). These methods involve several steps of sample preparation and extraction, are time-consuming and thus costly. However, there are other non-destructive techniques that can be used for screening purposes. One of these methods is handheld X-ray fluorescence spectroscopy (XRF), which has the advantage to be used on-site, i.e. measuring directly on boat hulls. The drawback of XRF is its inability to detect chemical species of an element. Hence, only information on total Sn concentrations will be available with XRF analysis. To our knowledge, Sn has exclusively been added into paint formulations as organotin compounds and thus the detection of tin is most likely originating from organotin compounds, e.g. TBT.

The aim of this study was to develop an empirical model for a handheld XRF analyzer that has the ability not only to detect but also quantify the area concentration of Sn on boat hulls. Cu and Zn were also included in the empirical model since these metals are included in the vast majority of today's antifouling paints.

2. Materials and methods

2.1. Test design

A handheld XRF analyzer was used for the purpose of creating an empirical model able to analyze the area concentration of Sn, Cu and Zn in antifouling paints coated on boat hulls. The XRF analyzer (DELTA-50, Innov-X) was manufactured by Olympus and is powered with a 4 W, 50 kV X-ray tube, which has the advantage to excite and detect heavy elements such as the K-lines of Sn. In addition, the analyzer is equipped with a software that enables the setup of own empirical models for quantification of elements in different matrices (e.g. antifouling paints). In the laboratory, calibration experiments for each of the element of interest (Sn, Cu and Zn) were performed. Compton adjusted Kα intensities were used to account for possible matrix effects. The calibration curves were used in our own empirical model and the models' ability to predict Sn, Cu and Zn concentrations in antifouling paints was determined in a blind test (Section 2.6).

2.2. Development of standards

Four different commercial biocide-free antifouling paints were used in the development of standards. Increasing amounts of Sn (as TBTO, Sigma Aldrich, 96%), Cu (as Cu_2O, Alfa Aeser, 99%) and Zn (as ZnO, Alfa Aeser, 98%) was added to the paints (both separately and in combination) to yield a concentration interval between 0% and 32% (in wet weight (ww)). After thorough mixing, the paints were applied on a 6.3 μm thick Mylar®-film (Chemplex Industries, Inc.) with a Quadruplex film applicator (VF2170, TQC), to obtain a
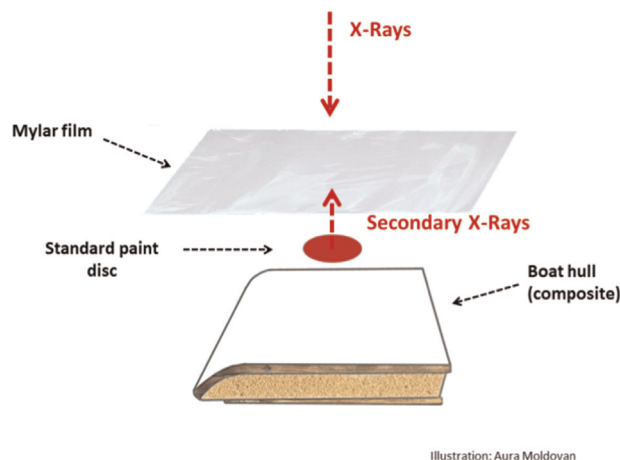

Fig. 1. XRF analysis procedure for the empirical model development. The standards were analyzed both individually and together by applying two, three, four or five standards on top of each other. The Mylar film is used to exclude possible contamination of the measurement window.

wet film thickness of 100 μm. After a drying period of at least 12 h, disks of 25 mm Ø were punched out, weighed and used as standards.

2.3. Empirical model development

The standards were analyzed under controlled conditions in the XRF work station by applying the disks on the X-ray tube/detector. For a more realistic scenario, a piece from a plastic boat hull was placed behind the standards during the analysis, in order to account for X-ray absorption by the boat hulls (Fig. 1).

During the analysis, an area of 28.3 mm^2 of the standards was analyzed using a 50 kV, 4 W setting beam. Since leisure boats usually have several layers of coatings applied on their hull, the standards were analyzed both individually and together by applying two, three, four or five standards on top of each other. If Sn is present on boat hulls, the most realistic scenario is that the organotin paint was applied decades ago and the hull is probably coated with Cu and Zn containing paint on top of the organotin paint layer. Hence, when Sn and Cu and/or Zn standards were used in the calibration, the Sn standard was always placed directly on the piece of boat hull and the Cu and/or Zn standards were always positioned closest to the instrument window. The calibration was done on the adjusted intensity of Kα signals, i.e. the intensity rates have been adjusted for air background and peak overlap, elemental interference from other elements in the sample that have peak energies close to the element of interest. To reduce for matrix effects, Compton normalization was performed, i.e. each element's adjusted rate was divided by the scatter produced in the light element (LE) region of the sample. An analytical time of 30 s was chosen for the buildup of calibration curves as the results showed sufficient reproducibility.

After being analyzed with XRF, the standards were chemically analyzed for total concentrations of Sn, Cu and Zn (see Section 2.7). The (chemically analyzed) total concentrations of Sn, Cu and Zn, the weight and area of the standards allowed us to calculate the area concentration, expressed as μg/cm^2.

The standards were used to examine the relationship between measured Compton adjusted Kα intensities of Sn, Cu and Zn, and known (chemically analyzed) concentrations of Sn, Cu and Zn in the standards. A regression analysis (for each element) was performed to calculate the slope and the intercept of the calibration curve.