



New analytical application for metal determination in antifouling paints



Erik Ytreberg^{a,b,*}, Lennart Lundgren^a, Maria Alexandra Bighiu^a, Britta Eklund^a

^a Department of Environmental Science, Stockholm University, SE-106 91 Stockholm, Sweden

^b Department of Shipping and Marine Technology, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden

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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 ($\mu\text{g}/\text{cm}^2$) 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 ($< 10 \text{ ng/L}$) [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

* Corresponding author at: Department of Shipping and Marine Technology, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden.
Tel.: +46 317722749.

E-mail address: erik.ytreberg@chalmers.se (E. Ytreberg).

[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 K_{α} 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 Aesar, 99%) and Zn (as ZnO , Alfa Aesar, 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

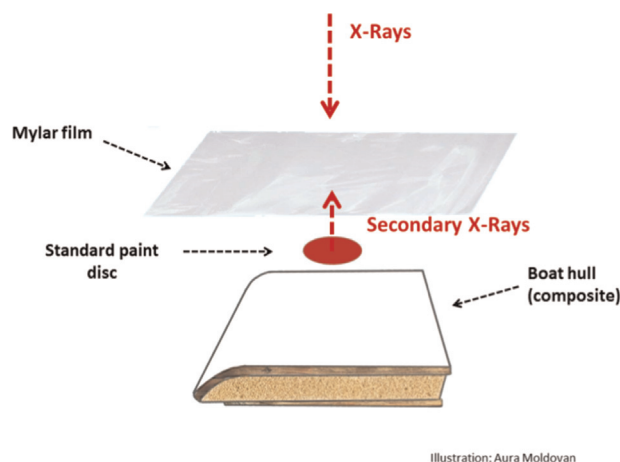


Fig. 1. XRF analysis procedure for the empirical model development. The standards were analyzed both individually and together by applying two, three, four or five standards on top of each other. The Mylar film is used to exclude possible contamination of the measurement window.

wet film thickness of 100 μm . After a drying period of at least 12 h, disks of 25 mm $\varnothing$ 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 K_{α} 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 $\mu\text{g}/\text{cm}^2$.

The standards were used to examine the relationship between measured Compton adjusted K_{α} 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.

2.4. Detection limit

For each of the element of interest, i.e. Sn, Cu and Zn, at least 10 blank samples (paint standard without the analyte of interest) were analyzed and mean blank value and standard deviation (SD) were calculated. The limit of detection (LOD) was determined as the mean blank value plus 3 SDs. The limit of quantification (LOQ) was determined as the mean blank value plus 10 SDs [12].

2.5. Validation of the empirical module

A blind test was conducted to assess how well our antifouling paint application predicts Sn, Cu and Zn concentrations in paint coatings with varying paint thickness/layers. The blind test was conducted by allowing coworkers to apply antifouling paints on Mylar® films with brushes. The coworkers had five different unlabeled antifouling paints (two commercially available containing Cu₂O and ZnO, one containing ZnO, and two of our own-made TBT-paints) to choose between and were instructed to use at least two of them. In total 20 different antifouling paint treatments, with painted layers varying between two and four (corresponds to a dry thickness between 250 and 500 µm), were produced. From all treatments, 25 mm Ø disks were punched out and analyzed for Sn, Cu and Zn concentrations with our (Compton adjusted) antifouling paint module. The analysis was performed as described in Section 2.3., i.e. the disks were put directly on the

instrument window with a plastic piece from a boat hull allocated behind and analyzed with a 50 kV beam for 30 s. Thereafter, the paint disks were sent to a commercial laboratory to be chemically analyzed for Sn, Cu and Zn concentrations.

2.6. Chemical analysis

Sample digestion and chemical analysis were performed by a commercial accredited laboratory (ALS Scandinavia). The standards were digested in a solution containing 5 mL concentrated HNO₃ and 5 mL concentrated HCl on a hotplate for 1 h. The sample solutions were diluted with Milli-Q water and analyzed for total Sn, Cu and Zn concentrations by inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) according to EPA method 200.8 rev 5.4 (1994) and SS EN ISO 17294-1 (2006).

2.7. Statistical analysis

A regression analysis was performed to fit the model between XRF-analyzed logarithm value of K_α-Compton adjusted intensities for Sn, Cu and Zn and the corresponding logarithm value of chemically analyzed concentrations of the specific element (Sn, Cu and Zn) (Fig. 2). By the use of these log–log regression formulas for Sn, Cu and Zn, XRF-analyzed area concentrations were calculated for every measurement included in the regression line (i.e. on disks applied individually or on top of each other). The logarithm

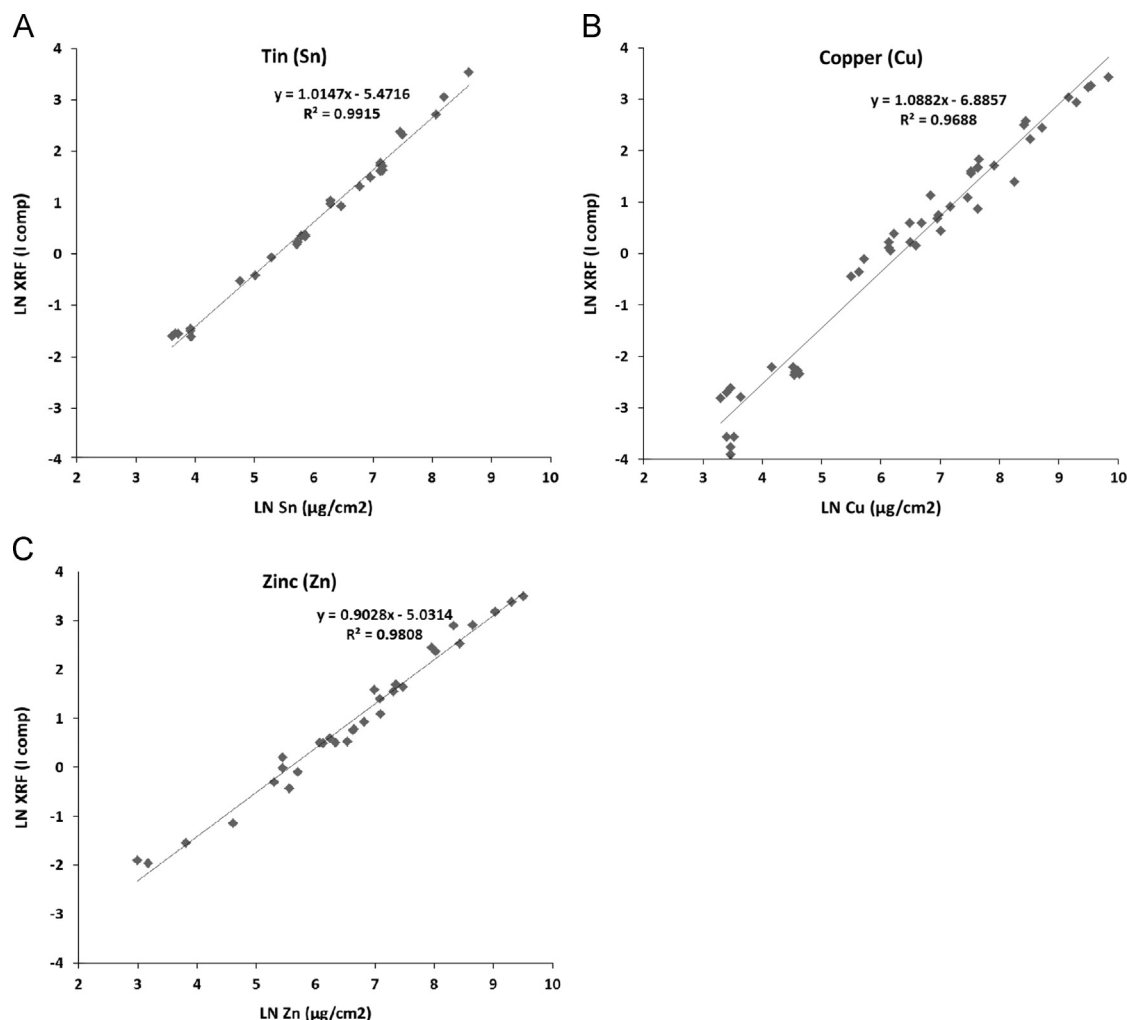


Fig. 2. Regression (calibration curve) for tin (A), copper (B) and zinc (C). The x-axis shows the logarithm value of the chemically analyzed concentration of tin, copper and zinc, respectively while the y-axis display the logarithm value of K_α-Compton adjusted intensity.

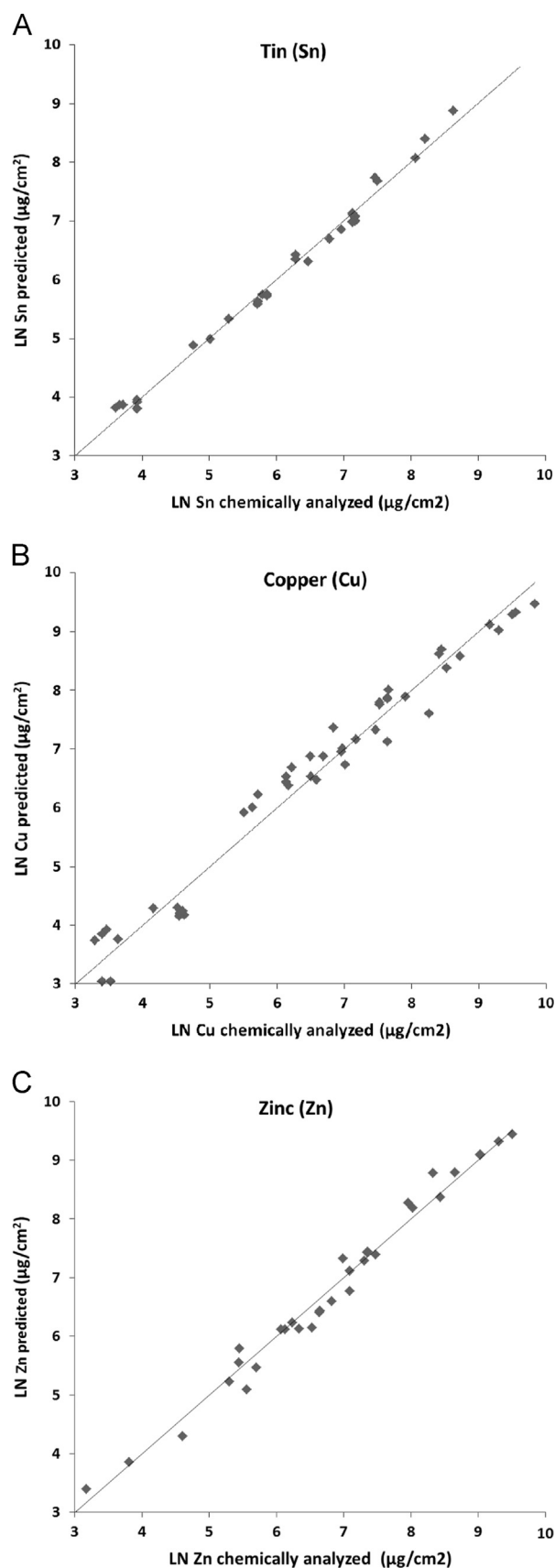


Fig. 3. Logarithm value of XRF-analyzed (predicted) tin (A), copper, (B) and zinc (C) concentration plotted as a function of logarithm value of chemically analyzed concentration ($k=1$).

value of XRF-analyzed (predicted) concentrations were then plotted as a function of logarithm value of chemically analyzed concentration (Fig. 3). The correlation between XRF-analyzed concentrations was assumed to be proportional to the chemically analyzed concentration ($k=1$). A 90% prediction interval (PI) was calculated with the statistical software Stata.

3. Results

3.1. Empirical model

The calibration curves of Sn, Cu and Zn are shown in Fig. 2. Sn showed the best relationship between logarithm value of K_{α} -Compton adjusted intensities and logarithm value of chemically measured concentrations ($R^2=0.99$). For Cu and Zn the corresponding R^2 values were 0.97 and 0.98, respectively. The LOD and LOQ for Sn were determined to be 2.9 and 9.4 $\mu\text{g}/\text{cm}^2$, respectively. The LOD and LOQ for Cu were determined to be 13.3 and 35.9 $\mu\text{g}/\text{cm}^2$, respectively. For Zn, the LOD and LOQ were quantified to be 23.0 and 73.0 $\mu\text{g}/\text{cm}^2$, respectively.

In Fig. 3, the correlation between logarithm value of predicted (XRF-analyzed) concentration and logarithm value of chemically analyzed concentration is shown. Based on these regression data 90-percent prediction intervals (90% PI) were calculated for XRF-measured Sn, Cu and Zn concentrations. For Sn the 90% PI were determined to be between 0.78 and 1.28, i.e. with 90% certainty the Sn concentration is between 78% and 128% of the XRF-analyzed concentration. For Cu and Zn the 90% PI were calculated to be 0.50–2.02 and 0.64–1.58, respectively.

3.2. Empirical model validation

The blind test was performed to study how well our antifouling paint application predicts Sn, Cu and Zn concentration in paint coatings with varying paint thickness/layers. The regression analysis between XRF-measured concentrations and chemically analyzed concentrations is shown in Fig. 4. The chemically analyzed concentration was in most cases within the 90% PI, indicating that the module's prediction of metal concentrations in antifouling paints is adequate at least when the paint thickness is $< 500 \mu\text{m}$.

4. Discussion

XRF measurements on antifouling paints have been performed in several previous studies [13–15]. In these studies, XRF applications developed for other matrixes, e.g. soil and plastic, have been used and are thus not calibrated for antifouling paint matrixes. Also these applications express the analytical data as mass-per-mass concentrations, e.g. parts per million, which is not ideal if the data shall be used for determining the total mass of toxic elements in antifouling paints applied on a boat hull. In this study, we have developed a novel XRF antifouling paint application that can be used directly on-site for analyzing area concentrations ($\mu\text{g}/\text{cm}^2$) of Sn, Cu and Zn in paint applied on boat hulls.

4.1. Tin (Sn) in TBTO

The results from the linear regression analysis of Sn, i.e. the relationship between logarithm value of Sn concentration and logarithm value of K_{α} -Compton adjusted intensity showed that the model works well (Fig. 2). The R^2 -value of the regression analysis was determined to be 0.99 and the relationship between logarithm value of XRF-analyzed (predicted) concentrations plotted as

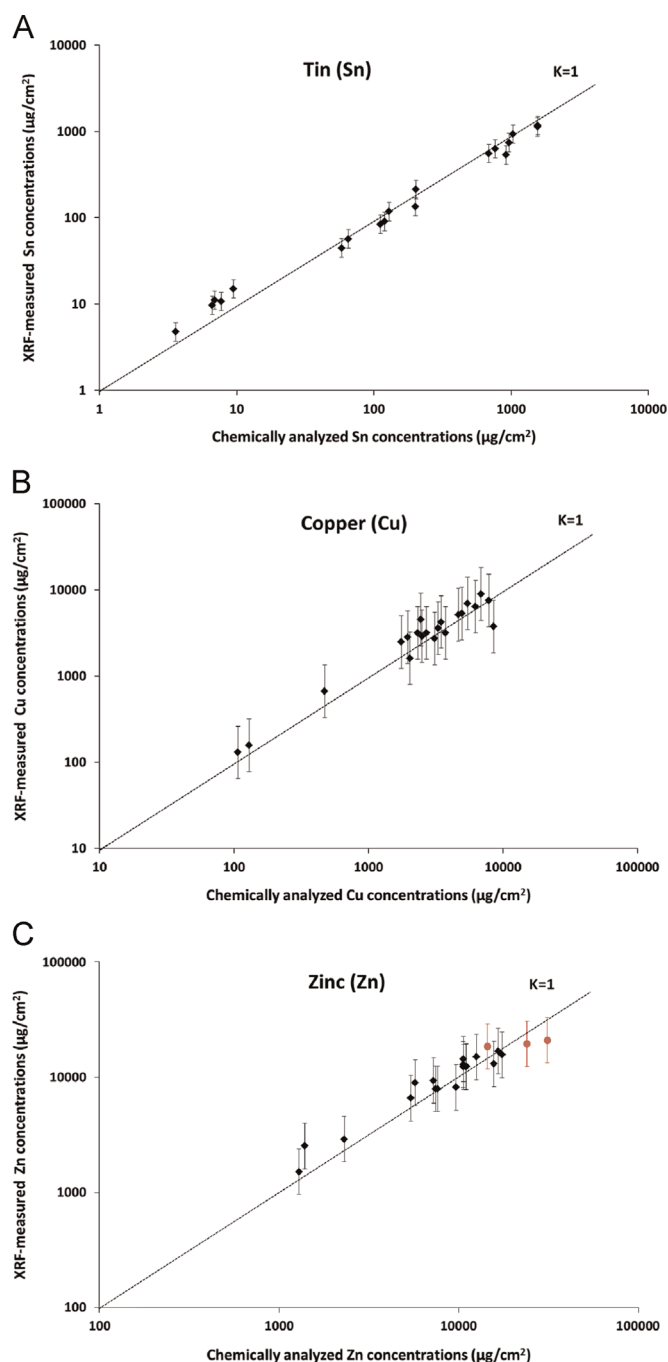


Fig. 4. Validation study on how well the XRF antifouling module predicts true (chemically analyzed) concentrations of tin (A), copper (B) and zinc (C) in different antifouling paints holding a dry paint thickness between 250 and 500 μm . Error bars represent 90% Prediction Intervals. Red dots and error bars (for zinc) indicate concentrations outside the XRF applications calibration curve. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

a function of logarithm value of chemically analyzed concentrations showed the 90% PI to be between 0.78 and 1.28.

We used TBTO in our standards since TBTO has been the dominating organotin compound added in antifouling paints, and to our knowledge inorganic Sn has never been used in antifouling paints. No measurement of degradation of TBT in paint formulation has been found in the literature. However, the degradation of TBT has in sediments been shown to be very slow with half-life up to 87 years [16]. Given that knowledge, we hypothesize that if Sn is

present in high area concentrations on boat hulls, it most likely originates from old organotin paint.

4.2. Copper (Cu) and zinc (Zn)

The linear regression for Cu and Zn, i.e. the relationship between logarithm value of concentration and logarithm value of $K\alpha$ -Compton adjusted intensity, showed the model to work adequately yielding a R^2 -value of 0.97 and 0.98, respectively. However, compared to Sn, the 90% PI was considerable wider, i.e. between 0.5–2.02 (Cu) and 0.64–1.58 (Zn). The disparity in prediction interval can be explained by the ability of fluorescent X-rays to penetrate through the sample matrix and reach the detector. Since Sn is a heavier element, as compared to Cu and Zn, its (Sn) fluorescent X-rays is more energetic and will thus be able to pass through a larger distance within the sample. Therefore, the effect of paint thickness is larger for Cu and Zn as compared to Sn.

For many years, cuprous oxide has been the most commonly used active ingredient in antifouling paints and zinc is used as a binder/pigment in many formulations [3]. Thus, knowledge on the total area concentrations of Sn, Cu and Zn in the coatings will provide valuable data for future environmental risk assessments of leisure boats.

4.3. Empirical model validation

The blind test showed good agreement between the empirical model used in the XRF measurements and the chemical determination. The blind test confirmed that the used model also worked under conditions where several different paints had been applied on a boat hull (simulated with a piece of plastic from a boat hull added behind the paints). The results showed most of the data points' 90% PI to overlap the $K=1$ line, indicating the model to work well in predicting the "true" (chemically analyzed) concentration despite that the (dry) paint thickness varied between 250 and 500 μm .

5. Conclusions

The boat paint application presented here can be used for identifications of boats with high area concentrations of Sn, Cu and Zn. If Sn is detected in high concentration, the boat hull most likely contains organotin-based paint residues. Thus the method has the potential of discriminating boats that contain different amounts of toxicants. It is our ambition to continue this work by determining the proportion of organotin compounds present on boat hulls and in the long run develop a system by which boats will be tested with the XRF antifouling paint application and receive a certification according to the amount of toxicants on the boat. Such a system would be a useful tool for the environmental authorities and enable them to adopt effective measures to reduce the emissions of biocides to the environment during boat maintenance. A certification system may also be useful on the second hand market for leisure boats and provide information to the buyer about the risk of hazardous substance that he may be exposed to in connection with different paint removal techniques (e.g. scraping, sanding and blasting).

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