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Analytical capabilities of two-phase hollow-fiber liquid phase microextraction for trace multielement determination in aqueous samples by means of portable total reflection X-ray instrumentation

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Abstract: Liquid phase microextraction (LPME) procedures have been widely used in combination with atomic and emission spectroscopic techniques for the isolation and preconcentration of trace elements. However, its application in combination with total reflection X-ray spectrometry (TXRF) is still scarce. In this paper, we evaluate the possibilities and drawbacks of a two-phase hollow fiber LPME procedure in combination with TXRF for the simultaneous determination of trace amounts of Cr, Ni, Cu, Zn, Pb, and Cd in aqueous samples.

After extraction of the analytes by using the optimum conditions (sample volume: 25 mL, complexing agent: APDC, organic solvent: hexylbenzene, extraction time: 2 h, extraction speed: 660 rpm), 10 μL of the preconcentrated sample was deposited on a preheated quartz reflector, dried on a hot plate at 80 °C, and analyzed by TXRF. Using such conditions, limits of detection lower than 3 $\mu\text{g L}^{-1}$ were obtained for all metals.

In spite of LODs improvement in comparison with the direct analysis of the aqueous samples (up to a factor of 100), precision of the results was not optimal (RSD ~20%). This fact may be related to the use of a low volatility solvent as extractant phase that hampers the later TXRF analysis.

Key words: HF-LPME, TXRF, lead, cadmium, chromium, zinc, copper, nickel

1. Introduction

Multielement determination and quantification in liquid samples is a topic of great interest in many fields. Usually environmentally important elements are present in water samples at the low $\mu\text{g L}^{-1}$ range and the analytical techniques used for their determination include electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS).^{1–3} Although less used, total reflection X-ray spectrometry (TXRF) is also applicable for this purpose.⁴ Over the last decades, most of the published TXRF analyses were performed using large-scale instruments with high-power X-ray tubes that required water-cooling systems and liquid-nitrogen cooled detectors.⁵ However, in recent years, the development and commercialization of benchtop TXRF instrumentation, offering extreme simplicity of operation in a low-cost compact design, have promoted its application in industry as well as in research activities.^{6,7} However, these systems present limited sensitivity and usually a sample treatment procedure is needed to preconcentrate analytes and improve the detection limits. Many pre-

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concentration methods for the analysis of water samples by X-ray spectrometric techniques (including TXRF) have been developed so far.^{8,9} Taking into account the microanalytical capability of TXRF,¹⁰ recent preconcentration strategies used in combination with TXRF have focused on the use of nanomaterials as well as liquid phase microextraction (LPME) procedures.¹¹ LPME is a solvent-miniaturized sample pretreatment procedure of the conventional liquid-liquid extraction (LLE) in which only several microliters of solvent are required to concentrate analytes rather than hundreds of milliliters needed in traditional LLE.¹² Since its development in the mid-to-late 1990s, LPME has been widely used to preconcentrate organic analytes¹³ as well as inorganic analytes mostly in combination with electrothermal atomic absorption spectrometry (ETAAS), flame atomic absorption spectrometry (FAAS), or electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS).^{14,15} Different LPME modes have been developed including hollow fiber LPME (HF-LPME), dispersive liquid-liquid microextraction (DLLME), and single drop LPME (SD-LPME). Some recently published papers have shown the possibilities of DLLME as a preconcentration strategy to be used in combination with TXRF for the determination of trace levels of Cd as well as Sb species in waters.^{16,17} However, there is an absolute lack of information about the possibilities of HF-LPME in combination with TXRF for multielement analysis of aqueous samples. Therefore, the aim of this contribution was to develop a method based on HF-LPME for the simultaneous determination of Cr, Ni, Cu, Zn, Pb, and Cd in aqueous samples by TXRF and to explore the analytical capabilities for such purpose. For that, in the first stage, parameters affecting both the extraction procedure and TXRF analysis were carefully evaluated to ensure the best sensitivity for multielement determination. Then analytical figures of merit including limits of detection, linearity, accuracy, and precision were evaluated.

2. Results and discussion

2.1. Selection of experimental conditions for multielement extraction by HF-LPME

According to the literature,¹⁵ in HF-LPME systems, the extractant phase should have low solubility in water to avoid its dissolution and low volatility to reduce evaporation of the solvent during extraction. Moreover, the extractant should have an adequate polarity so that it can be immobilized within the pores of the hollow fiber, avoiding solvent leakage. In the present contribution, the suitability of several organic solvents including undecane, dihexyl ether, decalin, hexylbenzene, and toluene was tested for such purpose. In a previous work, we demonstrated the usefulness of carbon tetrachloride as extractant solvent in a DLLME-TXRF system.¹⁶ Therefore, in spite of the higher volatility of this solvent compared to the aforementioned ones, we evaluated also the possibilities of using this solvent in the HF-LPME configuration. It is well known that hydrophobic analytes are easily extracted into organic solvents from aqueous solutions. Therefore, for proper extraction of metals present in an aqueous solution, an adequate complexing agent should be added to the sample to form metal chelates with low solubility in water. For that, APDC and 8-hydroxyquinoline were tested taking into account their widespread use as complexing agents in metal preconcentration procedures.^{18,19}

Preliminary extraction tests were carried out with 25 mL of an aqueous solution containing Cr, Ni, Cu, Zn, Cd, and Pb at the level of $50 \mu\text{g L}^{-1}$. First, an adequate amount of APDC and 8-hydroxyquinoline was added to the aqueous sample to obtain a final concentration of 0.25% (w/v) and then the pH was adjusted to 7 and 8, respectively, taking into consideration previous reported studies dealing with the use of such complexing agents.^{18,19} In both cases, $100 \mu\text{L}$ of all the organic solvents mentioned above were tested as extraction phase placed inside the HF. The impregnated HF was then immersed into the aqueous solution and the extraction was carried out for 2 h under magnetic agitation.

For both systems (APDC/8-hydroxyquinoline), toluene and carbontetrachloride were not recovered from the HF after the preconcentration procedure. For that, these solvents were discarded to be used in the HF-LPME configuration. In the case of 8-hydroxyquinoline, only a significant Cu signal was obtained when using dihexyl ether as organic phase. In contrast, when using APDC as complexing agent, interesting results were obtained for most of the studied elements using decalin or hexylbenzene as extractant phases (see Figure 1). Since the aim of this manuscript was the development of a multielement method of preconcentration, APDC was finally selected as complexing agent and decalin and hexylbenzene as extractant phases for further experiments.

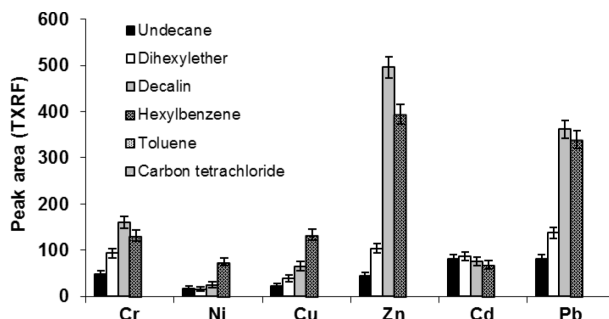


Figure 1. Effect of organic solvent used for multielement extraction when using HF-LPME (configuration 2: 50 $\mu\text{g L}^{-1}$ metals, 25 mL aqueous sample, APDC 0.25% (w/v), pH 6–7, extraction time: 2 h, 50 μL organic solvent inside the hollow fiber).

In addition to the extractant and the complexing agent, other parameters affecting metal extraction (extraction time, sample pH, sample volume, and extraction speed) were evaluated to obtain high analyte preconcentration rates. One variable at a time optimization was used to obtain the best favorable conditions for the HF-LPME procedure. All the experiments were carried out using an aqueous standard containing Cr, Ni, Cu, Zn, Cd, and Pb at the level of 50 $\mu\text{g L}^{-1}$ and an APDC concentration of 0.25%. HF dimensions were 4.5 cm length (4.0 effective length) with an internal diameter of 600 μm . The use of a thinner HF was discarded due to the insufficient organic solvent volume recovered after the preconcentration procedure to carry out later TXRF analyses.

Extraction time is a significant parameter in HF-LPME systems and it was firstly evaluated. In Figure 2A, as an example, the analytical TXRF signal for Zn is shown at different extraction times (from 30 to 600 min) using hexylbenzene and decalin as extractant phases. As shown, for both solvents, metal extraction is increasing up to 600 min. However, as a compromise between the extraction rate and the extraction time, 120 min was used to perform the subsequent experiments. Moreover, from Figure 2A, it can be deduced that analytical TXRF signals obtained when using decalin as extractant phase were lower than when using hexylbenzene. Similar trends were found for other studied elements (for additional information see Supporting information). Therefore, hexylbenzene was selected as organic phase to recover metals inside the HF.

The effect of pH on the formation and extraction of the ADPC-metal complexes was also studied and it was found that the metal signals were higher and relatively constant in the pH range of 6–8. Taking into account that the pH of natural waters is usually within the range of 6–7, the pH adjustment of the sample was not necessary.

Another parameter that can affect the sensitivity of the preconcentration procedure is the volume of the aqueous sample. To evaluate this effect, we compared TXRF spectra obtained for the analysis of a preconcentrated sample using aliquots of 25 mL or 500 mL of the initial aqueous sample. The results obtained

are displayed in Figure 2B. As shown, the improvement in the analytical signal was almost negligible increasing the volume 20 times. This fact can be explained considering a worst contact between the fiber and the solution when using higher sample volumes that lead to a limited extraction of the metals inside the HF. Therefore, a volume of 25 mL was set since, within the two volumes studied, it entails less consumption of reagents.

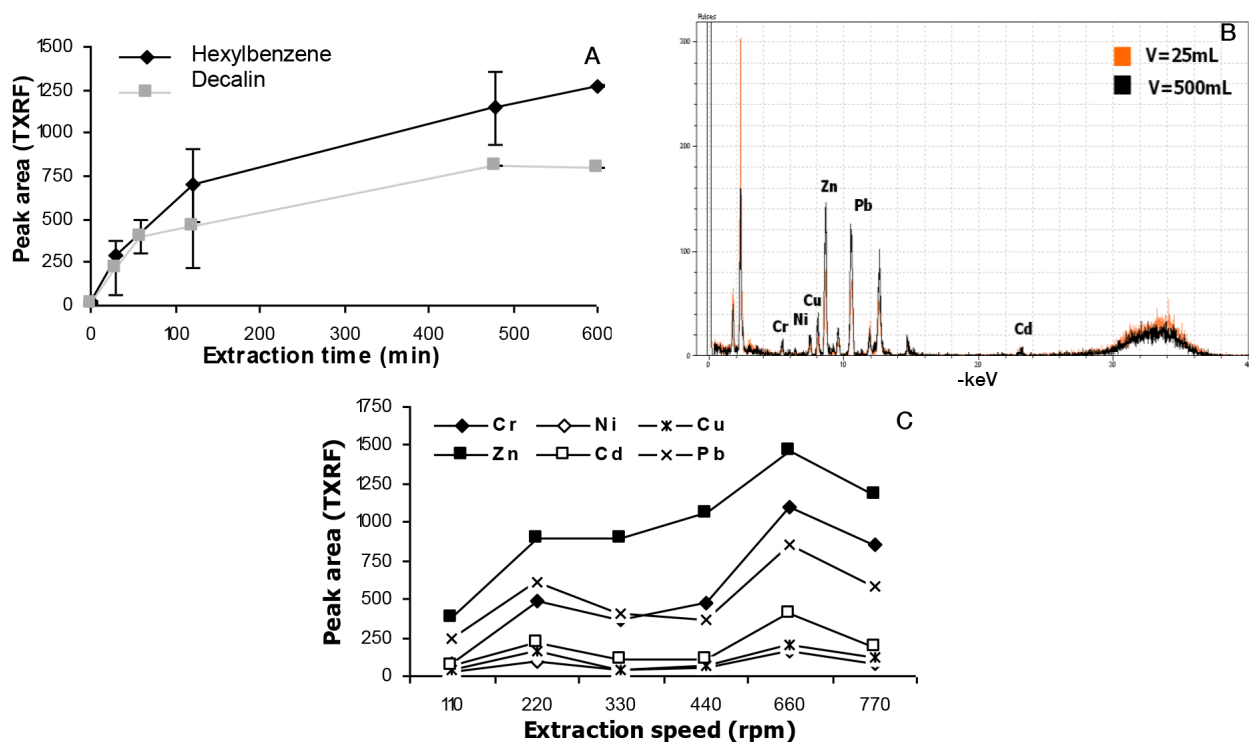


Figure 2. Effect of: (A) extraction time ($50 \mu\text{g L}^{-1}$ metals, 25 mL aqueous sample, APDC 0.25% (w/v), pH 6–7), (B) aqueous sample volume ($50 \mu\text{g L}^{-1}$ metals, 50 μL hexylbenzene, APDC 0.25% (w/v), pH 6–7, extraction time: 2 h), (C) extraction speed ($50 \mu\text{g L}^{-1}$ metals, 50 μL hexylbenzene, APDC 0.25% (w/v), pH 6–7, extraction time: 2 h) on element determination using the HF-LPME-TXRF system.

To speed up the extraction process when using HF-LPME procedures, usually the sample is stirred. Stirring rate is therefore another significant parameter to be tested. Increasing stirring speeds (within the range 110–770 rpm) were used for the extraction (2 h) of standard solutions containing $50 \mu\text{g L}^{-1}$ of the target metals. The obtained results in terms of TXRF signal are displayed in Figure 2C. In general, an increase in the analytical signal was obtained when using stirring speeds up to 660 rpm. Using higher speeds (770 rpm) a strong wave was originated at the top-center of the solution that hampers the extraction process and, as shown in Figure 2C, the analytical signal decreased. Based on the obtained results, a stirring rate of 660 rpm was selected.

2.2. Selection of operating conditions for TXRF measurements

As stated in the introduction section, in order to work under conditions of total reflection, samples must be presented as thin layers ($<100 \mu\text{m}$) on a reflective carrier. Moreover, the diameter of the sample spot on the sample carrier has to be within the beam size to ensure the entire exposition of the drop to the X-ray beam. For aqueous samples this is accomplished by depositing 5–50 μL of the sample on the carrier and drying the drop

under heating.²⁰ However, when analyzing organic solvents, a careful evaluation of the sample volume as well as of the drying mode should be carried out in order to ensure proper preparation for the later TXRF analysis.

For that reason, a first test was performed in order to study the effect of the sample deposition volume (sample pre-concentrated in hexylbenzene) on the obtained TXRF results. The use of volumes higher than 10 μL was discarded because of the long time required to dry the organic drop. The data obtained are presented in Figure 3. As seen, a significant increase in the elements' TXRF response was found when using a total volume of 10 μL but using two consecutive depositions of 5 μL in the same location with time allowed for droplet drying between depositions. Based on the obtained results, this sample deposition approach was used in further experiments.

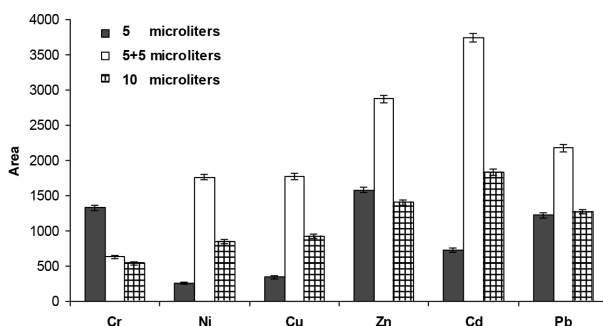


Figure 3. Effect of pre-concentrated sample deposition volume on the quartz reflector for TXRF analysis (analytical conditions: [Metals] = 50 $\mu\text{g L}^{-1}$, 25 mL aqueous phase, extraction time: 2 h, stirring rate: 660 rpm).

Another set of tests was conducted to select the best way to dry the drop as a centered film on the reflector: (i) drying at room temperature (under a laminar flow hood), (ii) drying under an IR-lamp, (iii) drying on a hot plate ($T = 80\text{ }^{\circ}\text{C}$). It was found that the only way to avoid the unwanted movement of the organic drop to the reflector's edges during the drying step and thus obtaining a centered thin film on the reflector surface was the deposition of the drop on a preheated reflector and using an additional heating step on a hot plate set at $80\text{ }^{\circ}\text{C}$.

Regarding the instrumental conditions, the rate of kV/mA (50/1) of the X-ray tube was selected to work under conditions of maximum efficiency of excitation (max. power of the X-ray tube 60 W). Measurement time was set at 1000 s as a trade-off between an acceptable instrumental sensitivity, repeatability of measurements, and total analysis time.

2.3. Analytical figures of merit and analytical possibilities of HF-LPME-TXRF system

Limits of detection for the HF-LPME-TXRF system were theoretically estimated from the element peak intensities and background values obtained in the TXRF analysis of a pre-concentrated aqueous standard containing 50 $\mu\text{g L}^{-1}$ of each element, according to the following equation:

$$LOD = \frac{3C_i \sqrt{N_{bkg}}}{N_i}$$

where C_i is the concentration of a given analyte, N_{bkg} is the background area, and N_i is the net area of the analyte.

Obtained values are shown in Table 1. For comparison purposes, limits of detection calculated for the direct analysis (without pre-concentration) of an aqueous standard containing 500 $\mu\text{g L}^{-1}$ of each element are

also displayed. As can be seen, limits of detection when using the HF-LPME procedure as preconcentration step are, for all the studied elements, at the low $\mu\text{g L}^{-1}$ level. These values are significantly improved in comparison to the direct TXRF analysis. This fact is particularly interesting when using portable TXRF systems that offer extreme simplicity of operation in a low-cost compact design (no cooling media or gas consumption are required for operation) but they also present limited sensitivity compared with high-scale instrumentation. Although the LODs achieved are rather higher than those associated with other popular spectrometric techniques such as ETAAS²¹ and ICP-MS (after electrothermal vaporization)²² in combination with HF-LPME, they are low enough for most environmental studies.

Table 1. Analytical figures of merit for the HF-LPME-TXRF system. Concentrations are expressed in $\mu\text{g L}^{-1}$.

Element	LOD ^a	Linearity			RSD (% , n = 4) ^b	
		Range	Slope	R ²	Without IS	With IS (Mo)
Cr	1.8 (180)	5–50	3.257	0.996	26	4
Ni	2.8 (100)	5–70	4.858	0.991	40	17
Cu	2.3 (105)	5–40	3.488	0.990	6	20
Zn	1.0 (102)	5–50	13.853	0.993	14	70
Pb	0.5 (22)	10–70	10.726	0.999	24	15
Cd	3 (34)	5–50	1.695	0.991	16	4

LOD: limit of detection, IS: internal standard correction.

^a in parentheses are reported the detection limits without preconcentration (direct analysis of an aqueous sample).

^b RSD was calculated from four-replicate analysis of an aqueous standard containing $30 \mu\text{g L}^{-1}$ of each metal.

The linearity of the proposed analytical methodology was examined for the concentration of analytes in the range of 5–100 $\mu\text{g L}^{-1}$. The obtained results showed that the linear concentration range is highly dependent on the element (see Table 1 for details). However, for all the studied elements, the linear range is up to 50–70 $\mu\text{g L}^{-1}$ concentration level. This is in agreement with other published scientific papers dealing with the use of HF-LPME as preconcentration procedure.^{23,24} As is widely known, the slope of the calibration curve is related to method sensitivity. Taking into account the slope values displayed in Table 1, it is apparent that the sensitivity for the proposed HF-LPME-TXRF method is higher for Pb and Zn and lower for Cd.

The global precision of the developed analytical procedure was evaluated in terms of relative standard deviation (RSD) of four-replicate analysis of solutions containing $30 \mu\text{g L}^{-1}$ of the target metals. As shown in Table 1, RSD values obtained (RSD \sim 6%–40%) were in most cases higher than those in other published studies dealing with the use of HF-LPME in combination with electrothermal vaporization ICPMS (RSD \sim 6%–13%).²⁵ This may be related to the uncertainty associated with the deposition and drying of few microliters of an organic solvent (preconcentrated sample) on the reflective carrier to perform TXRF analysis. When analyzing organic solvents, due to their higher boiling points, the deposition of a proper sample volume on the reflector as well as the drying mode is critical. In order to minimize the uncertainty associated with sample deposition on the global precision, the use of an internal standard was tested. For that, an adequate volume of a Mo stock solution of 1000 mg kg^{-1} in oil matrix was diluted with hexylbenzene up to 10 mg kg^{-1} . Then the resulting solution was used as organic phase for the preconcentration of 25 mL of an aqueous standard containing $30 \mu\text{g L}^{-1}$ of the target metals. However, it was found that part of the Mo initially located inside the HF moved to the aqueous phase during the extraction procedure and therefore this approach was discarded as a strategy to correct sample deposition uncertainties. Taking into account these results, it was considered appropriate to add

the internal standard to the organic phase after performing the preconcentration procedure. In this case, 30 μL of a preconcentrated aqueous standard containing 30 $\mu\text{g L}^{-1}$ of the target metals was carefully mixed with 10 μL of a Mo standard solution of 10 mg kg^{-1} . This procedure was repeated four times and RSD values from the obtained results were calculated and are displayed in the last column of Table 1. As can be seen, there is not a clear improvement tendency for all the metals using internal standard correction. Moreover, using such an approach the sample is diluted by a factor of 1/4, which is critical for trace analysis. For these reasons, internal standard correction was discarded.

Finally, in order to check the analytical possibilities of the developed HF-LPME-TXRF method for the analysis of water samples, the system was applied to the analysis of a spiked river water at the level of 30 $\mu\text{g L}^{-1}$ of the target metals (ICP-MS analysis of the raw river water showed that all the studied metals were present at concentrations less than 1 $\mu\text{g L}^{-1}$). In Figure 4 the TXRF spectrum for the aforementioned spiked river water sample is displayed. As shown, in addition to the peaks of the studied metals (Cr, Ni, Cu, Zn, Pb, and Cd) detectable peaks of Si (from the reflector), S (from the APDC), Ar (from the air), and Fe are also present. Calculated recoveries were 105% for Cr, 97% for Ni, 81% for Cu, 115% for Zn, 115% for Cd, and 112% for Pb.

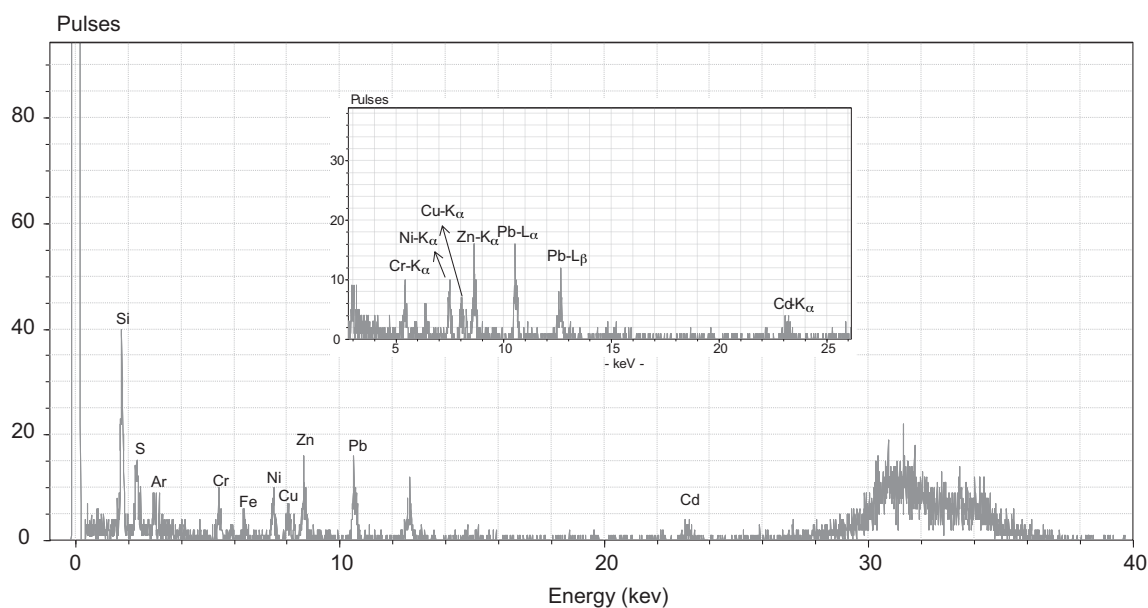


Figure 4. TXRF spectrum for a spiked aqueous sample with 30 $\mu\text{g L}^{-1}$ of Cr, Ni, Cu, Zn, Pb, and Cd (analytical conditions: 25 mL aqueous sample, 0.25% APDC, pH 6–7, 50 μL hexylbenzene, 2 h extraction time, 660 rpm agitation speed, 5 + 5 μL deposition volume, drying at 80 °C on a hot plate, 1000 s measurement time).

3. Experimental

3.1. Reagents and solutions

Stock solutions of $1000 \pm 0.5 \mu\text{g mL}^{-1}$ (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 and samples was obtained from a Milli-Q purifier system operated at 18 $\text{M}\Omega$ (Millipore Corp., Bedford, MA, USA). The solution of 10 mg/kg of Mo used for internal standardization was obtained by appropriate

dilution of Mo stock solution of 1000 $\mu\text{g/g}$ in an oil matrix (High-Purity standards, USA). This metallorganic standard shows high solubility and could be easily employed as an internal standard in organic matrices.

All organic solvents used through the work (hexylbenzene, undecane, carbon tetrachloride, dihexyl ether, decalin, and toluene) were of analytical grade quality (Sigma-Aldrich, Spain). The complexing agents, ammonium pyrrolidine dithiocarbamate-APDC (>99%) and 8-hydroxyquinoline, were also purchased from Sigma-Aldrich (Spain). The pH values were adjusted by addition of ammonia and nitric acid solutions (Merck, Spain). The hollow fiber polypropylene membrane (600 μm i.d., 200- μm wall thickness, 0.2- μm pore size) was obtained from AKZO Nobel (Germany).

3.2. Hollow fiber liquid phase microextraction procedure and TXRF analysis

In the present contribution a two-phase HF-LPME procedure in combination with TXRF was tested for the simultaneous determination of Cr, Ni, Cu, Zn, Cd, and Pb in aqueous solutions. Extraction parameters (HF-LMPE) and operating conditions (TXRF) were carefully evaluated in order to ensure best results for multielement analysis. In Figure 5 a schematic overview of the proposed method is displayed. In brief, first the polypropylene hollow fiber (HF) was cut into 4.5-cm length segments. A plastic pipette tip was connected to one of the ends of the fiber and the other end was thermally sealed. The fiber was immersed into the organic solvent for about 30 s to impregnate the pores of the hollow fiber with the organic solvent. Then a 100- μL microsyringe with a needle of 0.5 mm outer diameter was used to introduce the organic solvent into the lumen of the hollow fiber for extraction. Care was taken to avoid any air bubbles. By this preparation, the effective fiber length was 4.0 cm with an organic phase volume of $\sim 90 \mu\text{L}$. The impregnated HF was then immersed into 25 mL of the aqueous sample solution containing 0.25% (w/v) of APDC and adjusted to pH 6–7 (by addition of ammonia or nitric acid solutions). The extraction was carried out for 2 h under a magnetic agitation speed of 660 rpm, and then the acceptor solution (containing the analytes) was collected by using a microsyringe. For TXRF analysis, a preconcentrated sample aliquot of 5 μL was transferred onto a preheated quartz sample carrier and dried on a hot plate ($T \sim 80^\circ\text{C}$). This procedure was performed twice (5 + 5 μL) before TXRF analysis.

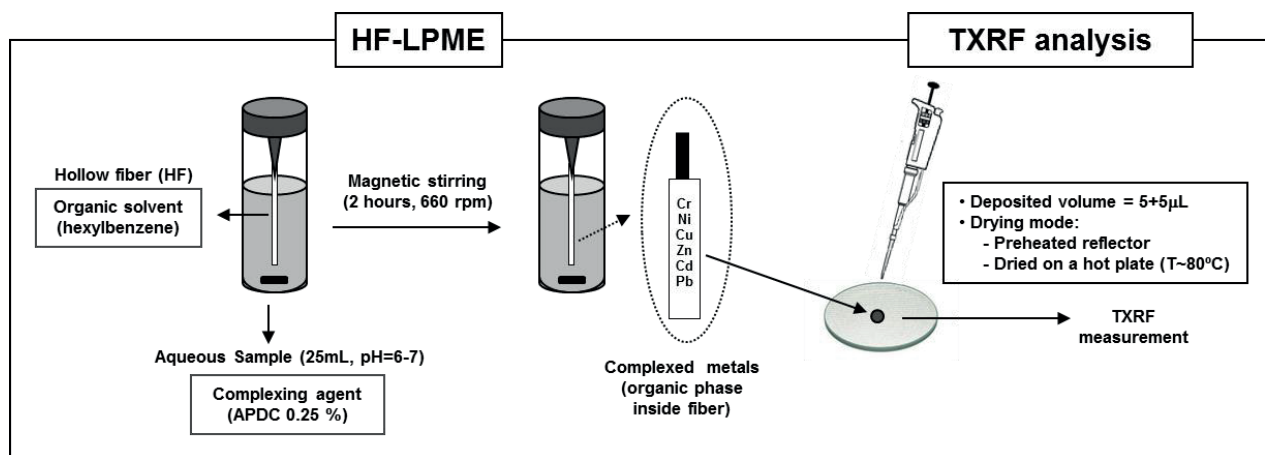


Figure 5. Schematic setup for the HF-LPME-TXRF system for multielement determination of Cd, Cr, Zn, Cu, Pb, and Ni in aqueous samples.

3.3. Instrumental and operating conditions

TXRF analysis of the preconcentrated samples was performed with the benchtop spectrometer S2 PICOFOX (Bruker AXS Microanalysis GmbH, Berlin, Germany). The spectrometer specifications and operating conditions used are summarized in Table 2. This instrument is equipped with a W X-ray tube that allows TXRF analysis using K-lines of high atomic number elements such as Cd. An additional advantage of this spectrometer compared to other existing systems is that it uses an air-cooled low-power X-ray tube and a Peltier cooled silicon drift detector and thus no cooling media and gas consumption are required.

Table 2. Instrumental parameters and measurement conditions.

S2 PICOFOX TXRF benchtop spectrometer (Bruker AXS, Germany)	
X-ray tube	W
Rating	50 kV, 1 mA (maximum power 50 W)
Optics	Multilayer Ni/C, 35.0 keV, 80% reflectivity
Detector	Si drift detector, 10 mm ² , <160 eV resolution Mn-K _α
Working environment	Air
Sample station	Cassette changer for 25 samples
Size, weight	600 × 300 × 450 mm, 37 kg
Measurement time	1000 s
Analytical lines	Cr-K _α (5.415 keV)
	Ni-K _α (7.480 keV)
	Cu-K _α (8.046 keV)
	Zn-K _α (8.637 keV)
	Pb-L _α (10.551 keV)
	Cd-K _α (23.173 keV)

4. Conclusions

In this contribution we tested the possibilities and drawbacks of two-phase HF-LPME as a relatively simple and inexpensive preconcentration procedure to improve the elemental sensitivity of low-power TXRF systems for aqueous sample analysis. The results showed that using such an analytical approach limits of detection can be improved by a factor of 100 (depending on the analyte) in comparison with direct analysis of the aqueous samples. Another interesting advantage of HF-LPME-TXRF configuration is the possibility of simultaneous determination of several elements (Cr, Ni, Cu, Zn, Cd, and Pb). Most of the published contributions dealing with the use of LPME procedures are focused on the determination of a single or a limited number of elements.

However, despite the advantages in terms of sensitivity improvement of two-phase HP-LPME procedures, the use of a low volatility solvent as extractant phase hampers the attainment of precise results (RSD ~20%) and hinders the application of this analytical approach for multielemental analysis of water samples by TXRF. To tackle this issue, further experiments will be focused on the possibilities of three-phase HP-LPME systems in combination with TXRF. In such extraction mode, analytes are extracted from an aqueous sample through the organic solvent (immobilized into the pores of the hollow fiber) into an aqueous acceptor solution. Therefore, this mode seems more compatible with the later TXRF analysis.

Acknowledgments

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Supporting Information

Effect of extraction time on element determination using the HF-LPME+TXRF system
(Analytical conditions: $50 \mu\text{g L}^{-1}$ metals, 25 mL aqueous sample, APDC 0.25 % (w/v),
pH = 6-7).

