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Determination of Mercury(II) in Drinking Water by Total Reflection X-ray Fluorescence Spectrometry and Liquid–Liquid Microextraction

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ABSTRACT

The total reflection X-ray fluorescence determination of mercury(II) in drinking water at concentrations of 7×10^{-2} to 3.0 $\mu\text{g/L}$ is reported. The mercury(II) preconcentration protocol includes directly suspended droplet microextraction with benzene as a molecular iodine complex. The proposed approach is highly selective. The elements Cr, Mn, Fe, Co, Ni, Zn, and Pb at concentrations up to 0.1 g/L did not interfere with the extraction of trace mercury(II). The method is characterized by high sensitivity (limit of detection of 21 ng/L) and suitable reproducibility (relative standard deviation of 0.12 for 100 ng/L). The accuracy of the results was confirmed by recovery and the method of standard addition.

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Directly suspended droplet microextraction; drinking water; liquid–liquid microextraction; mercury(II); total reflection X-ray fluorescence analysis

Introduction

Total reflection X-ray fluorescence (TXRF) is one of the most effective methods for the simultaneous determination of metal ions in waters. The advantages of TXRF are high sensitivity and selectivity, wide range of concentrations may be determined, and the express and simple analysis of liquid samples (Alov 2011; Klockenkämper and von Bohlen 2015). However, the sensitivity of TXRF for the direct determination of the most toxic metals at the level of limit permitted concentration is insufficient for the determination of mercury in drinking (500 ng/L) and bottled (200/500 ng/L) water, wastewater (100–200 ng/L), seawater (100 ng/L), and fisheries (10 ng/L).

In the most recent 20 years, several strategies for TXRF determination of mercury in waters with preconcentration have been developed. In particular, the formation of an amalgam with Ag and Au was proposed to capture and concentrate Hg in liquids (Greaves et al. 1997; Bennun, Greaves, and Bloshtein 2002). An electrochemical enrichment procedure was also reported (Bennun and Gomez 1997; Bennun, Gillette, and Greaves 1999; Ritschel et al. 1999), as well as trapping complexation (Gusto et al. 2006), preconcentration using polyvinyl chloride membranes on the reflector (Koulouridakis, Kallithrakas-Kontos, and Gekas 2006), and quartz activation with immobilization (Aretaki, Koulouridakis, and Kallithrakas-Kontos 2006). Margui et al. (2010) developed a rapid and

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reliable TXRF approach for the determination of mercury in wastewater. This method is based on the trapping of Hg by thiourea complexation before its quantification by TXRF that prevents the losses of Hg during drying process on the reflector. Unfortunately, the detection limits are so high for Hg determination in drinking water despite of the high-power (0.8–3 kW) of the X-ray tube. The reasons include spectral overlapping and high background signal. However, the main reason that only a small portion of the Hg in the analyzed solution participates in signal formation. A comparison of these approaches shows that the sample preparation in the TXRF analysis of waters is favorably combined with liquid–liquid extraction. It is more advantageous compared to other methods of separation and preconcentration based on characteristics that include efficiency, technical simplicity, cost, and analysis time. A significant advantage is that the concentrate is originally located in the liquid and low-boiling phase.

Usually ions of mercury(II) are extracted from aqueous solution in the form of complex compounds with organic reagents such as dithizone (Gladyshev, Levitskaya, and Filippova 1974). Mercury(II) determination has been reported with extraction from water by methyl isobutyl ketone in the form of pyrrolidinedithiocarbamate (Holyńska et al. 1996). The high sensitivity of the developed approach (from 200 ng/L) is due to the preconcentration step and spectral measurements with a TXRF module with a high-power X-ray tube (1.5 kW). To obtain a more objective view, it is necessary to establish the analytical characteristics of combined method with use of a commercially available TXRF spectrometer with a low power X-ray tube (30 W).

The recovery of mercury(II) from water described by Holyńska et al. (1996) can be optimized by considering modern variants of extraction technique (Pena-Pereira, Lavilla, and Bendicho 2009; Dadfarnia and Shabani 2010). The establishment of another extraction system for this analytical problem is very interesting. As an example, we can give efficient recovery of mercury(II) from water by benzene in the form of the molecular iodine complex (Kish et al. 1977). In contrast to Holyńska et al. (1996), this approach is highly selective and it does not require the use of expensive reagents.

The preliminary extraction was successfully used for the preconcentration of micro-impurities (Misra, Dhara, and Singh Mudher 2006; Sitko et al. 2011; Marguí et al. 2013; Marguí, Hidalgo, and Queralt 2013) and for the removal of interfering matrix components (Misra et al. 2005; Misra et al. 2008) in the analysis of various samples by TXRF. Because the volume of liquid sample for TXRF measurements is several microliters, liquid–liquid microextraction (LLME) is the most effective for the preconcentration of metal ions (De La Calle et al. 2013; Marguí, Zawisza, and Sitko 2014). Extremely small volumes of extract allow using a larger portion for the formation of the analytical signal and leads to an increase in the sensitivity. Small volumes of toxic organic solvents minimize the harm caused to the analyst and the environment. One of the most inexpensive, available and effective ways of liquid–liquid microextraction is based on directly suspended droplet microextraction (Yangcheng et al. 2006). An example of successful combination of this approach with the X-ray determination of trace substances is presented in a recent publication (Pytlakowska 2014). The goal of this work is to develop the TXRF determination of mercury(II) in drinking water after liquid–liquid microextraction in the form of a molecular iodine complex using the directly suspended droplet approach.

Experimental

Reagents

Mercury(II) sulfate (ACS reagent, $\geq 99\%$), potassium iodide (anhydrous, free-flowing, Redi-Dri, ACS reagent, $\geq 99\%$), sulfuric acid (ACS reagent, 95.0–98.0%), and benzene (for HPLC, $\geq 99.9\%$) were used in this work. All reagents were from Sigma-Aldrich. The mercury(II) solution with an approximate concentration of 10 mg/mL is prepared by dissolving mercury(II) sulfate in 1 M sulfuric acid. The accurate concentration of obtained solution was determined by a complexometric titration. The solutions of mercury(II) with lower concentration were obtained by serial dilution of the stock solution in deionized water (15–18 M Ω · cm). Deionized water was also used for the preparation of the solutions of potassium iodide and for the dilution of sulfuric acid. For quantitative TXRF analysis, we used gallium atomic absorption standard solution (Fluka Analytical) that contains 995.0 ppm of Ga in 1 wt% HNO₃. For hydrophobization of the quartz reflector, we used a silicone solution for siliconizing the glass and metal in isopropanol (Serva).

Preconcentration of mercury(II)

A total of 5.00 mL of mercury(II) solution, 0.7 mL 0.001 M potassium iodide aqueous solution, 1.3 mL sulfuric acid (1:1) and 50 μ L benzene are placed in 10 mL vial. The extraction conditions for molecular complex HgI₂ were optimized by Kish et al. (1977). The vial was stoppered and its contents were mixed with a Teflon stirrer (length of 12 mm, diameter of 4.5 mm) on a magnetic stirrer at 25°C. The extraction time was not less than 3 min. The rotation speed of magnetic stirrer is 1250 rpm. Since the density and volume of benzene are lower than for water, stirring in the central part of the funnel on a surface of liquid formed a well-localized suspended drop of the organic phase (Yangcheng et al. 2006).

The organic phase was recovered through a microsyringe Hamilton (100 μ L) without turning off the magnetic stirrer and was placed in 200 μ L microinserts for glass vials (Akvilon ND9) and was evaporated carefully in a water bath heated to 50°C. The dried concentrated residue was dissolved in 70 μ L of 0.01% potassium iodide aqueous solution containing internal standard (Ga at 3 μ g/L). A total of 50 μ L of the obtained concentrate were applied with a microsyringe (5 \times 10 μ L) on hydrophobized silicone solution quartz reflector surface.

To obtain the concentrated sample in a homogeneous spot (spot size does not exceed the working area of detector), the surface of the quartz reflector was coated with a hydrophobic silicone solution in isopropanol (Serva). A total of 20 μ L of this solution were applied to the clean reflector and dried in vacuum for 30 min at 80°C. Direct application of the benzene extract on the unmodified substrate leads to spreading of drops and to the exit of uncontrolled concentrate from the detection zone which is a circle with a diameter of 3 mm in the central part of the reflector. To solve this problem, it is necessary to replace benzene by significantly more polar solvent. To minimize the losses of mercury droplets, the concentrated deposit on the reflector was dried in vacuum at 25°C for 1 min.

TXRF measurements

The TXRF spectra of the samples were measured using a S2 Picofox spectrometer (Bruker Nano GmbH, Germany). MoK α radiation was used for the X-ray fluorescence excitation

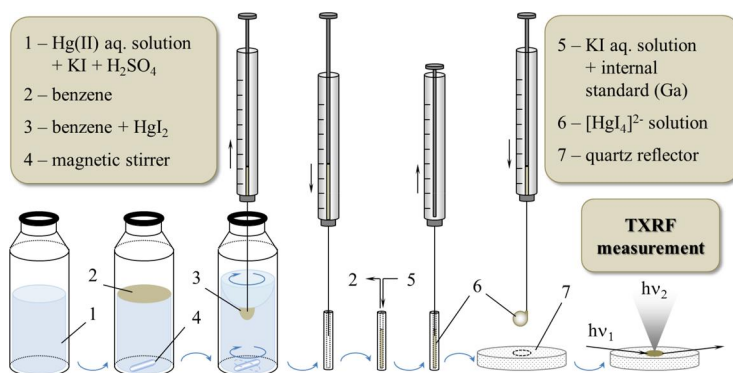


Figure 1. TXRF determination of Hg(II) in water with microextraction as HgI₂ using benzene.

(17.4 keV). The operating voltage of the X-ray tube was 50 kV and the current was 600 μ A. The instrument was equipped with a high-efficiency module to increase the determination sensitivity and with XFlash silicon drift detector with thermoelectric cooling. The energy resolution at the MnK α line (5.90 keV) was better than 150 eV. The spectral acquisition time was 1000s. The TXRF determination of mercury was performed by the internal standard technique using the Spectra 7 software (Bruker Nano GmbH, Germany). The calculation of mercury content was performed using L β ₁-line of Hg (11.82 keV). The spectral line comparison for the internal standard was GaK α (9.25 keV). The full scheme of experiment including preconcentration of mercury(II) and TXRF measurements is presented on Figure 1.

Results and discussion

Direct Hg determination in water

The limit of detection for mercury was 26 pg. This value was determined for an aqueous solution of mercury(II) sulfate on the quartz reflector (Figure 2). To illustrate the validity

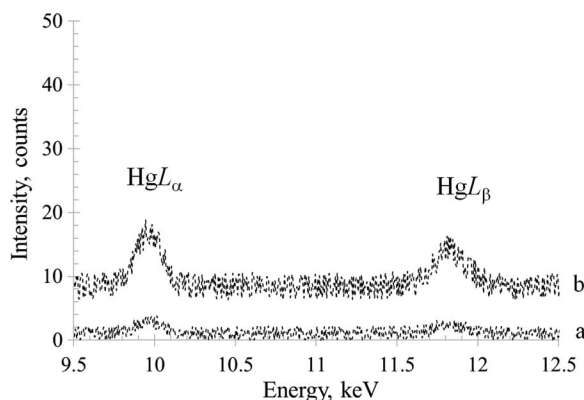


Figure 2. TXRF spectrum (fragment) of an aqueous solution of mercury(II) sulfate. The concentration of mercury(II) is 13 μ g/L and the volume is 2 μ L using a quartz reflector. The spectrum acquisition times were (a) 250 and (b) 1000s.

of the assessment, a model solution with a mercury concentration equal to the detection limit was prepared and the spectrum was measured. The limit of detection for mercury in water determined by Margui et al. (2010) was 7 pg. In spite of the significantly lower power of X-ray tube (by 100 times), the sensitivity is less only by four times due to focusing of primary X-ray radiation by the high-efficiency module. The sample placed in the central zone of diameter less than 3 mm on the reflector surface has a significant influence on the formation of the analytical signal. The diameter of the drop on the quartz reflector does not exceed the specified value if the volume of analyzed water solution is not more than 2 μL . One application of the analyzed water samples to the reflector detected mercury at levels of 10–15 $\mu\text{g/L}$.

The approach based on coating and drying alternating drops of analyzed solution is widely used to improve the sensitivity. Using this approach the quantity of the analyzed sample excited by X-ray beam can be increased by tens of times (Klockenkämper and von Bohlen 2015). However, the opportunity of TXRF analysis and the accuracy of analysis results strongly depend on the level of salinity. A high concentration of salts leads to disruption of the total external reflection of the exciting X-ray radiation. The introduction to the substrate of a low salinity water sample (tenth shares g/L) volume of more than 50–60 μL does not lead to an increase of sensitivity, but it is accompanied by a significant increase in the error of determination (Pashkova, Revenko, and Finkelshtein 2013). Reducing the number of applied droplets of the solution while increasing their volume leads to a decrease in the error of the results. To achieve this goal, the quartz reflector surface was hydrophobized by a silicone solution. Drops of aqueous solution up to 10 μL in volume do not spread across the modified surface (Pashkova and Revenko 2015).

Using the sample preparation technique described above, mercury may be determined at the permitted concentration for drinking water (500 ng/L). However, the direct determination of mercury using portable TXRF spectrometers is still impossible. Thus, the described procedure of mechanical accumulation of analyte on the surface of the quartz reflector needs to be combined with preliminary recovery of mercury from the water phase.

Extraction of mercury(II)

Preconcentration allows an additional increase of sensitivity for mercury(II) determination. For this purpose, microextraction was used in this work. The conditions for the extraction of mercury(II) from aqueous solution in the form of uncharged molecular complexes of HgHal_2 have been studied in detail (Kish et al. 1977). It was shown that the degree of mercury recovery varies among HgI_2 ($\log\beta_2$ 23.82) > HgBr_2 ($\log\beta_2$ 17.33) > HgCl_2 ($\log\beta_2$ 13.22). The optimum concentration of iodide ions in solution is 10^{-4} – 10^{-3} M. At the concentrations of less than 10^{-4} M and more than 10^{-3} M, the recovery, is reduced due to increasing fraction of the charged complexes in solution— HgI^+ ($\log\beta_2$ 12.87) and HgI_3^- ($\log\beta_2$ 27.60), respectively. It was found by Kish et al. (1977) that by varying the concentration of sulfuric acid from 0.05 to 3M the recovery of mercury(II) was changed from 90 to 98%. The recovery almost does not depend on the ratio of volumes of the aqueous and organic phases in the range of 1:1 to 1:200 and allows mercury(II) preconcentration from highly dilute solutions. When comparing several organic solvents, it was shown that the use of benzene provides the most complete extraction of HgI_2 (Kish et al. 1977).

The TXRF spectrum of benzene extract is presented in Figure 3. Calculation of the ratio of iodine and mercury contents in obtained concentrate with the use of Sherman equation

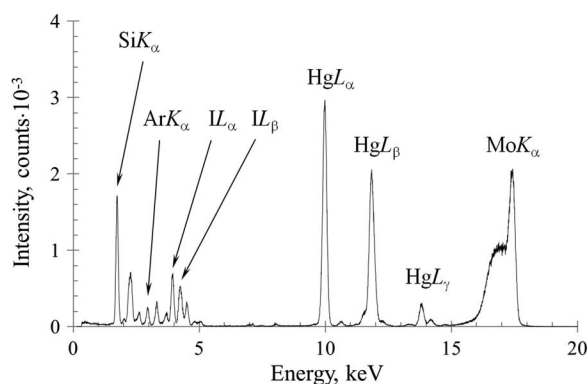


Figure 3. TXRF spectrum of Hg concentrate. The volume is 2 μL using a quartz reflector and an acquisition time of 250 s. The mercury was extracted as HgI_2 with benzene from aqueous mercury(II). The concentration of mercury(II) in the aqueous solution is 3.5 mg/L. The ratio of organic and water phases volumes is 1:5. The SiK_α peak originated from the quartz reflector. The ArK_α peak is produced by the air between the reflector and the Be-window of the detector.

(Van Grieken and Markowicz 2001) indirectly confirms the extraction of mercury(II) from aqueous solutions in the form of uncharged molecular complexes HgI_2 .

$$\frac{c^{\text{I}}}{c^{\text{Hg}}} = \frac{I_{\text{IL}_\alpha} S_{\text{L}_{\text{III}}}^{\text{I}} \tau_{\text{MoK}_\alpha}^{\text{Hg}} (S_{\text{L}_{\text{III}}}^{\text{Hg}} - 1) \omega_{\text{L}_{\text{III}}}^{\text{Hg}}}{I_{\text{HgL}_\alpha} \tau_{\text{MoK}_\alpha}^{\text{I}} (S_{\text{L}_{\text{III}}}^{\text{I}} - 1) \omega_{\text{L}_{\text{III}}}^{\text{I}} S_{\text{L}_{\text{III}}}^{\text{Hg}}} = 2.0 \pm 0.1 (P = 0.95, n = 5) \quad (1)$$

where $S_{\text{L}_{\text{III}}}^{\text{I}}$, $S_{\text{L}_{\text{III}}}^{\text{Hg}}$ are the absorption jumps of the I and Hg L-series; $\omega_{\text{L}_{\text{III}}}^{\text{I}}$, $\omega_{\text{L}_{\text{III}}}^{\text{Hg}}$ are the fluorescence yields of the I and Hg L-series; $\tau_{\text{MoK}_\alpha}^{\text{I}}$, $\tau_{\text{MoK}_\alpha}^{\text{Hg}}$ are the values of the MoK_α radiation absorption coefficients for I and Hg; I_{IL_α} , I_{HgL_α} are the intensities of IL_α and HgL_α -lines, respectively.

The results of the evaluation of mercury(II) recovery from sulfate solutions using directly suspended droplet microextraction (Table 1) correspond to the results obtained by a classical liquid–liquid extraction protocol (Kish et al. 1977).

Limit of detection

The limit of detection for mercury was estimated from peak/background ratio in the TXRF spectrum of a standard Hg(II) solution in a concentration of 400 ng/L using the following equation (Greaves et al. 1997):

$$\text{LOD} = \frac{3c}{S} \sqrt{\frac{B}{t}}, \quad (2)$$

Table 1. Hg(II) recovery from aqueous solution by microextraction.

Concentration of mercury(II) in aqueous solution, mg/L	Ratio of intensities of line $\text{HgL}_{\beta 1}$ in TXRF spectra of aqueous solutions before and after Hg(II) microextraction ($P = 0.95$; $n = 10$)
10	52 ± 3
1.0	54 ± 4
0.1	49 ± 4

Table 2. TXRF determination of Hg(II) in drinking water: Analytical figures of merit.

Limit of detection, ng/L	Limit of quantification, ng/L	Preconcentration factor	Relative standard deviation for 100 ng/L mercury(II)
21	70	68	0.12

where LOD is limit of detection, c is the concentration of the mercury standard, B is the spectral background count rate, S is the signal count rate, and t is the counting time.

A total of 26 pg of mercury may be detected (line HgL_{α}) on the quartz reflector when Hg (II) solution prepared in deionized water or the benzene extract containing only HgI_2 (measurement time is 1000s). In this technique, 26 pg of mercury correspond to a Hg concentration of 8 ng/L, if the volume of benzene extract is equals 50 μ L. However, to apply this large volume of organic extract on quartz reflector without the drop spreading is a very difficult task. Replacement of benzene by KI solution solves this problem, but leads to four times increase in the background signal that raises the limit of detection of mercury(II) to 15 ng/L.

Mercury(II) in water was determined by the internal standard method. Because the HgL_{α} (9.99 keV) line partially overlaps the GaK_{β} (10.26 keV) line, the HgL_{β} (11.82 keV) line was used for analytical measurements. Using this line, the limit of detection is 21 ng/L (Table 2). The decrease in the limit of detection by less than a factor of two is statistically insignificant. The TXRF spectrum of Hg concentrate obtained by the extraction of HgI_2 with benzene from aqueous solution of mercury(II) ($c_{Hg} = 300$ ng/L) and subsequent solvent replacement is presented on Figure 4.

Accuracy

The accuracy of the Hg TXRF measurements was characterized by analyzing two samples of drinking water from the Southwest District of Moscow spiked at a Hg concentration of 250 ng/L. Good agreement was obtained between Hg concentrations determined by TXRF and the initial Hg concentration in the spiked samples ($I(HgL_{\beta})/I(GaK_{\alpha}) = (3.1 \pm 0.2)c_{Hg}$

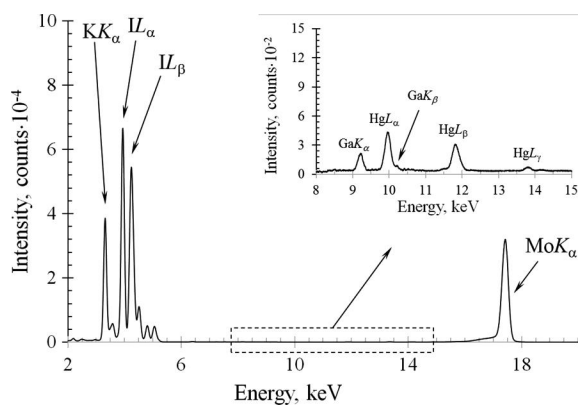


Figure 4. TXRF spectrum of Hg concentrate. The volume is 50 μ L using a quartz reflector with an acquisition time of 1000s. The mercury was extracted as HgI_2 with benzene from aqueous mercury(II). The concentration of mercury(II) is 300 ng/L. The content of Ga as the internal standard in the Hg concentrate is 3 μ g/L.

Table 3. TXRF determination of Hg(II) in drinking water from Southwest Moscow.

Drinking water	Concentration of mercury(II), ng/L ($P = 0.95$; $n = 10$)	
	Original water	Water spiked with 250 ng/L of Hg
Sample 1	<limit of detection	244 ± 20
Sample 2	<limit of detection	257 ± 22

($\mu\text{g/L}$), $R^2 = 0.9984$) (Table 3). The calibration curve is presented in Figure 5. The linear range of the calibration curve is 7×10^{-2} to $3.0 \mu\text{g/L}$.

Precision

The precision of the methodology was evaluated in terms of relative standard deviation of ten replicate measurements of a standard solution containing 100 ng/L of Hg(II). A relative standard deviation of 0.12 was obtained for the relative Hg intensity $I(\text{HgL}_{\beta})/I(\text{GaK}_{\alpha})$ (Table 2).

Evaluation of chemical interferences

According to Kish et al. (1977), Cr, Mn, Fe, Co, Ni, Zn, and Pb (up to concentration $0.1\text{--}0.5 \text{ g/L}$) did not interfere with the extraction of trace concentrations of mercury(II). An equal concentration of gold and 25-fold excess concentration of thallium (III) also did not interfere with the extraction of mercury(II) (Kish et al. 1977). Considering the composition of natural waters, we can expect the extraction of other elements with mercury(II), including As, Se, Sb, and Sn (Grimanis and Hadzistelios 1968). However, the most intense lines of these elements do not overlap with the mercury lines and do not interfere with the TXRF determination.

For the evaluation of chemical interferences of metal ions during Hg(II) microextraction, two solutions were prepared using deionized water. One solution only contained 200 ng/L Hg(II) and the other 0.1 g/L Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Zn(II), and

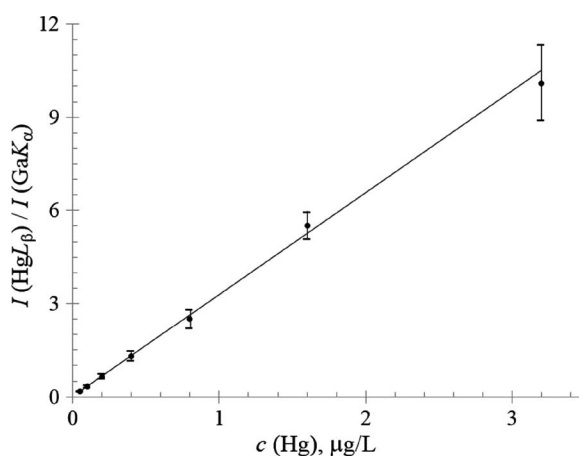


Figure 5. Relative signal intensity ($\text{HgL}_{\beta}/\text{GaK}_{\alpha}$) from the TXRF spectra as a function of the Hg(II) concentration in water ($P = 0.95$; $n = 10$).

Table 4. Influence of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Zn(II), and Pb(II) on the determination of Hg(II) in water by TXRF ($P = 0.95$, $n = 10$). The mercury(II) concentration is 200 ng/L. Details of measurement conditions are provided in the text.

Aqueous solution	Measured concentration of mercury(II), ng/L ($P = 0.95$; $n = 10$)
1	205 ± 17
2	210 ± 15

Pb(II) and 200 ng/L Hg(II). The difference for Hg determination in these solutions was statistically insignificant (Table 4).

Conclusion

The proposed approach to the determination of small quantities of mercury in aqueous solutions is based on its recovery as mercury(II) iodide using directly suspended droplet microextraction with subsequent measurement by TXRF. The developed sample preparation technique is simple and rapid. The results of Hg determination have favorable analytical figures of merit. Almost quantitative and selective recovery of mercury(II) from aqueous solution with the subsequent use of the most part of the received concentrate when forming an analytical signal provides high sensitivity for Hg in drinking water using a portable TXRF spectrometer with a low-power X-ray tube.

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