



Simple method for Cr(VI) determination by liquid-liquid microextraction combined with total reflection X-ray fluorescence spectrometry: Application to water samples and industrial extracts

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ABSTRACT

In the present contribution, a simple and inexpensive method for the determination of hexavalent chromium in aqueous solutions was developed. The analytical methodology consists of the combined use of a low cost Cr(VI) isolation procedure followed by the analysis using total reflection X-ray spectrometry (TXRF). The liquid-liquid microextraction procedure (LLME) used is based on the formation of an ion-pair between the cationic part of the surfactant cetyltrimethylammonium bromide (CTAB) and the corresponding anionic Cr(VI) species, which is extracted in few microliters of chloroform. TXRF analysis can be performed directly by deposition of 15 μL of the preconcentrated sample on a sample carrier, without any additional sample treatment.

Experimental parameters affecting Cr(VI) extraction and TXRF analysis were studied in detail. Under optimum conditions, a good linearity was obtained in the range of 5–5000 $\mu\text{g/L}$ with a limit of detection for hexavalent chromium of 0.9 $\mu\text{g/L}$. This fact opens the possibility of Cr determination in aqueous samples characterized by different concentration levels. The methodology was successfully applied for the determination of Cr(VI) species in different type of water matrices (tap, well, river and sea water) as well as industrial aqueous samples including in industrial waste water from a galvanic industry and aqueous clinker extracts. For comparison purposes, the determination of Cr(VI) in industrial samples was also carried out by using the colorimetric method EPA Method 7196.

1. Introduction

Chromium is one of the major inorganic pollutants in the environment resulting from industrial activities [1]. It is a redox-sensitive transition metal that mainly exists as trivalent and hexavalent species [2]. These species have different chemical properties, being hexavalent chromium (Cr(VI)) the most toxic one [3]. Therefore, in addition to the limit of total Cr content in waters, there are specific maximum levels for Cr(VI). The World Health Organization (WHO) and the US Environmental Protection Agency (EPA) recommend that the concentration of Cr(VI) in drinking water should be <50 $\mu\text{g/L}$ and 100 $\mu\text{g/L}$, respectively [4]. The amount of Cr(VI) is also restricted in some industrial applications. For instance, the Directive 2003/53/EC provides a strict limitation regarding the use of cements containing >2 mg/kg of water-soluble Cr(VI) of the total cement weight [5]. When dissolved, Cr(VI) present in cement penetrates the skin, where it is transformed into Cr(III) and

combines with epidermal proteins leading to a general irritation of the skin (cement dermatitis) [6].

There are a considerable number of analytical methods available for specific determination of Cr(VI) in aqueous samples. In fact, several reviews about this topic have been published in the scientific literature [7–9]. Among them, it is interesting to highlight the use of analytical methods based on solvent microextraction, especially dispersive liquid-liquid microextraction (DLLME). DLLME is based on a cloudy solution formed when an appropriate mixture of an extractant in an organic solvent and a disperser is injected into an aqueous sample. The fine droplets of extractant are dispersed through the aqueous sample, allowing its interaction with the analyte [10]. The major benefit of this rapid and inexpensive method is the reduced usage of organic solvents during the extraction since only several microliters of solvent are needed to concentrate analytes from the sample [11]. Moreover, in some applications, the disperser agent is substituted by a surfactant, which could

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afford more effective emulsification and make the extraction greener. In this case, the extraction method is named surfactant-assisted DLLME (SA-DLLME) [12]. In Table 1, a summary of the DLLME methods published in the period 2014–2022 for Cr(VI) determination in aqueous samples is displayed. As it is shown, most of these methods are specifically designed for the extraction of Cr(VI) but some of them enable the sequential determination of both inorganic species (Cr(VI) and Cr(III)) using different extraction conditions [1,13,14,18]. In view of the small amount of organic solvent in which the analyte is extracted, usually DLLME has been combined with microanalytical techniques such as electrothermal atomic absorption spectrometry (ETAAS) [1,12–14]. Other techniques such as UV-spectrophotometry, spectrofluorimetry and flame atomic absorption spectrometry (FAAS) have also been used but using microvolume cells [4,18,19] or after a dilution of the sample to get an adequate volume to perform the analysis [15,16]. Other less explored techniques include tungsten coil atomic emission spectrometry (WCAES) [20] and laser induced breakdown spectroscopy (LIBS) [21]. In a previous publication, we also demonstrated the potential combination of total reflection X-ray spectrometry (TXRF) with DLLME for the determination of Cr(VI) in drinking and municipal water samples [22]. In order to work under conditions of total reflection, the sample has to be prepared as a very thin film on a reflective carrier by deposition of few microliters of sample. Therefore, it is an ideal technique to be used in combination with microextraction procedures.

In spite of the wide range of analytical methods for Cr(VI) determination, most of them have proved to be useful only for the analysis of water samples (see Table 1). The matrix of industrial waste water samples as well as cement-related materials is more complex and contains a variety of potential interfering elements and compounds that may cause problems with the accurate determination of Cr(VI). Another drawback of most of the published methods in Table 1 is the limited linear concentration range, which hampers their application for the analysis of aqueous samples characterized by different analyte concentration levels. In view of that, the main aim of this contribution is the development of a simple and fast SA-DLLME strategy in combination with TXRF for Cr(VI) determination in different types of aqueous samples including waters of different sources (tap, well, river and sea) as well as different types of industrial aqueous extracts (industrial waste water from a galvanic industry and aqueous clinker extracts). In the latter case, to demonstrate the suitability of the developed method, the determination of Cr(VI) was also carried out by using the EPA Method 7196 based on a colorimetric determination.

2. Material and methods

2.1. Reagents and solutions

All solutions were prepared using analytical reagent grade chemicals and bidistilled water, purified through a Milli-Q Plus system (Millipore). Chromium (VI) and chromium (III) stock solutions of 1000 mgL⁻¹ were prepared by dissolving appropriate amounts of K₂CrO₄ (Panreac AppliChem, Spain) and CrCl₃·6H₂O (Panreac AppliChem, Spain), respectively. The cationic surfactant CTAB (Merck, Darmstadt, Germany) and the commercial quaternary ammonium salt Aliquat®336 (Merck, Darmstadt, Germany) were used as extractants. Stock solutions of 1000 mgL⁻¹ (ROMIL PrimAg@ Mono-component reference solutions) of target elements were used to prepare standard solutions for inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. Other chemical reagents used (HCl 37%, HNO₃ 69%, CHCl₃, H₂SO₄ 96%, NaCl, NaNO₃, Na₂SO₄, Na₃PO₄) were purchased from Panreac AppliChem (Spain). Quartz glass sample carriers with a 30 mm diameter and a thickness of 3 mm ± 0.1 mm were employed for TXRF analysis.

2.2. Water and aqueous industrial samples

2.2.1. Water samples

In this study, different types of waters (tap, well, river and sea water) were sampled and used in Cr(VI) extraction experiments. All samples were collected in different areas belonging to Girona region (Catalonia located in the northeast of Spain). Water samples were analysed after filtration using a 0.45 µm pore size cellulose acetate membrane filter. To test the efficiency of the SA-DLLME+TXRF method, spiked water samples at the levels of 25 and 50 µg/L Cr(VI) were also prepared and analysed.

2.2.2. Aqueous industrial extracts

The viability to use the SA-DLLME +TXRF method for Cr(VI) determination in aqueous samples from industrial activities was also studied by analysing a waste water sample from a galvanic industry effluent and two different clinker aqueous extracts from a concrete industry. In the latter case, the extraction of the water-soluble Cr(VI) in clinker samples was carried out according to the UNE-EN 196–10 (Appendix C) procedure [23]. This regulation is the official version, in Spain, of the European Standard EN 196–10:2006. This method consists mainly on the solubilisation of the Cr(VI) by stirring the clinker sample (25 g) in water (25 mL) for a predetermined period of time (15 ± 1 min). For practical reasons, the above mixture was filtered using acetate cellulose filters of 0.2 µm (Millipore) instead of using filtration plates, after checking that absorption of Cr(VI) on the filter did not occur.

Table 1

Dispersive liquid-liquid microextraction (DLLME) methods published for Cr(VI) determination in water samples (Period: 2014–2022).

Extraction method	Technique	LD (µg/L)	Range (µg/L)	Cr species ¹	Sample type	Reference
IL-DSPE-DLLME		0.015	0.06–5	Cr(VI) + Cr(III)	Tap, river, well water	[1]
SA-DLLME	ETAAS	0.0052	0.02–2.5	Cr(III)	Drinking, tap water	[12]
M-MM-DLLME		0.0005	0.02–1	Cr(VI) + Cr(III)	Lake, tannery effluent samples	[13]
In situ IL-DLLME		0.0021	0.07–0.25	Cr(VI) + Cr(III)	Tap, ground water	[14]
UA-SUPRAS-DLLME	FAAS	0.03	0.1–350	Cr(VI)	Tap, waste water	[15]
In situ IL-DLLME		11.3	50–600	Cr(VI) + Cr(III)	Drinking, tap, underground, well water	[16]
DES-DLLME		1.5	5–200	Cr(VI)	Tap, waste water	[17]
SA-DLLME	UV-Spectrophotometry	5	5–100	Cr(VI)	Tape, surface, well water	[18]
DLLME		7.5	25–900	Cr(VI)	Tap, sea water	[4]
USA-IA-DLLME	Spectrofluorimetry	0.57	1–1000	Cr(VI)	Tap, sea water	[19]
In situ IL-DLLME	WCAES ²	3	10–60	Cr(VI)	Tap, bottled, mineral water	[20]
DLLME	LIBS	3.1	0–300	Cr(VI)	Drinking water	[21]
DLLME	TXRF	0.8	5–4000	Cr(VI)	Drinking, municipal waste water	[22]

Nomenclature Extraction methods → IL: ionic liquid, DSPE: dispersive solid phase, SA: surfactant-assisted, M-MM: micelle and mixed-micelles, UA-SUPRAS: ultrasound-assisted supramolecular solvent, DES: deep eutectic solvent, USA-IA: ultrasound-assisted ion association.

¹ Cr(VI) + Cr(III): sequential determination of both species, ² WCAES: tungsten coil atomic emission spectrometry.

2.3. SA-DLLME procedure and TXRF analysis

Different experimental tests were performed to select the best conditions for Cr(VI) extraction and TXRF analysis (see Sections 3.1 and 3.2 for details). Finally, the extraction procedure was as follows: 10 mL of aqueous sample was acidified to pH = 0.2 (using the suitable amount of HCl) and then 100 μ L of a 0.01 M CTAB solution in chloroform were added. After manual shaking of the mixture for 60 s, a cloudy white suspension appeared. Phase separation was performed by centrifuging the mixture at 3000 rpm (990 relative centrifugal force) for 2 min. A small volume (~30 μ L) of organic phase, containing the Cr(VI) – CTAB species, was placed at the bottom of the tube. Then, 7.5 μ L of the pre-concentrated sample was deposited on a quartz reflector and dried on a hot plate set at 40 °C. The deposition procedure was repeated twice and thus the final sample volume deposited on the reflector was 15 μ L. TXRF analysis was carried out using a commercial benchtop TXRF spectrometer S2 PICOFOX (BrukerNano, Germany) with a low-power tungsten X-ray tube (50 kV, 1 mA) and a silicon drift detector (SSD, resolution <150 eV at Mn K α). The commercial software (Spectra Plus 5.3, Bruker AXS Microanalysis GmbH, Berlin, Germany) was used to evaluate TXRF spectra and get quantitative results. TXRF measurements were performed using an acquisition time of 1000 s.

2.4. Reference techniques

For comparison purposes, the determination of Cr(VI) in industrial waste water samples and aqueous clinker extracts was also performed by using the EPA Method 7196 [24]. In this method, dissolved Cr(VI) is determined colorimetrically by reaction with diphenylcarbazide in acid solution. In brief: 50 μ L of diphenylcarbazide was mixed with 5 mL of sample. Then, 100 μ L of H₂SO₄ solution was added to give a pH of 2.0 \pm 0.5. The resulting solution was let stand 5 to 10 min for full color (red-violet) development and after, an appropriate portion of the solution was transferred to a 1-cm absorption cell. Absorbance was recorded at 540 nm using a spectrophotometer (Agilent Technologies Cary 8454 UV-vis). Concentration of Cr(VI) in the samples was estimated by reference to the calibration curve obtained from the measurement of a set of Cr(VI) standards prepared following the same derivatization procedure.

Industrial waste water samples and aqueous clinker extracts were also analysed by ICP-OES in order to get information of the metal content (K, Ca, Ni, Fe, Cu and Zn) and the total amount of Cr. For these measurements, an Agilent ICP-OES 5100 Synchronous Vertical Dual View (SVDV) spectrometer was used. The system was equipped with a concentric nebulizer, a polychromatic wavelength selector and a silicon based multichannel array CCD detection system. The plasma was operated at 12 L/min argon flow. Analytical wavelengths were: K (769.897 nm), Ca (315.887 nm), Fe (259.940 nm), Cu (327.395 nm), Zn (213.857 nm), Ni (216.555 nm) and Cr (205.560 nm).

3. Results and discussion

3.1. Evaluation of the SA-DLLME procedure

Experimental factors influencing the extraction of Cr(VI) from aqueous samples were evaluated. In all cases, an aqueous standard solution containing 200 μ g/L of Cr(VI) was used.

Two different ammonium quaternary salts were tested as extracting agents to isolate Cr(VI) from aqueous samples: cetyltrimethylammonium bromide (CTAB) and *N*-methyl-*N,N,N*-triethylammonium chloride (Aliquat®336) (see Fig. S1 (Appendix)). Both extractants can efficiently extract Cr(VI) species in acid media on the basis of the formation of an ion-pair between their cationic part and the corresponding anionic Cr(VI) species [25,26]. As previously reported, the predominant Cr species at acidic pH is HCrO₄⁻ that can be extracted by CTAB and Aliquat®336 via an anion-exchange mechanism. In the

same conditions, Cr(III) species cannot be extracted since at acidic pH Cr(III) is present in cationic form. Fig. 1A displays the results obtained (in terms of Cr TXRF signal) when using CTAB and Aliquat®336 as extractants at different acidic pH values. In both cases, chloroform was used as organic solvent. As it is shown in Fig. 1A, higher Cr signals were obtained using Aliquat®336 but the dispersion of the results for triplicate analysis was very high (RSD(%): 10–80%). In a previous publication, we demonstrated the suitability of using multiwalled carbon nanotubes modified with Aliquat®336 for extraction of Cr(VI) in a dispersive micro solid phase extraction system and TXRF analysis [27]. However, it seems that the use of Aliquat®336 as extractant in LLME systems in combination with TXRF analysis is not a good strategy, probably due to the difficulty to get a proper deposition of the organic drop containing the extractant on the quartz reflector surface. In view of the obtained results, next experiments were performed using CTAB and adjusting the aqueous samples at pH = 0.2.

In view of the solubility of CTAB in water and chloroform, two different extraction modes were tested (see Fig. S2 (Appendix)). In the first one, CTAB was dissolved in the organic solvent and added to the aqueous sample containing Cr(VI). In the second approach, CTAB was added to the aqueous sample containing Cr(VI) and after a manual mixing procedure an appropriate amount of organic solvent was introduced to the mixture. As it is shown in Fig. S2 (Appendix), a higher response for Cr was obtained using the first mode, which was used to perform further experiments.

As mentioned above, chloroform was used as organic solvent in the SA-DLLME procedure developed. This solvent presents low water solubility, high stability but also a high vapour pressure, which is a requisite for TXRF analysis [28]. In Fig. 1B the effect of the volume of chloroform used to perform the extraction (75–200 μ L) on the Cr response is displayed. As expected, Cr response is decreased when increasing the volume of organic solvent. However, as it is shown, a significant dispersion of the results is obtained when using the lower amount of organic solvent tested (75 μ L), probably due to the difficulty of isolating efficiently the organic drop from the aqueous phase. According to the obtained results, a volume of 100 μ L of solvent was finally selected.

Different concentrations of CTAB were also tested to evaluate its influence on Cr extraction (see Fig. 1C). Results indicated that the chromium analytical signal increased with increasing CTAB concentration. In view of that, and taking into account the likely competitive reaction of CTAB with other anionic species in real water and aqueous samples, a CTAB concentration of 0.01 M was chosen.

Finally, the influence of the extraction time on Cr response was also evaluated. As it is shown in Fig. 1D, best results in terms of analytical response and precision of the obtained results were by using an extraction time of 60 s.

3.2. Evaluation of TXRF measurement conditions

The aim of the sample preparation process in TXRF is to obtain the target sample as a thin layer on a sample carrier with high reflectivity. Therefore, the choice of adequate sample deposition volume is of crucial importance in order to ensure the conditions of total reflection [29]. The area of the sample spot on the sample holder has to be also appropriate, taking into account the volume spanned by the excitation beam and the detector viewing. For that, a study was conducted to evaluate the sample deposition volume effect (in the range of 2–15 μ L) on the limits of detection and precision of the obtained Cr results ($n = 3$). As it is shown in Fig. 2, limits of detection were improved when increasing the volume of sample deposited on the reflector. However, for disposition volumes in the range of 2–10 μ L, the uncertainty of the results obtained for triplicate analysis was very high (RSD > 25%). Best results in terms of limits of detection and precision were obtained when depositing a total volume of 15 μ L of the preconcentrated sample in two successive depositions of 7.5 μ L with time allowed for droplet drying between depositions (7.5 μ L + 7.5 μ L). Finally, this strategy was the selected one for

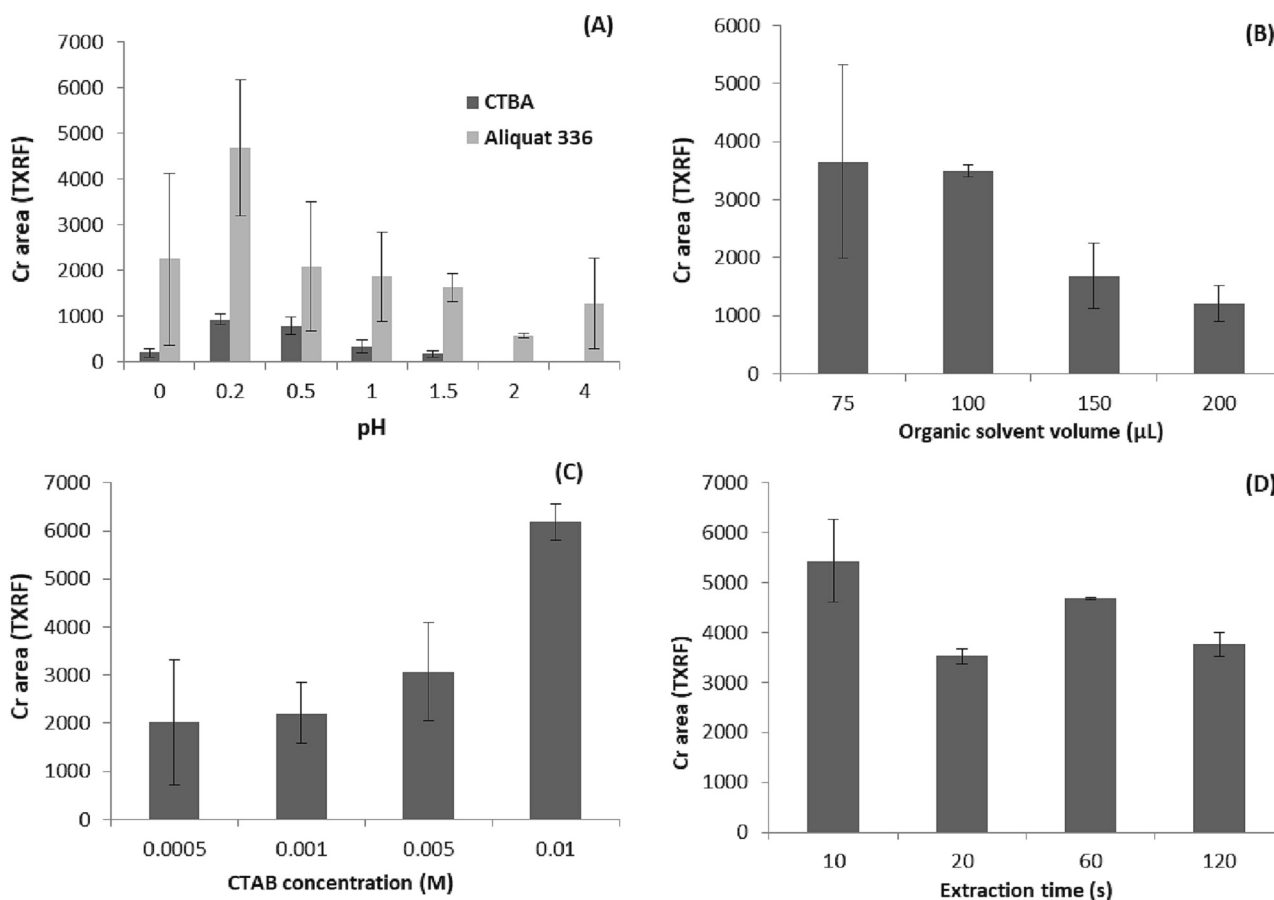


Fig. 1. Evaluation of SA-DLLME conditions: (A) Effect of pH and extractants, (B) Effect of organic solvent volume, (C) Effect of CTAB concentration, (D) Effect of extraction time. In all cases, tests were performed using an aqueous standard containing 200 µg/L of Cr (VI). Error bars represent mean values ± standard deviation, $n = 3$.

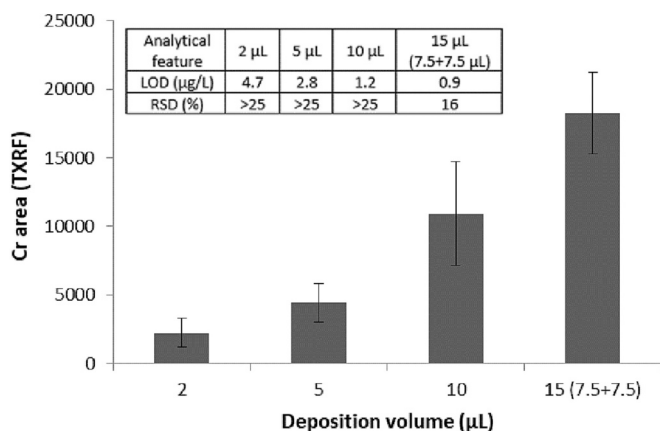


Fig. 2. Effect of deposition volume on the quartz reflector. Error bars represent mean values ± standard deviation, $n = 3$.

Limits of detection (LOD) were estimated using the expression: $LOD = \frac{3C_i \sqrt{N_{bkg}}}{N_i}$ Where: C_i is the analyte concentration, N_{bkg} is the background area under the analyte peak and N_i is the net area of the analyte peak.

the deposition of the preconcentrated samples on the reflector for the subsequent TXRF analysis.

The effect of measurement time on the repeatability of the Cr response was also tested. For that, three different solutions containing Cr (VI) in the range of 25–5000 µg/L Cr(VI) were treated with the SA-DLLME procedure and the resulting drop on the reflector was

measured six times at 500, 1000, 2000 and 2500 s. A summary of the obtained results, in terms of RSD, is displayed in Fig. S3 (Appendix). As it is shown, for high concentration levels (expected in industrial aqueous extracts), there was not any significant improvement on RSD values if measurements were performed at 500 s compared to longer measurement times. On the contrary, for low Cr(VI) levels, a longer measurement time was necessary to obtain similar RSD values. In view of the obtained results, a measurement time of 1000 s was selected as a trade-off between an acceptable repeatability of the results (RSD ~ 5%) and the total analysis time.

3.3. Analytical figures of merit of the LLME+TXRF system

Once the best conditions to determine Cr(VI) were established, analytical figures of merit of the SA-DLLME +TXRF method were evaluated and a summary of the obtained results is presented in Table 2. It was found that the minimum Cr content that can be detected was 0.9 µg/L Cr. This value is significantly lower than the maximum Cr(VI) permissible in drinking water, indicating the potential of the proposed method for such purpose. It is also interesting to remark that this limit of detection can be significantly reduced using TXRF systems equipped with Mo X-ray tubes. In a previous contribution we demonstrated that limits of detection for mid-Z elements (such as Cr) were 1 order of magnitude lower for Mo TXRF systems in comparison with W TXRF systems [30].

As reported in Table 2, the SA-DLLME +TXRF method proved to be applicable to determine Cr (VI) in a wide concentration range (5–5000 µg/L, $R^2 = 0.990$) expanding the possibility of Cr determination not only in water samples but also in industrial aqueous extracts. Usually, the

Table 2

Analytical figures of merit of the developed SA-DLLME +TXRF method for Cr (VI) determination.

Parameter	Analytical feature
Limit of detection ¹	0.9 µg/L
Linear range	5–5000 µg/L
R ²	0.990
Method precision (n = 6, 1 measurement) 25 µg/L/200 µg/L/5000 µg/L	RSD = 15.4% RSD = 11.7% RSD = 10.2%
Instrumental precision (n = 1, 6 measurement) 25 µg/L 200 µg/L 5000 µg/L	RSD = 5.5% RSD = 1.9% RSD = 0.1%

¹ Limit of detection (LOD) was estimated using the expression: $LOD =$

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

Where: C_i is the analyte concentration, N_{bkg} is the background area under the analyte peak and N_i is the net area of the analyte peak.

linearity range in microextraction procedures is limited (see Table 1) and this fact hampers their application for the analysis of aqueous samples characterized by different analyte concentration levels. The extraction efficiency of the method was evaluated from the difference between Cr concentration measured at the beginning of the experiment and the concentration after application of the SA-DLLME procedure, determined by the analysis of the aqueous extracts by means of ICP-OES. It was found that the extraction efficiency was nearly constant ($65 \pm 4\%$) in the linear concentration range. Global precision of the method was also tested by analysing six independent replicates of solutions containing different concentrations of Cr (VI). Besides, one of the replicates at each concentration level was measured six times and relative standard deviation of the obtained results was calculated. This uncertainty is related only to TXRF measurement. As it is shown in Table 2, global precision of the method is acceptable with RSD values in the range of 10–15%. It is also interesting to mention that the contribution of instrumental uncertainty decrease when increasing the concentration of Cr(VI) in the initial aqueous solution, being <2% for concentration levels higher than 200 µg/L.

A set of experiments were also performed to evaluate the effect of potential interferences on the determination of Cr(VI). Firstly, the selectivity of the method for Cr(VI) determination in the presence of Cr (III) was evaluated. As stated in Section 3.1, in acidic conditions, Cr(III) is present in cationic form and thus it cannot be extracted via an anion-exchange mechanism using CTAB. To prove that, several synthetic aqueous samples containing different concentration ratios of Cr(VI) and Cr(III) were analysed using the SA-DLLME -TXRF method. Results obtained confirmed that the presence of Cr(III) in the aqueous samples did not affect the quantitative determination of Cr(VI) (see Table 3). The effect of other ions that can be present at relative high concentrations in water and/or industrial aqueous samples was also studied. For that, several Cr(VI) standards were spiked with different amounts of metals,

Table 3

Cr(VI) concentration determined at different concentration ratios of Cr(VI) and Cr(III) using the system SA-DLLME +TXRF (results are expressed as mean values \pm standard deviation, $n = 3$).

Cr(VI) / Cr(III) ratio	Cr(VI) found (µg/L)
20/100	17 \pm 2
100/20	108 \pm 6
40/40	42 \pm 2
3000/3000	3200 \pm 200
700/5000	690 \pm 90

humic acids (HA) and anions (see Fig. S4 (Appendix) for details). As it is shown, Cr(VI) determination was not affected by the presence of high concentrations of metals and anions but the presence of HA at a concentration level of 25 mgL⁻¹ decrease the Cr signal to about 20%. This fact limits the application of the method to waste water samples with a high organic matter loading (i.e., waste waters from tannery industry) but it is not an important drawback for the application of the method to other industrial aqueous samples or natural water samples (expected level of HA \sim 5 mgL⁻¹).

3.4. Application of the SA-DLLME +TXRF method to water samples and aqueous industrial extracts

3.4.1. Water samples

The developed SA-DLLME +TXRF method was applied to the determination of Cr(VI) in different type of water samples including tap, well, river and sea water. In Table 4, chemical characterization of samples including pH, conductivity, anions (chloride, nitrate, sulphate) and metal (K, Ca, Fe, Cu, Zn) content is displayed. As it is shown, Cr(VI) concentration was below the detection limit for all the analysed samples. However, in order to validate the method for the different types of water matrices, the target samples were spiked at different concentration levels of Cr (VI). Recovery values estimated were in all cases in the range of 88–100%. Only for sea water samples spiked at low Cr(VI) concentration levels was around 80% (see Table 4). To study in more detail the saline effect on Cr(VI) extraction, an aqueous solution containing 25 µg/L Cr(VI) was spiked with sodium chloride at a concentration level of 20 g/L (to simulate salt content in sea water). The results obtained were compared with those from the analysis of a 25 µg/L Cr(VI) standard (pure water) and a spiked sea water sample at the same concentration level. As it is shown in Fig. S5 (Appendix), the presence of salt in the aqueous matrix led to a clear reduction of the Cr signal. Nevertheless, for sea water sample analyses, the SA-DLLME -TXRF method may still be used if matrix matching standards (containing 20 g/L sodium chloride) are used for quantitative purposes. In fact, using this approach, a clear improvement of the recovery value for the spiked sea water samples was assessed (from 80% to 104%).

3.4.2. Aqueous industrial extracts

Finally, the method was also applied for the determination of Cr(VI) in different types of aqueous industrial extracts. Obtained results are reported in Table 5. For comparison purposes, Cr(VI) concentration determined by using a standardized colorimetric method (EPA Method 7196) and total Cr determined by ICP-OES are also displayed (see Section 2.4 for specific details).

As it is shown in Table 5, in the case of the waste water sample from a galvanic industry, a slightly higher Cr(VI) concentration was obtained using the colorimetric method in comparison with SA-DLLME +TXRF. It is interesting to mention that the industrial waste water sample was turbid and although a correction of the sample absorbance was carried out (as recommended by the EPA Method 7196) it is possible to get a somewhat overestimation of the Cr(VI) content. That fact is corroborated taking into account that the Cr(VI) content determined by the colorimetric method is also slightly higher than the total amount of chromium in the sample determined by ICP-OES.

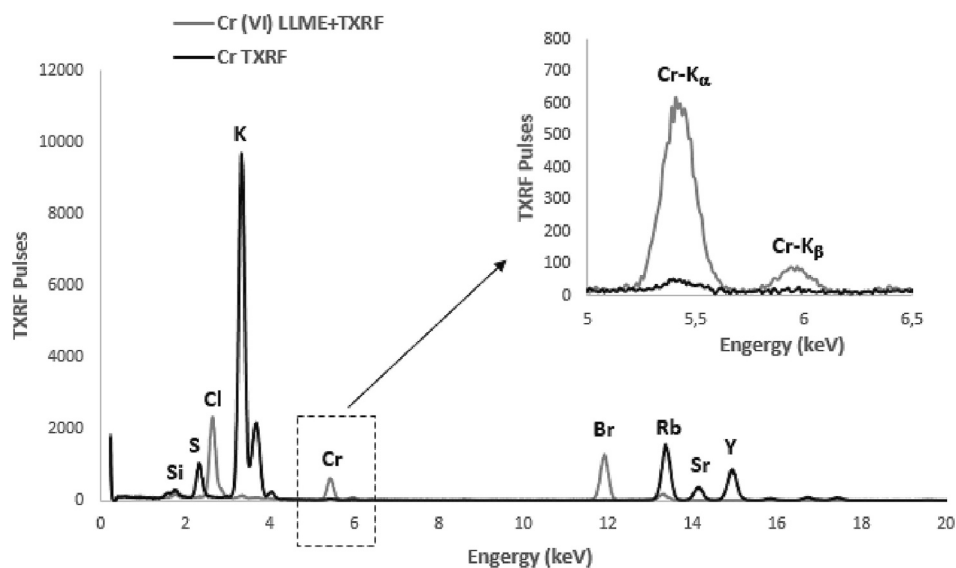
The developed method was also applied to monitor water-extractable Cr(VI) in several clinker samples (see Section 2.2.2 for specific sample details). As it is shown in Table 5, good agreement was obtained between SA-DLLME +TXRF and references values, demonstrating the suitability of the developed method for this kind of application. As mentioned in the introduction section, the European Directive 2003/53/EC provides a rigorous limitation regarding the use of cements containing >2 mg/kg of water-soluble Cr(VI) of the total cement weight. In view of the obtained results, the analysed clinkers should be treated with chemical reducing agents to decrease the level of soluble Cr(VI) and comply with this strict directive on the final cement product. In Fig. 3,

Table 4Physicochemical properties and determination of Cr(VI) in different type of water samples (results are expressed as mean values \pm standard deviation, $n = 3$).

Sample	pH	Conductivity (mS/cm)	Anions (mgL ⁻¹)	Metals (mgL ⁻¹)	Cr(VI) added (μ g/L)	Cr(VI) found (μ g/L)
Tap water	7.52	0.363	Cl ⁻ :23.0	K:0.003,Ca:0.056, Fe < 0.01, Cu:0.04, Zn:0.01	0	n.d. ¹
			NO ₃ ⁻ :1.3		25	24.1 \pm 0.9
			SO ₄ ²⁻ :14.0		50	50.0 \pm 0.6
Well water	6.75	0.567	Cl ⁻ :52.5	K:0.002,Ca:0.056, Fe < 0.01, Cu:0.05, Zn:3.06	0	n.d. ¹
			NO ₃ ⁻ :21.3		25	20.9 \pm 0.7
			SO ₄ ²⁻ :28.5		50	47.0 \pm 0.2
River water	8.15	0.173	Cl ⁻ :9.5	K:0.001,Ca:0.013, Fe:0.02, Cu < 0.01, Zn < 0.01	0	n.d. ¹
			NO ₃ ⁻ :0.2		25	22 \pm 2
			SO ₄ ²⁻ :2.2		50	48.0 \pm 0.2
Sea water	7.81	50.9	Cl ⁻ :21114.3	K:0.455,Ca:0.357, Fe < 0.01, Cu < 0.01, Zn:0.33	0	n.d. ¹
			NO ₃ ⁻ : n.d.		25	20.4 \pm 0.2
			SO ₄ ²⁻ :98.1		50	49.0 \pm 0.3

¹ n.d. = not detected.**Table 5**Determination of Cr(VI) in different type of industrial aqueous extracts (results are expressed as mean values \pm standard deviation, $n = 3$).

(A) Industrial waste waters (galvanic industry)						
Sample	pH	Conductivity (mS/cm)	Metals (mgL ⁻¹)	Cr(VI) LLME+TXRF (mgL ⁻¹)	Cr(VI) Ref. method ¹ (mgL ⁻¹)	Cr total ICP-OES (mgL ⁻¹)
IG2	8.13	3.59	K: 0.072, Ca:0.056, Cu:0.033, Zn:0.173, Ni:0.023	1.4 \pm 0.2	1.79 \pm 0.1	1.58
(B) Aqueous clinker extracts (cement industry)						
Sample	Cr(VI) SA-DLLME +TXRF (mgL ⁻¹) ²		Cr(VI) Ref. method (mgL ⁻¹) ¹		Cr total ICP-OES (mgL ⁻¹)	
Clinker-1	2.5 \pm 0.3		2.28 \pm 0.4		2.99 \pm 0.01	
Clinker-2	6.5 \pm 0.6		6.10 \pm 0.4		6.74 \pm 0.01	

¹ Ref. method: colorimetric method (see Section 2.4 for details).² Results are expressed in mg Cr (VI)/L aqueous extract. Taking into account an extraction ratio between the amount of clinker (in g) and the amount of water used in the extraction (in mL), 1 mg Cr (VI)/L in the aqueous extract corresponds to 1 mg Cr (VI)/kg clinker (see Section 2.2.2 for details).**Fig. 3.** TXRF spectra obtained for the analysis of clinker-1 aqueous extract (see Table 5 for details).

TXRF spectra obtained from the analysis of clinker-1 water extract before and after the SA-DLLME procedure are displayed. In the case of SA-DLLME +TXRF spectrum, in addition to Cr, Cl and Br peaks are also detected arising from the hydrochloric acid used to adjust sample pH and the CTAB, respectively. As it can be seen, with the direct analysis of the water extract by TXRF it is possible to get information about the total amount of water-soluble Cr (and other elements present in the sample).

Therefore, by the difference with the hexavalent chromium determined by SA-DLLME +TXRF, it is possible to estimate the proportion of Cr(VI) in the water extract. The possibility to get information of inorganic chromium speciation (Cr (VI), Cr (III)) can be of special interest for cement laboratories.

4. Conclusions

A simple and inexpensive analytical method for hexavalent chromium determination in aqueous samples has been developed. Limit of detection obtained (0.9 µg/L Cr (VI)) indicated that SA-DLLME +TXRF is suitable to monitor hexavalent chromium in water samples considering the current legislation. However, the high linear concentration range of the method opens also the possibility to apply it for the analysis of industrial aqueous extracts. In fact, the developed method has been applied not only in different type of water matrices (tap, well, river and sea water) but also in industrial waste water from a galvanic industry and aqueous clinker extracts. The microextraction procedure used to isolate Cr(VI) only involves the use of a cationic surfactant and few microliters of an organic solvent. It is not necessary to add a dispersing agent as in most of the existing dispersive liquid-liquid microextraction procedures. Therefore, it can be easily applied even to quality control industrial laboratories. Moreover, the analytical technique used for Cr detection (low power TXRF system) involves very low consumption of consumables which reinforce the applicability of the method.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.sab.2023.106682>.

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