



Technical Note

Cr speciation in water samples by dispersive liquid–liquid microextraction combined with total reflection X-ray fluorescence spectrometry



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ABSTRACT

A novel method based on dispersive liquid–liquid microextraction (DLLME) and total-reflection X-ray fluorescence spectrometry (TXRF) is proposed for the determination and preconcentration of inorganic Cr species (Cr(VI) and Cr(III)) in water samples.

Parameters affecting the extraction procedure for Cr speciation (pH, sample volume, disperser solvent, complexing agent, organic solvent, temperature) and TXRF conditions (sample volume, drying mode, measurement time, internal standardization) have been carefully evaluated to ensure the highest sensitivity for Cr determination. It was found that the minimum Cr content that can be detected was $0.8 \mu\text{g L}^{-1}$. This value is significantly lower than the maximum Cr content permissible in drinking waters and it is better or comparable with those obtained in other published works based on the use of solid phase extraction or liquid phase microextraction in combination with atomic absorption spectrometry techniques. A good linearity ($R^2 = 0.9937$) was obtained in the range of 5 to $4000 \mu\text{g L}^{-1}$ demonstrating the suitability of the DLLME + TXRF for both the analysis of drinking and waste water samples.

Additional advantages of the DLLME-TXRF systems include the use of very small amount of reagents and the simplicity and low cost of operation of the benchtop instrument used (no cooling media and gas consumption are needed).

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1. Introduction

Cr is an environmental pollutant resulting mainly from industrial activities including electroplating, wood preservation, leather tanning and steel industries [1,2]. The main forms of Cr found in the environment are trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Cr(III) appears to be one of the essential elements for the proper functioning of living organisms. On the contrary, water soluble Cr(VI) species are highly toxic and irritant for human tissues due to their high oxidation potential as well as their ability to cross biological membranes [3–5]. Therefore, in addition to the limit of total Cr content in waters, there are specific maximum levels for Cr(VI). For instance, the World Health Organization (WHO) recommends that the level of Cr(VI) in drinking water should be less than $50 \mu\text{g L}^{-1}$ [6]. Consequently, the determination and speciation of inorganic species of Cr are a subject of considerable interest.

There are a large number of analytical techniques that have been suggested for this purpose. In Table 1, a summary of selected examples of analytical procedures published for Cr speciation in water samples is presented. The analytical method proposed by the Environmental Protection Agency of the United States (EPA) is based on the use of ionic chromatography (IC) [7]. Using this method Cr species can be determined at very low levels but the linear concentration range is limited and IC is a relatively expensive analytical tool. Another analytical alternative is the combination of preconcentration strategies with atomic spectrometry. Cloud-point extraction (CPE) and solid phase extraction (SPE) have been widely applied for Cr speciation in different types of water samples (see Table 1) [9–12]. However, recent research trends include the use of more environmental friendly analytical preconcentration procedures such as liquid phase microextraction (LPME). The major benefit of this rapid and inexpensive method is the reduction of the use of organic solvents during the extraction step since only several microliters of solvent are needed to concentrate analytes from the sample. Several reviews about the basic principles and main applications of LPME procedures are at present available in the scientific literature [13,14]. Since 2006, LPME procedures have

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Table 1
Selected examples of analytical procedures published for Cr speciation in water samples.

Extraction preconcentration	Analytical technique	Detection limit ($\mu\text{g L}^{-1}$)	Linear range ($\mu\text{g L}^{-1}$)	Sample water type	Reference
	IC + UV detection	0.01	0.02–5	Drinking water	[7]
LLE	Spectrophotometry	7.5	7.5–350	Natural water	[8]
CPE	FAAS	0.08	Up to 100	Tap, well, dam, industrial water	[9]
CPE	ETAAS	0.01	0.5–10	Lake, river, tap	[10]
SPE	FAAS	45	n.a	Tap water	[11]
SPE	FAAS	2.3	0–250	Natural water	[12]
SA-LLME	FAAS	1.25	3–150	Mineral, sea, river water	[15]
RTIL-HFLPME	FAAS	0.7	3–200	Tap, river, waste water	[16]
UA-DLLME	ETAAS	0.002	0.005–0.2	Bottled, tap, sea water	[17]
IL-DLLME	FAAS	0.41	3–800	Tap, purified, lake water	[6]
IL-DLLME	ETAAS	0.002	0.025–0.150	Tap, river, sea water	[19]
IL-DLLME	ETAAS	0.002	0.005–0.1	Bottled, tap, sea water	[20]
DLLME	FAAS	0.08	0.3–20	Tap, river, sea water	[21]

IC: ion chromatography, UV: ultraviolet, CPE: cloud point extraction, SPE: solid phase extraction, SA: salt-assisted, LLME: liquid–liquid microextraction, RTIL: room temperature ionic liquid, HFLPME: hollow fiber liquid phase microextraction, UA: ultrasound-assisted, DLLME: dispersive liquid–liquid microextraction, IL: ionic liquid, FAAS: flame atomic absorption spectrometry, ETAAS: electrothermal atomic absorption spectrometry, TXRF: total reflection X-ray fluorescence spectrometry.

been applied for the preconcentration of inorganic species, including Cr species, in environmental samples [6,15–20]. As it is shown in Table 1, most of them are based on the use of dispersive liquid–liquid microextraction (DLLME) combined with flame or electrothermal atomic absorption spectrometry. In the present contribution, we propose a low cost analytical alternative combining DLLME with benchtop total reflection X-ray spectrometry (TXRF).

Total reflection X-ray fluorescence (TXRF) spectrometry is a suitable analytical technique for multielemental determination in various sample types, especially liquids and powdered micro samples [21]. In the 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 for trace element analysis [22,23].

In TXRF, the sample has to be prepared as a very thin film. For liquid samples this is done by depositing few microliters of the sample on a reflective carrier with a subsequent drying of the drop [24]. Therefore, it is an ideal technique to be used in combination with DLLME systems since only few microliters of preconcentrated sample are available after the preconcentration step. We have recently demonstrated the usefulness of this analytical approach for the determination of Se [25], Cd [26] and Sb [27] in different types of environmental samples.

In this work, parameters affecting the extraction procedure for Cr speciation (pH, sample volume, disperser solvent, complexing agent, organic solvent, temperature) as well as the operating conditions for TXRF analysis (sample volume, drying mode, measurement time, internal standardization) have been carefully evaluated to ensure the highest sensitivity for Cr determination/speciation. The usefulness of the proposed DLLME + TXRF system has been tested by means of the analysis of several type of samples including tap, mineral, river and waste water samples. As far as we know, it is the first time that a DLLME procedure is combined with TXRF for Cr speciation analysis.

2. Material and methods

2.1. Reagents and solutions

All reagents and solvents used were of analytical quality grade. Ultra purewater (MilliQ Plus system, Millipore Corp., Bedford) was used for dilutions and standard preparations in all experiments. Stock solutions of 100 mg L^{-1} Cr(VI) and Cr(III) ions were prepared by dissolving appropriate amounts of $\text{K}_2\text{Cr}_2\text{O}_7$ (Panreac, Spain) and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (Merck D-6100, Darmstadt, Germany), respectively.

Working solutions of Cr(VI) and Cr(III) were obtained daily by appropriate dilution of stock solutions. The pH of solutions was adjusted by using nitric acid (Suprapure, 65%, Merck, Germany) or sodium hydroxide (98%, Panreac, Spain). Other chemical reagents such as acetonitrile, acetone, methanol, ethanol, carbon tetrachloride and chloroform were purchased from Merck (Darmstadt, Germany). Ammonium pyrrolidinecarbodithioate (99%, Sigma Aldrich) was used as complexing agent.

The solution of 10 mg kg^{-1} of Mo used for internal standardization was obtained by appropriate dilution of Mo stock solution of 1000 mg L^{-1} in oil matrix (High-Purity standards, USA) using carbon tetrachloride. This metalorganic standard shows high solubility and could be easily employed as an internal standard in organic matrices.

Quartz glass sample carriers with a 30 mm diameter and a thickness of $3 \text{ mm} \pm 0.1 \text{ mm}$ were applied for TXRF analysis.

2.2. Instrumentation

TXRF analysis was performed using a portable spectrometer S2 PICOFOX™ (Bruker AXS Microanalysis GmbH, Berlin, Germany). The spectrometer is equipped with a low power tungsten target X-ray tube. This fact allows performing TXRF analysis using K-lines of high atomic number elements such as Sn and Cd (in conventional Mo-based X-ray tubes less intense L-lines have to be used for this purpose) and thus the limits of detection for heavy elements are improved. However, limits of detection for the 4th period elements ($Z = 19\text{--}36$) are higher than those associated with Mo anode X-ray tubes ($\sim 1\text{--}10 \mu\text{g L}^{-1}$). The system is also equipped with a Si drift detector (SDD) (10 mm^2 , $<160 \text{ eV}$ resolution Mn- K_α) and a multilayer Ni/C monochromator (17.5 keV, 80% reflectivity).

An 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. The evaluation of TXRF spectra and calculation of analytes net peak areas was performed using the software (Spectra Picofox 6.2.0.0, Bruker AXS Microanalysis GmbH, Berlin, Germany) linked to the equipment [28]. For the quantification in TXRF analysis, the software applies a deconvolution routine which uses measured mono-element profiles for the evaluation of peak areas. A summary of the technical features of the instrument and measuring conditions are given in Table 2. In order to evaluate the extraction efficiency for the developed preconcentration procedure, Cr content in aqueous samples (before and after the extraction) was determined by a quadrupole-based ICP-MS system equipped with an octapole collision cell (Agilent 7500c, Agilent Technologies, Tokyo, Japan). Instrumental parameters and measuring conditions for Cr monitoring are also displayed in Table 2.

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