Talanta 82 (2010) 821–827

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Analytical approaches for Hg determination in wastewater samples by means of total reflection X-ray fluorescence spectrometry

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ARTICLE INFO

Article history:
Received 7 March 2010
Received in revised form 18 May 2010
Accepted 30 May 2010
Available online 4 June 2010

Keywords:
Hg
TXRF
Wastewater samples

ABSTRACT

At present, there is a considerable interest in Hg monitoring in wastewater samples due to its widespread occurrence and the high toxicity of most of its compounds. Hg determination in water samples by means of total reflection X-ray fluorescence spectrometry (TXRF) entails some difficulties due to the high vapor pressure and low boiling point of this element that produce evaporation and loss of Hg from the surface of the reflector during the drying process, commonly used for sample preparation in TXRF analysis.

The main goal of the present research was to develop a fast and simple chemical strategy to avoid Hg volatilization during the analysis of wastewater samples by TXRF spectrometry. Three different analytical procedures were tested for this purpose: (i) increasing the viscosity of the wastewater sample by adding a non-ionic surfactant (Triton® X-114), (ii) Hg immobilization on the quartz reflectors using the extractant tri-isobutylphosphine (Cyanex 471X) and (iii) formation of a stable and non-volatile Hg complex into the wastewater sample. The best analytical strategy was found to be the formation of a Hg complex with thiourea (pH = 10) before the deposition of 10 μL of sample on the reflector for following TXRF analysis. Analytical figures of merit such as linearity, limits of detection, accuracy and precision were carefully evaluated. Finally, the developed methodology was applied for the determination of Hg in different types of wastewater samples (industrial effluents, municipal effluents from conventional systems and municipal effluents from constructed wetlands).

1. Introduction

Heavy metals have many industrial applications which considerably influence their appearance in wastewaters of various industrial treatment plants. Part of these metals may eventually reach biological wastewater treatment plants and might produce also significant changes in their microbial communities and reduce their treatment efficiency [1]. Among the heavy metals, there is a considerable interest in Hg monitoring due to its widespread occurrence and the high toxicity of most of its compounds [2]. In this sense, the United States Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) lists Hg and its compounds in third place on the "Priority list of hazardous substances" and the European Water Framework Directive (2000/60/EC) classifies Hg as one of the 33 "Priority pollutants" [3]. Consequently, the determination of Hg in wastewaters is, at present, regulated by law.

Hg concentrations in wastewater samples are typically in the low $\mu g\,L^{-1}$ to $ng\,L^{-1}$ range, which makes their reliable determination a major analytical challenge [4]. Recently reported techniques for trace Hg analysis at this concentration levels are direct neutron activation (NAA) [5], inductively coupled plasma mass spectrometry (ICP-MS) [6], inductively coupled plasma atomic emission spectrometry (ICP-OES) [7], cold vapor atomic absorption spectrometry (CVAAS) [8] and atomic fluorescence spectrometry (AFS) [7].

Total reflection X-ray fluorescence spectrometry (TXRF) is a well-established analytical technique for trace element determination in various sample types, especially liquids and powdered or micro-samples [9]. TXRF is a variation of energy-dispersive XRF where the primary beam strikes the sample at a very small angle (~0.1°). The TXRF system makes use of the fact that, at very low glancing angles, primary X-ray photons are almost completely absorbed within thin specimens, and the high background that would generally occur due to scatter from the sample support is absent leading to an improvement of detection limits [10]. To perform analysis under total-reflection conditions, samples must be provided as thin films. For liquid samples, this is done by depositing

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doi:10.1016/j.talanta.2010.05.066

Table 1
Published methods based on TXRF spectrometry for the determination of Hg in liquid samples.

Analytical strategy	Instrumentation	Measuring time (s)	Sample volume[a] (mL)	Type of sample	LOD ($\mu g\,L^{-1}$)	Ref.
Forming a Hg–Ag amalgam	Mo X-ray tube (40 kV, 20 mA) Si(Li) detector (159 eV at 5.9 keV)	1000	2	Diluted HNO_3 solutions	15	[11]
Forming a Hg–Au amalgam	Mo X-ray tube (40 kV, 20 mA) Si(Li) detector (190 eV at 5.9 keV)	500	(20–30)	Hg standard solutions	100	[12]
		1000	(10)	Hg standard solutions	5000	[13]
		2000	(10)	Hg standard solutions	250	[14]
Electrochemical enrichment procedure	Mo X-ray tube (45 kV, 40 mA) (45 kV, 40 mA) (159 eV at 5.89 keV)	1000	N.A.	Hg standard solutions	0.004	[15]
Trapping complexation (Ac, Ox, EDTA, APDC)	Mo X-ray tube (50 kV, 30 mA) Si(Li) detector (165 eV at 5.9 keV)	200	1 (10)	TiO_2 photocatalytic reaction solutions	10[b]	[16]
Preconcentration using PVC membranes (containing ditizone) on the reflector	Mo X-ray tube (55 kV, 20 mA) Si(Li) detector (155 eV at 5.9 keV)	100	50	Sea water	0.4	[17]
		300	50	Drinking water	0.2	[3]
CDI quartz activation with 4-(2-pyridylazo-resorcinol) immobilization	Mo X-ray tube (55 kV, 20 mA) Si(Li) detector (155 eV at 5.9 keV)	900	30	Drinking water	5	[18]
				Distilled water	2.5	

LOD: limit of detection; Ac: acetate; Ox: oxalate; EDTA: ethylendiamintetracetic acid; APDC: ammoniumpyrrolidine-dithiocarbamate; CDI: 1,1-carbonyldiimidazole; N.A.: not available.

[a] In brakets is presented the deposited sample volume on the reflector (μL).

[b] Limit of quantification (LOQ) value.

5–50 μL of sample on a reflective carrier with a subsequent drying by applying heat or vacuum. Preparation of samples as thin layer excludes matrix effects, like absorption and secondary excitation and thus, the quantification in TXRF analysis can be done directly by the addition of an internal standard to the sample. However, in the particular case of Hg quantification, this procedure is unsuitable due to the high vapor pressure and low boiling point of this element that produce evaporation and loss of Hg from the surface of the reflector during the drying process [11]. Last years, several analytical strategies have been developed to avoid Hg volatilization during sample preparation for subsequent TXRF analysis. In Table 1, a summary of published methods based on TXRF spectrometry for the determination of Hg in liquid samples is presented. Some authors proposed the formation of an amalgam with a noble metal (Ag and Au) to capture and preconcentrate Hg contained in liquids [12–14]. However, such methods are characterized by high detection limits (up to 5000 $\mu g\,L^{-1}$) which are not suitable for most environmental applications. The use of an electrochemical enrichment procedure employing a polished disk of pure Nb has been also proposed as a possible contender [15]. Despite that low Hg detection limits (ng L^{-1} range) were obtained with this approach, some drawbacks of the method include a long enrichment time (up to 2 h) and the need of specially constructed electrolytic cells, not always available in most laboratories. To determine Hg in TiO_2 photocatalytic reaction solutions, a methodology based on trapping Hg into the solution by forming stable complexes was also developed [16]. It must be noted that EDTA in this application was indeed added as a sacrificial electron donor to enhance Hg(II) transformation, turning easier the analytical procedure.

Last years, selective membranes containing a few micrograms of complexing reagents in a polymeric matrix and placed on the centre of quartz reflectors have also been employed as Hg preconcentration strategy prior TXRF analysis. This methodology has been applied for Hg determination in different types of water samples (including seawater) in the low $\mu g\,L^{-1}$ range using a sample volume of 50 mL and an equilibration time of 1 day [17,2]. Another approximation to create selective membranes for Hg determination was performed by activating the quartz reflector using 1,1-carbonyldiimidazole (CDI) and a subsequent coupling reaction between the activated surface and 4-(2-pyridazo-resorcinol). Using this method, determination of Hg was feasible at detection levels of 2.5 $\mu g\,L^{-1}$ for distilled water and 5 $\mu g\,L^{-1}$ for drinking water, respectively [18]. However, again, the Hg extraction using selective membranes was time consuming (~22 h), limiting the application of this procedure to routine analysis.

Considering the number of samples to be handled in order to get valid information in environmental studies, the main goal of the present research was to develop a fast and simple chemical strategy to avoid Hg volatilization during the analysis of wastewater samples by means of TXRF spectrometry. Three different analytical procedures were tested for this purpose: (i) increasing the viscosity of the wastewater sample by adding a non-ionic surfactant (Triton® X-114), (ii) Hg immobilization on the quartz reflectors using the extractant tri-isobutylphosphine (Cyanex 471X) and (iii) formation of a stable and non-volatile Hg complex into the wastewater sample. In this latter case, several complexing agents were studied including relatively large organic molecules (ethylendiaminetetraacetic acid and 8-hidroxyquinoline) and molecules containing sulfur groups in their structure (sodium thiosulphate, thiourea, sodium tiocyanate). The use of these complexing agents was chosen due to their ability to create stable complexes with the analyzed trace element.

For the best analytical strategy, analytical figures of merit such as linearity, limits of detection, accuracy and precision were carefully evaluated. Finally, the developed methodology was applied for the determination of Hg in different types of wastewater samples (industrial effluents, municipal effluents from conventional systems and municipal effluents from constructed wetlands).

2. Experimental

2.1. Reagents and solutions

Stock solutions of $1000 \pm 0.5\,\mu g\,mL^{-1}$ (Spectroscan, TECKNOLAB A/S, Norway) of appropriate elements were used to prepare standard solutions and spiked samples. High purity water used for dilution of stock solutions was obtained from a Milli-Q purifier system operated at $18\,M\Omega$ (Millipore Corp., Bedrod, MA). The solution (10% in water) of the commercial non-ionic detergent Triton® X-114 (polyethylene glycol tert-octylphenyl ether) was purchased from Sigma–Aldrich (Spain). All complexing agents used were high quality reagents for laboratory use (PA-ACS-ISO): ethylendiaminetetraacetic, sodium thiosulphate, thiourea and sodium tiocyanate were purchased from Sigma–Aldrich (Spain) and 8-hidroxyquinoline was acquired from Panreac S.A. (Spain). The extractant tri-isobutylphosphine (Cyanex 471X) was supplied by CYTEC Industries (Woodland, NJ, USA) and the ethanol absolute used for Cyanex 471X dissolution was purchased from Panreac (Spain).

In TXRF analysis, the sample carrier plays an important role with regard to the achievement of optimal analytical results. In most cases, the reflective sample carrier is made of quartz or acrylic glass. In this work, taking into account the higher resistance and the lower background, quartz glass discs with a diameter of 30 mm and a thickness of 3 ± 0.1 mm were used as sample holders for introducing the sample into the TXRF equipment.

2.2. Instrumentation

The analysis by TXRF was performed using a TXRF 8030C spectrometer (Atomika Instruments GmbH), equipped with a 3 kW X-ray tube with a Mo/W alloy anode and a double-W/C multilayer monochromator, adjusted to obtain an excitation energy of 17.4 keV (Mo K_α). In this equipment, the characteristic radiation emitted by the elements present in the sample is detected by a Si(Li) detector with an active area of $80\,mm^2$ with a resolution of 150 eV at 5.9 keV. The measurements were performed working at 50 kV and the current was adjusted automatically as a trade-off between the detector dead time and total analysis time. A fixed acquisition time of 1000 s was used.

2.3. Sample preparation

2.3.1. Samples

To test the applicability and robustness of the developed methodology for the intended purpose, different types of wastewater samples were analyzed: (i) industrial wastewater effluents from metallurgical and tanning-leather factories ($n = 2$), (ii) municipal effluents from conventional treatment plants ($n = 3$) and (iii) municipal effluents from constructed wetlands ($n = 5$). From the last few decades, the application of constructed wetlands as wastewater treatment systems has gained the popularity throughout the word as an effective and inexpensive alternative for traditional wastewater treatment methods. These engineered systems have been designed to employ natural processes including vegetation, soil and microbial activity to treat contaminated water [19].

2.3.2. Sample treatment procedures

In all the analytical procedures tested for Hg quantification purposes, Y was selected as internal standard due to compatibility with the studied system. An appropriate amount of a $1000 \pm 0.5\,\mu g\,mL^{-1}$ Y solution (to reach a final Y concentration of $500\,\mu g\,L^{-1}$) was added to the target sample or standard for internal standardization.

As commented in Section 1, three different chemical strategies were tested for Hg quantification by TXRF spectrometry.

2.3.2.1. Increasing the viscosity of the sample. To study the efficiency of increasing the viscosity of the sample to avoid Hg volatilization during the drying procedure in TXRF analysis, a dilution of the liquid sample (1:1) using a 10% solution of the commercial non-ionic detergent (Triton® X-114) was performed. After, the resulting solution was thoroughly homogenized (Vortex device) and an aliquot of $10\,\mu L$ was transferred onto a quartz glass sample carrier and dried before TXRF analysis.

2.3.2.2. Hg immobilization on the quartz reflectors. Hg extraction on the quartz reflectors was tested using the extractant tri-isobutylphosphine (Cyanex 471X) due to its high mercury selectivity [20]. A stock solution of Cyanex 471X (0.004 M) was prepared by dissolving the appropriate amount of extractant in ethanol. In the present work, two types of extraction experiments were carried out. On one hand, $10\,\mu L$ of the extractant solution were transferred to the centre of the quartz reflector and they were left to dry at room temperature. Then, $10\,\mu L$ of the standardized liquid sample were added on the reflector and dried before TXRF analysis (Method 1). In a second group of experiments, the extraction solution was added to the standardized liquid sample (1:1), followed by homogenization with the use of an orbital shaker (Vortex device). The mixture was left to rest at room temperature for 30 min and then $10\,\mu L$ of the liquid were transferred on the reflector and dried for subsequent TXRF analysis (Method 2).

2.3.2.3. Trapping complexation. Stock solutions of 0.01 M of each complexing agent (ethylendiaminetetraacetic acid, sodium thiosulphate, thiourea, sodium tiocyanate and 8-hidroxyquinoline) were prepared. Then, the complexing solution was added to the standardized liquid sample (1:1), followed by homogenization with the use of an orbital shaker (Vortex device) for 1 min. The mixture was left to rest at room temperature for 30 min and then $10\,\mu L$ of the liquid were transferred on the reflector and dried for subsequent TXRF analysis.

3. Results and discussion

3.1. Procedure 1: increasing the viscosity of the sample

As reported in the literature, non-ionic detergents such as Triton® X-114 could be used to adjust the viscosity of solutions and enhance the homogeneity of the analyzed samples [21]. In the present work it was tested if the high density of this surfactant could also avoid the Hg volatilization during the drying procedure for subsequent TXRF analysis. From the obtained results it was found that an improvement of the Hg signal when using such reagent as a diluting agent did not occur. On the contrary, the background of the obtained TXRF spectrum increased considerably when using Triton® X-114 (see Fig. 1). This fact also difficult the quantification of Hg due to the proximity of the K-lines of Y (internal standard) to the increased background that hampers the Y K-lines fitting. Taking into account all these facts, it was decided that this procedure was not suitable for the intended purpose.

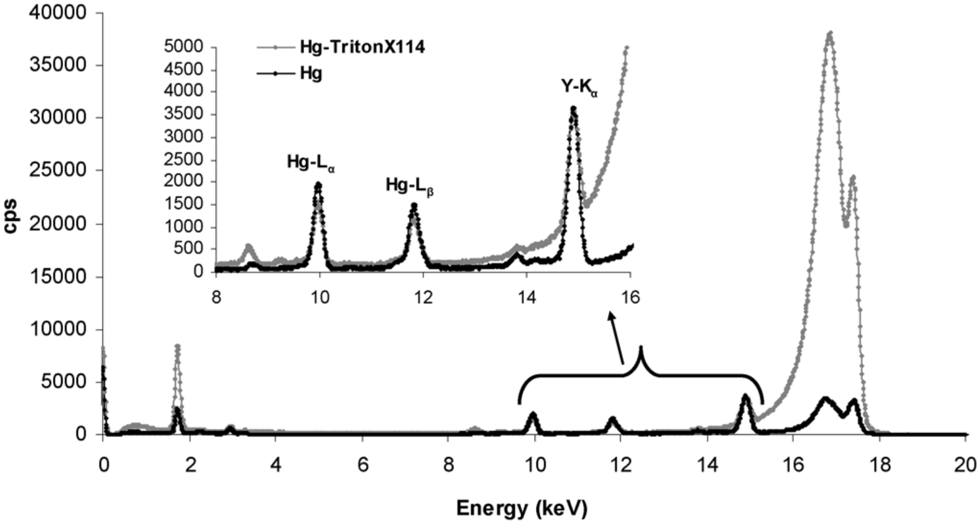

Fig. 1. TXRF spectrum of a 1 mg L^{-1} Hg standard solution with and without using Triton® X-114 for sample preparation.

3.2. Procedure 2: Hg immobilization on the quartz reflectors

As commented in Section 2, two different experimental methodologies were tested using the extractant tri-isobutylphosphine sulphide (Cyanex 471X) for Hg immobilization on the quartz reflectors. In both cases (Methods 1 and 2), a slightly higher improvement of the recovery calculated for the analysis of a Hg standard containing 1 mg L^{-1} of Hg (~80%) was obtained compared to that calculated for the direct analysis of the same Hg standard (~60%). However, it was found that the Hg recovery obtained when using Cyanex 471X was dependent on the initial Hg concentration and also on the drying procedure used (see Fig. 2). Therefore, the Hg collected on the reflector using this analytical approach was not directly related to the initial Hg content in the reflector and it could not be used for quantitative purposes.

3.3. Procedure 3: trapping complexation

3.3.1. Effect of pH

The pH plays an important role with respect to the Hg complexation in the liquid solution. For this reason, the effect of pH on the relative Hg signal was examined analyzing 0.1 M solutions of the complexing agents studied in the pH range of 2–10 at the level of 1 mg L^{-1} of Hg (Fig. 3). From the obtained results it was found that the best candidates to be used as complexing agents for Hg determination were ethylendiaminetetraacetic acid (EDTA) at pH = 10, thiourea at pH = 10 and sodium thiosulphate at pH = 6.

3.3.2. Effect of Hg concentration

In order to test if the Hg collected on the reflector after the complexation procedure could be directly related to the initial Hg content on the reflector, Hg recovery at different concentration levels was calculated. Results obtained using different drying procedures (vacuum, hot plate at 100 °C, IR lamp) are displayed in Fig. 4. Low Hg recoveries (~60%) were obtained when performing Hg determination without the addition of a complexing agent. Moreover in this case, a significant fluctuation of recovery values was obtained depending on the initial Hg concentration in the liquid solution. A higher Hg recovery was calculated when the trapping complexation procedure was carried out (~80%). However, when using EDTA or sodium thiosulphate as complexing agents, the calculated recoveries were dependent on the initial Hg concentration. The best results were obtained if thiourea at pH = 10 was employed to complexate Hg since in this case a constant recovery of 80% was achieved at Hg concentrations ranging from 1 mg L^{-1} to 10 µg L^{-1} (corresponding to 10 ng and 0.1 ng of Hg on the reflector, respectively) for all the drying procedures tested. According to this results, thiourea at pH = 10 was used for following experiments.

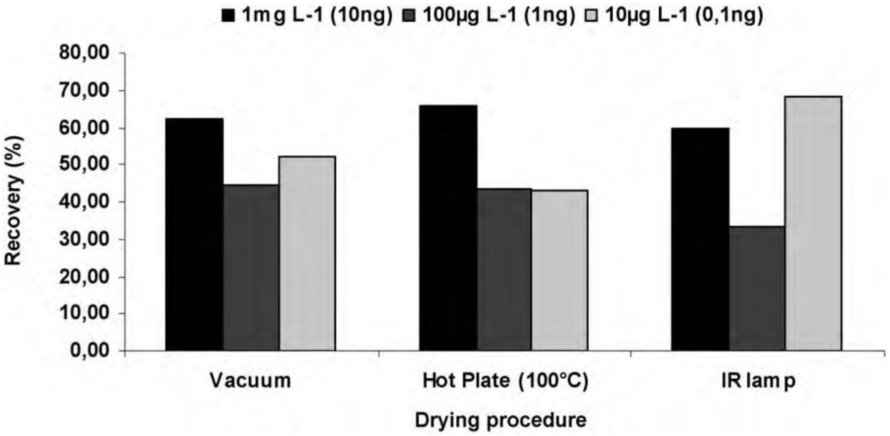

Fig. 2. Hg recovery *vs.* drying procedure when using Cyanex 471X immobilized on the reflector at different Hg concentration levels (in brackets Hg content on the reflector).

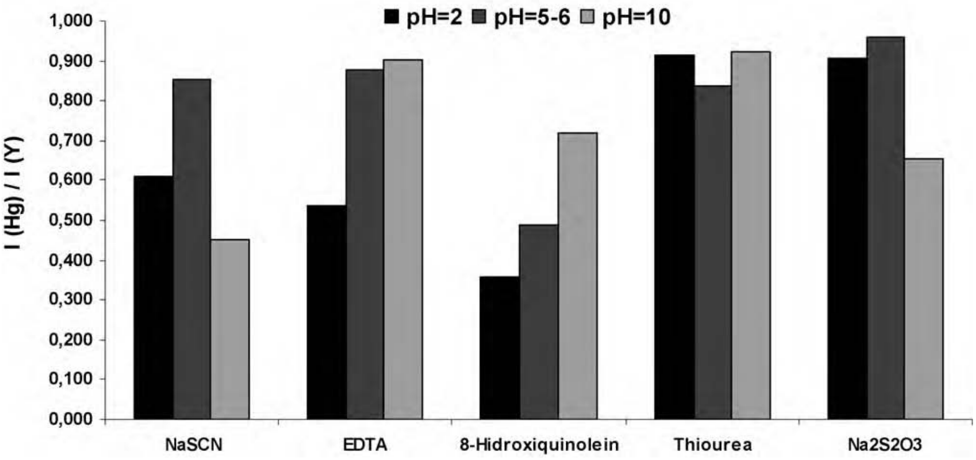

Fig. 3. Effect of pH on Hg complexation ([Hg] = 1 mg L^{-1} and [complexing agent] = 0.1 M).

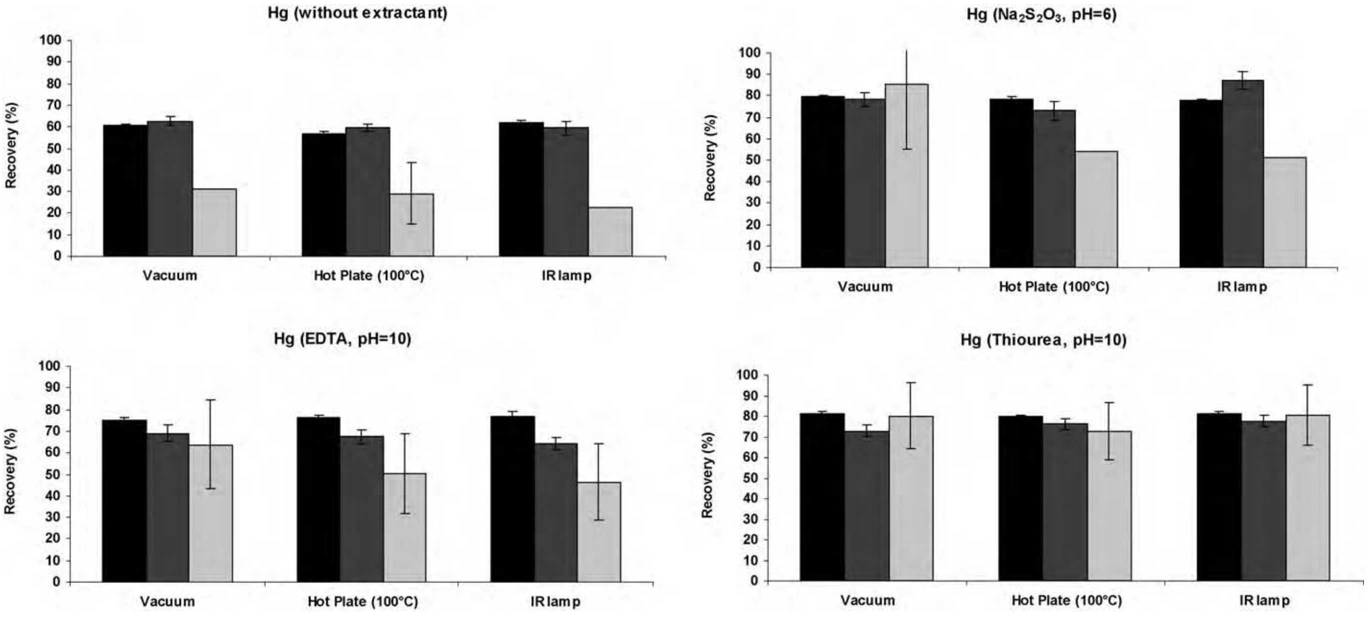

Fig. 4. Hg recovery *vs.* drying procedure using several complexing agents at different Hg concentration levels (black: 1 mg L^{-1} Hg (10 ng Hg), dark grey: 100 μg L^{-1} Hg (1 ng Hg), light grey: 10 μg L^{-1} Hg (0.1 ng Hg)).

3.3.3. *Effect of complexing agent concentration*

The effect of complexing agent concentration on the analytical response for Hg was also studied. In Fig. 5 TXRF spectra of 100 μg L^{-1} Hg standard solutions using different concentrations of thiourea are shown. In view of the obtained results, a 0.01 M thiourea solution was established for further experiments since this concentration proved to be sufficient to complex Hg and moreover, a lower background of the TXRF spectrum was achieved compared to that obtained when using a concentration of 0.1 M of thiourea.

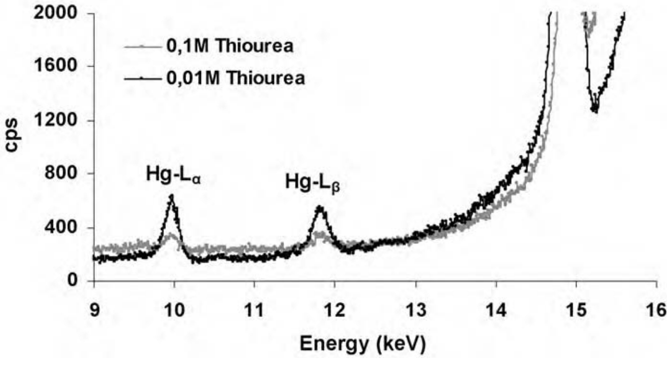

Fig. 5. TXRF spectrum of a 100 μg L^{-1} Hg standard solution using different concentrations of complexing agent (thiourea pH = 10).

3.3.4. *Analytical figures of merit*

3.3.4.1. Linearity. The linearity of the methodology was determined by analyzing 9 aqueous samples containing Hg in the range 10–1000 μg L^{-1} (corresponding to 10–0.1 ng Hg on the reflector). Intensity ratios between the Hg L_α and Y K_α lines were plotted *vs.* known concentrations of Hg in the solutions and a straight line was fitted to measured points by the least-square method (confidence limit 95%). Fig. 6 depicts the obtained calibration lines obtained when applying the trapping complexation procedure using thiourea and the direct analysis of Hg. It is clearly noted that a higher sensitivity and linearity was obtained in the presence of thiourea in the solution, also in the lower concentration range (10–200 μg L^{-1}). The regression coefficient was higher than 0.99,

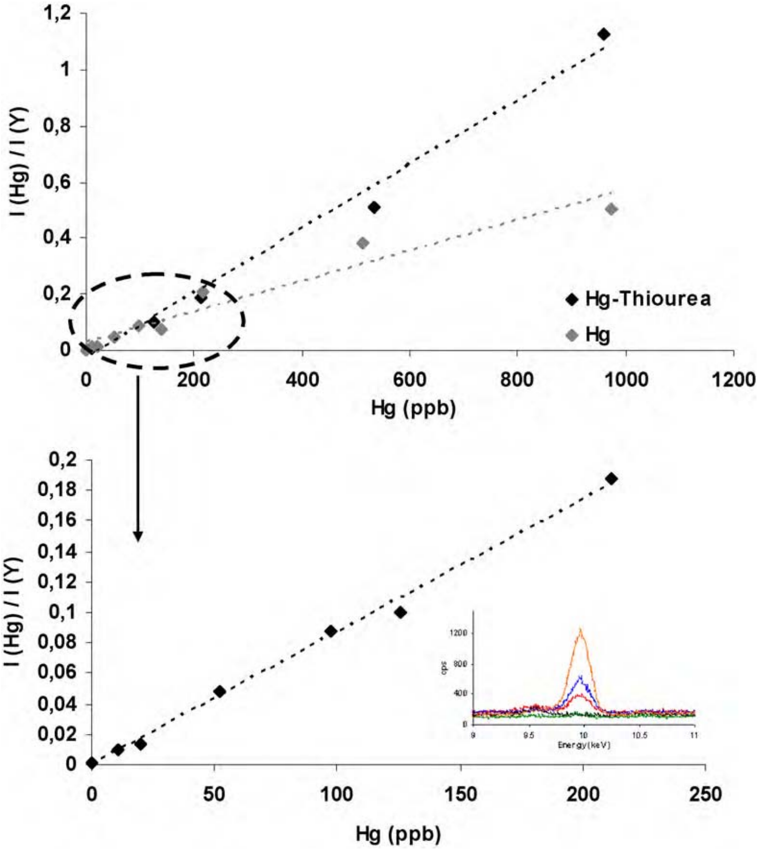

Fig. 6. Relative signal intensity (Hg L_α/Y K_α) as a function of Hg concentration (analytical conditions: thiourea 0.1 M at pH = 10, 10 μL, 1000 s).

indicating a good linearity and a wide working range under experimental conditions. This fact confirms the suitability of using this analytical approach since Hg collected on the reflector is related with the initial metal content in the aqueous solution.

3.3.4.2. Limit of detection. Limit of detection for Hg was estimated as 3 times the background standard deviation (square root of the background) in the TXRF spectrum of a standard solution of Hg in a concentration of 10 μg L^{-1} [10]. Different sample volumes and measuring conditions were tested to assess the lowest Hg concentration that could be detected using the developed methodology. A measuring time of 1000 s was selected as a trade-off between an acceptable limit of detection and total analysis time. It was found that using a measuring time of 1000 s and a sample volume of 50 μg L^{-1} the Hg content that could be detected was as low as 0.7 μg L^{-1}, corresponding to 7 pg of Hg on the reflector. The limit of detection achieved in this work is comparable to or better than some of the previous reported methods (see Table 1).

3.3.4.3. Accuracy. Accuracy of the Hg TXRF measurements in wastewater samples was examined by analyzing five municipal wastewater samples spiked at different Hg concentration levels in the range of 20–500 μg L^{-1}. Good agreement was obtained between Hg concentrations determined by the TXRF method and the initial Hg concentration in the spiked samples ($y = 1.0789x - 1.9451$, $R^2 = 0.9997$). This fact confirms the suitability of the trapping complexation procedure developed for the determination of Hg in wastewater samples.

3.3.4.4. Precision. The precision of the methodology was evaluated in terms of relative standard deviation (RSD) of five replicate analyses of a standard solution containing 100 μg L^{-1} of Hg. A RSD of 7% was obtained for the relative Hg intensity (Hg L_α/Y K_α).

3.3.4.5. Evaluation of chemical interferences. Wastewater samples are usually characterized by high levels of organic load [22]. On the other hand, high Ca concentrations are also frequently encountered in outlet effluents as a result of coagulation–flocculation processes used in the treatment of raw wastewaters [23]. Taking into account these facts, it was considered appropriate to study the influence of Ca and organic matter (humic acids) content on Hg determination. For that, several synthetic water samples containing increasing amounts of Ca (0–500 mg L^{-1}) and humic acids (0–150 mg L^{-1}) were spiked with Hg at a concentration of 100 μg L^{-1} and analyzed. The effect of the presence of Ca and humic acids on the element signal-to-internal standard signal relationship is shown in Table 2A and B, respectively. As it can be seen, the presence of high amounts of Ca and humic acids did not affect Hg determination. Only in the case of high Ca contents (500 mg L^{-1}) the ratio Hg L_α/Y K_α signal exhibits a small increase. This fact demonstrated that probably when working with high salt contents in the sample matrix, the condition of thin layer is broken and then the analysis is not performed under total-reflection conditions.

3.3.5. Application to wastewater samples

To test the real capability of the TXRF methodology for the intended purpose, the developed procedure was applied to the determination of Hg in different types of wastewaters including, industrial wastewater effluents from metallurgical and tanning-leather factories (IND), municipal effluents from conventional treatment plants (MUN_C) and municipal effluents from constructed wetlands (MUN_W). As it is shown in Table 3, Hg concentration was below the detection limit for most analyzed

Table 2
Influence of Ca and organic matter content on Hg determination by TXRF spectrometry.

(A) Ca effect ([Hg] = 100 μg L^{-1})

[Ca] mg L^{-1}	Hg/Y signal	Std. dev. (Hg/Y)
0	0.0875	0.0032
10	0.0849	0.0045
50	0.0957	0.0042
100	0.0924	0.0044
500	0.1057	0.0082

(B) Organic matter content (OM) effect ([Hg] = 100 μg L^{-1})

[OM] mg L^{-1}	Hg/Y signal	Std. dev. (Hg/Y)
0	0.0875	0.0032
50	0.0976	0.0067
100	0.0816	0.0057
150	0.0886	0.0034

Table 3
Hg determination using the developed methodology in: industrial wastewaters (IND), municipal wastewaters from conventional systems (MUN_C) and municipal wastewaters from wetlands constructed systems (MUN_W).

Sample	Hg (μg L^{-1})	Recovery (%)[a]
IND-1	18.9	96.7
IND-2	n.d.	85.0
MUN_C-1	n.d.	109.8
MUN_C-2	n.d.	104.3
MUN_C-3	n.d.	99.4
MUN_W-1	n.d.	109.1
MUN_W-2	n.d.	95.9
MUN_W-3	n.d.	97.1
MUN_W-4	n.d.	96.8
MUN_W-5	n.d.	109.4

[a] Added concentration: 100 μg L^{-1}.

samples. Only in one of the analyzed industrial wastewater samples, coming from a metallurgical factory, a concentration of Hg of 18.9 μg L^{-1} was determined.

However, in order to validate the methodology for the different types of wastewater samples, the target samples were spiked with 100 μg L^{-1} of Hg. The recovery of the spiked samples as shown in Table 3 was, in most cases, in the range of 95–105% which demonstrates the suitability of the TXRF methodology for monitoring Hg in industrial and municipal wastewater samples.

4. Conclusions

A rapid and reliable TXRF analytical approach has been developed and validated for the determination of Hg in wastewater samples. This method, which is based on the trapping of Hg by thiourea complexation (pH = 10) previous to its quantification by TXRF, represents a suitable strategy to avoid losses of Hg during the drying process on the reflector. Additional advantages of this sample preparation are the simplicity of the chemical treatment, offering an interesting and easy alternative to the sophisticated and time-consuming treatment methods described so far (e.g., electrochemical enrichment procedure, formation of a Ag or Au amalgam) when dealing with Hg determination by means of TXRF spectrometry.

The analysis of different Hg standard solutions using the developed TXRF methodology showed a linear response between the Hg concentration in the aqueous solution and the relative Hg signal in the range of 10–1000 μg L^{-1} Hg, with a detection limit of 0.7 μg L^{-1} (corresponding to 7 pg of Hg on the reflector) for a measuring time of 1000 s.

The accuracy of the proposed method was confirmed by analyzing spiked industrial and municipal wastewater samples at the level of 100 μg L^{-1} Hg. The results of this study clearly show the potential and versatility of this method, which could be applied to monitoring Hg in various types of wastewater samples.

Acknowledgments

This work was supported by the Spanish “Consolider Ingenio 2010” Program (Project ref. CSD2006-00044) and the Spanish National Research Progam (Project ref. CGL2007-66861-C4). E. Marguí gratefully acknowledges the research-contract from the Spanish Council for Scientific Research (CSIC, JAE-Doc Program contract) and also a mobility grant within the framework of the “research stages in foreigners' research centers” funded by the Spanish Council for Scientific Research (CSIC).

Industrial wastewater samples were kindly supplied by SIGMA Consortium (La Garrotxa, Spain). The authors are also grateful to Dr. Victor Matamoros from the Chemistry Department (University of Girona) for his help during the sampling of municipal wastewater samples.

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