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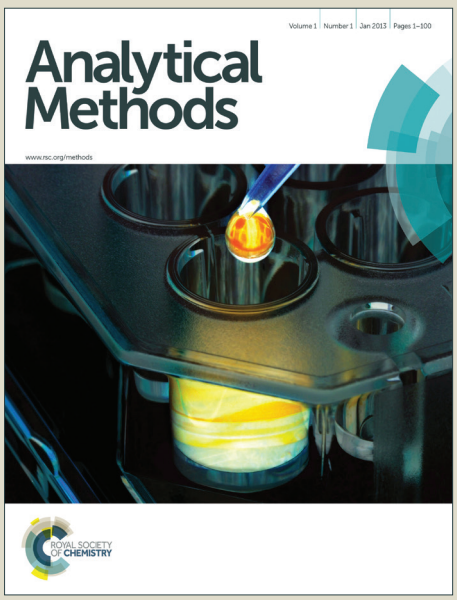

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Directly suspended droplet microextraction coupled with electrothermal atomic absorption spectrometry for the speciation of chromium(III)/chromium(VI)

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Abstract: A novel procedure for the speciation of Cr(III)/Cr(VI) by directly suspended single droplet microextraction combined with electrothermal atomic absorption spectrometry was presented. In this method, Cr(III) can be extracted by 1-decanol at pH 6.0 due to the hydrophobic complex of Cr(III)-8-hydroxyquinoline (8-HQ), whereas Cr(VI) remains in aqueous solution. Cr(VI) concentration was calculated by subtracting Cr(III) from the total chromium after reducing Cr(VI) to Cr(III) by hydroxylamine hydrochloride. Different factors affecting the extraction of Cr(III), such as pH, 8-HQ concentration, stirring rate, extraction temperature and time, and interfering ions, were schematically evaluated. Under the selected conditions, the limit of detection for Cr(III) was 0.03 ng mL^{-1} with the relative standard deviation of 4.7% (C=1.0 ng mL^{-1}, n=5). The calibration curve was highly linear in the Cr(III) concentration range of 0.10–2.0 ng mL^{-1}. The proposed method was validated against certified reference materials of environmental water (GSBZ50027-94, GBW(E)080642), and successfully applied to the speciation of chromium in well and tap water samples.

Keywords: Chromium speciation, directly suspended single droplet microextraction, electrothermal atomic absorption spectrometry, water samples

1. Introduction

The heavy metals contamination in the environment is a global concern because of their toxicity and threat to human life and environment.[1] Sufficient evident has revealed that the toxicological and physiological characteristics of many elements like chromium are strongly related to chemical forms. Chromium is the naturally occurring element in gases, soils, rocks, and volcanic dust.[2] It is mainly present in two oxidation states as Cr(III) and Cr(VI) in nature differing in their toxicological effects and health risks.[3] Cr(III) is essential for mammals to maintain several metabolism (such as lipid, carbonate, and protein metabolism), while Cr(VI) has extremely hazardous and carcinogenic impact on lung, liver, and kidney owing to its high water solubility, oxidizing ability, and free penetration into cells.[4-6] Although being essential, Cr(III) in evaluated concentrations may exhibit toxicity towards living organisms.[2,3] Cr(III) is far less toxic than Cr(VI), and their toxicities can differ up to 100-fold. Chromium and its compounds are often applied in electroplating, leather tanning, metallurgy, wood preservation, artificial fertilizers, cement products, and textile industry, which are probably discharged into surrounding ecosystems and easily end up in river watersheds through runoff from industrial effluents.[7] Both chromium species can also enter the drinking water distribution system from the corrosion inhibitors used in water pipes and containers, or via contamination of ground water from sanitary landfill.[4,7,8] So, there is a potential risk of contaminating river and drinking water sources. The toxic effect of environmental exposure to excessive chromium contaminants on population health has raised special concerns, and chemical speciation of Cr(III)/Cr(VI) has correspondingly become a pressing issue around the world. The U.S. Environmental Protection

Agency and the World Health Organization regulate the maximum residual level of Cr(VI) at 0.1 and 0.05 mg L^{-1} in drinking water, respectively.[1,9] In this respect, the development of sensitive and reliable analytical methods for the speciation of Cr(III) and Cr(VI) is of great interest.

Advanced techniques for Cr(III)/Cr(VI) quantification in different matrices are based on ultraviolet-visible spectrophotometry (UV-Vis),[7,10,11] flame atomic absorption spectrometry (FAAS),[12,13] electrothermal atomic absorption spectrometry (ETAAS),[14,15] inductively coupled plasma optical emission spectrometry (ICP-OES),[16] and inductively coupled plasma mass spectrometry (ICP-MS),[17,18] high performance liquid chromatography (HPLC),[19,20] and fluorescence spectrometry.[21] Of these methods, ETAAS and ICP-MS have become sensitive, powerful, and important tools for testing chromium. Despite the great potential of ICP-MS for chromium detection, this technique actually involves an expensive and sophisticated instrumentation, restricting its widespread application on the routine analysis. Additionally, severe carbon, nitrogen, chlorine and sulfur polyatomic interferences can disturb the ICP-MS measurements of ^{52}Cr and ^{53}Cr isotopes.[2] In comparison with ICP-MS, ETAAS is a more cost-effective and affordable alternative for most laboratories, and gives comparable sensitivity with respect to ICP-MS after using precocentration procedures. Furthermore, organic matrix in samples can be partially eliminated during the pyrolysis step in ETAAS. However, the straight determination of individual chromium species is still hampered owning to various factors, particularly their extremely lower concentrations in complicated matrices. To address such defects, appropriate sample pretreatment is highly required before chromium determination by the techniques such as ETAAS. Relevant strategies like liquid-liquid extraction (LLE),[4] solid phase extraction (SPE),[22,23] coprecipitation,[24] cloud point extraction (CPE),[8,25] dispersive

liquid-liquid microextraction (DLLME),[15,26] and solidified floating organic drop microextraction (SFODME)[27] are available for the separation and preconcentration of Cr(III)/Cr(VI).

Directly suspended droplet microextraction (DSDME) has recently engendered tremendous attention in virtue of its simplicity, low cost, effectiveness, and solvent-minimized extraction.[28] In DSDME, a well-defined organic droplet is directly exposed to a continuously stirred aqueous solution, and the target analytes are quickly extracted into the droplet. Unlike single drop microextraction, DSDME can effectively obviate the risk of the droplet dislodgement and cross contamination without use of supporting materials. It also showed more flexibility in the choice of experimental parameters, especially for extraction solvent volume and stirring frequency.[29] The mass transfer of analytes from aquatic phase to organic phase would be speeded up at larger volumes of extraction solvent and higher stirring rates during the DSDME process, which increases extraction efficiency and reduces extraction time. Many efforts have been devoted to develop chromatographic and UV-Vis strategies after DSDME for the determination of environmental pollutant,[30-32] pharmaceuticals,[33,34] and bioactive substance.[35,36] Nevertheless, DSDME in conjunction with atomic spectrometry has not yet been explored to analyze metals and their species.

The aim of the present work was to explore a efficient DSDME method coupled to ETAAS for the speciation of Cr(III) and Cr(VI). Experimental variables affecting the extraction efficiency of chromium species were examined in detail. The developed method was applied to determine Cr(III)/Cr(VI) in tap and well samples with good results.

2. Experimental

2.1 Instrumentation

A ZEEnit 700 electrothermal atomic absorption spectrometer (Jenna Analytic Instrument Co., Ltd. Germany) equipped with a Zeeman-based background corrector and a transversely heated graphite furnace atomizer was used for the detection of chromium. Measurements were carried out in the peak area mode using a chromium hollow cathode lamp (General Research Institute for Nonferrous Metals, Beijing, China) operated at 4 mA and 357.9 nm with a spectral bandwidth of 0.8 nm. Pyrolytic platform graphite tubes were used following the temperature program: drying 1 at 90 °C (ramp 10 °C s^{-1}, hold 10 s), drying 2 at 105 °C (10 °C s^{-1}, 10 s), drying 3 at 110 °C (5 °C s^{-1}, 15 s), pyrolysis at 400 °C (250 °C s^{-1}, 40 s), atomization at 2400 °C (1500 °C s^{-1}, 4 s), and cleaning at 2700 °C (500 °C s^{-1}, 4 s). pH measurements were conducted with a PHS-25B pH meter (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China) supplied with a combined glass electrode. A SZCL-3A constant-temperature magnetic stirrer (Yuhua Instrument Co., Ltd., Gongyi, China) and a TU-1810 UV-visible spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China) were used

2.2 Chemicals and reagents

All chemicals used were of analytical reagent grade or better, unless otherwise stated. Doubly deionized water was used throughout the experiments. A stock standard solution of 1.00 mg L^{-1} Cr(VI) was prepared from $K_2Cr_2O_7$ (Shanghai Reagent Factory, Shanghai, China). A stock solution of 1.00 mg mL^{-1} Cr(III) was prepared by dissolving 0.1000 g metallic chromium powder (Tokyo, Japan 5N) in appropriate concentrated hydrochloric acid and diluting to 100 mL

with doubly deionized water. Working standard solutions were prepared by stepwise dilution from the stock solutions. 1-Octanol and 1-decanol (98%) were purchased from Aladdin Reagents (Shanghai) Company (Shanghai, China) and tried as potential extraction solvents. 2.5% (*w/v*) of 8-hydroxyquinoline (8-HQ, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was prepared in ethanol. 1.0 mol L^{-1} of hydroxylamine chloride (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was acted as a reducing reagent. Buffer solutions of sodium acetate-acetic acid (pH 3.0–6.0), ammonium acetate ammonia (pH 7.0), and ammonium chloride-ammonia (pH 8.0–10.0) were used for pH adjustments. All glassware and plastic were stored in 10% (*v/v*) nitric acid for at least 24 h, and thoroughly rinsed with doubly deionized water before use.

2.3 General procedure for DSDME

A 30.0 mL of working standard solution (or sample solution), 2.0 mL 2.5% (*w/v*) 8-HQ, and 6.0 mL of pH 5.0 acetate buffer solution were hold in a 50 mL screw cap glass vial with a PTFE stirring bar (25 mm × 9 mm). The mixture in the vial was incubated at 45 °C and was agitated at 450 rpm to form a steady vortex. A 130 μL of 1-decanol was then added at the bottom of the vortex, and the vial was sealed to prevent evaporation of the extraction solvent. After 50 min, the supernatant droplet was retracted into a micropipette and dissolved in 0.60 mL methanol containing nitric acid (0.10 mol L^{-1}) in an inert vial. 20 μL of resultant solution was automatically injected into the ETAAS atomizer for further analysis. The typical schematic of DSDME-ETAAS method is illustrated in Fig. 1.

<Fig. 1>

2.4 UV-Vis measurement

Aliquots of 10.0 mL solution containing 2.0 μg mL^{-1} of Cr(III) [or Cr(VI)] and 0.70 mL 2.5% (*w/v*) 8-HQ were adjusted to the corresponding pH 6.0 and were introduced into the 1-cm quartz cell for UV-Vis measurements. Absorbance of the blank solution was deducted for all tests.

2.5 Sample preparation

Local tap and well water samples were filtered through 0.45 μm membrane filters immediately and stored at 4 °C. Certified reference water samples for the total chromium (GBW(E)080462, Shanghai Institute of Measurement and Testing Technology, Shanghai, China) and the Cr(VI) (GSBZ50027-94, Institute for Environmental Reference Materials of the Ministry of Environmental Protection, Beijing, China) were directly analyzed after appropriate dilution with doubly deionized water.

2.6 Determination of chromium species

The concentration of Cr(III) in the sample solution was determined as described above procedure. Total chromium was obtained after the reduction of Cr(VI) to Cr(III) by hydroxylamine chloride, and the concentration of Cr(VI) was calculated from the difference between the total chromium and Cr(III). Reduction of Cr(VI) to Cr(III) was performed according to our previous work.[23]

3. Results and discussion

3.1 Effect of pH

pH is a critical factor for the speciation of Cr(III)/(VI), which plays an important role in the hydrophobic complex formation between chromium species and 8-HQ, and its subsequent extraction. The effect of pH on the extraction efficiency of Cr(III) and Cr(VI) was investigated separately over the pH range of 3.0–10.0. The results in Fig. 2 indicated that the quantitative extraction (> 90.6%) for Cr(III) was achieved with the pH range from 5.0 to 8.0, while Cr(VI) was almost not extracted in the whole tested pH range. The reason for the selective extraction of Cr(III) may be explained that the extractable complex of Cr(III)-8-HQ formed in the presence of 8-HQ. At pH 6.0, Cr(III) mainly exists as $Cr(OH)^{2+}$ and $Cr(OH)_2^{+}$, which would be easily chelated with N atom of 8-HQ to form a hydrophobic complex and subsequently extracted by 1-decanol, leading to the quantitative extraction of Cr(III). However, Cr(III) tends to be precipitated as $Cr(OH)_3$ after pH 9.0, decreasing the recovery of Cr(III). In view of Cr(VI), its dominant species are $HCrO_4^-$ (pH 1~6.5) and $Cr_2O_4^{2-}$ (pH >6.5).[2] In addition, $Cr_2O_4^{2-}$ could not react with 8-HQ at the tested pH range, probably owing to extremely high and negative hydration enthalpy (1490.3 kJ mol^{-1}) and free energy (1301.1 kJ mol^{-1}).[37] UV-visible absorption spectra in Fig. 2 (inset) further verified that the complex of 8-HQ-Cr(III) has a maximum absorption at the wavelength of 395 nm, when the sample solution was set at pH 6.0. But no absorption was found for Cr(VI) and 8-HQ at this pH value. Therefore, pH 6.0 was determined and chosen for extracting Cr(III) in this study.

<Fig. 2>

3.2 Extraction solvent and its volume

The criterion of solvent selection in DSDME includes high enrichment factor, poor volatility and water solubility, lower density than water, and environmental friendship.[33,38] In addition, a high viscosity is necessary and favorable for the organic solvent to form a stable and well-defined phase during extraction.[36] Based on these considerations, 1-octanol and 1-decanol were tested as possible extraction solvents for the extraction of Cr(III). A 130 μL of the organic solvent mentioned above was studied using a stirring rate of 450 rpm. 1-Octanol and 1-decanol provided the extraction efficiency of 78.9% and 94.0%, respectively. Furthermore, the 1-decanol droplet was more stable than 1-octanol, which facilitated the collection of the extraction phase after the agitation of the sample solution. Hence, 1-decanol was selected in this work.

The effect of 1-decanol volume on the extraction efficiency of Cr(III) was also evaluated in the range from 80 to 150 μL. The results showed that the extraction efficiency was continuously enhanced with an increase of 1-decanol volume below 120 μL, and kept relatively constant for higher volumes. A lower volume of 1-decanol tended to cause instability of the extraction droplet during agitation, and was difficultly isolated from the aqueous sample by a microsyringe at the end of the DSDME process. Consequently, 130 μL of 1-decanol was employed.

3.3 Effect of 8-HQ concentration

The effect of 8-HQ concentration on the extraction efficiency of Cr(III) was optimized, and the results are disclosed in Fig. 3. The extraction efficiency of Cr(III) increased gradually as

8-HQ concentration increased from 0.2% to 2.0% (*w/v*), and attained the maximum in the presence of 8-HQ concentration over 2.0% (*w/v*). Accordingly, 2.5% (*w/v*) of 8-HQ was selected.

<Fig. 3>

3.4 Stirring rate

Agitation of the sample solution can effectively strengthen the mass transfer and accelerate the extraction kinetics in DSDME by reducing the thickness of the Nernst diffusion film.[31,34] Different stirring rates (200–550 rpm) were surveyed for better extraction of Cr(III). The extraction efficiency was ascended and reached the maximum as the stirring rate was at 450 rpm, but declined obviously for greater agitation. It may be that a higher stirring speed (more than 450 rpm) would generate a more unstable fluid field, which resulted in the break of the 1-decanol droplet and its dispersion in the aqueous phase.[33,35] After dispersion of the organic droplet(1-decanol droplet), Cr(III) was very difficult collected into the microsyringe, and subsequently the extraction efficiency of Cr(III) was poor. As a result, 450 rpm of stirring rate was executed as the optimum.

3.5 Extraction temperature and time

The effect of extraction temperature on the extraction efficiency of Cr(III) was checked by varying the temperature within 20–50 °C at the interval of 5 °C. The obtained results illustrated that the extraction efficiency augmented with the increase of extraction temperature up to 40 °C exceeding 90% thereafter. A temperature of 45 °C was set for all extractions.

The dependence of extraction efficiency of Cr(III) upon equilibrium time was carefully

observed with a range of 10–70 min. The increment of extraction time brought a remarkable increase in the extraction efficiency of the analyte, and the equilibrium state was subsequently gained after extracting beyond 45 min. Thus, 50 min of extraction time was finally performed.

3.6 Effect of salt addition

The influence of ionic strength on the extraction efficiency of Cr(III) was evaluated at different amounts of NaCl. The obtained results stated that NaCl concentration up to 4% (*w/v*) did not affect the extraction of Cr(III). All extractions were performed without salt addition.

3.7 Sample volume

The effect of sample volume from 20.0 to 40.0 mL on the recovery of 30.0 ng Cr(III) was explored since other variables constant. The evidence demonstrated that above 90.0% of Cr(III) could be extracted in the sample volume range of 20.0–30.0 mL.

3.8 Interferences

The interferences of coexisting ions on the determination of 1.0 ng mL^{-1} Cr(III) were examined. The tolerance limits of interfering ions, defined as the largest amount of the substance causing ±5% error of absorbance, were as follows: 2000-fold of K(I), 1000-fold of Ca(II), Mg(II), 300-fold of Cu(II), 200-fold of Co(II), 100-fold of Mn(II), Cd(II), Fe(III), Al(III), and 50-fold of Pb(II), Zn(II), Cr(VI). The results deduced that the probably encountered matrix did not significantly interfere determining Cr(III) at the given level. The interference of Fe(III) can be completely avoided by using EDTA.[11] Therefore, the presented method was good selective for studied species.

3.9 Method evaluation

Under the optimum conditions, the calibration curve equation was A= 0.047+0.476C (R=0.9978) with a linear range of 0.10–2.0 ng mL^{-1}, where A and C corresponded absorbance and original concentration of Cr(III) (ng mL^{-1}) in the sample solutions, respectively. The limit of detection (LOD) for Cr(III) was 0.03 ng mL^{-1}. The relative stand deviation (RSD, n=5) was 4.7% at 1.0 ng mL^{-1} of Cr(III). The enrichment factor (EF, calculated as the slope ratio of calibration graphs after and before extraction) was 46.9 for Cr(III). Table 1 compares the characteristic data of the present method with those reported in literatures. As could be seen, this method showed a higher sensitivity for analyzing chromium.

<Table 1>

3.10 Method validation and application

Validation of the method was performed by analyzing two certified reference materials of environmental water, GSBZ50027-94 and GBW(E)080642. As listed in Table 2, the analytical results were in good agreement with the certified values. The proposed method was also applied for the speciation of Cr(III) and Cr(VI) in well and tap water samples (Table 3). It was found that the concentration of Cr(VI) was not detected in these water, and the recoveries of Cr(III) and Cr(VI) in spiked water samples ranged from 90% to 114%, implying the applicability and feasibility of this method.

<Table 2>

<Table 3>

4. Conclusions

A flexible method of DSDME coupled to ETAAS was successfully established for the speciation of Cr(III) and Cr(VI) in tap and well water samples. This procedure takes additional advantages including easy manipulation, reasonable recovery, and lower detection limit.

Acknowledgments

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Figure captions

Fig. 1 The typical schematic of DSDME-ETAAS: (a) setup of DSDME; (b) extraction steps.

Fig. 2 Effect of pH on the selective extraction of Cr(III) and Cr(VI). Conditions: Cr(III) or Cr(VI), 1.0 ng mL^{-1}; buffer solutions, pH 3.0–10.0; 8-HQ, 2.0 mL 2.5% (*w/v*); 1-decanol, 130 μL. Inset shows UV-visible absorption spectra of (curve 1) Cr(III)+8-HQ and (curve 2) Cr(VI)+8-HQ. Conditions: Cr(III) or Cr(VI), 2.0 μg mL^{-1}; 8-HQ, 0.70 mL 2.5% (*w/v*).

Fig. 3 Effect of 8-HQ concentration on the extraction of Cr(III). Conditions: Cr(III), 1.0 ng mL^{-1}; buffer solution, pH 6.0; 8-HQ, 2.0 mL; 130 μL 1-decanol.

Fig. 1

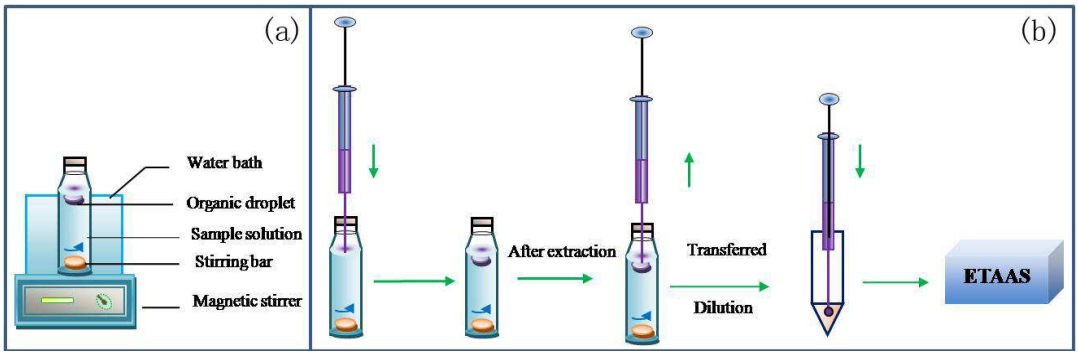

Fig. 2

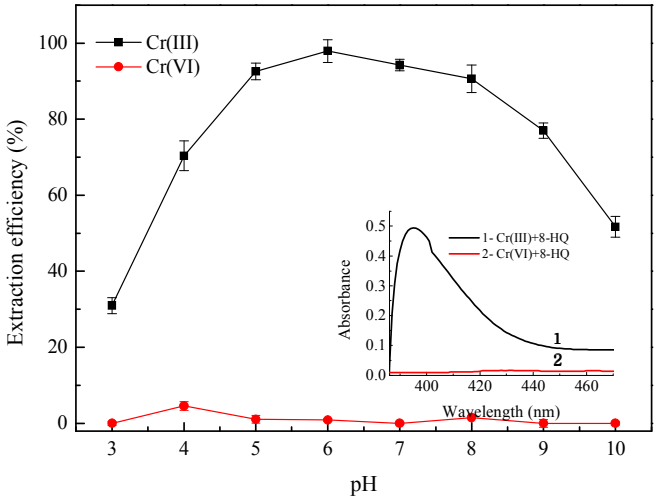

Fig. 3

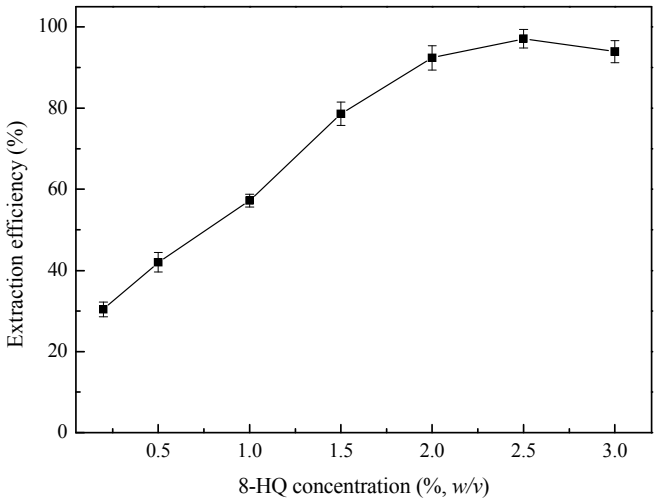

Table 1

Table 1 Comparison of analytical performance of the proposed method with other methods for the speciation of chromium.

Method	Chelating agent	LOD (ng mL^{-1})		Linear range (ng mL^{-1})		RSD (%)		Ref.
		Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
DEME-HPLC	APDC	5.4	2.8	10-500	20-500	10.7	13.1	1
CME-ICP-MS	-	0.074	0.018	-	-	3.9	2.8	17
SPE-ETAAS	PAR	0.056	-	2.0-160.0	-	2.5	-	23
SFODME-ETAAS	TTA	0.006	-	0.03-0.13	-	5.1	-	27
CPE-ICP-MS	APDC	0.025	0.010	0.3-5	0.2-10	3	0.6	18
DLLME-ETAAS	APDC	-	0.002	-	0.005-0.1	8.1	7.2	15
DLLME-ETAAS	-	-	0.002	-	0.005-0.2	8.1	7.2	26
DSDME-ETAAS	8-HQ	0.03	-	0.10-2.0	-	4.7	-	This work

APDC, ammonium pyrrolidinedithiocarbamate; CME, capillary microextraction; DEME, dual electromembrane extraction; PAR, 4-(2-pyridylazo)resorcinol; TTA, 2-thenoyltrifluoroacetone.

Table 2

Table 2 Analytical results for the certified reference water samples.

Sample	Species	Certified value (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
GSBZ50027-94	Cr(VI)	0.40±0.01	0.38±0.02	95.0
GBW(E)080642	Total Cr	100.0±5.0	93.6±5.1	93.6
	Cr(III)	-	69.9±2.6	-
	Cr(VI) [a]	-	23.7±1.1	-

[a] The concentration of Cr(VI) was calculated by subtracting Cr(III) from the total chromium.

Table 3

Table 3 Determination of chromium species in real water samples (Mean ± S.D., *n*=3).

Sample	Added (ng mL^{-1})		Found (ng mL^{-1})			Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI) [a]	Total Cr	Cr(III)	Cr(VI)
Well water	0	0	0.61±0.03	ND	0.61±0.05	-	-
	0.3	0.3	0.88±0.05	0.28±0.02	1.16±0.08	90.0	93.3
	0.5	0.5	1.08±0.06	0.57±0.03	1.65±0.04	94.0	114.0
Tap water	0	0	0.47±0.02	ND	0.47±0.03	-	-
	0.2	0.2	0.69±0.05	0.21±0.01	0.90±0.04	110.0	105.0
	0.4	0.4	0.84±0.09	0.39±0.03	1.23±0.11	92.5	97.5

ND: not detected.

[a] The content of Cr(VI) was calculated by subtraction of Cr(III) from the total chromium.