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(72) Inventors; and

(71) Applicants : **EKLUND, Britta** [SE/SE]; Lundagatan 11, S-619 34 Trosa (SE). **LUNDGREN, Lennart** [SE/SE]; Råsundavägen 135, S-169 50 Solna (SE). **YTREBERG, Erik** [—/SE]; Enskiftesvägen 5, S-433 41 Partille (SE).

(74) Common Representative: **EKLUND, Britta**; Lundagatan 11, S-619 34 Trosa (SE).

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(54) Title: SET OF CALIBRATION STANDARDS AND THEIR USE IN A METHOD OF QUANTIFYING BIOCIDES IN ANTI-FOULING PAINTS WITH A PORTABLE XRF INSTRUMENT

(57) Abstract: The invention relates to a set of calibration standards for use in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a portable XRF instrument. Further disclosed is a method for manufacturing the set of calibration standards as well as their use in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a portable XRF instrument.



SET OF CALIBRATION STANDARDS AND THEIR USE IN A METHOD OF QUANTIFYING BIOCIDES IN ANTI-FOULING PAINTS WITH A PORTABLE XRF INSTRUMENT

5 FIELD OF INVENTION

The present invention relates to a set of calibration standards for use in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a portable XRF instrument. Further disclosed is a method for manufacturing the set of calibration standards as well as their use in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a portable XRF instrument.

BACKGROUND OF INVENTION

15 Marine biofouling, a natural process of undesirable attachment and accumulation of microorganisms, plants and animals on submerged surfaces, has been combated by maritime transporters the last 3000 years (1, 2). The adverse effects of biofouling are well-known and include higher frictional resistance, which translates to higher costs due to increased fuel consumption and hull maintenance. Since the mid-19th century the most common strategy to prevent biofouling is to coat the boat hull with anti-fouling paints containing various toxicants (2). Around 1950, organometallic paints (with e.g. tin, mercury and arsenic) were developed which later (early 1960s) gave rise to tributyltin (TBT)-based paints. TBT-based paints became increasingly popular due to its 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, French oyster growers reported shell malformations which rendered their produce worthless (4, 5). This effect was traced back to TBT in the water (6, 4, 7, 5). Other populations of mollusk species were shown to be sensitive to extremely low TBT concentrations (< 10 ng/L) (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 EU for more than
5 20 years, several studies indicate that it is still being spread to the aquatic environment (9, 10). 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 (mean value 1,600 ng/L, n=15). What is not known, though, is the quantity of TBT that are still present on leisure boats. This knowledge is of im-
10 portance in order to perform adequate measures to reduce or eliminate the spread of TBT. This is particularly essential since the countries in the European Union are obligated under the EU Water Framework Directive to implement necessary measures to cease or phase out emissions, discharges and losses of so called "priority hazardous substances", which includes TBT.

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However, the treatment systems' efficiency in removing organotin compounds has been questioned since recent data suggest only 50 percent efficiency in removing TBT. A more effective measure would be to remove organotin-based paint from leisure boat hulls. There is therefore a need for to determine the concentrations of
20 organotin compounds on boat hulls in order to identify boats that have to undergo removal of anti-fouling paint.

To accurately determine the concentrations of organotin compounds on boat hulls, the anti-fouling paint need to be scraped off and analyzed by advanced, chemical
25 analytical methods, such as ICP-SFMS. However, these methods involve several steps of sample preparation and extraction, are time-consuming and thus costly.

Hence, there is a need for a non-destructible technique that could be used for screening purposes. One candidate is handheld X-ray fluorescence spectroscopy
30 (XRF), which is a non-destructible technique having the advantage that it can be used on-site, i.e. measure directly on boat hulls.

Handheld XRF techniques are practical and effective analytical tools having the advantage to determine environmental samples directly on-site. Today, several

applications exist including in-situ analysis of metals in soils and sediments (11). The advantage with XRF is that the analyses are non-destructible and the analytical time is in order of seconds which compared to chemical analysis reduces the analytical cost substantially. However, since the soil application is calibrated using soil standards, it is not compatible for anti-fouling paint matrixes. Moreover, the methods for screening compounds in soil samples are not applicable for quantifying compounds in anti-fouling paints due to several reasons, including the fact that there are several layers of paints wherein each layer comprises different compositions of metal containing compounds which gives rise to matrix effects as well as other unwanted effects. Consequently, there is a need to develop an anti-fouling paint quantification method for a handheld XRF instrument which has the ability to quantify tin compounds in anti-fouling paints.

Additionally, it has been shown that copper and zinc compounds also have toxic effects on the environment. However, a non-destructive method for quantifying copper and/or zinc compounds in anti-fouling paints applied on boat hulls doesn't exist in the present. Hence, there is a need to develop an XRF-based method for quantifying tin, copper and zinc compounds at the same time in anti-fouling paints applied on boat hulls.

SUMMARY OF THE INVENTION

It is a *first object of the invention* to provide a method for manufacturing a set of calibration standards for use in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument.

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It is a *second object of the invention* to provide said set of calibration standards for use in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument.

- 10 It is a *third object of the invention* to provide a method for calibration with said set of calibration standards wherein said method for calibration is used in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument.

- 15 It is a *fourth object of the invention* to use said set of calibration standards in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument.

- It is a *fifth object of the invention* to provide a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument by using said set of calibration standards.
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- It is of importance to note that the below disclosed embodiments of the first and second objects of the inventions will be used in the preferred embodiments of the third, fourth and fifth objects of the invention. Hence, when the technical effects and advantages of the embodiments of the first and second objects are described below, these effects and advantages also relate to the preferred embodiments of the third, fourth and fifth objects of the invention.
- 25

- 30 The definition of the word "set" used in the present invention is "a group of things of the same kind that belong together and are so used". Hence, a "set of calibration standards" relates to calibration standards for Sn, Cu and Zn that are prepared according to the same method as well as used for the same purpose.

According to a preferred embodiment, **the first object of the invention** is attained by a method comprising the steps of:

a. Manufacturing calibration standards for tin compounds comprising the steps of:

- 5 i. Applying increasing amounts of tin compounds to anti-fouling paints both separately and in combination with copper compounds and/or zinc compounds to yield a concentration interval between 0-64 % (weight:weight) for each of tin, copper and zinc compounds, wherein said anti-fouling paint to be used in step ai) does not comprise tin, copper and zinc compounds, and
- 10 ii. mixing the paints with respective compounds, and
- iii. applying paints on a thin film to obtain a wet layer of paint, and
- 15 iv. drying the paint, and

b. Manufacturing calibration standards for copper compounds comprising the steps of:

- 20 i. Applying increasing amounts of copper compounds to anti-fouling paints both separately and in combination with zinc compounds to yield a concentration interval between 0-64 % (weight:weight) for each of copper and zinc compounds, wherein said anti-fouling paint to be used in step bi) does not comprise tin, copper and zinc compounds, and
- ii. mixing the paints with respective compounds, and
- 25 iii. applying paints on a thin film to obtain a wet layer of paint, and
- iv. drying the paint, and

c. Manufacturing calibration standards for zinc compounds comprising the steps of:

- 30 i. Applying increasing amounts of zinc compounds to anti-fouling paints to yield a concentration interval between 0-64 % (weight:weight) for zinc compounds, wherein said anti-fouling paint to be used in step ci) does not comprise tin, copper and zinc compounds, and

- ii. mixing the paints with respective compounds, and
- iii. applying paints on a thin film to obtain a wet layer of paint, and,
- iv. drying the paint.

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According to a preferred embodiment, **the second object of the invention** is attained by:

- 10 a. Calibration standards for tin compounds comprising a thin film coated by a layer of anti-fouling paint comprising tin compounds both separately or in combination with copper compounds and/or zinc compounds with a concentration interval between 0-64% (weight:weight) for each of tin, copper and zinc compounds, and
- 15 b. Calibration standards for copper compounds comprising a thin film coated by a layer of anti-fouling paint comprising copper compounds both separately and in combination with zinc compounds with a concentration interval between 0-64% (weight:weight) for each of copper and zinc compounds, and
- 20 c. Calibration standards for zinc compounds comprising a thin film coated by a layer of anti-fouling paint comprising zinc compounds with a concentration interval between 0-64% (weight:weight) for each of tin, copper and zinc compounds, and

wherein said concentration interval 0-64% represents the concentration (weight:weight) of wet layer of tin, copper and zinc compounds applied to
25 the film in the method for manufacturing said set of calibration standards.

From hereafter (weight:weight) is left out from the present invention. Hence, when concentrations are disclosed in %, said concentration indicates % in weight:weight

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Thus the above mentioned preferred embodiments of the first and second objects of the invention provide a set of calibration standards comprising calibration

standards for tin, copper and zinc compounds. This allows using said set of calibration standards in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints, wherein inter-elemental effects (1) between elements (i.e. metals) of tin, copper and zinc compounds *within* a paint layer, as well as (2) between elements of tin, copper and zinc compounds *between* paint layers, can be eliminated by a method for calibration involving the use of said calibration standards. Moreover, also matrix effects within a paint layer, as well as, between paint layers are eliminated.

10 The greater the knowledge about the sample matrix and how it varies in the paint layers on boat hulls, the more representative the calibration model is and the more accurate the results. The calibration standards used to generate the set of calibration standards are therefore prepared in the same way as the samples that will be quantified at the site, i.e. on boat hulls. Consequently, the standards will exhibit the same characteristics as the real samples to be analyzed and will therefore provide a reliable method for calibrating the XRF instrument. Thus, the sample matrix which is used in the method of the preferred embodiment is an anti-fouling paint which originally does not comprise any of tin, copper and zinc compounds to be quantified. A concentration interval between 0-64 % of tin, copper and zinc compounds is applied to the anti-fouling paint in order to simulate the concentration of anti-fouling paints applied to boat hulls. Said concentration interval 0-64% represents the concentration of wet layer of tin, copper and zinc compounds applied to the film in the manufacture of the standards. Additionally, the mixed paints are applied with a thickness which results in a sample morphology representative of the distribution, uniformity, heterogeneity and surface conditions of the anti-fouling paints applied to boat hulls. Hence, said set of calibration standards are representative of the anti-fouling paints to be analyzed on boat hulls.

The mixed paint is applied on a thin film (i.e. foil) support (i.e. backing material). The backing material gives mechanical strength and is of a high-purity material which is able to withstand high beam intensities. The continuous background radiation produced by the backing material is as small as possible. The film being thin favors low background radiation. The film is preferably made of plastic material, more preferably polyester or polypropylene.

According to a further preferred embodiment of the first and second objects of the invention, the concentration for each of tin, copper and zinc compounds applied on the film is 0-32 %, more preferably, 0%, 1%, 2%, 4%, 8%, 16% and/or 32%. The set of calibration standards will consequently cover the full range of target compounds and interfering matrix element concentrations, as well as reflect variations in concentrations of tin, copper and zinc compounds to produce a representative calibration model when used in method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument.

10 The highest and lowest concentrations of tin, copper and zinc compounds in the set of the calibration standards will define the calibration range.

According to a further embodiment of the first and second objects of the invention, the paint is applied on a polyester film support. The chemical composition of polyester attenuates absorption of the primary X-rays and characteristic radiation emitted by the sample. The degree of attenuation is further controlled by the gauge of the film used; the thinner the gauge, the lower the absorption of x-rays. The inherent high strength of polyester film also permits safe sample handling and retention concurrent with maintaining taut film surfaces to define statistically reproducible target- to-sample distance.

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According to a further embodiment of the first and second objects of the invention, the film gauge thickness is preferably 2-10 μm . The lower the film gauge thickness, the more negligible are interelement matrix effects. Hence, the thinner film gauge material, then the set of calibration standards will provide a more linear relationship between the fluorescent intensity of tin, copper and zinc compounds in the film and the mass per unit area (i.e. area concentration) of tin, copper and zinc compounds in the film.

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According to a further embodiment of the first and second objects of the invention, the film has a gauge of 2.5 μm , 3.6 μm or 6.3 μm . The film with a gauge thickness of 2.5 μm is used for applications requiring reduced absorption of the primary X-rays and characteristic long wavelength, including the "L" spectral lines. The film with a gauge thickness of 3.6 μm is (a general purpose film) for both short- and

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long-wavelength investigations, and particularly well suited for analyzing samples containing mixtures of both heavy and light elements. The application of a 6.3 μm -gauge film, used primarily for short-wavelength, i.e. heavy element determinations, but may be extended to include moderately high concentrations of elements having long wavelengths. Preferably, 6.3 μm -gauge film is used since tin, copper and zinc compounds are to be quantified with the said set of calibration standards.

According to a further preferred embodiment of the first and second objects of the invention, the wet layer of paint applied to the film has a thickness of about 10-500 μm , more preferably about 50, 100, 150 and 200 μm . It is important to apply a wet layer of paint with the most optimal thickness since a too thick or thin wet layer of paint can result in a crackled dry layer of paint. Moreover, if the wet layer of paint is too thin, then it can be difficult to use paint with high concentrations of zinc and copper compounds, such as ZnO and Cu_2O , since these oxides are particulate and therefore do not mix easily in small volumes of paint. Moreover, the standards are to be used in a method for quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints, wherein the concentration is quantified as amount per area, i.e. $\mu\text{g}/\text{cm}^2$. Hence, if the painted surface is too thick so that the X-rays going IN but especially going OUT from plastic film coated with paint is absorbed significantly, then it is probable that the amount of tin, copper and zinc compounds are too high.

According to a further preferred embodiment of the first and second objects of the invention, the wet layer of paint has a thickness of about 100 μm since this thickness corresponds approximately to a thickness of a layer of anti-fouling paint on boat hulls of leisure boats.

According to a further preferred embodiment of the second object of the invention, the concentration interval 0-32% of wet layer of tin, copper and zinc compounds applied to the film corresponds to an area concentration of dry tin, copper and zinc compounds of 0-1800 $\mu\text{g}/\text{cm}^2$ Sn, 0-4700 $\mu\text{g}/\text{cm}^2$ Cu and 0-2800 $\mu\text{g}/\text{cm}^2$ Zn. The thickness of the wet layer of tin, copper and zinc compounds applied to the film is 100 μm in this preferred embodiment.

According to a further embodiment of the first and second objects of the invention, the calibration standards for each of tin, copper and zinc compounds comprise a minimum of 7-10 samples. As the number of analyzed elements analyzed increases, more calibration samples are required for each element to adequately characterize target element concentration ranges and correct for interelement matrix effects. Hence, the calibration standards for each of tin, copper and zinc compounds preferably comprise a minimum of 7-10 standards. This generates a linear model for the analytes when interelement matrix effects are significant.

According to a further preferred embodiment of the first and second objects of the invention, the punched out pieces for use as standards are preferably circular, and preferably have a diameter of 25 mm. This allows practical handling and storing of the standards.

According to a further preferred embodiment of the first object of the invention, the method for manufacturing a set of calibration standards for use in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument comprises the steps of:

- a. Manufacturing calibration standards for tin compounds comprising the steps of:
 - i. Preparing calibration standards comprising tin compounds, wherein said concentrations of tin compounds is between 0-32 %, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and
 - ii. Preparing calibration standards comprising both tin and copper compounds, wherein said concentrations of each of tin and copper compounds is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and
 - iii. Preparing calibration standards comprising both tin and zinc compounds, wherein said concentrations of each is between 0-32 %, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and,
 - iv. Preparing calibration standards comprising tin, copper and zinc compounds, wherein said concentrations of each com-

pound is between 0-32 %, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and,

b. Manufacturing calibration standards for copper compounds comprising the steps of:

- 5 i. Preparing calibration standards comprising copper compounds, wherein said concentrations of copper compounds is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and
- 10 ii. Preparing calibration standards comprising both copper compounds and zinc compounds, wherein said concentrations of each of copper and zinc compounds is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and,

c. Manufacturing calibration standards for zinc compounds comprising the steps of:

- 15 i. Preparing calibration standards comprising zinc compounds, wherein said concentrations of zinc compounds is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%.

20 According to a further preferred embodiment of the second object of the invention, the set of calibration standards for use in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument comprises:

a. Calibration standards for tin compounds comprising:

- 25 i. Calibration standards comprising tin compounds, wherein said concentrations of tin compounds is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and
- 30 ii. Calibration standards comprising both tin and copper compounds, wherein said concentrations of each of tin and copper compounds is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and
- iii. Calibration standards comprising both tin and zinc compounds, wherein said concentrations of each is between 0-

32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%,
and

- iv. Calibration standards comprising tin, copper and zinc compounds, wherein said concentrations of each compound is
5 between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16%
and/or 32%, and

b. Calibration standards for copper compounds comprising:

- i. Calibration standards comprising copper compounds ,
wherein said concentrations of copper compounds is be-
10 tween 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or
32%, and

- ii. Calibration standards comprising both copper and zinc
compounds, wherein said concentrations of each of copper
and zinc compounds is between 0-32%, preferably 0%, 1%,
15 2%, 4%, 8%, 16% and/or 32%, and

c. Calibration standards for zinc compounds comprising:

- i. Calibration standards comprising zinc compounds, wherein
said concentrations of zinc compounds is between 0-32%,
preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%.

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According to a further preferred embodiment of the first object of the invention, the
method for manufacturing a set of calibration standards for use in in a method of
quantifying the concentration of tin, copper and zinc compounds in anti-fouling
paints with a handheld XRF instrument comprises the steps of:

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a. Manufacturing calibration standards for tin compounds comprising
the steps of:

- i. Preparing calibration standards comprising 1%, 2%, 4%, 8%,
16% and 32% tin compounds, and
ii. Preparing calibration standards comprising both tin and zinc
30 compounds, wherein the concentration of tin compounds is
4% and the concentration of zinc compounds is 32%, and

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b. Manufacturing calibration standards for copper compounds compris-
ing the steps of:

- 5
- i. Preparing calibration standards comprising 1%, 2%, 4%, 8%, 16% and 32% copper compounds, and
 - ii. Preparing calibration standards comprising both copper compounds and zinc compounds, wherein the concentrations of copper and zinc compounds are:
 - 1% and 4% copper and zinc compounds respectively
 - 4% and 8% copper and zinc compounds respectively
 - 8% and 8% copper and zinc compounds respectively
 - 2% and 4% copper and zinc compounds respectively
 - 10 – 4% and 4% copper and zinc compounds respectively
 - 1% and 2% copper and zinc compounds respectively
- and,
- c. Manufacturing calibration standards for zinc compounds comprising the steps of:
 - 15 i. Preparing calibration standards comprising 2%, 4%, 8%, 16% and 32% zinc compounds, and
 - d. Manufacturing calibration standards free of tin, copper and zinc compounds.
- 20 According to a further preferred embodiment of the second object of the invention, the set of calibration standards for use in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument comprises:
- a. Calibration standards for tin compounds comprising:
 - 25 i. Calibration standards comprising 1%, 2%, 4%, 8%, 16% and 32% tin compounds, and
 - ii. Calibration standards comprising both tin and zinc compounds, wherein the concentration of tin compounds is 4 % and the concentration of zinc compounds is 32 %, and
 - 30 b. Calibration standards for copper compounds comprising:
 - i. Calibration standards comprising 1%, 2%, 4%, 8%, 16% and 32% copper compounds, and

ii. Calibration standards comprising both copper compounds and zinc compounds, wherein the concentrations of copper and zinc compounds are:

- 1% and 4% copper and zinc compounds respectively
- 4% and 8% copper and zinc compounds respectively
- 8% and 8% copper and zinc compounds respectively
- 2% and 4% copper and zinc compounds respectively
- 4% and 4% copper and zinc compounds respectively
- 1% and 2% copper and zinc compounds respectively

and,

c. Calibration standards for zinc compounds comprising:

i. Calibration standards comprising 2%, 4%, 8%, 16% and 32% zinc compounds, and

d. Calibration standards free of tin, copper and zinc compounds.

The above disclosed four embodiments for the first and second objects of the invention provide a set of calibration standards which are optimal for use in the third object of the invention, as well as fourth and fifth objects of the invention, i.e. method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF.

The set of calibration standards according to the above four preferred embodiments includes the relevant range of target compound concentrations to be quantified as well as possible anti-fouling paint matrix element concentrations. Thus the set of calibration standards reflects the variations in concentrations of tin, copper and zinc compounds in order to produce a representative calibration model in the preferred embodiments of the third, fourth and fifth objects of the invention. Moreover, the set of calibration standards includes several standards for tin, copper and zinc compounds with concentrations near the concentrations of anti-fouling paints applied on boat hulls in order to improve accuracy of the method for calibration disclosed in the third, fourth and fifth objects of the invention. Additionally, several standards are needed for each of tin, copper and zinc compounds in order to generate a linear model for multiple analytes when interelement matrix effects is sig-

nificant within a paint layer, as well as between paint layers, as in the method for calibration disclosed in the third, fourth and fifth objects of the invention. Since the number of elements analyzed is three (i.e. Sn, Cu and Zn) in the preferred embodiments of fourth and fifth objects of the invention, more calibration standards are
5 needed to accurately and with high precision quantify target elements concentrations and to correct for interelement matrix effects.

According to a further preferred embodiment of the first and second objects (as well as third, fourth and fifth objects) of the invention, said tin compounds is tin
10 metal, inorganic tin, or one or more organotin compounds.

According to a further preferred embodiment of the first and second objects (as well as third, fourth and fifth objects) of the invention, said copper compound is inorganic copper, preferably selected from one or more of Cu_2O , CuSCN and copper
15 metal (powder).

According to a further preferred embodiment of the first and second objects (as well as third, fourth and fifth objects) of the invention, said zinc compounds is inorganic zinc, preferably selected from one or more of zinc metal (powder), ZnO and
20 ZnSO_4

According to a further preferred embodiment of the first and second objects (as well as third, fourth and fifth objects) of the invention, one or more organotin compounds is selected from TBT (tributyltin), TPT (triphenyltin) and DBT (dibutyltin)
25 compounds.

According to a further preferred embodiment of the first and second objects (as well as third, fourth and fifth objects) of the invention, said TBT and TPT compounds are selected from one or more of TBTO (tributyltin oxide), Tributyltin hydride, Tributyltin adipate, Tributyltin dodecenyl succinate, Tributyltin sulfide, Tributyltin acetate, Tributyltin acrylate, TBT fluoride, Tributyltin methacrylate, Tributyltin resinate, Triphenyltin oxide, Triphenyltin hydride, Triphenyltin hydroxide, Triphenyltin chloride and Triphenyltin acetate. TBT, TPT and DBT compounds have been
30 used in anti-fouling paint and the calibration standards of the tin compounds there-

fore comprise one or more of TBT, TPT and DBT compounds. Consequently, the set of calibration standards is representative of the sample matrix on the boat hull.

According to a further preferred embodiment of the first and second objects (as well as third, fourth and fifth objects) of the invention, said tin compounds is TBTO. The set of calibration standards has to be representative of the sample matrix on the boat hull in order to provide accurate results in the method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument. Since, TBTO was the most used organotin compound in anti-fouling paint in the 1960s and 1970s, said calibration standards of organotin compound therefore comprise TBTO.

According to a further preferred embodiment of the first and second objects (as well as third, fourth and fifth objects) of the invention, the set of calibration standards comprises calibration standards for TBTO, Cu_2O and ZnO . This allows using said set of calibration standards in a method for quantifying the concentration of all three of TBTO, Cu_2O and ZnO in anti-fouling paints.

According to a further preferred embodiment of the first object of the invention, the calibration standards are chemically analyzed for total concentration of Sn, Cu and Zn, wherein the chemically analyzed total concentration of Sn, Cu and Zn and the weight and area of the standards are used to calculate the total concentration per area (i.e. area concentration) expressed as $\mu\text{g}/\text{cm}^2$.

According to a further preferred embodiment of the first object of the invention, said method also comprises the following step d:

d. Manufacturing calibration standards for a further compound comprising the steps of:

i. Applying increasing amounts of further compound to anti-fouling paints both separately and in combination with tin, copper and zinc compounds to yield a concentration interval between 0-64 %, preferably 0-32%, for each of further, tin, copper and zinc compounds, wherein said anti-fouling paint in

step di) does not comprise any of further, tin, copper and zinc compounds, and

- ii. mixing the paints with respective compounds, and
- iii. applying paints on a thin film to obtain a wet layer of paint,
- 5 and
- iv. drying the paint,

wherein said further compound is selected from one or more of organic mercury, inorganic mercury, inorganic lead, organic lead, arsenic, cadmium, chromium, barium and iron compounds.

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According to a further preferred embodiment of the second object of the invention, said set of calibration standards also comprises:

- d. Calibration standards for a further compound comprising a thin film coated by a dry layer of anti-fouling paint comprising said further compound both separately and in combination with tin, copper and
- 15 zinc compounds with a concentration interval between 0-64%, preferably 0-32%, for each of further, tin, copper and zinc compounds,

wherein said further compound is selected from one or more of organic mercury, inorganic mercury, inorganic lead, organic lead, arsenic, cadmium, chromium, barium and iron compounds.

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Mercury, lead, arsenic, cadmium and chromium compounds as well as other toxic compounds have in the past (and maybe in the present) been added to anti-fouling paints. Hence, in this preferred embodiment one or more of these compounds are

25 also included in the set of calibration standards so that they can also be quantified in the fourth and fifth objects of the invention.

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According to a preferred embodiment, the said second object of the invention is attained by using the above disclosed preferred embodiments of the method for attaining the first object of the invention. Hence, the preferred embodiments of the above mentioned set of calibration standards of the second object of the invention are obtained according to the method according to preferred embodiments of the first object of the invention. This product-by-process embodiment is necessary

since it is difficult to define the set of calibration standards without referring to the method for manufacturing said set of calibration standards. This is due to the fact that it is difficult to indicate the amount of dry tin, copper and zinc compounds on the film in $\mu\text{g}/\text{cm}^2$ since the anti-fouling paint can be applied with a thickness of 50, 100, 150 and 200 μm . Hence, the amount of dry tin, copper and zinc compounds in $\mu\text{g}/\text{cm}^2$ is dependent of the thickness of the paint layer. Consequently, it is difficult to define a preferred embodiment of the second object of the invention without including a product-by-process embodiment in the invention.

10 According to a preferred embodiment, an object of the invention is to provide a kit for use in quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF, comprising the above disclosed preferred embodiments of the first and/or second objects of the invention.

15 According to a further preferred embodiment, the **third object of the invention** is attained by the following method for calibration with the set of calibration standards described in the above preferred embodiment said method comprising the steps of:

a. Calibrating with calibration standards comprising the steps of:

20 Scanning the calibration standards of tin, copper and zinc compounds both individually and together by applying two, three, four or five standards on top of each other and wherein a piece of a boat hull material is placed behind the standards during the scanning,

25 b. Providing calibration curves of tin, copper and zinc compounds by plotting (log) $K\alpha$ -Compton adjusted intensities of Sn, Cu and Zn and (log) chemically measured concentrations ($\mu\text{g}/\text{cm}^2$) of Sn, Cu and Zn in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument,

30 wherein said method for calibration is used in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument.

As in a real boat hull, the boat hull material is situated underneath the most bottom layer, i.e. most the bottom calibration standard. The scan is performed by aiming the handheld-XRF instrument on the top layer, i.e. the top calibration standard.

- 5 The use of above disclosed set of calibration standards (of the first and second objects of the invention) in the method for calibration (of the third object of the invention) results in the technical effects and advantages described in the above preferred embodiments of said set of calibration standards.
- 10 Tin, copper and zinc compounds (such as organotin compounds Cu_2O and ZnO) have been included in anti-fouling paints in different time periods since the 1960s. Organotin compound based anti-fouling paints were used in the 1960s and 1970s before they were banned in many countries due to serious toxic effects on marine life. Copper and zinc based anti-fouling paints (such as Cu_2O and ZnO) have been
- 15 used since then as alternatives. Additionally, the use anti-fouling paints comprising more than one of tin, copper and zinc compounds shouldn't be ruled out. Due to these reasons, a boat hull can comprise several layers of paint wherein each layer comprises either (1) only tin, copper and zinc compounds, or (2) one or more of tin, copper and zinc compounds. Additionally, each layer can comprise varying
- 20 concentrations of tin, copper and zinc compounds. Since there can be several layers of paint on a boat hull, and that the chemical composition and concentration of the anti-fouling paint varies significantly in each paint layer, the method of calibration according to the preferred embodiment takes these variations into account in order to generate an accurate and precise calibration model.

25

- Hence, the method for calibration according to the present invention is adapted to be used in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument. Since the boat hull of a leisure boat is covered with several layers of paint, the method for calibration
- 30 is, as indicated below, designed to include several layers of paint.

X-ray measurements are susceptible to variable scattering of the source of X-rays from the boat hull material beneath the anti-fouling paint layers. Although, some XRF analyzers might provide corrections for substrate scattering, the most optimal

correction for this scattering is to emulate the scattering in the method for calibration. Hence, a piece of boat hull material is placed behind the first layer of calibration standards as indicated above. The piece of boat hull material is preferably non-metallic and does not comprise any layers of anti-fouling material. Moreover, the piece of boat hull material is made of the same material as a real boat hull material from a leisure boat and has the same thickness, preferably 3 mm – 100 mm, more preferably 5- 50, even more preferably 21 mm. The non-metallic piece of boat hull material is preferably chosen from the group comprising wood, fiberglass, carbon fiber, Kevlar, composite material, gelcoat, composite covered with gelcoat, plastic-based material, Roplene, rubber, polymer, or combinations of said non-metallic materials. Gelcoat is a material used to provide a high-quality finish on the visible surface of a fibre-reinforced composite material. The most common gelcoats are based on epoxy or unsaturated polyester resin chemistry. Gelcoats are modified resins which are applied to moulds in the liquid state. They are cured to form crosslinked polymers and are subsequently backed with composite polymer matrices, often mixtures of polyester resin and fiberglass or epoxy resin with glass. An example of a material which can be used as a boat hull material comprises an outer 4 mm layer of gelcoat, a 14 mm porous intermediary layer and an inner 3 mm layer of gelcoat.

20

The calibration curve is based on the adjusted intensity of K_{α} signals, i.e. the intensity rates have been adjusted for air background, peak overlap and elemental interference from other elements in the sample that have peak energies close to the element of interest. To correct for matrix effects, Compton normalization is performed, i.e. each element's adjusted rate was divided by the scatter produced in the light element (LE) region of the sample. A regression analysis (for each element to be detected) is performed to calculate the slope and the intercept of the calibration curve.

30

According to a further preferred embodiment of the third object of the invention, the method comprises the steps of:

- a. Calibrating with calibration standards comprising the steps of:
 - i.

- 1) Scanning each of the calibration standards for tin compounds when placed on a respective piece of a boat hull material, and
- 2) Scanning each of the calibration standards for copper or zinc compounds when placed on each of the calibration standards of tin compounds in step i1, and
- 3) Scanning each of the calibration standard for copper or zinc compounds when placed on each combination of calibration standards in step i2, and
- 4) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step i3, and
- 5) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step i4, and
- repeating previous steps i1-i5 by
 - exchanging calibration standards for copper or zinc compounds in step i1 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in step i1 and i2 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in steps i1- i3 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in steps i1-i4 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in steps i1-i5 with calibration standards for tin, and

ii.

- 1) Scanning each of the calibration standards for copper compounds when placed on a respective piece of a boat hull material, and
 - 5 2) Scanning each of the calibration standards for copper or zinc compounds when placed on each of the calibration standards of copper compounds in step ii1, and
 - 3) Scanning each of the calibration standard for copper or zinc compounds when placed on each combination of calibration standards in step ii2, and
 - 10 4) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step ii3, and
 - 5) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step ii4, and
 - 15
- iii.
- 1) Scanning each of the calibration standards for zinc compounds when placed on a respective piece of a boat hull material, and
 - 20 2) Scanning each of the calibration standards for copper or zinc compounds when placed on each of the calibration standards of zinc compounds in step iii1, and
 - 3) Scanning each of the calibration standard for copper or zinc compounds when placed on each combination of calibration standards in step iii2, and
 - 25 4) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step iii3, and
 - 5) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step iii4.
 - 30
- b. Providing calibration curves of tin, copper and zinc compounds by plotting (log) $K\alpha$ -Compton adjusted intensities of Sn, Cu and Zn and (log) chemically measured concentrations ($\mu\text{g}/\text{cm}^2$) of Sn, Cu and Zn

in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument,

- c. Aiming a handheld and handheld XRF analyzer on the boat hull to be analyzed,
- 5 d. Scanning $K\alpha$ -lines of Sn, Cu and Zn wherein scanning is preferably for 5, 10, 15, 20, 30, 60 and 120 seconds, more preferably for 30 seconds,
- e. Quantifying the concentration of tin, copper and zinc compounds by relating the detected $K\alpha$ lines of Sn, Cu and Zn in the boat hull to the
- 10 calibration curves of tin, copper and zinc compounds.

In a preferred embodiment, a scan doesn't have to be made in each of the above disclosed steps 1-5 in the above preferred embodiment.

- 15 According to a further preferred embodiment of the third object of the invention, the method comprises the steps of:

a. Calibrating with calibration standards comprising the steps of:

i.

- 20 – Placing each of the calibration standards for tin compounds comprising 1%, 1%, 4%, 8%, 8% and 32% tin compounds on a respective piece of boat hull material, wherein the resulting single layer of standard is referred to as layer 3, and
- 25 – Placing each of the calibration standards for tin compounds comprising 1%, 2%, 4%, 8%, 16% and 32% tin compounds on top of the previous standards comprising 1%, 1%, 4%, 8%, 8% and 32%, respectively, wherein the resulting single layer of standard is referred to as layer 2, and
- 30 – Placing each of the calibration standard for tin compounds comprising 1%, 2%, 4%, 8%, 16% and 32 % tin compounds on top of the previous standards comprising 1%, 2%, 4%, 8%, 16% and 32% tin compounds, re-

spectively, wherein the resulting single layer of standard is referred to as layer 1, and

- Performing a scan of each of the resulting 6 combinations of layers by aiming the handheld XRF instrument on each layer 1, and

ii.

- Placing each of the calibration standards for tin compounds comprising 1%, 16%, 8% and 16% tin compounds on a respective piece of a boat hull material, wherein the resulting single layer of standard is referred to as layer 3, and

- Placing each of the calibration standard for copper compounds comprising 2%, 2%, 8% and 8% copper compounds on top of the previous standards comprising 1%, 16%, 8% and 16% tin compounds, respectively, wherein the resulting single layer of standard is referred to as layer 2, and

- Placing each of the calibration standard for copper compounds comprising 2%, 2%, 8% and 8% copper compounds on top of the previous standards comprising 2%, 2%, 8% and 8% copper compounds, respectively, wherein the resulting single layer of standard is referred to as layer 1, and

- Performing a scan of each of the resulting 4 combinations of layers by aiming the handheld XRF instrument on each layer 1, and

iii.

- Placing each of the calibration standards for tin compounds comprising 8%, 4%, 1%, 16% tin compounds on a respective piece of a boat hull material, wherein

the resulting single layer of standard is referred to as layer 3, and

- Placing each of the calibration standard for zinc compounds comprising 2%, 4%, 8% and 16% zinc compounds on top of the previous standards comprising 8%, 4%, 1%, 16% tin compounds, respectively, wherein the resulting single layer of standard is referred to as layer 2, and
- Placing each of the calibration standard for zinc compounds comprising 2%, 4%, 8% and 16% zinc compounds on top of the previous standards comprising 2%, 4%, 8% and 16% zinc compounds, respectively, wherein the resulting single layer of standard is referred to as layer 1, and
- Performing a scan of each of the resulting 4 combinations by aiming the handheld XRF instrument on each layer 1, and

iv.

- Placing each of the calibration standards for tin compounds comprising 8%, 4%, 1% and 16% tin compounds on a respective piece of a boat hull material, wherein the resulting single layer of standard is referred to as layer 3, and
- Placing each of the calibration standards for zinc compounds comprising 4%, 2%, 8% and 16% zinc compounds on top of the previous standards comprising 8%, 4%, 1% and 16% tin compounds, respectively, wherein the resulting single layer of standard is referred to as layer 2, and
- Placing each of the calibration standard for copper compounds comprising 2%, 4% 16% and 18 % copper compounds on top of the previous standards compris-

ing 4%, 2%, 8% and 16 % zinc compounds, respectively, wherein the resulting single layer of standard is referred to as layer 1, and

- Performing a scan of all of the resulting 4 combinations by aiming the handheld XRF instrument on each layer 1, and

v. Scanning each of the calibration standards for tin compounds comprising 1% and 32% tin compounds when placed on a respective piece of a boat hull material, and

- vi. Scanning a calibration standard for tin compounds comprising 32% tin compounds when placed on a piece of a boat hull material, and then placing a calibration standard for tin compounds comprising 32% tin compounds on top of the previous standard placed on the piece of boat hull, and then performing a scan, and

vii. Scanning a calibration standard for tin compounds comprising 4% tin compounds and 32% zinc compounds, and

viii. Scanning a calibration standard free of tin, copper and zinc compounds, and

ix.

- Placing each of the calibration standards for copper compounds comprising 2%, 4%, 8%, 16%, 32% and 32 % copper compounds on a respective piece of a boat hull material, wherein the resulting single layer of standard is referred to as layer 3, and
- Placing the calibration standard for copper compounds comprising 2%, 4%, 8%, 16%, 32% and 32 % copper compounds on top of the previous standards comprising 2%, 4%, 8%, 16%, 32% and 32% copper com-

pounds, respectively, wherein the resulting single layer of standard is referred to as layer 2, and

- Placing the calibration standard for copper compounds comprising 2%, 4%, 8%, 16%, 32% and 16 % copper compounds on top of the previous standards comprising 2%, 4%, 8%, 16%, 32% and 32% copper compounds, respectively, wherein the resulting single layer of standard is referred to as layer 1, and
- Performing a scan of all of the resulting 6 combinations of layers by aiming the handheld XRF instrument on each layer 1, and

x.

- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on a piece of a boat hull material, wherein the resulting single layer of standard is referred to as layer 4, and
- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on top of the previous standard comprising 32% copper compounds, wherein the resulting single layer of standard is referred to as layer 3, and
- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on top of the previous standard comprising 32% copper compounds, wherein the resulting single layer of standard is referred to as layer 2, and
- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on top of the previous standard comprising 32% copper compounds, wherein the resulting single layer of standard is referred to as layer 1, and

xi.

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– Placing a calibration standard comprising 4% copper compounds and 8% zinc compounds on a piece of a boat hull material, wherein the resulting single layer of standard is referred to as layer 3, and

10

– Placing a calibration standard comprising 4% copper compounds and 8% zinc compounds on top of the previous standard comprising 4% copper compounds and 8 % zinc compounds, wherein the resulting single layer of standard is referred to as layer 2, and

15

– Placing a calibration standard comprising 8% copper and 8% zinc compounds on top of the previous standard comprising 4% copper compounds and 8% zinc compounds, wherein the resulting single layer of standard is referred to as layer 1, and

– Performing a scan by aiming the handheld XRF instrument on each layer 1 , and

xii.

20

– Placing a calibration standard for copper compounds comprising 4% copper compounds and 4% zinc compounds on a piece of a boat hull material, wherein the resulting single layer of standard is referred to as layer 3, and

25

– Placing a calibration standard comprising 1% copper compounds and 2% zinc compounds on top of the previous standard comprising 4% copper compounds and 4% zinc compounds, wherein the resulting single layer of standard is referred to as layer 2, and

30

– Placing a calibration standard comprising 0% copper, 0% zinc and 0% tin compounds on top of the previous standard comprising 1% copper compounds and 2%

zinc compounds, wherein the resulting single layer of standard is referred to as layer 1, and

- Performing a scan by aiming the handheld XRF instrument on each layer 1, and

5

- xiii. Scanning each of the calibration standards comprising 2%, 4%, 8%, 16% and 32 % copper compounds when placed on a respective piece of a boat hull material, and

10

- xiv. Scanning each of the calibration standards comprising 1%, 4%, 4%, 8% and 2 % copper compounds and 4%, 8%, 8%, 8% and 4% zinc compounds, respectively, when placed on a respective piece of a boat hull material, and

15

xv.

- Placing each of the calibration standards for zinc compounds comprising 2%, 4%, 8%, 16% and 32 % zinc compounds on a respective piece of a boat hull material, wherein the resulting single layer of standard is referred to as layer 3, and

20

- Placing each of the calibration standard for zinc compounds comprising 2%, 4%, 8%, 16% and 32 % zinc compounds on top of the previous standards comprising 2%, 4%, 8%, 16% and 32 % zinc compounds, respectively, wherein the resulting single layer of standard is referred to as layer 2, and

25

- Placing the calibration standard for zinc compounds comprising 2%, 4%, 8%, 16% and 32 % zinc compounds on top of the previous standards comprising 2%, 4%, 8%, 16% and 32% zinc compounds, respectively, wherein the resulting single layer of standard is referred to as layer 1, and

30

- Performing a scan of all of the resulting 5 combinations of layers by aiming the handheld XRF instrument on each layer 1, and

5

xvi.

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- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on a piece of a boat hull material, wherein the resulting single layer of standard is referred to as layer 5, and
- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, wherein the resulting single layer of standard is referred to as layer 4, and
- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, wherein the resulting single layer of standard is referred to as layer 3, and
- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, wherein the resulting single layer of standard is referred to as layer 2, and
- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, wherein the resulting single layer of standard is referred to as layer 1, and

- xvii. Scanning each of the calibration standards for zinc comprising 8%, 16% and 32% zinc compounds when placed on a respective piece of a boat hull material, and

- b. Providing calibration curves of tin, copper and zinc compounds by plotting (log) K_{α} -Compton adjusted intensities of Sn, Cu and Zn and (log) chemically measured concentrations ($\mu\text{g}/\text{cm}^2$) of Sn, Cu and Zn in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument,

wherein said method for calibration is used in a method of quantifying the concentration of tin copper and zinc compounds in anti-fouling paints with a handheld XRF instrument.

- Steps i-xvii in the above preferred embodiment is representative of the variations of paint layers that can be found in boat hulls. Hence, this preferred embodiment takes into consideration that boat hulls can have 1-5 layers of anti-fouling paints that each layer can comprise one or more of tin, copper and zinc compounds.

- Step i represents a boat hull comprising three layers of anti-fouling paint comprising tin compounds in each layer.

Step ii represents tin compounds in the paint layer closest to the boat hull and copper compounds in the next two layers of anti-fouling paint.

- Step iii represents tin compounds in the paint layer closest to the boat hull and zinc compounds in the next two layers of anti-fouling paint.

- Step iv represents tin compounds in the paint layer closest to the boat hull, zinc compounds in the next layer of anti-fouling paint and copper compounds in the layer after.

Step v represents a boat hull coated with a single layer of anti-fouling paint comprising of tin compounds.

- Step vi represents a boat hull coated with two layers of anti-fouling paint comprising of tin compounds.

Step vii represents a boat hull coated with a layer of anti-fouling paint comprising tin and zinc.

Step ix represents a boat hull comprising three layers of anti-fouling paint comprising copper compounds in each layer.

Step x represents a boat hull comprising one to four layers of anti-fouling paint comprising copper compounds in each layer.

Step xi represents a boat hull comprising three layers of anti-fouling paint comprising copper and zinc compounds in each layer.

Step xii represents a boat hull comprising three layers of anti-fouling paint comprising copper and zinc compounds in the two first layers closest to the boat hull and wherein the third layer comprising only anti-fouling paint without any tin, copper and zinc compounds.

Step xiii represents a boat hull coated with a single layer of anti-fouling paint comprising of copper compounds.

Step xiv represents a boat hull coated with a single layer of anti-fouling paint comprising of copper and zinc compounds.

Step xv represents a boat hull comprising three layers of anti-fouling paint comprising zinc compounds in each layer.

Step xvi represents a boat hull comprising one to four layers of anti-fouling paint comprising zinc compounds in each layer.

Step xvii represents a boat hull coated with a single layer of anti-fouling paint comprising of zinc compounds.

Anti-fouling paints comprising tin compounds such as organotin compounds (such as TBTO) were developed and used in the 1960s and 1970s. It can therefore be assumed that the oldest layers of anti-fouling paint on boat hulls comprise tin compounds such as organotin compounds. Hence, calibration standards for tin compounds are not placed on top of calibration standards of copper and zinc compounds.

According to a further preferred embodiment for said method for calibration, the said calibration curves are stored in the handheld XRF-instrument. Hence, the handheld XRF-instrument can be pre-calibrated by the manufacturer using the method for calibration and set of calibration standards disclosed in the present invention. This consequently allows for instant quantification of real samples, i.e. instant quantification of tin, copper and zinc compounds on boat hulls of leisure boats at the site where said leisure boats are harbored, stored, anchored etc.

15

According to a further preferred embodiment for the method for calibration, said piece of boat hull material is of non-metallic material and free of anti-fouling paint.

According to a further preferred embodiment for the method for calibration, steps a and b optionally comprise the steps of calibrating and providing calibration curves also of further compounds. Said further compound is selected from one or more of organic mercury, inorganic mercury, inorganic lead, organic lead, arsenic, cadmium, chromium, barium and iron compounds. Mercury, lead, arsenic, cadmium and chromium compounds as well as other toxic compounds have in the past been added to anti-fouling paints. Hence, in this preferred embodiment one or more of these compounds are also subjected to the method calibration so that they can also be quantified in the fourth and fifth objects of the invention.

According to further embodiments, the **fourth object of the invention** relating to the use of the set of calibration standards according to the above mentioned preferred embodiments (of the first and second objects) in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument, is attained by the following steps:

a. Calibrating according to the third object of the invention, and

- 5 b. Providing calibration curves of tin, copper and zinc compounds by plotting (log) K_{α} -Compton adjusted intensities of Sn, Cu and Zn and (log) chemically measured concentrations ($\mu\text{g}/\text{cm}^2$) of Sn, Cu and Zn in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument, and
- c. Aiming a handheld XRF analyzer on the boat hull to be analyzed, and
- d. Scanning K_{α} -lines of Sn, Cu and Zn wherein scanning is preferably for 5, 10, 15, 20, 30, 60 and 120 seconds, more preferably for 30
10 seconds, and
- e. Quantifying the concentration of tin, copper and zinc compounds by relating the detected K_{α} lines of Sn, Cu and Zn in the boat hull to the calibration curves of tin, copper and zinc compounds.

15

According to further embodiments, the **fifth object of the invention** relating to a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument, by using the set of calibration standards according to the above mentioned preferred embodiments (of the first
20 and second objects), comprising the steps of:

- a. Calibrating according to the third object of the invention, and
- b. Providing calibration curves of tin, copper and zinc compounds by plotting (log) K_{α} -Compton adjusted intensities of Sn, Cu and Zn and (log) chemically measured concentrations ($\mu\text{g}/\text{cm}^2$) of Sn, Cu and Zn
25 in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument, and
- c. Aiming a handheld XRF analyzer on the boat hull to be analyzed, and
- d. Scanning K_{α} -lines of Sn, Cu and Zn wherein scanning is preferably for 5, 10, 15, 20, 30, 60 and 120 seconds, more preferably for 30
30 seconds, and
- e. Quantifying the concentration of tin, copper and zinc compounds by relating the detected K_{α} lines of Sn, Cu and Zn in the boat hull to the calibration curves of tin, copper and zinc compounds.

Thus, the fourth and fifth object of the invention is attained by using preferred embodiments of above mentioned set of calibration standards (of the first and second objects of the invention) and method for calibration (of the third object of the invention). Consequently, the use of the preferred embodiments of the set of calibration standards and method for calibration, in said preferred embodiments of the fourth and fifth objects, results in the technical effects and advantages described in the above mentioned preferred embodiments of the set of calibration standards and method for calibration. Hence, these technical effects and advantages will not be repeated here once again.

According to a further preferred embodiment for the fourth and fifth objects of the invention, said calibration curves are stored in the handheld XRF-instrument.

According to a further preferred embodiment for the fourth and fifth objects of the invention, steps a-e comprise the steps of calibrating, providing calibration curves, scanning and quantifying also further compounds. Said further compound is selected from one or more of organic mercury, inorganic mercury, inorganic lead, organic lead, arsenic, cadmium, chromium, barium and iron compounds.

The technical effects and advantages of the preferred embodiment for the fourth and fifth objects have already been disclosed in above described preferred embodiment for the third object of the invention. Hence, these technical effects and advantages will not be repeated here once again.

FIGURES

Figure 1. Regression (calibration curve) for tin. The X-axis shows the log value of the chemically analyzed concentration of tin while the y-axis displays the log value of K_{α} -Compton adjusted intensity.

Figure 2. Regression (calibration curve) for copper. The X-axis shows the log value of the chemically analyzed concentration of copper while the y-axis displays the log value of K_{α} -Compton adjusted intensity.

Figure 3. Regression (calibration curve) for zinc. The X-axis shows the log value of the chemically analyzed concentration of zinc while the y-axis displays the log value of K_{α} -Compton adjusted intensity.

5

Figure 4. Log (Ln) XRF-analyzed (predicted) tin concentration plotted as a function of log (Ln) chemically analyzed (True) tin concentration ($k=1$).

Figure 5. Log (Ln) XRF-analyzed (predicted) copper concentration plotted as a
10 function of log (Ln) chemically analyzed (True) copper concentration ($k=1$).

Figure 6. Log (Ln) XRF-analyzed (predicted) zinc concentration plotted as a function of log (Ln) chemically analyzed (True) zinc concentration ($k=1$).

15 Figure 7. Validation study on how well the XRF anti-fouling module predicts true (chemically analyzed) concentrations of tin in different anti-fouling paints holding a dry paint thickness between 250 – 500 μm .

Figure 8. Validation study on how well the XRF anti-fouling module predicts true
20 (chemically analyzed) concentrations of copper in different anti-fouling paints holding a dry paint thickness between 250 – 500 μm .

Figure 9. Validation study on how well the XRF anti-fouling module predicts true
25 (chemically analyzed) concentrations of zinc in different anti-fouling paints holding a dry paint thickness between 250 – 500 μm .

DETAILED DESCRIPTION

30 The present invention relates to a set of calibration standards for use in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a portable XRF instrument. Further disclosed is a method for manufacturing the set of calibration standards as well as their use in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a portable XRF instrument.

While the present invention has been described with reference to the below specific Example 1, which is intended to be illustrative only and not to be limiting of the disclosure, it is noted that changes, additions and/or deletions may be made to the disclosed example without departing from the spirit and scope of the disclosure.
The scope of the disclosure is therefore not covered the specific example, but rather by the patent claims.

EXAMPLE 1

10 *Test design*

A handheld XRF analyzer was used for the purpose to build up an empirical model able to analyze the concentration of Sn, Cu and Zn in anti-fouling paints coated on boat hulls. The XRF analyzer (DELTA-50) was manufactured by Olympus and is powered with a 4W, 50kV 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 matrixes. In the laboratory, calibration experiments for each of the element of interest (Sn, Cu and Zn) were performed. K_{α} net intensity spectral peak were used since this electron transition, i.e. from L-shell to K-shell, is easiest to detect. Compton normalization was used to account for possible matrix effects. The calibration curves were used in our own empirical model and tested in field on boat hulls coated with anti-fouling paints.

Development of standards

25 Three different commercial biocide-free anti-fouling paints were used in the development of standards. Increasing amount 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 0-32% (weight:weight). After a thorough mixing, the paints were applied on a 6 μm thick Mylar film with a Quadruplex film applicator (VF2170, TQC), to obtain a wet layer of paint with thickness of 100 μm . After a drying period for at least 12 h, 25 mm $\varnothing$ pieces were punched out and used as standards.

Empirical model development

The standards were analyzed under controlled conditions in the XRF work station by applying the standards on the X-ray tube/detector. To simulate actual field conditions, i.e. boat hulls coated with anti-fouling paints, a plastic piece from a boat hull was allocated behind the standards during the analysis. The standards were
5 scanned with the 50kV beam. Since leisure boats usually have several layer 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 (see tables 1-3). The calibration was done on the adjusted intensity of K_{α} signals, i.e. the intensity rates have been adjusted for air background, peak overlap and ele-
10 mental interference from other elements in the sample that have peak energies close to the element of interest. To correct for matrix effects, Compton normalization were performed, i.e. each elements adjusted rate were divided by the scatter produced in the light element (LE) region of the sample. To assess the effect of analytical scan time on precision, a series of standards were scanned with the
15 50kV beam for 5, 10, 15, 20, 30, 60 and 120 seconds, respectively. The results showed that the scan time had no impact on the intensities of Sn, Cu and Zn. Based on this result we chose to use a scanning time of 30 seconds for the analyses of standards and build-up of calibration curves.

20 After being thoroughly analyzed with XRF, the standards were chemically analyzed for total concentration of Sn, Cu and Zn. The (chemically analyzed) total concentration of Sn, Cu and Zn, the weight and area of the standards allowed us to calculate the total concentration per area, expressed as $\mu\text{g}/\text{cm}^2$. (see the tables 1-3)

25

The standards were used to examine the relationship between measured Compton adjusted K_{α} intensities of Sn, Cu and Zn, respectively, and known 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 (see
30 Figures 1-3).

Detection limit

For each of the element of interest, i.e. Sn, Cu and Zn, at least ten blank samples (paint standard without the analyte of interest) were analyzed and mean blank val-

ue and SD were calculated. The 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).

5 *Validation of the empirical module*

A blind test was conducted to assess how well our anti-fouling paint application analysis Sn, Cu and Zn concentration in paint coatings with varying paint thickness/layers correlated. The blind test was conducted by allowing coworkers to apply anti-fouling paints on Mylar films with brushes. The coworkers had five different
10 unlabeled anti-fouling paints (three commercially available containing Cu and Zn and two own-made TBT-paints) to choose between and were instructed to use at least two of them. In total 20 different anti-fouling paint treatments, with painted layers varying between two and four (corresponds to a dry thickness between 250-500 μm), were produced. From all treatments, 25 mm diameter discs were
15 punched out and analyzed for Sn, Cu and Zn concentrations with our (Compton adjusted) anti-fouling paint module. The analysis was performed as described in section "Development of standards", i.e. the discs were put directly on the X-ray tube/detector with a plastic piece from a boat hull allocated behind and scanned with a 50kV beam for 30s. Thereafter, the paint discs were sent to a commercially
20 laboratory to be chemically analyzed for Sn, Cu and Zn concentrations.

Field survey

The aim of the present invention is to develop a XRF model that has the ability to quantify the total concentration of Sn, Cu and Zn on boat hulls. Today, the anti-
25 fouling paint market for leisure boats is dominating by copper (I) oxide-based anti-fouling paints (often in combination with zinc (I) oxide). Thus, the XRF-result for copper and zinc can be interpreted to arise primarily from copper (I) oxide and zinc (I) oxide, respectively. For Sn, the story is a bit more complex. Tin, has to our knowledge, been added to paint formulation as organotin compounds only (primarily TBT). However, organotin compounds can be degraded in several stages and
30 as a final step form non-toxic inorganic Sn. Thus, we wanted to study to what extent the XRF-analyzed tin concentration can explain the concentration of organotin compounds. Therefore, the present invention was used on leisure boats in order to quantify the amount of Sn present on the boats' hull. If Sn was present, the paint

was scraped off and collected in clean plastic bottles. In total paint scrapes from 31 boats were collected. The paint flakes were then send to a commercial laboratory (ALS Scandinavia), homogenized and analyzed for total tin and organotin compounds (see "Chemical analysis") in order to determine the proportion of TBT
 5 and other organotin compounds on leisure boat hulls.

Chemical analysis

Sample digestion and chemical analyze were performed by a commercial laboratory (ALS Scandinavia). The standards were digested in a solution containing 5mL
 10 concentrated HNO₃ and 5 mL concentrated HCl on a hotplate for 1 h. The samples 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).

Statistical analyze

15 The correlation between XRF analyzed concentrations was assumed to be proportional to the "true" chemically analyzed concentration with multiplicative log normally distributed random error through the formula:

$$Y = c * x * \epsilon$$

where Y is the XRF analyzed concentration, x is the chemically analyzed concentration and ϵ is the random error. Log transformation of the formula gives us;
 20

$$\log Y = a * \log x * \epsilon$$

where ϵ is the normally distributed random error, $a = \log c$ is a parameter to be estimated as well as the standard deviation (σ) of ϵ . σ and a where calculated through the formulas:

$$\hat{a} = \frac{1}{n} \sum_{i=1}^n d_i = \bar{d}$$

$$\hat{\sigma} = \frac{1}{n-1} \sum_{i=1}^n (d_i - \bar{d})^2$$

Where $d_i = \log y_i - \log x_i$

A 90% prediction interval of the forecasted value $\log y_0$ for $\log x_0$ was calculated with the formula:

$$\hat{a} + \log x_0 \pm t * \hat{\sigma} * \sqrt{1 + 1/n}$$

where t is the distribution critical value

Results

Empirical model

The calibration curves of Sn, Cu and Zn are shown in figures 1-3. Sn showed the best relationship between (log) K_{α} -Compton adjusted intensities and (log) 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 2.9 and 9.4 $\mu\text{g}/\text{cm}^2$, respectively. The LOD and LOQ for Cu were determined to 13.3 and 35.9 $\mu\text{g}/\text{cm}^2$, respectively. For Zn, the LOD and LOQ were quantified to 23.0 and 73.0 $\mu\text{g}/\text{cm}^2$, respectively.

10

In Figure 4-6, the correlation between predicted (XRF-analyzed) log concentration and true (chemically analyzed) log concentration are shown. Based on these regression data 90-percent confidence intervals (90% CI) were calculated for XRF-measured Sn, Cu and Zn concentrations. For Sn the 90% CI were determined to be between 0.78 – 1.28, i.e. with 90% certainty the true Sn concentration is between 78% and 128% of the XRF-analyzed concentration. For Cu and Zn the 90% CI were calculated to 0.50 – 2.02 and 0.64 – 1.58, respectively.

15

Empirical model validation

A blind test was performed to study how well our anti-fouling paint application predicts Sn, Cu and Zn concentration in paint coatings with varying paint thickness/layers. The regression analysis between XRF-measured concentrations and true (chemically analyzed) concentrations is shown in figures 7-9. The true (chemically analyzed) concentration was in most cases within the 90% CI of the predicted (XRF-measured) concentration for all metals, indicating that the module's prediction of true metal concentrations in anti-fouling paints is adequate at least when the paint thickness is $<500 \mu\text{m}$.

25

Tin (Sn)

The results from the linear regression analysis of Sn, i.e. the relationship between (log) Sn concentration and (log) K_{α} -Compton adjusted intensity, showed the model to work adequately. The R^2 -value of the regression analysis was 0.99 and the 90% CI was determined to be between 0.78-1.28. A blind test was performed to study how well the model predicted Sn, Cu and Zn concentrations under conditions were

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several different paints have 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% CI to overlap the $K=1$ line, indicating the model to work well in predicting the "true" (chemically analyzed) Sn concentration despite that the (dry) paint thickness varied between 250 and 500 μm .

Copper (Cu) and Zinc (Zn)

The linear regression for Cu and Zn, i.e. the relationship between (log) concentration and (log) K_{α} -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% CI was considerable wider, i.e. between 0.5 – 2.02 (Cu) and 0.64 – 1.58 (Zn). The disparity in confidence interval can be explained by the ability of fluorescent X-rays to penetrate through the sample matrix and reach the detector. Since Sn, as compared to Cu and Zn, has much more energetic X-rays and can hence travel through a larger distance within the sample, the effect of paint thickness is not that apparent. For Cu and Zn, which have less energetic X-rays, the effect of paint thickness is larger.

20 FURTHER EXAMPLES

The embodiment in Example 1 is modified by also including calibration standards for further compounds that might be toxic for the environment, such as one or more of organic mercury, inorganic mercury, inorganic lead, organic lead, arsenic, cadmium, chromium, iron and barium compounds in order to also quantify the concentrations of organic mercury, inorganic mercury, inorganic lead, organic lead, arsenic, cadmium, chromium, iron and/or barium compounds in anti-fouling paints on boat hulls.

The calibration standard for the above described further compounds is prepared by

- i. Applying increasing amounts of further compound to anti-fouling paints both separately and in combination with tin, copper and zinc compounds to yield a concentration interval between 0-64 %, preferably 0-32%, for each of further, tin,

copper and zinc compounds, wherein said anti-fouling paint in step di) does not comprise any of further, tin, copper and zinc compounds, and

- ii. mixing the paints with respective compounds, and
- 5 iii. applying paints on a thin film to obtain a wet layer of paint, and
- iv. drying the paint,

Consequently, the method of quantifying the concentration of tin, copper, zinc in anti-fouling paints with a handheld XRF instrument comprises the steps of:

- 10 a. Calibrating with calibration standards comprising the steps of:
Scanning the calibration standards of tin, copper, zinc and further compounds, both individually and together by applying two, three, four or five standards on top of each other and wherein a piece of a boat hull material is placed behind the standards during the scanning,
15 b. Providing calibration curves of tin, copper, zinc and further compounds by plotting (log) K_{α} -Compton adjusted intensities of Sn, Cu, Zn and further compounds and (log) chemically measured concentrations ($\mu\text{g}/\text{cm}^2$) of Sn, Cu, Zn and further compounds in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument,
20 c. Aiming a handheld XRF analyzer on the boat hull to be analyzed,
d. Scanning K_{α} -lines of Sn, Cu, Zn and further compounds wherein scanning is preferably for 5, 10, 15, 20, 30, 60 and 120 seconds, more preferably for 30 seconds,
25 e. Quantifying the concentration of tin, copper, zinc and further compounds by relating the detected K_{α} lines of Sn, Cu, Zn and further compounds in the boat hull to the calibration curves of tin, copper and zinc compounds.

Table 1. The column "Scan identity" indicates a scan performed on the a layer of standards; please observe that Scan 1, 2, 3 etc. in Tables 1-3 is the same scan, i.e. Sn, Cu and Zn are scanned at the same time. The column titled "Sn $\mu\text{g}/\text{cm}^2$ " discloses the total chemically analyzed area concentration of Sn in the standards that are scanned. The column "I Comp" indicates the detected Compton normalized XRF K α -intensities. The column "Number of layers" indicates the number of calibration standards placed on the piece of boat hull material; i.e. the number of layers which are scanned by the handheld XRF-instrument. The column "First paint layer" indicates the calibration standard closest to the XRF-instrument, i.e. the handheld XRF instrument is pointed towards the "First paint layer" and a scan is performed. The layer/standard underneath is referred to as "Second paint layer" and the one layer/standard underneath the "Second paint layer" is referred to as "Third paint layer". The most bottom layer is in contact with the piece of boat hull material. The % TBTO value in parenthesis represents the concentration (weight:weight) of wet layer of TBTO applied to the film in the method for manufacturing said set of calibration standards.

Scan identity	Sn $\mu\text{g}/\text{cm}^2$	I Comp	Number of layers	First paint layer	Second paint layer	Third paint layer
1	0	-0,002	3	Sn, Cu and Zn free (0% TBTO)	Cu and Zn (0% TBTO)	Cu and Zn (0% TBTO)
2	117	0,594	3	Sn (1% TBTO)	Sn (1% TBTO)	Sn (1% TBTO)
3	329	1,426	3	Sn (2% TBTO)	Sn (2% TBTO)	Sn (1% TBTO)
4	886	3,740	3	Sn (4% TBTO)	Sn (4% TBTO)	Sn (4% TBTO)
5	1056	4,411	3	Sn (8% TBTO)	Sn (8% TBTO)	Sn (8% TBTO)
6	3204	15,170	3	Sn (16% TBTO)	Sn (16% TBTO)	Sn (8% TBTO)
7	5596	34,256	3	Sn (32% TBTO)	Sn (32% TBTO)	Sn (32% TBTO)
8	199	0,939	1	Sn and Zn (4% TBTO)		
9	1254	5,665	1	Sn (16% TBTO)		
10	151	0,660	1	Sn (2% TBTO)		
11	538	2,837	1	Sn (8% TBTO)		
12	1745	10,753	1	Sn (32% TBTO)		
13	350	1,446	1	Sn (8% TBTO)		
14	0	-0,004	1	Cu and Zn (0% TBTO)		
19	0	-0,006	1	Cu (0% TBTO)		
20	0	-0,006	1	Cu (0% TBTO)		
21	0	-0,005	1	Cu (0% TBTO)		
22	0	-0,004	1	Cu (0% TBTO)		
23	0	0,000	1	Cu (0% TBTO)		
24	0	-0,006	3	Cu (0% TBTO)	Cu (0% TBTO)	Cu (0% TBTO)

25	0	0,000	3	Cu (0% TBTO)	Cu (0% TBTO)	Cu (0% TBTO)
26	0	-0,007	3	Cu (0% TBTO)	Cu (0% TBTO)	Cu (0% TBTO)
27	0	-0,002	3	Cu (0% TBTO)	Cu (0% TBTO)	Cu (0% TBTO)
28	0	0,003	3	Cu (0% TBTO)	Cu (0% TBTO)	Cu (0% TBTO)
31	50,6	0,232	3	Cu (0% TBTO)	Cu (0% TBTO)	Sn (1% TBTO)
32	1254	5,053	3	Cu (0% TBTO)	Cu (0% TBTO)	Sn (16% TBTO)
33	647,3	2,532	3	Cu (0% TBTO)	Cu (0% TBTO)	Sn (8% TBTO)
34	1303	5,490	3	Cu (0% TBTO)	Cu (0% TBTO)	Sn (16% TBTO)
35	0	-0,005	3	Zn (0% TBTO)	Zn (0% TBTO)	Zn (0% TBTO)
36	0	-0,005	3	Zn (0% TBTO)	Zn (0% TBTO)	Zn (0% TBTO)
37	0	-0,006	3	Zn (0% TBTO)	Zn (0% TBTO)	Zn (0% TBTO)
38	0	-0,007	3	Zn (0% TBTO)	Zn (0% TBTO)	Zn (0% TBTO)
39	0	0,001	3	Zn (0% TBTO)	Zn (0% TBTO)	Zn (0% TBTO)
40	538	2,638	3	Zn (0% TBTO)	Zn (0% TBTO)	Sn (8% TBTO)
41	304	1,207	3	Zn (0% TBTO)	Zn (0% TBTO)	Sn (4% TBTO)
42	51	0,200	3	Zn (0% TBTO)	Zn (0% TBTO)	Sn (1% TBTO)
43	1303	5,087	3	Zn (0% TBTO)	Zn (0% TBTO)	Sn (16% TBTO)
44	350	1,399	3	Cu (0% TBTO)	Zn (0% TBTO)	Sn (8% TBTO)
45	307	1,264	3	Cu (0% TBTO)	Zn (0% TBTO)	Sn (4% TBTO)
46	51	0,199	3	Cu (0% TBTO)	Zn (0% TBTO)	Sn (1% TBTO)
47	1254	5,019	3	Cu (0% TBTO)	Zn (0% TBTO)	Sn (16% TBTO)
48	1814	10,203	1	Sn (32% TBTO)		
49	3676	21,128	2	Sn (32% TBTO)	Sn (32% TBTO)	
50	1254	5,867	1	Sn (32% TBTO)		
51	0	0,004	1	Sn, Cu and Zn free (0% TBTO)		
52	0	-0,013	1	Zn (0% TBTO)		
53	0	-0,003	1	Zn (0% TBTO)		

54	0	-0,010	1	Zn (0% TBTO)			
55	0	-0,009	1	Zn (0% TBTO)			
56	41,1	0,212	1	Sn (1% TBTO)			
57	39,2	0,213	1	Sn (1% TBTO)			
58	50,6	0,222	1	Sn (1% TBTO)			
59	37,1	0,203	1	Sn (1% TBTO)			

Table 2. The column "Scan identity" indicates a scan performed on the a layer of standards; please observe that Scan 1, 2, 3 etc. in Tables1-3 is the same scan, i.e. Sn, Cu and Zn are scanned at the same time. The column titled "Zn $\mu\text{g}/\text{cm}^2$ " discloses the total chemically analyzed area concentration of Zn in the standards that are scanned. The column "I Comp" indicates the detected Compton normalized XRF K α -intensities. The column "Number of layers" indicates the number of calibration standards placed on the piece of boat hull material; i.e. the number of layers which are scanned by the handheld XRF-instrument. The column "First paint layer" indicates the calibration standard closest to the XRF-instrument, i.e. the handheld XRF instrument is pointed towards the "First paint layer" and a scan is performed. The layer/standard underneath is referred to as "Second paint layer" and the one layer/standard underneath the "Second paint layer" is referred to as "Third paint layer" etc. The most bottom layer is in contact with the piece of boat hull material. The % ZnO value in parenthesis represents the concentration (weight:weight) of wet layer of ZnO applied to the film in the method for manufacturing said set of calibration standards.

Scan identity	Zn $\mu\text{g}/\text{cm}^2$	I comp	Number of layers	First paint layer	Second paint layer	Third paint layer	Fourth paint layer	Fifth paint layer
1	688	1,678	3	Sn, Cu and Zn free (0% ZnO)	Cu and Zn (2% ZnO)	Cu and Zn (4% ZnO)		
2	0	0,004	3	Sn (0% ZnO)	Sn (0% ZnO)	Sn (0% ZnO)		
3	0	0,007	3	Sn (0% ZnO)	Sn (0% ZnO)	Sn (0% ZnO)		
4	0	0,006	3	Sn (0% ZnO)	Sn (0% ZnO)	Sn (0% ZnO)		
5	0	0,004	3	Sn (0% ZnO)	Sn (0% ZnO)	Sn (0% ZnO)		
6	0	0,006	3	Sn (0% ZnO)	Sn (0% ZnO)	Sn (0% ZnO)		
7	0	0,009	3	Sn (0% ZnO)	Sn (0% ZnO)	Sn (0% ZnO)		
8	4146	18,078	1	Sn and Zn (32% ZnO)				
9	0	0,052	1	Sn (0% ZnO)				
10	0	0,058	1	Sn (0% ZnO)				
11	0	0,052	1	Sn (0% ZnO)				
13	0	0,051	1	Sn (0% ZnO)				
14	457	1,631	1	Cu and Zn (4% ZnO)				
15	1090	4,859	1	Cu and Zn (8% ZnO)				
16	761	2,117	1	Cu and Zn (8% ZnO)				

17	1203	2,943	1	Cu and Zn (8% ZnO)					
18	432	1,639	1	Cu and Zn (4% ZnO)					
19	45	0,212	1	Cu (0% ZnO)					
20	20	0,149	1	Cu (0% ZnO)					
21	24	0,140	1	Cu (0% ZnO)					
22	231	0,980	1	Cu (2% ZnO)					
23	232	1,219	1	Cu (2% ZnO)					
31	0	0,041	3	Cu (0% ZnO)	Cu (0% ZnO)		Sn (0% ZnO)		
32	0	0,045	3	Cu (0% ZnO)	Cu (0% ZnO)		Sn (0% ZnO)		
35	298,3	0,904	3	Zn (2% ZnO)	Zn (2% ZnO)		Zn (2% ZnO)		
36	771,4	2,171	3	Zn (4% ZnO)	Zn (4% ZnO)		Zn (4% ZnO)		
37	1768	5,157	3	Zn (8% ZnO)	Zn (8% ZnO)		Zn (8% ZnO)		
38	4623	12,484	3	Zn (16% ZnO)	Zn (16% ZnO)		Zn (16% ZnO)		
39	8390	23,854	3	Zn (32% ZnO)	Zn (32% ZnO)		Zn (32% ZnO)		
40	200	0,733	3	Zn (2% ZnO)	Zn (2% ZnO)		Sn (0% ZnO)		
41	512,6	1,811	3	Zn (4% ZnO)	Zn (4% ZnO)		Sn (0% ZnO)		
42	1202	4,029	3	Zn (8% ZnO)	Zn (8% ZnO)		Sn (0% ZnO)		
43	3052	10,552	3	Zn (16% ZnO)	Zn (16% ZnO)		Sn (0% ZnO)		
44	259	0,646	3	Cu (0% ZnO)	Zn (4% ZnO)		Sn (0% ZnO)		
45	100	0,317	3	Cu (0% ZnO)	Zn (2% ZnO)		Sn (0% ZnO)		
46	567	1,651	3	Cu (0% ZnO)	Zn (8% ZnO)		Sn (0% ZnO)		
47	1497	4,707	3	Cu (0% ZnO)	Zn (16% ZnO)		Sn (0% ZnO)		
52	915	2,518	1	Zn (8% ZnO)					
53	1571	5,383	1	Zn (16% ZnO)					
60	1555	5,352	1	Zn (16% ZnO)					
61	2856	11,456	1	Zn (32% ZnO)					
62	5720	18,289	2	Zn (32% ZnO)	Zn (32% ZnO)				

63	8390	23,994	3	Zn (32% ZnO)	Zn (32% ZnO)	Zn (32% ZnO)		
64	11015	29,353	4	Zn (32% ZnO)	Zn (32% ZnO)	Zn (32% ZnO)	Zn (32% ZnO)	
65	13530	32,944	5	Zn (32% ZnO)	Zn (32% ZnO)	Zn (32% ZnO)	Zn (32% ZnO)	
66	0	0,053	1	Sn (0% ZnO)				
67	0	0,051	1	Sn (0% ZnO)				
68	0	0,050	1	Sn (0% ZnO)				
69	0	0,057	1	Sn (0% ZnO)				
56	0	0,055	1	Sn (0% ZnO)				
57	0	0,058	1	Sn (0% ZnO)				
58	0	0,051	1	Sn (0% ZnO)				
59	0	0,049	1	Sn (0% ZnO)				

Table 3. The column "Scan identity" indicates a scan performed on the a layer of standards; please observe that Scan 1, 2, 3 etc. in Tables1-3 is the same scan, i.e. Sn, Cu and Zn are scanned at the same time. The column titled "Cu $\mu\text{g}/\text{cm}^2$ " discloses the total chemically analyzed area concentration of Cu in the standards that are scanned. The column "I Comp" indicates the detected Compton normalized XRF K α -intensities. The column "Number of layers" indicates the number of calibration standards placed on the piece of boat hull material; i.e. the number of layers which are scanned by the handheld XRF-instrument. The column "First paint layer" indicates the calibration standard closest to the XRF-instrument, i.e. the handheld XRF instrument is pointed towards the "First paint layer" and a scan is performed. The layer/standard underneath is referred to as "Second paint layer" and the one layer/standard underneath the "Second paint layer" is referred to as "Third paint layer" etc. The most bottom layer is in contact with the piece of boat hull material. The % CuO value in parenthesis represents the concentration (weight:weight) of wet layer of CuO applied to the film in the method for manufacturing said set of calibration standards.

Scan identity	Cu $\mu\text{g}/\text{cm}^2$	I comp	Number of layers	First paint layer	Second paint layer	Third paint layer	Forth paint layer
1	1111	1,550	3	Sn, Cu and Zn free	Cu and (1% CuO)	Cu an Zn (4% CuO)	
2	102	0,096	3	Sn	Sn	Sn	
3	94	0,094	3	Sn	Sn	Sn	
4	95	0,099	3	Sn	Sn	Sn	
5	99	0,103	3	Sn	Sn	Sn	
6	92	0,110	3	Sn	Sn	Sn	
7	64	0,109	3	Sn	Sn	Sn	
10	38	0,061	1	Sn			
11	32	0,073	1	Sn			
12	27	0,060	1	Sn			
13	30	0,067	1	Sn			
14	305	0,894	1	Cu and Zn (1% CuO)			
15	1065	2,101	1	Cu and Zn (4% CuO)			
16	1048	1,972	1	Cu and Zn (4% CuO)			
17	1753	2,943	1	Cu and Zn (8% CuO)			
18	661	1,802	1	Cu and Zn (2% CuO)			

19	4663	13,152	1	Cu (32% CuO)				
20	2083	5,357	1	Cu (16% CuO)				
21	2083	2,374	1	Cu (8% CuO)				
22	806	1,804	1	Cu (4% CuO)				
23	5022	9,264	1	Cu (32% CuO)				
24	666,7	1,248	3	Cu (2% CuO)	Cu (2% CuO)		Cu (2% CuO)	
25	727	1,165	3	Cu (2% CuO)	Cu (2% CuO)		Cu (2% CuO)	
26	1300,5	2,481	3	Cu (4% CuO)	Cu (4% CuO)		Cu (4% CuO)	
27	2732	5,496	3	Cu (8% CuO)	Cu (8% CuO)		Cu (8% CuO)	
28	6134	11,546	3	Cu (16% CuO)	Cu (16% CuO)		Cu (16% CuO)	
29	13373	25,174	3	Cu (32% CuO)	Cu (32% CuO)		Cu (32% CuO)	
30	10936	18,802	3	Cu (16% CuO)	Cu (32% CuO)		Cu (32% CuO)	
31	476,4	1,058	3	Cu (2% CuO)	Cu (2% CuO)		Sn (0% CuO)	
32	461	1,121	3	Cu (2% CuO)	Cu (2% CuO)		Sn (0% CuO)	
33	1859	4,713	3	Cu (8% CuO)	Cu (8% CuO)		Sn (0% CuO)	
34	1855	4,952	3	Cu (8% CuO)	Cu (8% CuO)		Sn (0% CuO)	
35	0	-0,011	3	Zn (0% CuO)	Zn (0% CuO)		Zn (0% CuO)	
36	0	-0,011	3	Zn (0% CuO)	Zn (0% CuO)		Zn (0% CuO)	
37	0	-0,007	3	Zn (0% CuO)	Zn (0% CuO)		Zn (0% CuO)	
38	0	0,003	3	Zn (0% CuO)	Zn (0% CuO)		Zn (0% CuO)	
40	32	0,023	3	Zn (0% CuO)	Zn (0% CuO)		Sn (0% CuO)	
41	32	0,020	3	Zn (0% CuO)	Zn (0% CuO)		Sn (0% CuO)	
42	34	0,028	3	Zn (0% CuO)	Zn (0% CuO)		Sn (0% CuO)	
43	30	0,028	3	Zn (0% CuO)	Zn (0% CuO)		Sn (0% CuO)	
44	279	0,700	3	Cu (2% CuO)	Zn (0% CuO)		Sn (0% CuO)	
45	502	1,463	3	Cu (4% CuO)	Zn (0% CuO)		Sn (0% CuO)	
46	2117	6,215	3	Cu (16% CuO)	Zn (0% CuO)		Sn (0% CuO)	

	47	932	3,085	3	Cu (8% CuO)	Zn (0% CuO)	Sn (0% CuO)	
	70	4663	13,152	1	Cu (32% CuO)			
	71	2083	5,270	1	Cu (16% CuO)			
	72	461	1,241	1	Cu (4% CuO)			
	73	4512	12,117	1	Cu (32% CuO)			
	74	9565	20,841	2	Cu (32% CuO)	Cu (32% CuO)		
	75	14062	26,259	3	Cu (32% CuO)	Cu (32% CuO)	Cu (32% CuO)	
	76	18748	30,64	4	Cu (32% CuO)	Cu (32% CuO)	Cu (32% CuO)	Cu (32% CuO)
	77	246	0,637	1	Cu (2% CuO)			
	78	3866	4,01	3	Cu and Zn (8% CuO)	Cu and Zn (4% CuO)	Cu and Zn (4% CuO)	
	51	0	-0,006		Sn, Cu and Zn free (0% CuO)			
	52	0	-0,002		Zn (0% CuO)			
	53	0	-0,001		Zn (0% CuO)			
	54	0	-0,006		Zn (0% CuO)			
	55	0	0,006		Zn (0% CuO)			

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CLAIMS

1. A method for manufacturing a set of calibration standards for use in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument, wherein said method for manufacturing comprises the steps of:
 - a. Manufacturing calibration standards for tin compounds comprising the steps of:
 - i. Applying increasing amounts of tin compounds to anti-fouling paints both separately and in combination with copper compounds and/or zinc compounds to yield a concentration interval between 0-64% for each of tin, copper and zinc compounds, wherein said anti-fouling paint to be used in step ai) does not comprise tin, copper and zinc compounds, and
 - ii. mixing the paints with respective compounds, and
 - iii. applying paints on a thin film to obtain a wet layer of paint, and
 - iv. drying the paint, and
 - b. Manufacturing calibration standards for copper compounds comprising the steps of:
 - i. Applying increasing amounts of copper compounds to anti-fouling paints both separately and in combination with zinc compounds to yield a concentration interval between 0-64% for each of copper and zinc compounds, wherein said anti-fouling paint to be used in step bi) does not comprise tin, copper and zinc compounds, and
 - ii. mixing the paints with respective compounds, and
 - iii. applying paints on a thin film to obtain a wet layer of paint, and
 - iv. drying the paint, and
 - c. Manufacturing calibration standards for zinc compounds comprising the steps of:
 - i. Applying increasing amounts of zinc compounds to anti-fouling paints to yield a concentration interval between 0-64% for zinc compounds, wherein said anti-fouling paint to be used in step ci) does not comprise tin, copper and zinc compounds, and
 - ii. mixing the paints with respective compounds, and

- iii. applying paints on a thin film to obtain a wet layer of paint, and,
 - iv. drying the paint,
- and optionally

d. Manufacturing calibration standards for further compounds comprising the steps of:

- i. Applying increasing amounts of further compound to anti-fouling paints both separately and in combination with tin, copper and zinc compounds to yield a concentration interval between 0-64 %, preferably 0-32%, for each of tin, copper and zinc compounds, wherein said anti-fouling paint in step di) does not comprise any of tin, copper and zinc compounds, and
- ii. mixing the paints with respective compounds, and
- iii. applying paints on a thin film to obtain a wet layer of paint, and
- iv. drying the paint,

and wherein said further compounds is selected from one or more of organic mercury, inorganic mercury, inorganic lead, organic lead, arsenic, cadmium, chromium, iron and barium compounds.

2. A method according to claim 1, wherein said film is plastic film, preferably polyester film or polyethylene film, more preferably polyester film, and even more preferably Mylar® film, and wherein said film has thickness of 2-10 μm , preferably a thickness of 2.5 μm , 3.6 μm or 6.3 μm , and more preferably a thickness of 6.3 μm .
3. Method according to any one of claims 1 or 2, wherein the wet layer of paint has a thickness of about 10-500 μm , preferably 50, 100, 150 and 200 μm , and more preferably 100 μm .
4. Method according to any one of claims 1-3, wherein the wet layer of paint has a thickness of 100 μm , and a concentration interval 0-32% of wet layer of tin, copper and zinc compounds applied to the film, wherein said 0-32% corresponds to an area concentration of dry tin, copper and zinc compounds of 0-1800 $\mu\text{g}/\text{cm}^2$ Sn, 0-4700 $\mu\text{g}/\text{cm}^2$ Cu and 0-2800 $\mu\text{g}/\text{cm}^2$ Zn.

5. Method according to any one of claims 1-4, wherein the concentration for each of tin, copper and zinc compounds applied on the film is 0-32 %, more preferably, 0%, 1%, 2%, 4%, 8%, 16% and/or 32%.
6. Method according to any one of claims 1-5, comprising the steps of:
 - a. Manufacturing calibration standards for tin compounds comprising the steps of:
 - i. Preparing calibration standards comprising tin compounds, wherein said concentrations of tin compounds is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and
 - ii. Preparing calibration standards comprising both tin and copper compounds, wherein said concentrations of each of tin and copper compounds is between 0-32 %, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and
 - iii. Preparing calibration standards comprising both tin and zinc compounds, wherein said concentrations of each compound is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and,
 - iv. Preparing calibration standards comprising tin, copper and zinc compounds, wherein said concentrations of each compound is between 0-32 %, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and,
 - b. Manufacturing calibration standards for copper compounds comprising the steps of:
 - i. Preparing calibration standards comprising copper compounds, wherein said concentrations of copper compounds is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and
 - ii. Preparing calibration standards comprising both copper compounds and zinc compounds , wherein said concentrations of each of copper and zinc compounds is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and,
 - c. Manufacturing calibration standards for zinc compounds comprising the steps of:

- i. Preparing calibration standards comprising zinc compounds, wherein said concentrations of zinc compounds is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%.

7. Method according to any one of claims 1-6, comprising the steps of:

- a. Manufacturing calibration standards for tin compounds comprising the steps of:
 - i. Preparing calibration standards comprising 1%, 2%, 4%, 8%, 16% and 32% tin compounds, and
 - ii. Preparing calibration standards comprising both tin and zinc compounds, wherein the concentration of tin compounds is 4% and the concentration of zinc compounds is 32%, and
- b. Manufacturing calibration standards for copper compounds comprising the steps of:
 - i. Preparing calibration standards comprising 1%, 2%, 4%, 8%, 16% and 32% copper compounds, and
 - ii. Preparing calibration standards comprising both copper compounds and zinc compounds, wherein the concentrations of copper and zinc compounds are:
 - 1% and 4% copper and zinc compounds respectively
 - 4% and 8% copper and zinc compounds respectively
 - 8% and 8% copper and zinc compounds respectively
 - 2% and 4% copper and zinc compounds respectively
 - 4% and 4% copper and zinc compounds respectively
 - 1% and 2% copper and zinc compounds respectivelyand,
- c. Manufacturing calibration standards for zinc compounds comprising the steps of:
 - i. Preparing calibration standards comprising 2%, 4%, 8%, 16% and 32% zinc compounds, and
- d. Manufacturing calibration standards free of tin, copper and zinc compounds.

8. A method according to any one of claims 1-7, wherein said tin compounds is tin metal powder, inorganic tin or one or more organotin compounds, wherein said organotin compounds is preferably selected from one or more of, tributyltin, triphenyltin and dibutyltin compounds, wherein said tributyltin and triphenyltin compounds are preferably selected from tributyltin oxide, tributyltin hydride, tributyltin adipate, tributyltin dodecenyl succinate, tributyltin sulfide, tributyltin acetate, tributyltin acrylate, tributyltin fluoride, tributyltin methacrylate, tributyltin resinate, triphenyltin oxide, triphenyltin hydride, triphenyltin hydroxide, triphenyltin chloride and triphenyltin acetate, and wherein said copper compounds is inorganic copper, preferably selected from Cu_2O , CuSCN and copper metal powder, and wherein said zinc compounds is inorganic zinc, preferably selected from zinc metal powder, ZnO and ZnSO_4 .
9. Method according to any one of claims 1-8, wherein said tin compounds is the tributyltin compound tributyltin oxide, and wherein said copper compounds is Cu_2O , and wherein said zinc compounds is ZnO .
10. A set of calibration standards for use in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument, comprising,
 - a. Calibration standards for tin compounds comprising a thin film coated by a layer of anti-fouling paint comprising tin compounds both separately or in combination with copper compounds and/or zinc compounds with a concentration interval between 0-64% for each of tin, copper and zinc compounds, and
 - b. Calibration standards for copper compounds comprising a thin film coated by a layer of anti-fouling paint comprising copper compounds both separately and in combination with zinc compounds with a concentration interval between 0-64% for each of copper and zinc compounds, and
 - c. Calibration standards for zinc compounds comprising a thin film coated by a layer of anti-fouling paint comprising zinc compounds with a concentration interval between 0-64% for each of tin, copper and zinc compounds, and

wherein said concentration interval 0-64% represents the concentration of wet layer of tin, copper and zinc compounds applied to the film in the method for manufacturing said set of calibration standards,

and optionally the set of calibration standards comprises,

- d. Calibration standards for further compounds comprising a thin film coated by a layer of anti-fouling paint comprising further compounds both separately and in combination with tin, copper and zinc compounds with a concentration interval between 0-64% for each of tin, zinc and copper compounds, and

wherein said further compounds is selected from one or more of organic mercury, inorganic mercury, inorganic lead, organic lead, arsenic, cadmium, chromium, iron and barium compounds

11. A set of calibration standards according to claim 10, wherein the said film is plastic, preferably polyester film, more preferably Mylar® film, and wherein said film has thickness of 2-10 μm , or preferably 2.5 μm , 3.6 μm or 6.3 μm , or more preferably 6.3 μm .

12. A set of calibration standards according to any one of claims 10 or 11, wherein the wet layer of paint has a thickness of about 10-500 μm , preferably 50, 100, 150 and 200 μm , more preferably 100 μm .

13. A set of calibration standards according to any one of claims 10-12, wherein the concentration for each of tin, copper and zinc compounds applied on the film is 0-32%, more preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%.

14. A set of calibration standards according to any one of claims 10-13, wherein said wet layer of paint has a thickness of 100 μm , and a concentration interval 0-32% of wet layer of tin, copper and zinc compounds applied to the film corresponding to an area concentration of dry tin, copper and zinc compounds of 0-1800 $\mu\text{g}/\text{cm}^2$ Sn, 0-4700 $\mu\text{g}/\text{cm}^2$ Cu and 0-2800 $\mu\text{g}/\text{cm}^2$ Zn.

15. A set of calibration standards according to any one of claims 10-14, comprising:

a. Calibration standards for tin compounds comprising:

- i. Calibration standards comprising tin compounds, wherein said concentrations of tin compounds is between 0-32 %, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and
- ii. Calibration standards comprising both tin and copper compounds, wherein said concentrations of each of tin and copper compounds is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and
- iii. Calibration standards comprising both tin and zinc compounds, wherein said concentrations of each is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and
- iv. Calibration standards comprising tin, copper and zinc compounds, wherein said concentrations of each compound is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and

b. Calibration standards for copper compounds comprising:

- i. Calibration standards comprising copper compounds, wherein said concentrations of copper compounds is between 0-32 %, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and
- ii. Calibration standards comprising both copper and zinc compounds, wherein said concentrations of each of copper and zinc compounds is between 0-32%, preferably chosen from the concentrations 0%, 1%, 2%, 4%, 8%, 16% and/or 32%, and

c. Calibration standards for zinc compounds comprising:

- i. Calibration standards comprising zinc compounds, wherein said concentrations of zinc compounds is between 0-32%, preferably 0%, 1%, 2%, 4%, 8%, 16% and/or 32%.

16. A set of calibration standards according to any one of claims 10-15, comprising:

a. Calibration standards for tin compounds comprising:

- i. Calibration standards comprising 1%, 2%, 4%, 8%, 16% and 32% tin compounds, and
- ii. Calibration standards comprising both tin and zinc compounds, wherein the concentration of tin compounds is 4 % and the concentration of zinc compounds is 32 %, and
- b. Calibration standards for copper compounds comprising:
 - i. Calibration standards comprising 1%, 2%, 4%, 8%, 16% and 32% copper compounds, and
 - ii. Calibration standards comprising both copper compounds and zinc compounds, wherein the concentrations of copper and zinc compounds are:
 - 1% and 4% copper and zinc compounds respectively
 - 4% and 8% copper and zinc compounds respectively
 - 8% and 8% copper and zinc compounds respectively
 - 2% and 4% copper and zinc compounds respectively
 - 4% and 4% copper and zinc compounds respectively
 - 1% and 2% copper and zinc compounds respectively and,
- c. Calibration standards for zinc compounds comprising:
 - i. Calibration standards comprising 2%, 4%, 8%, 16% and 32% zinc compounds, and
- d. Calibration standards free of tin, copper and zinc compounds.

17. A set of calibration standards according to any one of claims 10-16, wherein said tin compounds is tin metal powder, inorganic tin or one or more organotin compounds, wherein one or more organotin compounds is preferably selected from, tributyltin, triphenyltin and dibutyltin compounds, wherein said tributyltin and triphenyltin compounds are preferably selected from tributyltin oxide, tributyltin hydride, tributyltin adipate, tributyltin dodecenyl succinate, tributyltin sulfide, tributyltin acetate, tributyltin acrylate, tributyltin fluoride, tributyltin methacrylate, tributyltin resinate, triphenyltin oxide, triphenyltin hydride, triphenyltin hydroxide, triphenyltin chloride and triphenyltin acetate, and wherein said copper compounds is inorganic copper, preferably selected from

Cu₂O, CuSCN and copper metal powder, and wherein said zinc compounds is inorganic zinc, preferably selected from zinc metal powder, ZnO and ZnSO₄.

18. A set of calibration standards according to any one of claims 10-17 wherein said tin compounds is tributyltin oxide, and wherein said copper compounds is Cu₂O, and wherein said zinc compounds is ZnO.
19. A kit for use in quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument, comprising said set of calibration standards according to claims 10-17.
20. Use of the set of calibration standards according to claims 1-19 in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument, comprising the steps of:
- Calibrating with calibration standards comprising the steps of:
Scanning the calibration standards of tin, copper and zinc compounds, both individually and together by applying two, three, four or five standards on top of each other and wherein a piece of a boat hull material is placed behind the standards during the scanning,
 - Providing calibration curves of tin, copper and zinc compounds by plotting log K_α-Compton adjusted intensities of Sn, Cu and Zn and log chemically measured concentrations in µg/cm² of Sn, Cu and Zn in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument,
 - Aiming a handheld XRF analyzer on the boat hull to be analyzed,
 - Scanning K_α-lines of Sn, Cu and Zn, wherein scanning is preferably for 5, 10, 15, 20, 30, 60 and 120 seconds, more preferably for 30 seconds,
 - Quantifying the concentration of tin, copper and zinc compounds by relating the detected K_α lines of Sn, Cu and Zn in the boat hull to the calibration curves of tin, copper and zinc compounds,
- wherein steps a-e optionally comprise the steps of calibrating, providing calibration curves, scanning and quantifying also further compounds, wherein said further compound is selected from one or more of organic mercury,

inorganic mercury, inorganic lead, organic lead, arsenic, cadmium, chromium, barium and iron compounds.

21. Use according to claim 20, comprising the steps of:

a. Calibrating with calibration standards comprising the steps of:

i.

- 1) Scanning each of the calibration standards for tin compounds when placed on a respective piece of a boat hull material, and
 - 2) Scanning each of the calibration standards for copper or zinc compounds when placed on each of the calibration standards of tin compounds in step i1, and
 - 3) Scanning each of the calibration standard for copper or zinc compounds when placed on each combination of calibration standards in step i2, and
 - 4) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step i3, and
 - 5) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step i4, and
- repeating previous steps i1-i5 by
- exchanging calibration standards for copper or zinc compounds in step i1 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in step i1 and i2 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in steps i1- i3 with calibration standards for tin, and

- exchanging calibration standards for copper or zinc compounds in steps i1-i4 with calibration standards for tin, and
- exchanging calibration standards for copper or zinc compounds in steps i1-i5 with calibration standards for tin, and

ii.

- 1) Scanning each of the calibration standards for copper compounds when placed on a respective piece of a boat hull material, and
- 2) Scanning each of the calibration standards for copper or zinc compounds when placed on each of the calibration standards of copper compounds in step ii1, and
- 3) Scanning each of the calibration standard for copper or zinc compounds when placed on each combination of calibration standards in step ii2, and
- 4) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step ii3, and
- 5) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step ii4, and

iii.

- 1) Scanning each of the calibration standards for zinc compounds when placed on a respective piece of a boat hull material, and
- 2) Scanning each of the calibration standards for copper or zinc compounds when placed on each of the calibration standards of zinc compounds in step iii1, and
- 3) Scanning each of the calibration standard for copper or zinc compounds when placed on each combination of calibration standards in step iii2, and

- 4) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step iii3, and
 - 5) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step iii4.
- b. Providing calibration curves of tin, copper and zinc compounds by plotting log K_{α} -Compton adjusted intensities of Sn, Cu and Zn and log chemically measured concentrations in $\mu\text{g}/\text{cm}^2$ of Sn, Cu and Zn in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument,
 - c. Aiming a handheld XRF analyzer on the boat hull to be analyzed,
 - d. Scanning K_{α} -lines of Sn, Cu and Zn wherein scanning is preferably for 5, 10, 15, 20, 30, 60 and 120 seconds, more preferably for 30 seconds,
 - e. Quantifying the concentration of tin, copper and zinc compounds by relating the detected K_{α} lines of Sn, Cu and Zn in the boat hull to the calibration curves of tin, copper and zinc compounds.

22. Use according to claim 21, comprising the steps of:

- a. Calibrating with calibration standards comprising the steps of:
 - i.
 - Placing each of the calibration standards for tin compounds comprising 1%, 1%, 4%, 8%, 8% and 32% tin compounds on a respective piece of boat hull material, and
 - Placing each of the calibration standards for tin compounds comprising 1%, 2%, 4%, 8%, 16% and 32% tin compounds on top of the previous standards comprising 1%, 1%, 4%, 8%, 8% and 32%, respectively, and
 - Placing each of the calibration standard for tin compounds comprising 1%, 2%, 4%, 8%, 16% and 32% tin compounds on top of the previous standards

comprising 1%, 2%, 4%, 8%, 16% and 32 % tin compounds, respectively, and

- Performing a scan of each of the resulting 6 combinations of layers, and

ii.

- Placing each of the calibration standards for tin compounds comprising 1%, 16%, 8% and 16 % tin compounds on a respective piece of a boat hull material, and
- Placing each of the calibration standard for copper compounds comprising 2%, 2%, 8% and 8 % copper compounds on top of the previous standards comprising 1%, 16%, 8% and 16 % tin compounds, respectively, and
- Placing each of the calibration standard for copper compounds comprising 2%, 2%, 8% and 8% copper compounds on top of the previous standards comprising 2%, 2%, 8% and 8% copper compounds, respectively, and
- Performing a scan of each of the resulting 4 combinations of layers, and

iii.

- Placing each of the calibration standards for tin compounds comprising 8%, 4%, 1%, 16% tin compounds on a respective piece of a boat hull material, and
- Placing each of the calibration standard for zinc compounds comprising 2%, 4%, 8% and 16% zinc compounds on top of the previous standards comprising 8%, 4%, 1% and 16 % tin compounds, respectively, and

- Placing each of the calibration standard for zinc compounds comprising 2%, 4%, 8% and 16% zinc compounds on top of the previous standards comprising 2%, 4%, 8% and 16% zinc compounds, respectively, and
- Performing a scan of each of the resulting 4 combinations of layers, and

iv.

- Placing each of the calibration standards for tin compounds comprising 8%, 4%, 1% and 16% tin compounds on a respective piece of a boat hull material, and
- Placing each of the calibration standards for zinc compounds comprising 4%, 2%, 8% and 16% zinc compounds on top of the previous standards comprising 8%, 4%, 1% and 16% tin compounds, respectively, and
- Placing each of the calibration standard for copper compounds comprising 2%, 4% 16%, 18% copper compounds on top of the previous standards comprising 4%, 2%, 8% and 16% zinc compounds, respectively, and
- Performing a scan of all of the resulting 4 combinations of layers, and

v. Scanning each of the calibration standards for tin compounds comprising 1%, 2%, 8%, 16% and 32% tin compounds when placed on a respective piece of a boat hull material, and

vi. Scanning a calibration standard for tin compounds comprising 32% tin compounds when placed on a piece of a boat hull material, and then placing a calibration standard for tin compounds comprising 32% tin compounds on top of the

previous standard placed on the piece of boat hull, and then performing a scan, and

vii. Scanning a calibration standard for tin compounds comprising 4% tin compounds and 32% zinc compounds, and

viii. Scanning a calibration standard free of tin, copper and zinc compounds, and

ix.

- Placing each of the calibration standards for copper compounds comprising 2%, 4%, 8%, 16%, 32% and 32% copper compounds on a respective piece of a boat hull material, and
- Placing the calibration standards for copper compounds comprising 2%, 4%, 8%, 16%, 32% and 32% copper compounds on top of the previous standards comprising 2%, 4%, 8%, 16%, 32% and 32% copper compounds, respectively, and
- Placing the calibration standards for copper compounds comprising 2%, 4%, 8%, 16%, 32% and 16% copper compounds on top of the previous standards comprising 2%, 4%, 8%, 16%, 32% and 32% copper compounds, respectively, and
- Performing a scan of all of the resulting 6 combinations of layers, and

x.

- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on a piece of a boat hull material, and
- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on top of the previous standard comprising 32% copper compounds, and

- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on top of the previous standard comprising 32% copper compounds, and
- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on top of the previous standard comprising 32% copper compounds, and

xi.

- Placing a calibration standard comprising 4% copper compounds and 8% zinc compounds on a piece of a boat hull material, and
- Placing a calibration standard comprising 4% copper compounds and 8% zinc compounds on top of the previous standard comprising 4% copper compounds and 8% zinc compounds, and
- Placing a calibration standard comprising 8% copper and 8% zinc compounds on top of the previous standard comprising 4% copper compounds and 8% zinc compounds, and
- Performing a scan, and

xii.

- Placing a calibration standard for copper compounds comprising 4% copper compounds and 4% zinc compounds on a piece of a boat hull material, and
- Placing a calibration standard comprising 1% copper compounds and 2% zinc compounds on top of the previous standard comprising 4% copper compounds and 4% zinc compounds, and
- Placing a calibration standard comprising 0% copper, 0% zinc and 0% tin compounds on top of the previous

standard comprising 1% copper compounds and 2% zinc compounds, and

- Performing a scan, and
- xiii. Scanning each of the calibration standards comprising 2%, 4%, 8%, 16% and 32% copper compounds when placed on a respective piece of a boat hull material, and
- xiv. Scanning each of the calibration standards comprising 1%, 4%, 4%, 8% and 2% copper compounds and 4%, 8%, 8%, 8% and 4% zinc compounds, respectively, when placed on a respective piece of a boat hull material, and
- xv.
- Placing each of the calibration standards for zinc compounds comprising 2%, 4%, 8%, 16% and 32% zinc compounds on a respective piece of a boat hull material, and
 - Placing each of the calibration standard for zinc compounds comprising 2%, 4%, 8%, 16% and 32% zinc compounds on top of the previous standards comprising 2%, 4%, 8%, 16% and 32% zinc compounds, respectively, and
 - Placing the calibration standard for zinc compounds comprising 2%, 4%, 8%, 16% and 32% zinc compounds on top of the previous standards comprising 2%, 4%, 8%, 16% and 32% zinc compounds, respectively, and
 - Performing a scan of all of the resulting 5 combinations of layers, and
- xvi.

- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on a piece of a boat hull material, and
 - Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, and
 - Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, and
 - Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, and
 - Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, and
- xvii. Scanning each of the calibration standards for zinc comprising 8%, 16% and 32% zinc compounds when placed on a respective piece of a boat hull material, and
- b. Providing calibration curves of tin, copper and zinc compounds by plotting log K_{α} -Compton adjusted intensities of Sn, Cu and Zn and log chemically measured concentrations in $\mu\text{g}/\text{cm}^2$ of Sn, Cu and Zn in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument,
- c. Aiming a handheld XRF analyzer on the boat hull to be analyzed,
- d. Scanning K_{α} -lines of Sn, Cu and Zn wherein scanning is preferably for 5, 10, 15, 20, 30, 60 and 120 seconds, more preferably for 30 seconds,

- e. Quantifying the concentration of tin, copper and zinc compounds by relating the detected K_{α} lines of Sn, Cu and Zn in the boat hull to the calibration curves of tin, copper and zinc compounds.
23. Use according to any one of claims 20-22, wherein said piece of boat hull material is of non-metallic material and free of anti-fouling paint.
24. Use according to any one of claims 20-23, wherein said tin compounds is tin metal powder, inorganic tin or one or more organotin compounds, more preferably said one or more organotin compounds is selected from tributyltin, triphenyltin and dibutyltin compounds, wherein said tributyltin and triphenyltin compounds are preferably selected from tributyltin oxide, tributyltin hydride, tributyltin adipate, tributyltin dodecenyl succinate, tributyltin sulfide, tributyltin acetate, tributyltin acrylate, tributyltin fluoride, tributyltin methacrylate, tributyltin resinate, triphenyltin oxide, triphenyltin hydride, triphenyltin hydroxide, triphenyltin chloride and triphenyltin acetate, and wherein said copper compounds is inorganic copper, preferably selected from Cu_2O , CuSCN and copper metal powder, and wherein said zinc compounds is inorganic zinc, preferably selected from selected from zinc metal powder, ZnO and ZnSO_4 .
25. Use according to any one of claims 20-24, wherein said tin compounds is tributyltin oxide, and wherein said copper compounds is Cu_2O , and wherein said zinc compounds is ZnO .
26. Use according to any one of claims 20-25, wherein said calibration curves are stored in said handheld XRF-instrument.
27. Method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument, by using the set of calibration standards according to claims 1-19, comprising the steps of:
- a. Calibrating with calibration standards comprising the steps of:
Scanning the calibration standards of tin, copper and zinc compounds, both individually and together by applying two, three, four or five

standards on top of each other and wherein a piece of a boat hull material is placed behind the standards during the scanning,

- b. Providing calibration curves of tin, copper and zinc compounds by plotting $\log K_{\alpha}$ -Compton adjusted intensities of Sn, Cu and Zn and $\log$ chemically measured concentrations in $\mu\text{g}/\text{cm}^2$ of Sn, Cu and Zn in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument,
- c. Aiming a handheld XRF analyzer on the boat hull to be analyzed,
- d. Scanning K_{α} -lines of Sn, Cu and Zn wherein scanning is preferably for 5, 10, 15, 20, 30, 60 and 120 seconds, more preferably for 30 seconds,
- e. Quantifying the concentration of tin, copper and zinc compounds by relating the detected K_{α} lines of Sn, Cu and Zn in the boat hull to the calibration curves of tin, copper and zinc compounds, wherein steps a-e optionally comprise the steps of calibrating, providing calibration curves, scanning and quantifying also further compounds, wherein said further compound is selected from one or more of organic mercury, inorganic mercury, inorganic lead, organic lead, arsenic, cadmium, chromium, barium and iron compounds.

28. Method according to claim 27, comprising the steps of:

- a. Calibrating with calibration standards comprising the steps of:
 - i.
 - 1) Scanning each of the calibration standards for tin compounds when placed on a respective piece of a boat hull material, and
 - 2) Scanning each of the calibration standards for copper or zinc compounds when placed on each of the calibration standards of tin compounds in step i1, and
 - 3) Scanning each of the calibration standard for copper or zinc compounds when placed on each combination of calibration standards in step i2, and
 - 4) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step i3, and

5) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step i4, and

- repeating previous steps i1-i5 by
 - exchanging calibration standards for copper or zinc compounds in step i1 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in step i1 and i2 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in steps i1- i3 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in steps i1-i4 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in steps i1-i5 with calibration standards for tin, and

ii.

- 1) Scanning each of the calibration standards for copper compounds when placed on a respective piece of a boat hull material, and
- 2) Scanning each of the calibration standards for copper or zinc compounds when placed on each of the calibration standards of copper compounds in step ii1, and
- 3) Scanning each of the calibration standard for copper or zinc compounds when placed on each combination of calibration standards in step ii2, and
- 4) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step ii3, and

- 5) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step ii4, and

iii.

- 1) Scanning each of the calibration standards for zinc compounds when placed on a respective piece of a boat hull material, and
- 2) Scanning each of the calibration standards for copper or zinc compounds when placed on each of the calibration standards of zinc compounds in step iii1, and
- 3) Scanning each of the calibration standard for copper or zinc compounds when placed on each combination of calibration standards in step iii2, and
- 4) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step iii3, and
- 5) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step iii4.

- b. Providing calibration curves of tin, copper and zinc compounds by plotting $\log K_{\alpha}$ -Compton adjusted intensities of Sn, Cu and Zn and $\log$ chemically measured concentrations in $\mu\text{g}/\text{cm}^2$ of Sn, Cu and Zn in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument,
- c. Aiming a handheld XRF analyzer on the boat hull to be analyzed,
- d. Scanning K_{α} -lines of Sn, Cu and Zn wherein scanning is preferably for 5, 10, 15, 20, 30, 60 and 120 seconds, more preferably for 30 seconds,
- e. Quantifying the concentration of tin, copper and zinc compounds by relating the detected K_{α} lines of Sn, Cu and Zn in the boat hull to the calibration curves of tin, copper and zinc compounds.

29. Method according to claims 27 or 28, comprising the steps of:

- a. Calibrating with calibration standards comprising the steps of:
 - i.

- Placing each of the calibration standards for tin compounds comprising 1%, 1%, 4%, 8%, 8% and 32% tin compounds on a respective piece of boat hull material, and
- Placing each of the calibration standards for tin compounds comprising 1%, 2%, 4%, 8%, 16% and 32% tin compounds on top of the previous standards comprising 1%, 1%, 4%, 8%, 8% and 32 %, respectively, and
- Placing each of the calibration standard for tin compounds comprising 1%, 2%, 4%, 8%, 16% and 32% tin compounds on top of the previous standards comprising 1%, 2%, 4%, 8%, 16% and 32% tin compounds, respectively, and
- Performing a scan of each of the resulting 6 combinations of layers, and

ii.

- Placing each of the calibration standards for tin compounds comprising 1%, 16%, 8% and 16% tin compounds on a respective piece of a boat hull material, and
- Placing each of the calibration standard for copper compounds comprising 2%, 2%, 8% and 8% copper compounds on top of the previous standards comprising 1%, 16%, 8% and 16% tin compounds, respectively, and
- Placing each of the calibration standard for copper compounds comprising 2%, 2%, 8% and 8% copper compounds on top of the previous standards comprising 2%, 2%, 8% and 8% copper compounds, respectively, and

- Performing a scan of each of the resulting 4 combinations of layers, and

iii.

- Placing each of the calibration standards for tin compounds comprising 8%, 4%, 1%, 16% tin compounds on a respective piece of a boat hull material, and
- Placing each of the calibration standard for zinc compounds comprising 2%, 4%, 8% and 16% zinc compounds on top of the previous standards comprising 8%, 4%, 1% and 16 % tin compounds, respectively, and
- Placing each of the calibration standard for zinc compounds comprising 2%, 4%, 8% and 16% zinc compounds on top of the previous standards comprising 2%, 4%, 8% and 16% zinc compounds, respectively, and
- Performing a scan of each of the resulting 4 combinations of layers, and

iv.

- Placing each of the calibration standards for tin compounds comprising 8%, 4%, 1% and 16% tin compounds on a respective piece of a boat hull material, and
- Placing each of the calibration standards for zinc compounds comprising 4%, 2%, 8% and 16% zinc compounds on top of the previous standards comprising 8%, 4%, 1% and 16% tin compounds, respectively, and
- Placing each of the calibration standard for copper compounds comprising 2%, 4% 16%, 18% copper compounds on top of the previous standards comprising

4%, 2%, 8% and 16 % zinc compounds, respectively,
and

- Performing a scan of all of the resulting 4 combinations of layers, and
- v. Scanning each of the calibration standards for tin compounds comprising 1%, 2%, 8%, 16% and 32% tin compounds when placed on a respective piece of a boat hull material, and
- vi. Scanning a calibration standard for tin compounds comprising 32% tin compounds when placed on a piece of a boat hull material, and then placing a calibration standard for tin compounds comprising 32% tin compounds on top of the previous standard placed on the piece of boat hull, and then performing a scan, and
- vii. Scanning a calibration standard for tin compounds comprising 4% tin compounds and 32% zinc compounds, and
- viii. Scanning a calibration standard free of tin, copper and zinc compounds, and
- ix.
 - Placing each of the calibration standards for copper compounds comprising 2%, 4%, 8%, 16%, 32% and 32 % copper compounds on a respective piece of a boat hull material, and
 - Placing the calibration standard for copper compounds comprising 2%, 4%, 8%, 16%, 32% and 32% copper compounds on top of the previous standards comprising 2%, 4%, 8%, 16%, 32% and 32% copper compounds, respectively, and
 - Placing the calibration standard for copper compounds comprising 2%, 4%, 8%, 16%, 32% and 16% copper

compounds on top of the previous standards comprising 2%, 4%, 8%, 16%, 32% and 32% copper compounds, respectively, and

- Performing a scan of all of the resulting 6 combinations of layers, and

x.

- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on a piece of a boat hull material, and
- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on top of the previous standard comprising 32% copper compounds, and
- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on top of the previous standard comprising 32% copper compounds, and
- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on top of the previous standard comprising 32% copper compounds, and

xi.

- Placing a calibration standard comprising 4% copper compounds and 8% zinc compounds on a piece of a boat hull material, and
- Placing a calibration standard comprising 4% copper compounds and 8% zinc compounds on top of the previous standard comprising 4% copper compounds and 8 % zinc compounds, and
- Placing a calibration standard comprising 8% copper and 8% zinc compounds on top of the previous standard

comprising 4% copper compounds and 8% zinc compounds, and

- Performing a scan, and

xii.

- Placing a calibration standard for copper compounds comprising 4% copper compounds and 4% zinc compounds on a piece of a boat hull material, and
- Placing a calibration standard comprising 1% copper compounds and 2% zinc compounds on top of the previous standard comprising 4% copper compounds and 4% zinc compounds, and
- Placing a calibration standard comprising 0% copper, 0% zinc and 0% tin compounds on top of the previous standard comprising 1% copper compounds and 2% zinc compounds, and
- Performing a scan, and

xiii. Scanning each of the calibration standards comprising 2%, 4%, 8%, 16% and 32% copper compounds when placed on a respective piece of a boat hull material, and

xiv. Scanning each of the calibration standards comprising 1%, 4%, 4%, 8% and 2% copper compounds and 4%, 8%, 8%, 8% and 4% zinc compounds, respectively, when placed on a respective piece of a boat hull material, and

xv.

- Placing each of the calibration standards for zinc compounds comprising 2%, 4%, 8%, 16% and 32% zinc compounds on a respective piece of a boat hull material, and

- Placing each of the calibration standard for zinc compounds comprising 2%, 4%, 8%, 16% and 32% zinc compounds on top of the previous standards comprising 2%, 4%, 8%, 16% and 32% zinc compounds, respectively, and
- Placing the calibration standard for zinc compounds comprising 2%, 4%, 8%, 16% and 32% zinc compounds on top of the previous standards comprising 2%, 4%, 8%, 16% and 32% zinc compounds, respectively, and
- Performing a scan of all of the resulting 5 combinations of layers, and

xvi.

- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on a piece of a boat hull material, and
- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, and
- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, and
- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, and
- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, and

- xvii. Scanning each of the calibration standards for zinc comprising 8%, 16% and 32% zinc compounds when placed on a respective piece of a boat hull material, and
 - b. Providing calibration curves of tin, copper and zinc compounds by plotting $\log K_{\alpha}$ -Compton adjusted intensities of Sn, Cu and Zn and $\log$ chemically measured concentrations in $\mu\text{g}/\text{cm}^2$ of Sn, Cu and Zn in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument,
 - c. Aiming a handheld XRF analyzer on the boat hull to be analyzed,
 - d. Scanning K_{α} -lines of Sn, Cu and Zn wherein scanning is preferably for 5, 10, 15, 20, 30, 60 and 120 seconds, more preferably for 30 seconds,
 - e. Quantifying the concentration of tin, copper and zinc compounds by relating the detected K_{α} lines of Sn, Cu and Zn in the boat hull to the calibration curves of tin, copper and zinc compounds.
30. Method according to any one of claims 27-29, wherein said piece of boat hull material is of non-metallic material and free of anti-fouling paint.
31. Method according to any one of claims 27-30, wherein said tin compounds is tin metal powder, inorganic tin or one or more organotin compounds, wherein said one or more organotin compounds is preferably selected from tributyltin, triphenyltin and dibutyltin compounds, wherein said tributyltin and triphenyltin compounds are preferably selected from tributyltin oxide, tributyltin hydride, tributyltin adipate, tributyltin dodecenyl succinate, tributyltin sulfide, tributyltin acetate, tributyltin acrylate, tributyltin fluoride, tributyltin methacrylate, tributyltin resinate, triphenyltin oxide, triphenyltin hydride, triphenyltin hydroxide, triphenyltin chloride and triphenyltin acetate, and wherein said copper compounds is inorganic copper, preferably selected from Cu_2O , CuSCN and copper metal powder, and wherein said zinc compounds is inorganic zinc, preferably selected from zinc metal powder, ZnO and ZnSO_4 .

32. Method according to any one of claims 27-31, wherein said tin compounds is tributyltin oxide, and wherein said copper compounds is Cu_2O , and wherein said zinc compounds is ZnO .
33. Method according to any one of claims 27-32, wherein said calibration curves are stored in said handheld XRF-instrument.
34. A method for calibration with a set of calibration standards according to claims 1-19, said method comprising the steps of:
- a. Calibrating with calibration standards comprising the steps of:
Scanning the calibration standards of tin, copper and zinc compounds both individually and together by applying two, three, four or five standards on top of each other and wherein a piece of a boat hull material is placed behind the standards during the scanning, and
 - b. Providing calibration curves of tin, copper and zinc compounds by plotting $\log K_\alpha$ -Compton adjusted intensities of Sn, Cu and Zn and $\log$ chemically measured concentrations in $\mu\text{g}/\text{cm}^2$ of Sn, Cu and Zn in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument, and
- wherein said method for calibration is used in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument,
- and optionally steps a and b comprise the steps of calibrating and providing calibration curves also of further compounds, wherein said further compound is selected from one or more of organic mercury, inorganic mercury, inorganic lead, organic lead, arsenic, cadmium, chromium, barium and iron compounds.
35. Method according to claim 34, comprising the steps of:
- a. Calibrating with calibration standards comprising the steps of:
 - i.

- 1) Scanning each of the calibration standards for tin compounds when placed on a respective piece of a boat hull material, and
- 2) Scanning each of the calibration standards for copper or zinc compounds when placed on each of the calibration standards of tin compounds in step i1, and
- 3) Scanning each of the calibration standard for copper or zinc compounds when placed on each combination of calibration standards in step i2, and
- 4) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step i3, and
- 5) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step i4, and
 - repeating previous steps i1-i5 by
 - exchanging calibration standards for copper or zinc compounds in step i1 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in step i1 and i2 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in steps i1- i3 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in steps i1-i4 with calibration standards for tin, and
 - exchanging calibration standards for copper or zinc compounds in steps i1-i5 with calibration standards for tin, and

ii.

- 1) Scanning each of the calibration standards for copper compounds when placed on a respective piece of a boat hull material, and
- 2) Scanning each of the calibration standards for copper or zinc compounds when placed on each of the calibration standards of copper compounds in step ii1, and
- 3) Scanning each of the calibration standard for copper or zinc compounds when placed on each combination of calibration standards in step ii2, and
- 4) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step ii3, and
- 5) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step ii4, and

iii.

- 1) Scanning each of the calibration standards for zinc compounds when placed on a respective piece of a boat hull material, and
 - 2) Scanning each of the calibration standards for copper or zinc compounds when placed on each of the calibration standards of zinc compounds in step iii1, and
 - 3) Scanning each of the calibration standard for copper or zinc compounds when placed on each combination of calibration standards in step iii2, and
 - 4) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step iii3, and
 - 5) Scanning the calibration standards for copper or zinc compounds when placed on each combination of calibration standards in step iii4,
- b. Providing calibration curves of tin, copper and zinc compounds by plotting $\log K_{\alpha}$ -Compton adjusted intensities of Sn, Cu and Zn and $\log$ chemically measured concentrations in $\mu\text{g}/\text{cm}^2$ of Sn, Cu and Zn in the

standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument.

36. A method according to claim 34 or 35, said method comprising the steps of:

a. Calibrating with calibration standards comprising the steps of:

i.

- Placing each of the calibration standards for tin compounds comprising 1%, 1%, 4%, 8%, 8% and 32% tin compounds on a respective piece of boat hull material, and
- Placing each of the calibration standards for tin compounds comprising 1%, 2%, 4%, 8%, 16% and 32% tin compounds on top of the previous standards comprising 1%, 1%, 4%, 8%, 8% and 32%, respectively, and
- Placing each of the calibration standard for tin compounds comprising 1%, 2%, 4%, 8%, 16% and 32% tin compounds on top of the previous standards comprising 1%, 2%, 4%, 8%, 16% and 32% tin compounds, respectively, and
- Performing a scan of each of the resulting 6 combinations of layers, and

ii.

- Placing each of the calibration standards for tin compounds comprising 1%, 16%, 8% and 16% tin compounds on a respective piece of a boat hull material, and
- Placing each of the calibration standard for copper compounds comprising 2%, 2%, 8% and 8% copper compounds on top of the previous standards comprising 1%, 16%, 8% and 16% tin compounds, respectively, and

- Placing each of the calibration standard for copper compounds comprising 2%, 2%, 8% and 8% copper compounds on top of the previous standards comprising 2%, 2%, 8% and 8% copper compounds, respectively, and
- Performing a scan of each of the resulting 4 combinations of layers, and

iii.

- Placing each of the calibration standards for tin compounds comprising 8%, 4%, 1% and 16% tin compounds on a respective piece of a boat hull material, and
- Placing each of the calibration standard for zinc compounds comprising 2%, 4%, 8% and 16% zinc compounds on top of the previous standards comprising 8%, 4%, 1%, 16% tin compounds, respectively, and
- Placing each of the calibration standard for zinc compounds comprising 2%, 4%, 8% and 16% zinc compounds on top of the previous standards comprising 2%, 4%, 8% and 16% zinc compounds, respectively, and
- Performing a scan of each of the resulting 4 combinations of layers, and

iv.

- Placing each of the calibration standards for tin compounds comprising 8%, 4%, 1% and 16% tin compounds on a respective piece of a boat hull material, and
- Placing each of the calibration standards for zinc compounds comprising 4%, 2%, 8% and 16% zinc

- compounds on top of the previous standards comprising 8%, 4%, 1% and 16% tin compounds, respectively, and
- Placing each of the calibration standard for copper compounds comprising 2%, 4%, 16%, 18% copper compounds on top of the previous standards comprising 4%, 2%, 8% and 16% zinc compounds, respectively, and
 - Performing a scan of all of the resulting 4 combinations of layers, and
- v. Scanning each of the calibration standards for tin compounds comprising 1%, 2%, 8%, 16% and 32% tin compounds when placed on a respective piece of a boat hull material, and
- vi. Scanning a calibration standard for tin compounds comprising 32% tin compounds when placed on a piece of a boat hull material, and then placing a calibration standard for tin compounds comprising 32% tin compounds on top of the previous standard placed on the piece of boat hull, and then performing a scan, and
- vii. Scanning a calibration standard for tin compounds comprising 4% tin compounds and 32% zinc compounds, and
- viii. Scanning a calibration standard free of tin, copper and zinc compounds, and
- ix.
- Placing each of the calibration standards for copper compounds comprising 2%, 4%, 8%, 16%, 32% and 32% copper compounds on a respective piece of a boat hull material, and
 - Placing the calibration standard for copper compounds comprising 2%, 4%, 8%, 16%, 32% and 32% copper

compounds on top of the previous standards comprising 2%, 4%, 8%, 16%, 32% and 32% copper compounds, respectively, and

- Placing the calibration standard for copper compounds comprising 2%, 4%, 8%, 16%, 32% and 16% copper compounds on top of the previous standards comprising 2%, 4%, 8%, 16%, 32% and 32% copper compounds, respectively, and
- Performing a scan of all of the resulting 6 combinations of layers, and

x.

- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on a piece of a boat hull material, and
- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on top of the previous standard comprising 32% copper compounds, and
- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on top of the previous standard comprising 32% copper compounds, and
- Scanning a calibration standard for copper compounds comprising 32% copper compounds when placed on top of the previous standard comprising 32% copper compounds, and

xi.

- Placing a calibration standard comprising 4% copper compounds and 8% zinc compounds on a piece of a boat hull material, and

- Placing a calibration standard comprising 4% copper compounds and 8% zinc compounds on top of the previous standard comprising 4 % copper compounds and 8 % zinc compounds, and
- Placing a calibration standard comprising 8% copper and 9 % zinc compounds on top of the previous standard comprising 4% copper compounds and 8% zinc compounds, and
- Performing a scan, and

xii.

- Placing a calibration standard for copper compounds comprising 4% copper compounds and 4% zinc compounds on a piece of a boat hull material, and
- Placing a calibration standard comprising 1% copper compounds and 2% zinc compounds on top of the previous standard comprising 4% copper compounds and 4% zinc compounds, and
- Placing a calibration standard comprising 0% copper, 0% zinc and 0% tin compounds on top of the previous standard comprising 1% copper compounds and 2% zinc compounds, and
- Performing a scan, and

xiii. Scanning each of the calibration standards comprising 2%, 4%, 8%, 16% and 32% copper compounds when placed on a respective piece of a boat hull material, and

xiv. Scanning each of the calibration standards comprising 1%, 4%, 4%, 8% and 2% copper compounds and 4%, 8%, 8%, 8% and 4% zinc compounds, respectively, when placed on a respective piece of a boat hull material, and

xv.

- Placing each of the calibration standards for zinc compounds comprising 2%, 4%, 8%, 16% and 32% zinc compounds on a respective piece of a boat hull material, and
- Placing each of the calibration standard for zinc compounds comprising 2%, 4%, 8%, 16% and 32% zinc compounds on top of the previous standards comprising 2%, 4%, 8%, 16% and 32% zinc compounds, respectively, and
- Placing the calibration standard for zinc compounds comprising 2%, 4%, 8%, 16% and 32% zinc compounds on top of the previous standards comprising 2%, 4%, 8%, 16% and 32% zinc compounds, respectively, and
- Performing a scan of all of the resulting 5 combinations of layers, and

xvi.

- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on a piece of a boat hull material, and
- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, and
- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, and
- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, and

- Scanning a calibration standard for zinc compounds comprising 32% zinc compounds when placed on top of the previous standard comprising 32% zinc compounds, and
- xvii. Scanning each of the calibration standards for zinc comprising 8%, 16% and 32% zinc compounds when placed on a respective piece of a boat hull material, and
- b. Providing calibration curves of tin, copper and zinc compounds by plotting log K_{α} -Compton adjusted intensities of Sn, Cu and Zn and log chemically measured concentrations in $\mu\text{g}/\text{cm}^2$ of Sn, Cu and Zn in the standards, respectively, and optionally storing said calibration curves in the memory of said XRF-instrument,

wherein said method for calibration is used in a method of quantifying the concentration of tin, copper and zinc compounds in anti-fouling paints with a handheld XRF instrument.

37. A method according to any one of claims 34-36, wherein said piece of boat hull material is of non-metallic material and free of anti-fouling paint.
38. Method according to any one of claims 34-37, wherein said tin compounds is tin metal powder, inorganic tin or one or more organotin compounds, wherein said one or more organotin compounds is preferably selected from tributyltin, triphenyltin and DBT (dibutyltin) compounds, wherein said tributyltin and triphenyltin compounds are preferably selected from tributyltin oxide, tributyltin hydride, triphenyltin hydride, triphenyltin hydroxide, tributyltin adipate, tributyltin dodecenyl succinate, tributyltin sulfide, tributyltin acetate, tributyltin acrylate, tributyltin fluoride, tributyltin methacrylate, tributyltin resinate, triphenyltin oxide, triphenyltin chloride and triphenyltin acetate, and wherein said copper compounds is inorganic copper, preferably selected from Cu_2O , CuSCN and copper metal powder, and wherein said zinc compounds is inorganic zinc, preferably selected from zinc metal powder, ZnO and ZnSO_4 .

39. Method according to any one of claims 34-38, wherein said tin compounds is tributyltin oxide, and wherein said copper compounds is Cu_2O , and wherein said zinc compounds is ZnO .
40. A method according to any one of claims 34-39, wherein said calibration curves are stored in said handheld XRF-instrument.

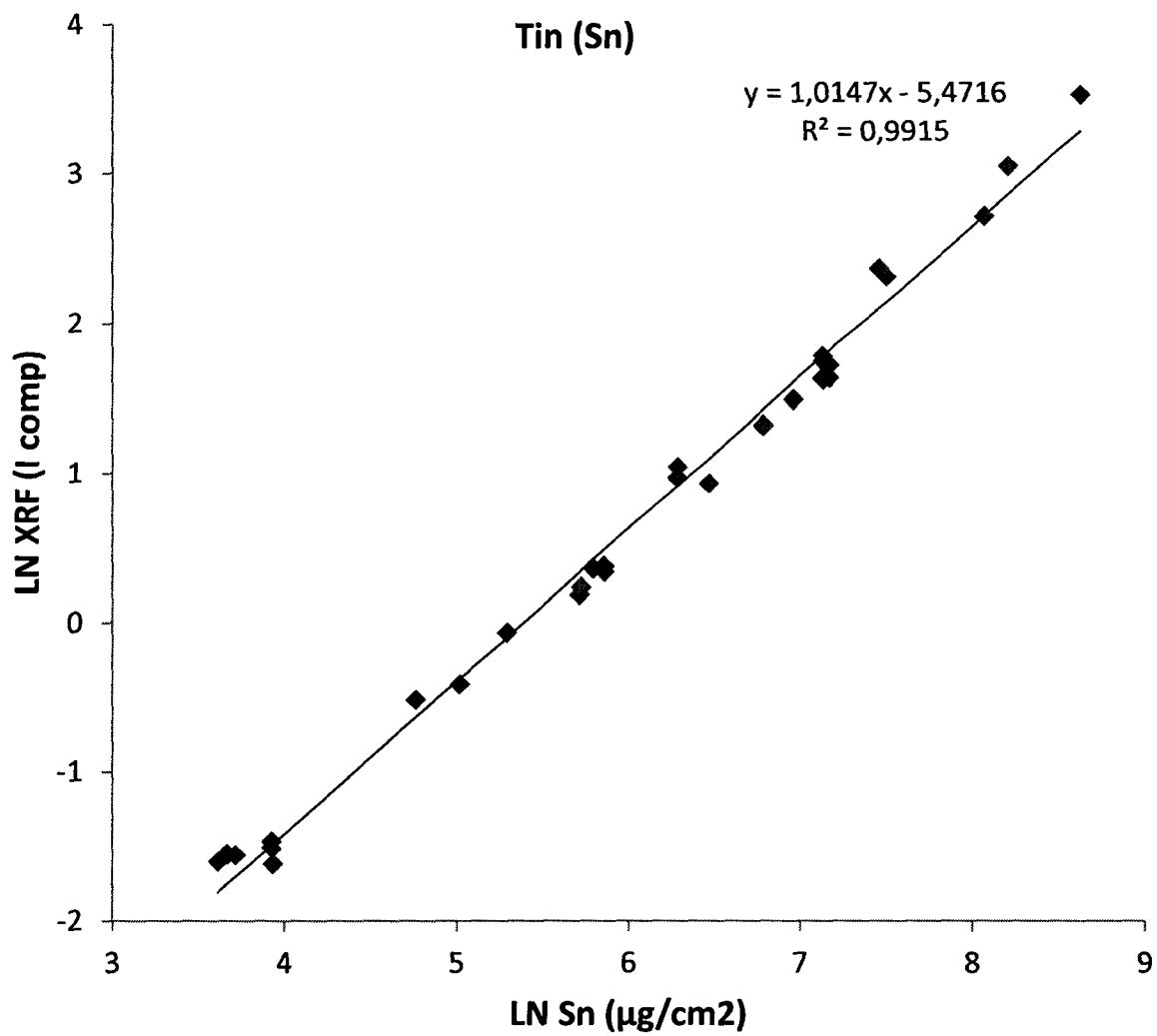


Fig. 1

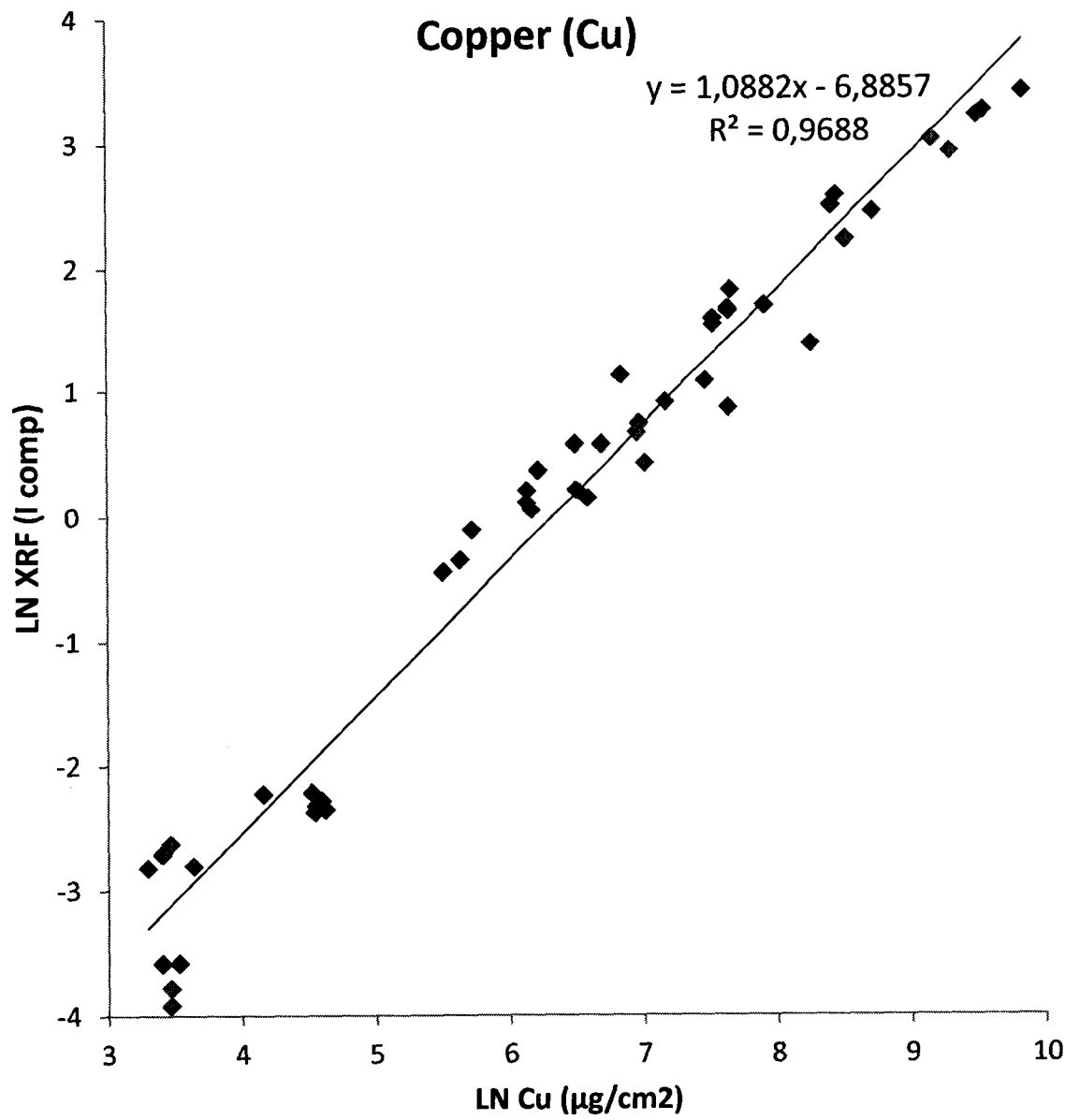


Fig. 2

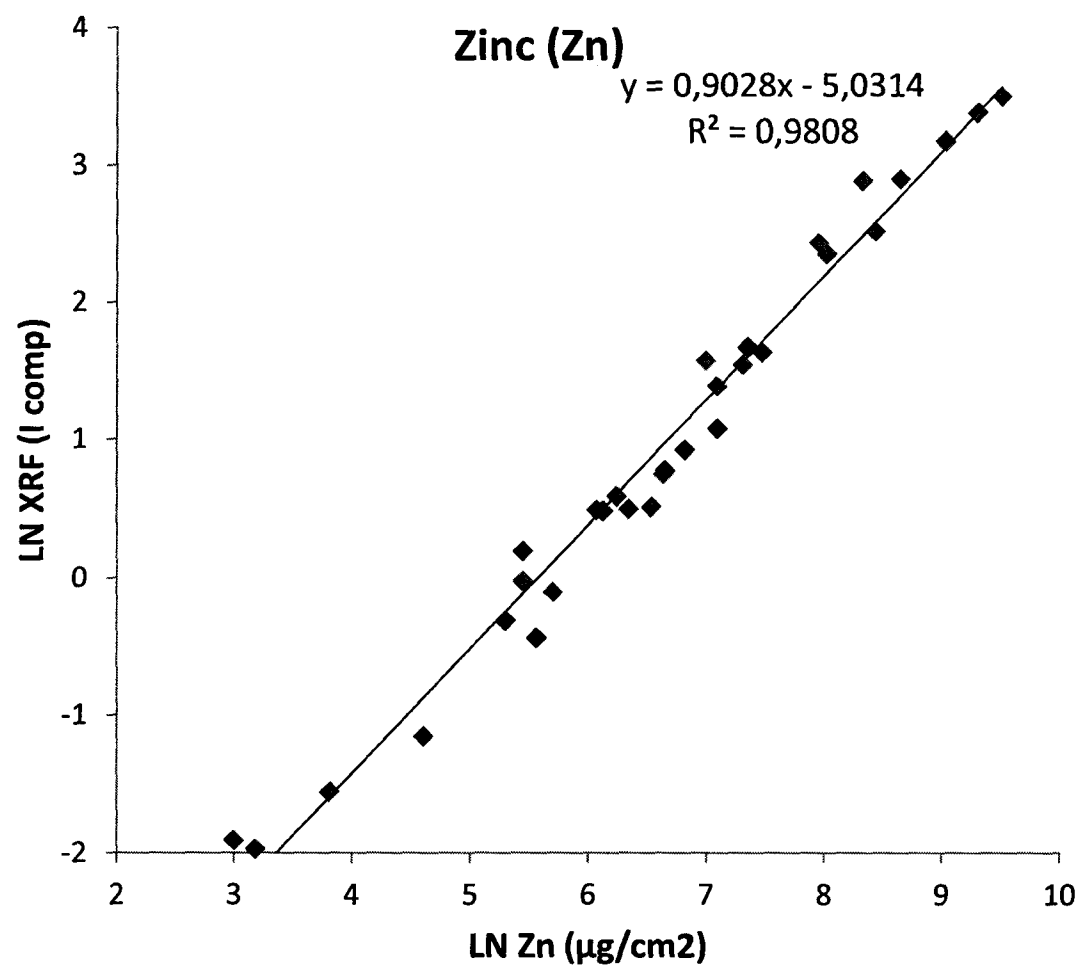


Fig. 3

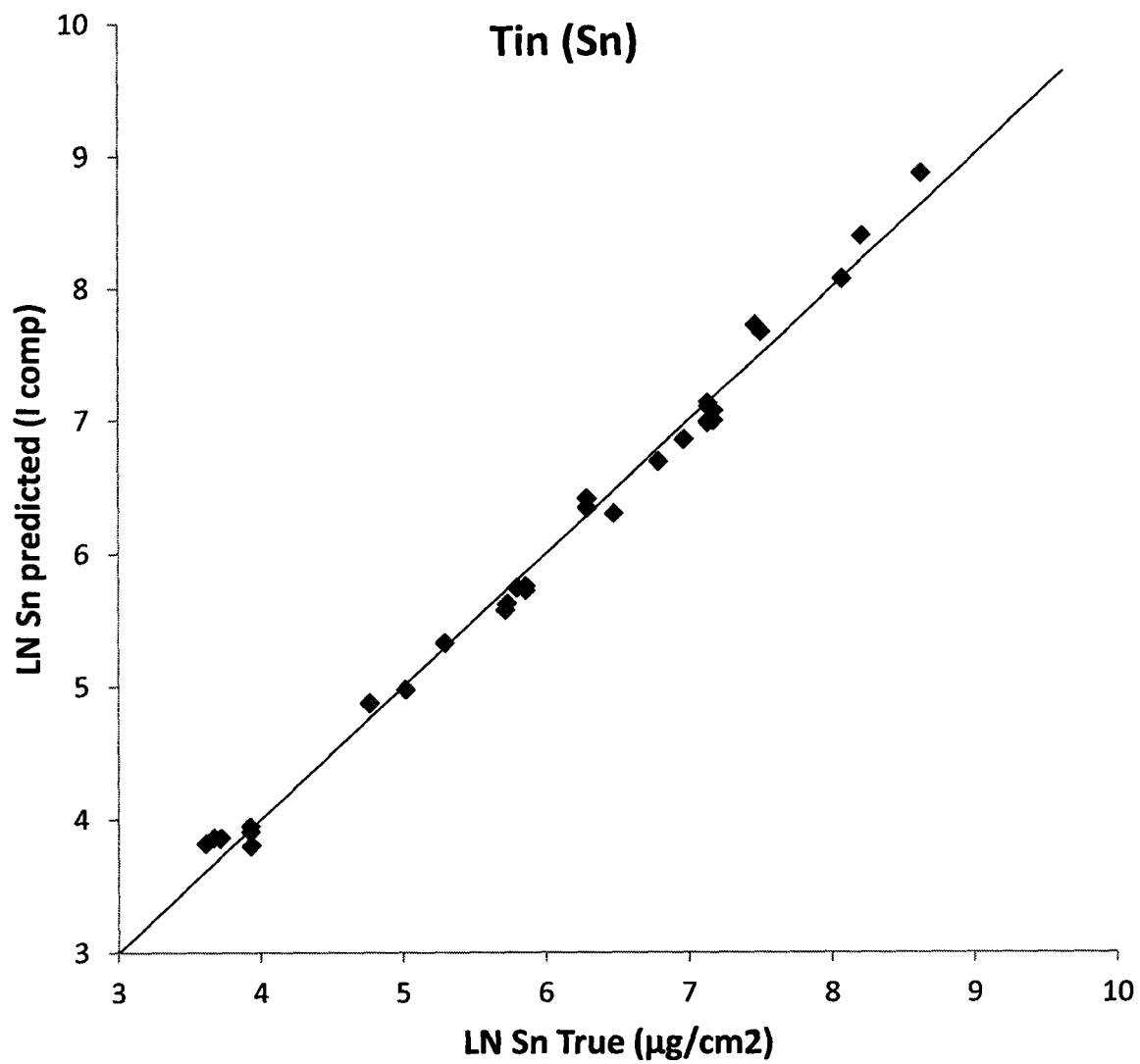


Fig. 4

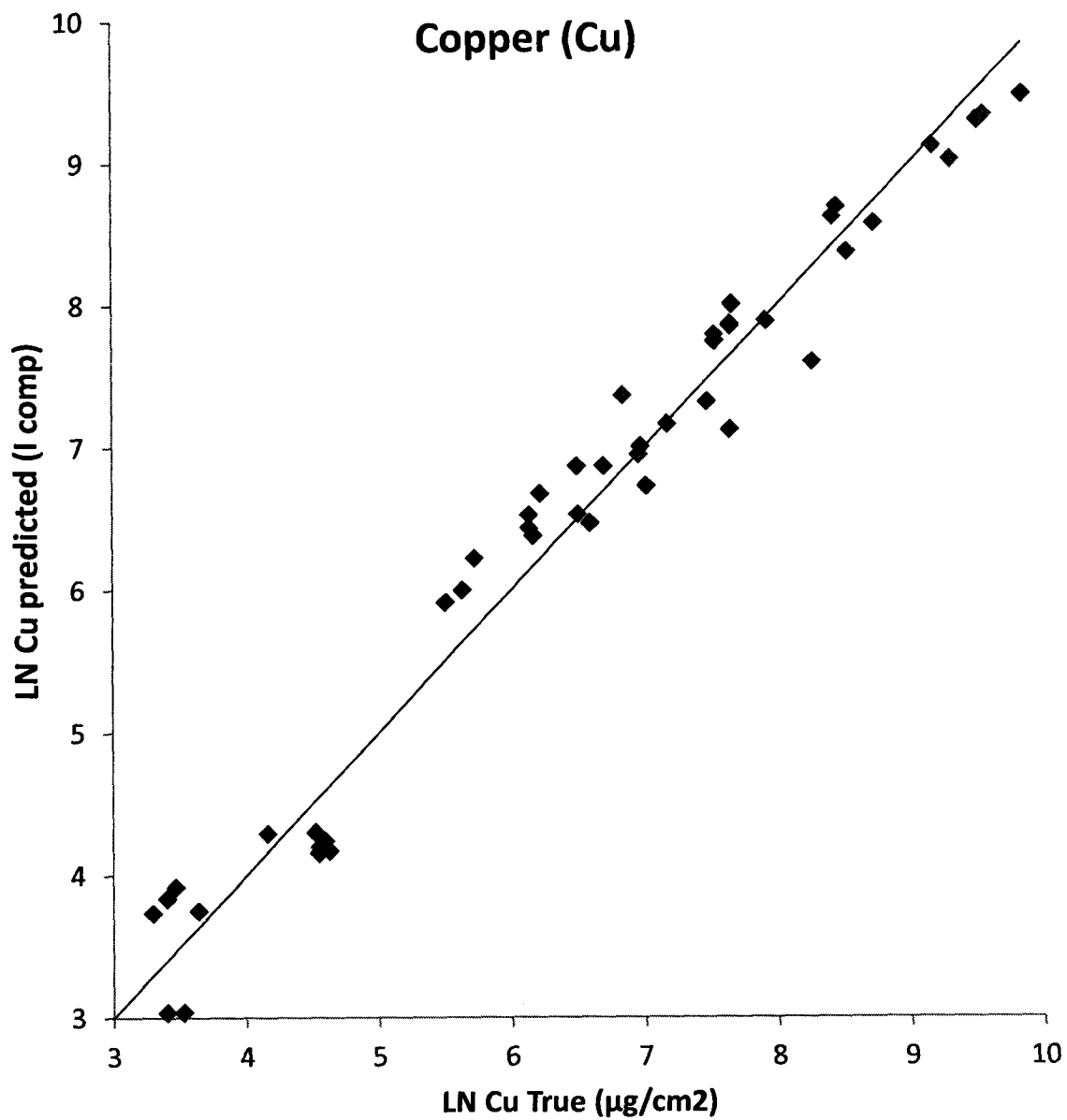


Fig. 5

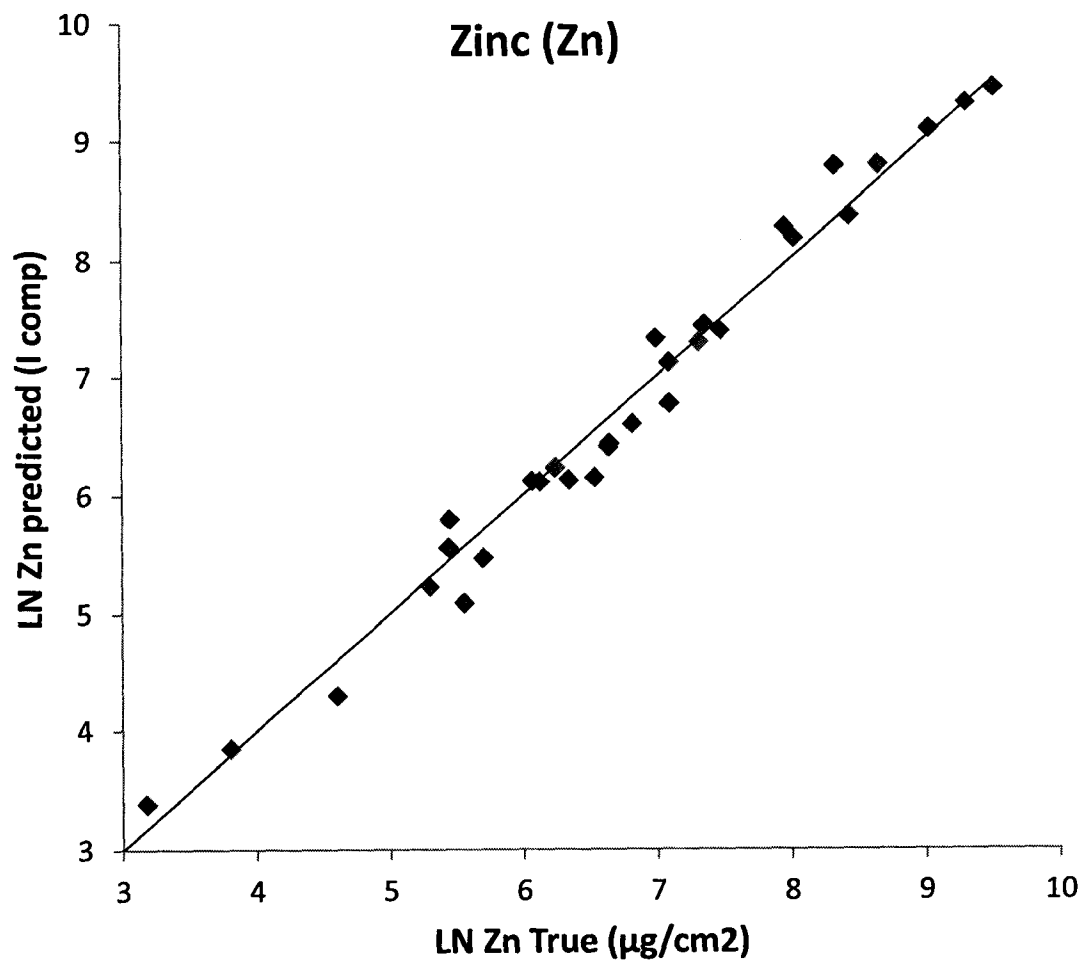


Fig. 6

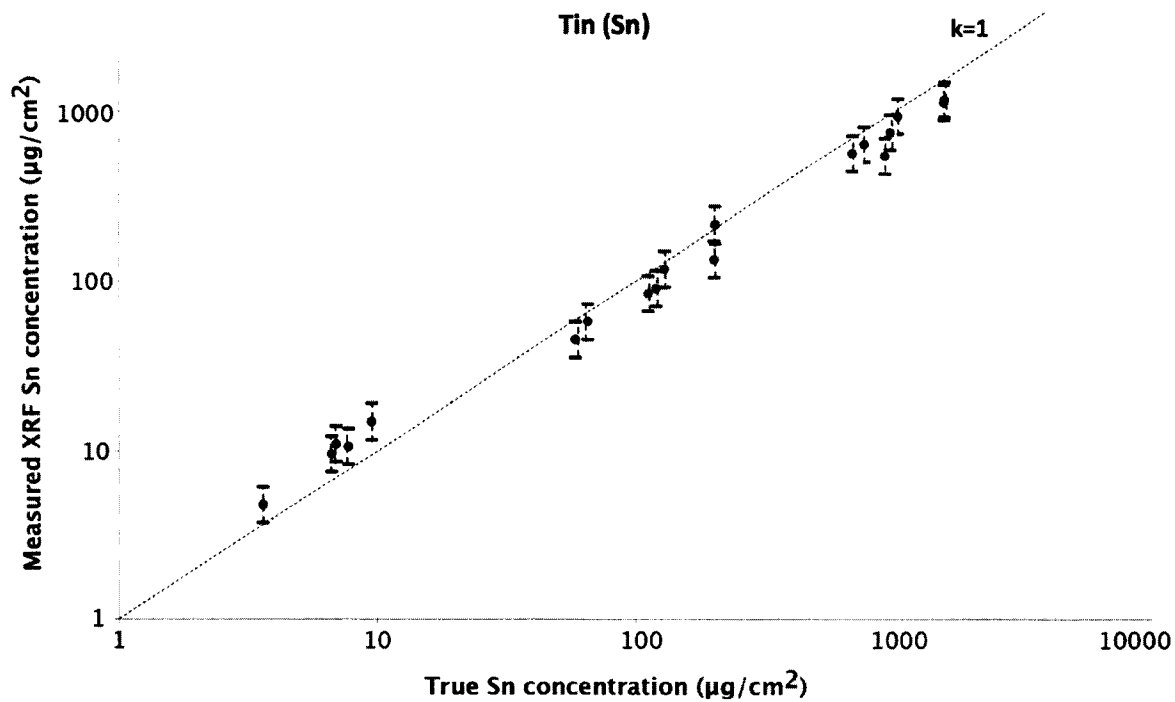


Fig. 7

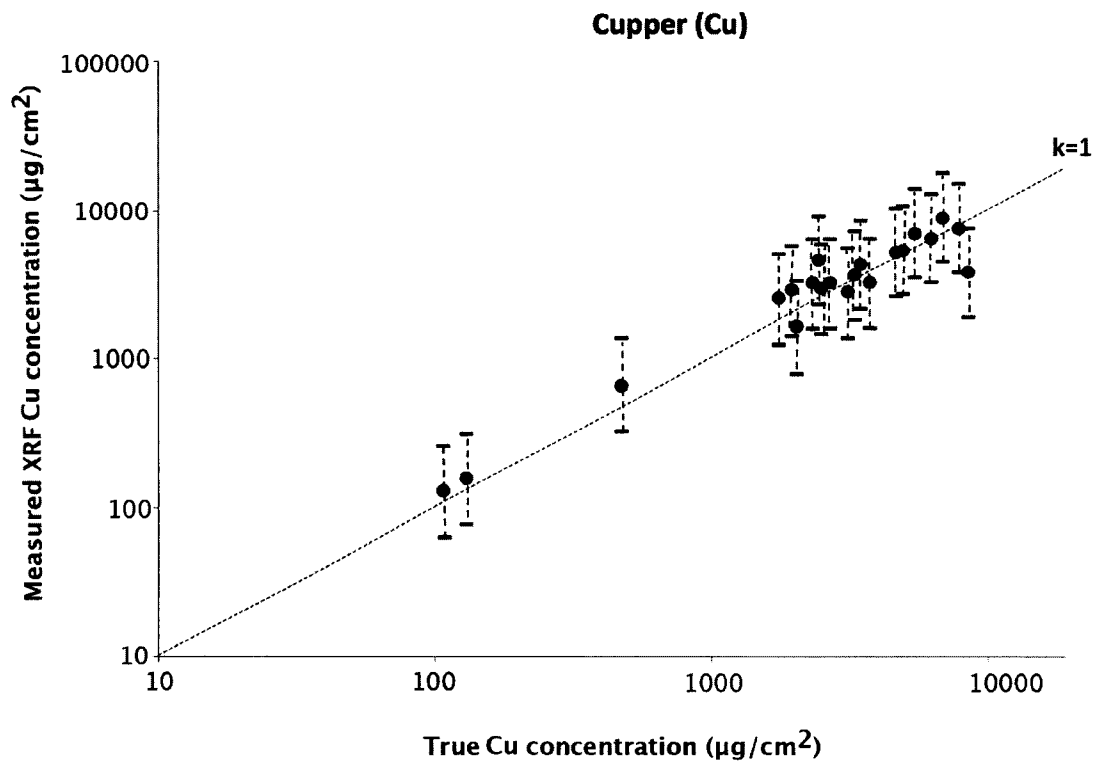


Fig. 8

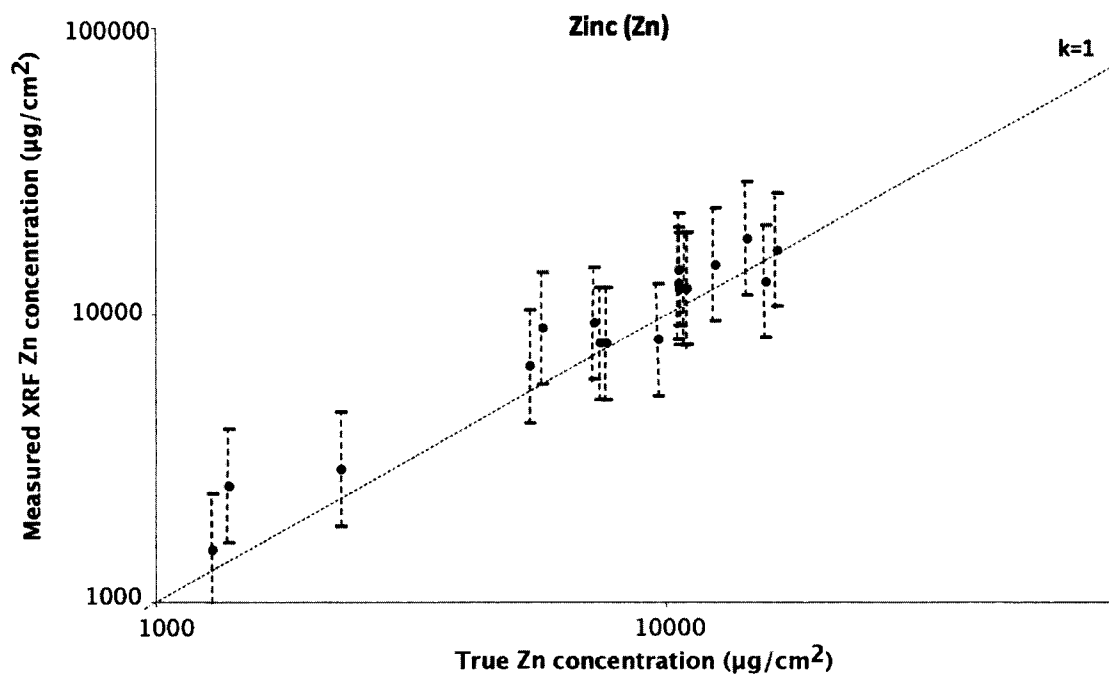


Fig. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2015/000044

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: G01N, G01T

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, PAJ, WPI data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 20140140473 A1 (CHEN XUNMING), 22 May 2014 (2014-05-22); abstract --	1-40
A	WO 2008105782 A2 (THERMO NITON ANALYZERS LLC ET AL), 4 September 2008 (2008-09-04); abstract --	1-40
A	JP 2003083852 A (MITSUBISHI HEAVY IND LTD), 19 March 2003 (2003-03-19); abstract --	1-40
A	US 20060016250 A1 (SWAIN GEOFFREY ET AL), 26 January 2006 (2006-01-26); abstract --	1-40



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

21-08-2015

Date of mailing of the international search report

24-08-2015

Name and mailing address of the ISA/SE

Patent- och registreringsverket

Box 5055

S-102 42 STOCKHOLM

Facsimile No. + 46 8 666 02 86

Authorized officer

Fredrik Arnesson

Telephone No. + 46 8 782 28 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2015/000044

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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