Analysis of inlet and outlet industrial wastewater effluents by means of benchtop total reflection X-ray fluorescence spectrometry

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ABSTRACT

The monitoring of heavy metals in industrial waste water effluents is an important activity in many laboratories. Of special interest is the screening of elemental composition of inlet effluents and quantitative analysis of outlet effluents to study the efficiency of chemical treatment process to eliminate metals and to comply with current established concentration limits, respectively. In this sense, fast analytical methodologies which entail simple sample preparation are desired.

In the present work, the possibilities and drawbacks of a benchtop total reflection X-ray fluorescence spectrometer (TXRF) for the rapid and simple determination of some inorganic impurities (As, Ba, Cd, Cu, Cr, Sn, Fe, Mn, Ni, Pb, Se and Zn) in inlet and outlet industrial waste water effluents from metallurgical and tanning leather factories have been tested. An evaluation of different simple sample treatments is presented and it is followed by a discussion of spectral and chemical matrix effects when dealing with this type of samples. Analytical figures of merit such as accuracy, precision and limits of detection have also been carefully studied. Finally, the data obtained by direct TXRF analysis has been compared to that obtained by ICP-OES/ICP-MS after a microwave digestion.

1. Introduction

Many industrial processes are chemical and water consuming and thus, they produce large quantities of waste water (Lofrano et al., 2006). High heavy metal concentrations (up to some hundred of mg L^{-1}) are frequently found in industrial waste water effluents which may cause detrimental effects on all forms of life upon direct discharge on the environment (Yunus Pamukoglu and Kargi, 2008). On the other hand, if these metals may eventually reach biological wastewater treatment plants could produce also significant changes in their microbial communities and reduce their treatment efficiency (Frank and Harangozó, 1994). The most widely known mechanism for heavy metal toxicity is the inhibition of extracellular or intracellular enzymes in activated sludge bacteria upon binding of metal ions, which is known to be irreversible in many cases (Vilchez et al., 2007). In view of that, permissible levels of heavy metals in industrial waste water effluents are usually defined by regulatory agencies and controlled by limit tests. In Spain the requirements to industrial waste waters to be discharged to a sewage system are established in each region individually. In Table 1, the concentration limits for heavy metals in industrial

waste water effluents according to the Catalan Water Agency are displayed.

Various treatment technologies in industrial plants have been developed to decrease the metal content in industrial waste water effluents and to comply the regulations of waste water discharges. Perhaps one of the most commonly used is the coagulation–flocculation process, generally using inorganic coagulants such as aluminum sulphate, ferric chlorides and ferrous sulphate. In some applications, to enhance the removal of metals, the addition of Ca(OH)$_2$ is also performed (Lofrano et al., 2006). In view of that, it is of significance to have adequate analytical methodologies to determine heavy metals not only in the treated industrial wastewaters (outlet effluents) but also in the raw waste waters (inlet effluents) to know the efficiency of the treatment process employed.

Usually, the presence of trace amounts of toxic elements in environmental samples is determined by using spectrophotometric techniques including flame atomic absorption spectrometry (FAAS) (Method 7000B, US Environmental Projection Agency, 2008), electrothermal atomic absorption spectrometry (ETAAS) (Method 7010, US Environmental Projection Agency, 2008), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Method 6101C, US Environmental Projection Agency, 2008) and inductively coupled plasma mass spectrometry (ICP-MS) (Method

Table 1
Concentration limits for heavy metals in industrial waste water effluents according to the regulation from the Catalonia Water Agency (Spain) and calculated detection limits from the analysis of the waste water reference material SPS-WW2 by TXRF spectrometry. Concentration values are expressed as mg L^{-1}.

Element	Limit value	Limits of detection (TXRF analysis)	
		Without treatment	Microwave digestion
Cr	3	0.24	0.24
Mn	2	0.17	0.12
Fe	5	0.09	0.07
Ni	5	0.11	0.07
Cu	3	0.10	0.06
Zn	10	0.08	0.05
As	1	0.03	0.02
Se[a]	0.5	0.02	0.09
Cd	0.5	0.009	0.003
Sn[a]	5	0.04	0.03
Ba[a]	10	0.49	0.48
Pb	1	0.01	0.01

Measuring time: 1000 s.
[a] Elements added to the SPS-WW2 reference material to calculate the limits of detection.

6020A, US Environmental Projection Agency, 2008). However, the direct analysis of some complex liquid environmental samples like wastewaters presents significant problems related to the complicated matrix of this type of samples. On the one hand, industrial inlet effluents are usually characterized by high levels of organic load and suspended solids. According to the reported literature, concentration contents with regards to total organic carbon contents (TOC) and total suspended solids (TSS) in inlet effluents could be up to 150 mg L^{-1} (Kutseva et al., 2000) and 1520 mg L^{-1}(Lofrano et al., 2006), respectively. An additional problem of the inlet effluents is the higher viscosity compared to water that also difficult the sample introduction system of most spectroscopic techniques. On the other hand, high Ca concentrations are frequently encountered in outlet industrial effluents as a result of coagulation–flocculation processes used in the treatment of raw waste waters that may also hamper the analysis. Therefore, in such cases, a typical dilution or digestion of the sample may be necessary before the analysis or a preliminary separation step may be required to eliminate interferences. For instance, the United States European Protection Agency (US-EPA) provides an analytical methodology based on the use of a microwave acid digestion (Method 3015A) to determine available metals in aqueous samples and wastes that contain suspended solids (Method 3015A, US Environmental Projection Agency, 2008). Although effective, the digestion approach is time-consuming and requires the use of corrosive and harmful reagents.

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 (Streli, 2006). 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 (Klockenkämper, 1997). To perform analysis under total-reflection conditions, samples must be provided as thin films. For liquid samples, this is done by depositing 5–50 µL of sample on a reflective carrier with a subsequent drying by applying heat or vacuum. Preparation of samples as thin layer exclude 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, when dealing with the analysis of some complex liquid samples, usually a special preparation

method has to be also applied to the sample to avoid inaccuracies associated with the drying step (Marguí et al., 2010).

Last decades, most of the published TXRF analyses were performed using large-scaled instruments with high-power X-ray tubes, demanding water-cooling systems and liquid-nitrogen cooled detectors. However, in recent years, the development and commercialization of bench top TXRF instrumentation, which offer extreme simplicity of operation in a low-cost compact design, have promoted its application in industry as well as in research activities (Stosnach, 2005).

The main goal of the present research is to develop a fast TXRF method with a sample preparation as simple as possible, without losing analytical performance compared to atomic spectroscopic techniques, for metal residues determination in industrial waste water samples. An evaluation of different simple sample treatments is presented and it is followed by a discussion of spectral and chemical matrix effects when dealing with this type of samples. Analytical figures of merit such as accuracy, precision and limits of detection have also been carefully evaluated. Finally, the developed methodology has been applied to the determination of heavy metals (listed in Table 1) in metallurgical and tanning industrial wastewater samples before (inlet effluents) and after the chemical treatment in the respective industrial plants (outlet effluents).

2. Experimental

2.1. Materials and reagents

Stock solutions of 1000 ± 0.5 µg 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 and samples was obtained from a Milli-Q purifier system operated at 18 MΩ (Millipore Corp., Bedrod, MA). The solution (10% in water) of the commercial non-ionic detergent Triton® X-114 (polyethylene glycol tert-octylphenyl ether) used for sample dilution was purchased from Sigma–Aldrich (Spain). All reagents used for sample microwave digestion were analytical grade Suprapur quality: nitric acid (Suprapur, Merck, Darmstadt, Germany) and hydrogen peroxide (Trace Select, Fluka, Gilligham, Dorset, UK).

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 mm ± 0.1 mm were used as sample holders for introducing the sample into the TXRF equipment.

The certified reference material SPS-WW2 ("Reference Material for Measurement of Elements in Wastewaters", Spectrapure Standard, Manglerud, Oslo, Norway) was employed to test the sample treatment for the analysis of wastewaters and the whole developed methodology.

2.2. Instrumentation

An ETHOS PLUS Millestone microwave with HPR-1000/10S high pressure rotor (Sorisole, Bergamo, Italy) was employed for acid digestion of samples.

Elemental content in digested waste water samples was determined by using an ICP-AES spectrometer Varian Liberty (Springvale, Australia) with a V-groove nebuliser. Metal concentrations below the detection limit of ICP-AES were determined by a quadrupole-based ICP-MS system (Agilent 7500c, Agilent Technologies, Tokyo, Japan) equipped with an octapole collision cell. The instrumental parameters and measurement conditions are displayed in Table 2.