Speciation and determination of ultra trace amounts of chromium by solidified floating organic drop microextraction (SFODME) and graphite furnace atomic absorption spectrometry

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ABSTRACT

Solidified floating organic drop microextraction (SFODME) method in combination with graphite furnace atomic absorption spectrometry (GFAAS) has been used for the determination of chromium species in water and urine samples. 1-undecanol containing 2-thenoyltrifluoroacetone (TTA) was used as a selective chelating agent for the extraction of Cr(III). The total Cr was determined after the reduction of Cr(VI) to Cr(III) with hydroxylamine. The concentration of Cr(VI) was determined from the difference between the concentration of total chromium and the Cr(III). Several variables such as the sample pH, concentration of TTA, salt concentration, extraction time and the sample volume were investigated in detail. Under the optimum conditions, the limit of detection of the proposed method was $0.006\,\mu g\,l^{-1}$ for Cr(III) and the relative standard deviation for six replicate determinations at $0.1\,\mu g\,l^{-1}$ Cr(III) was 5.1%. The proposed method was successfully applied for the determination of chromium species in tap water, well water, mineral water, and urine samples.

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1. Introduction

Speciation of chromium as a trace element in environmental and biological samples has become an interesting topic in analytical techniques. The interest in speciation is governed by the fact that toxicological and biological characteristics of this element are related to its oxidation states. Although chromium can exist in several oxidation states, Cr(III) and Cr(VI) are known as the only stable species in solution [1,2]. Cr(III) appears to be essential for the living organisms especially human beings. It has an important role in glucose, lipid and protein metabolism [3], while Cr(VI) is known as a toxic species that can easily penetrate the cell wall and exert its noxious influence in the cell. Cr(VI) is also known as a cause of various cancer diseases [4,5]. Thus, due to the difference in toxicities of Cr(III) and Cr(VI), their separate determination is necessary.

Various analytical techniques such as atomic absorption spectrometry (AAS) [6–8], spectrophotometry [9], spectrofluorometry [10], stripping voltametry [11], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [12], inductively coupled plasma-mass spectrometry (ICP-MS) [13,14], and high performance liquid chromatography (HPLC) [15] have been frequently used for accurate determination of chromium in various samples. However, due to its good sensitivity, graphite furnace atomic absorption spectrometry (GFAAS) is one of the most extensively used techniques for the determination of trace amounts of various elements, but it suffers from matrix interferences and the direct determination of the species of the elements presented in the samples is not possible. Thus, speciation of trace elements at sub-ppb level by GFAAS requires a separation and preconcentration step.

The most widely used techniques for separation and preconcentration of chromium are cloud-point extraction [16–18], coprecipitaton [19,20], solid phase extraction [21–23], ion exchange separation [24] and liquid–liquid extraction [25]. Although satisfactory results can be obtained with the above mentioned separation/preconcentration techniques, they have some drawbacks such as large consumption of reagent, low enrichment factor, multistage operation and lengthy separation.

Microextraction methods such as drop-in-drop system [26], single-drop microextraction (SDME) [27], homogenous liquid–liquid microextraction (HLLME) [28], solid phase microextraction (SPME) [29], dispersive liquid–liquid microextraction (DLLME) [30,31], and solidified floating organic drop microextraction (SFODME) [32] have been developed to overcome these problems. The major idea behind these techniques is a great reduction in the volume ratio of acceptor to donor phase.

Solidified floating organic drop microextraction (SFODME) that was reported by Khalili Zanjani et al. [32] is a new liquid phase microextraction technique in which small volume of an organic solvent with a melting point near the room temperature (in the range of 10–30°C) is floated on the surface of aqueous solution.

The aqueous phase is then stirred for a prescribed period of time, and the sample is transferred into the ice bath. When the organic solvent is solidified, it is transferred into a small conical vial and the melted organic solvent is used for the analytes determination. This method is inexpensive, sensitive and effective for the removal of the interfering matrices. Compared with conventional solvent extraction, it also has the advantage of great reduction in the amount of organic solvent and subsequently great enhancement of the preconcentration factor [33,34]. Recently, our research group were able to successfully combine SFODME with GFAAS and flame atomic absorption spectrometry (FAAS) for trace elements separation and determination [35–37]. Later, this method was also used by other researchers for the determination of trace metals in various samples [38–41]. However, to the best of our knowledge there is no report on the use of the SFODME technique for speciation of elements. Thus, in this study the possibility of implementation of SFODME for trace metal speciation was considered and a simple method for speciation of chromium(III) and (VI) was developed. Thenoyltrifluoroacetone (TTA) was used as a selective chelating agent for the extraction of chromium(III). Furthermore, the applicability of the approach was demonstrated for the determination of chromium in urine and water samples.

2. Experimental

2.1. Reagents and standard solutions

All reagents used were of analytical reagent grades and were purchased from the Merck Company (Darmstadt, Germany). Doubly distilled deionized water was used throughout this study. Stock standard solution ($1000\,mg\,l^{-1}$) of Cr(VI) and Cr(III) was prepared by dissolving proper amount of $K_2Cr_2O_7$ and $CrCl_3 \cdot 6H_2O$ in water. Thenoyltrifluoroacetone (TTA) solution ($0.1\,mol\,l^{-1}$) was prepared by dissolving 0.111 g of TTA in 5 ml of 1-undecanol, and then $0.001\,mol\,l^{-1}$ of TTA solution was prepared by proper dilution with 1-undecanol. Hydroxylamine hydrochloride solution ($4\,mol\,l^{-1}$) was prepared by dissolving 6.95 g of the reagent in 25 ml of distillated water. Sodium fluoride solution ($1\,mol\,l^{-1}$) was prepared by dissolving sufficient amount of NaF in distilled water. Buffer solution (pH = 3.5) was prepared by dissolving 13.609 g of KH_2PO_4 and an appropriate amount of hydrochloric acid, adjusting the pH and diluting to the mark by distilled water in a 100 ml volumetric flask.

2.2. Apparatus

Varian Zeeman spectra atomic absorption spectrometer, model 220Z was used for all metal measurements throughout this study. A PC computer was used to record the absorbance signal profile. A Varian Spectra-AA hollow cathode lamp for chromium was used as the light source. The furnace tube was a standard plateau tube with a pyrolytic graphite coating. The analytical wavelength (357.9 nm), spectra bandwidth (0.5 nm) and lamp current (7 mA) were used as recommended by manufacturers. The sample injection volume was 10 μl in all experiments. The pH measurements were carried out with a Metrohm pH meter (model 691, Switzerland) using a combined glass calomel electrode.

2.3. Extraction procedure

(A) Determination of Cr(III): Ten ml solution of the Cr(III) and Cr(VI), 0.2 ml of $1\,mol\,l^{-1}$ NaF and 1 ml of phosphate buffer solution (pH = 3.5) were added to a suitable vial containing a stirring bar. 30 μl of TTA in 1-undecanol ($0.001\,mol\,l^{-1}$) was added, the magnetic stirrer was turned on and the solution was mixed for 30 min at 1250 rpm. In this step the organic drop was dispersed to some

extents in the sample solution, the Cr(III) reacted with TTA and extracted into 1-undecanol while Cr(VI) remained in the aqueous solution. After the extraction time was over, the stirring rate was lowered so that the drop was coagulated. The stirring was then terminated and the sample vial was transferred into an ice bath for 5 min. The solidified solvent was transferred into a conical vial where it melted immediately. 10 μl of the extract was manually injected into graphite furnace atomic absorption spectrometer for quantification.

(B) Determination of total Cr and Cr(VI): To determine the total concentration of chromium in the solution, Cr(VI) was efficiently reduced to Cr(III) upon the addition of 1 ml of $0.05\,mol\,l^{-1}$ of the hydroxylamine hydrochloride solution. The solution was then treated according to the procedure given in part A.

The concentration of Cr(VI) was determined from the difference between the concentration of total chromium and Cr(III).

3. Results and discussion

In the preliminary analysis of the extract with GFAAS, it was illustrated that 2-thenoyltrifluoroacetone (TTA) dissolved in 1-undecanol can extract Cr(III) via the solidified floating organic drop microextraction (SFODME) method, while Cr(VI) remained in aqueous phase, a similar behavior was reported by the other workers [16,42]. TTA forms a complex with Cr(III) as follows:

1-Undecanole was used as an extracting solvent because of its low volatility, low water solubility and melting point (13–15 °C) near to room temperature. Furthermore, to obtain a high enrichment factor, different parameters affecting the complex formation, extraction and analysis process were optimized in a univariable approach. The percentage of extraction and enhancement factors was calculated according to the Eqs. (1) and (2) as described earlier [35–37].

$$\text{Percent of extraction} = \left(\frac{C_O V_O}{C_{aq} V_{aq}} \right) \times 100 \tag{1}$$

$$\text{Enrichment factor} = \frac{C_O}{C_{aq}} \tag{2}$$

where V_O, C_O and V_{aq}, C_{aq} are the volumes and the concentration in organic and initial aqueous phases, respectively. C_O was calculated from the calibration graph of standard solution of Cr(III)–TTA complex in ethanol.

3.1. Optimization of furnace temperature program

It was previously reported that TTA complex of Cr(III) is volatile and vaporized at 700 °C [16,42]. Thus, in order to avoid the loss of the interested metal ion and to eliminate or alleviate the background signal during the pyrolysis step, the time and temperature program of GFAAS during the analysis process were optimized, the results of which are demonstrated in Fig. 1. The optimal ashing and atomization temperatures were 550 and 2400 °C respectively. Under these conditions the background was low and the Cr peak had a normal shape. The optimum temperature program of GFAAS used for the determination of chromium in the extract is given in Table 1.

3.2. Selection of organic solvent

Several extracting solvents, including 1-undecanol (m.p. 13–15 °C), 1-dodecanol (m.p. 22–24 °C), 1,10-dichlorodecane (m.p. 14–16 °C) and n-hexadecane (m.p. 18 °C) which fulfill the needed conditions for extracting solvents of SFODME, were investigated [35–37]. 1-Undecanol was found to give the best extraction efficiency, with 2-dodecanol the extraction efficiency was about 65%
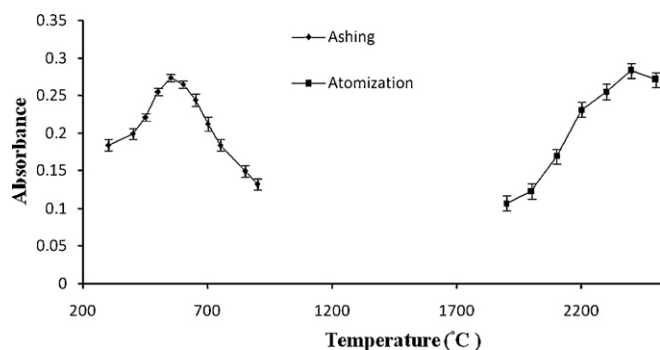
Fig. 1. Effect of ashing and atomization temperature on absorption of 12 μg l^{-1} of Cr(III) in present of 2×10^{-2} mol l^{-1} of TTA.

Table 1
Temperature program of GFAAS for determination of Cr.

Steps	Temp. (°C)	Time (s)	Argon flow rate (l min^{-1})
Dry	85	5	3
Dry	95	10	3
Dry	200	30	3
Ashing	550	6	3
Ashing	550	2	0
Atomization	2400	3.2	0
Cleaning	2600	2	3

of 1-undecanol, while 1,10-dichlorodecane and n-hexadecane produced high backgrounds during the analysis with GFAAS which interfere with determination of the analyte. Thus, in the present study, 1-undecanol was selected as the extracting solvent.

3.3. Effect of pH

The separation and preconcentration of metal ions by SFODME is based on the formation of a complex with sufficient hydrophobicity that can be extracted into small volume of 1-undecanol. Thus the pH of aqueous phase has a unique role in the extraction method as it effects the metal–chelate formation and its subsequent extraction. The extraction of Cr(III) was studied in the pH range of 1.5–8 using hydrochloric acid or ammonium hydroxide solution and keeping the other variable constants. The results are shown in Fig. 2 demonstrating that the recovery is nearly constant in the pH range of 3–4. The progressive decrease in extraction of Cr at pH < 3 might be due to the competition of proton with the analyte for reaction with TTA, while the reduction in signal at high pH might be due to the hydrolysis of the chromium ions. Therefore, a pH of 3.5 was selected as the optimum pH for the subsequent work.
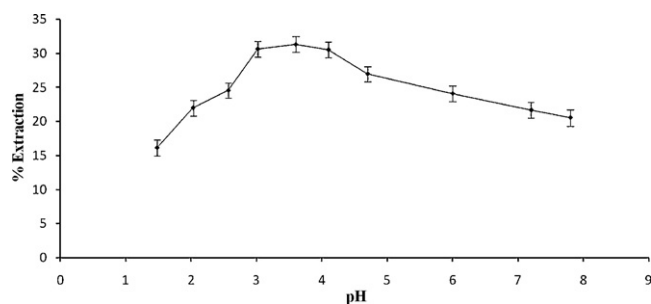

Fig. 2. Effect of pH on extraction of Cr^{3+} by SFODME method. Extraction conditions: sample volume, 10 ml; amount of Cr^{3+}, 1 ng; organic phase volume, 30 μl; TTA concentration, 2×10^{-3} mol l^{-1}; extraction time, 20 min.
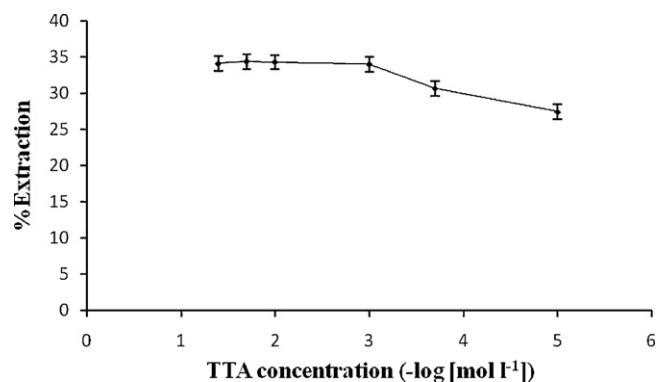

Fig. 3. Effect of TTA concentration on extraction of Cr^{3+} by SFODME method. Extraction conditions: sample volume, 10 ml; amount of Cr^{3+}, 1 ng; organic phase volume, 30 μl; sample pH = 3.5; extraction time, 20 min.

3.4. Effect of TTA concentration

The efficiency of analyte extraction was dependent on the TTA concentration in 1-undecanol as shown in Fig. 3. The analyte signal reached a maximum at a concentration of 1×10^{-3} mol l^{-1} of TTA and was independent of further increase in the amount of TTA. So a concentration of 1×10^{-3} mol l^{-1} of TTA was selected as optimum for further studies.

3.5. Effect of salt

To study the influence of salt on the performance of SFODME, the effect of concentrations of different salts such as NaCl, NaF, NaH$_2$PO$_4$, KBr and NaClO$_4$ in the range of 0.0–0.08 mol l^{-1} on extraction efficiency was considered. The pH of solution was adjusted to ~3.5 using either nitric acid or ammonium hydroxide and the extraction was done for 20 min. The results are shown in Fig. 4. It was observed that addition of NaCl has no significant effect on the extraction efficiency but when the concentration of KBr and NaClO$_4$ was greater than 0.02 mol l^{-1}, the extraction signal was decreased. Furthermore, as Fig. 4 reveals, an increase in concentration of NaF up to 0.02 mol l^{-1} causes an increase in the extraction of chromium and remains constant up to 0.04 mol l^{-1}. This observation was in agreement with the previous report which stated that the extraction of Cr(III) with TTA is accelerated by the addition of fluoride ions due to the formation of an intermediate fluoride complex. This intermediate complex destroys the hydrated shell of Cr(III) but does not prevent the formation of extractable chromium(III)–TTA complex [43]. The slight decrease in extraction at higher concentration of NaF might be due to competition of fluoride with TTA for complex formation with Cr(III) ions. It was also observed that an increase in phosphate concentration up to
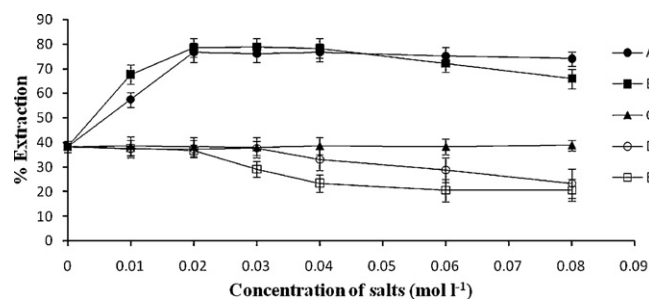

Fig. 4. Effect of various salts concentration (A: NaH$_2$PO$_4$, B: NaF, C: NaCl, D: NaHClO$_4$, E: KBr) on extraction of Cr^{3+} by SFODME method. Extraction conditions: sample volume, 10 ml; amount of Cr^{3+}, 1 ng; organic phase volume, 30 μl; TTA concentration, 1×10^{-3} mol l^{-1}; sample pH = 3.5; extraction time, 20 min.
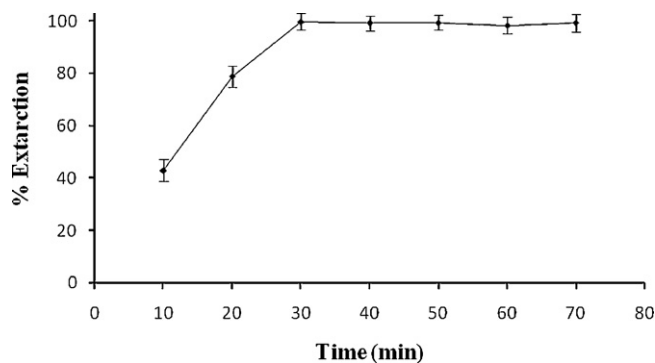
Fig. 5. Effect of time on extraction of Cr^{3+} by SFODME method. Extraction conditions: sample volume, 10 ml; amount of Cr^{3+}, 1 ng; organic phase volume, 30 μl; TTA concentration, 1×10^{-3} lmol l^{-1}; NaF concentration, 0.02 mol l^{-1}; sample pH = 3.5.

0.02 mol l^{-1} causes an increase in extraction efficiency and remains constant at higher concentration of phosphate.

3.6. Extraction time

Extraction time is an important factor influencing the extraction efficiency and speed of analysis. In order to have a good precision, high sensitivity and speed, it is necessary to select an extraction time that guarantees the achievement of equilibrium between aqueous and organic phases and maximizes the extraction of the analyte. The effect of the extraction time on the extraction efficiency was assessed by varying the extraction time between 20 and 70 min at a constant experimental condition. The result demonstrated in Fig. 5 revealed that the formation of adduct and its extraction was relatively slow and after 30 min, the signal of Cr was independent of the extraction period. An exposure time of 30 min was selected for the subsequent experiments.

3.7. Effect of sample volume

Demonstration of the preconcentration capability of the SFODME system is an important aspect of the method development. An increase in the ratio of the volume of the aqueous phase to the organic phase will increase the preconcentration factor, but it may reduce the extraction efficiency at a given extraction time. The effect of the sample volume on the extraction of 1 ng of Cr(III) from a different sample volume (1–35 ml) was examined. The result in Fig. 6 showed that the extraction was quantitative with the aqueous phase volume in the range of 1–10 ml, and then decreased
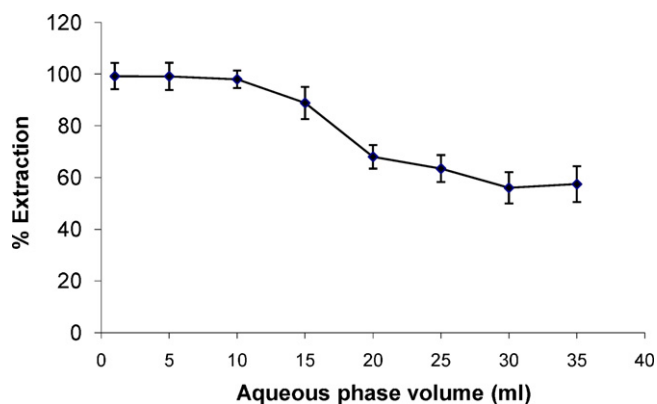

Fig. 6. Effect of volume of aqueous phase on extraction of Cr^{3+} by SFODME method. Extraction conditions: amount of Cr^{3+}, 1 ng; organic phase volume, 30 μl; TTA concentration, 1×10^{-3} mol l^{-1}; NaF concentration, 0.02 mol l^{-1}; sample pH = 3.5; extraction time, 30 min.

Table 2
Effect of diverse ions on the recovery of Cr: concentrated volume 10 ml, Cr(III) at a concentration of 100 ng l^{-1}.

Diverse ions	Molar ratio (ion/Cr)	Cr(III)[a] recovery (%)
K^+	10,000[b]	97.1 ± 6.4
Na^+	10,000[b]	96.1 ± 4.3
Ca^{2+}	10,000[b]	96.5 ± 5.1
Mg^{2+}	10,000[b]	101.2 ± 4.5
Fe^{2+}	1000[b]	96.5 ± 6.4
Cd^{2+}	1000[b]	96.2 ± 6.8
Cu^{2+}	1000[b]	96.0 ± 5.6
Hg^{2+}	1000[b]	105.1 ± 3.1
Ag^+	1000	104.7 ± 3.3
Pb^{2+}	800	104.6 ± 4.8
Fe^{3+}	500	96.6 ± 3.2
Zn^{2+}	400	96.6 ± 6.9
NO_3^-	10,000[b]	101.7 ± 2.9
I^-	10,000[b]	101.3 ± 7.7
SO_4^{2-}	10,000[b]	96.1 ± 6.2
Br^-	10,000[b]	95.9 ± 5.3
Cl^-	10,000[b]	98.8 ± 3.8

[a] Results are mean and standard deviation of three independent measurements.
[b] Maximum amount tested.

with further increase in sample the volume. Thus, based on the organic phase volume (30 μl) and the maximum sample volume that the extraction was quantitative (10 ml) an enrichment factor of 333 was determined. Based on the slope ratio of the calibration curves of standard solution with microextraction preconcentration and without preconcentration, an enhancement factor of 327 was determined which indicates that the extraction is about 98% completed.

3.8. Effect of diverse ions

The effect of potential interference ions in natural waters on the preconcentration and determination of analyte was examined. For this purpose, according to the recommended precedence, 10 ml of the solution of 100 ng l^{-1} of Cr(III) and various amounts of interfering ions were preconcentrated and analyzed. The tolerance limit of coexisting ions is defined as the largest amount making variation of less than 5% in the recovery of analyte. The result of this investigation is summarized in Table 2 and no significant interference in the determination of chromium was observed at the given level. This proves that the Cr recoveries are almost quantitative in the presence of excessive amount of the possible interfering cations and anions.

3.9. Figures of merit

Performance characteristics of the method were obtained by processing standard solution of Cr(III) are summarized in Table 3. Under the optimized conditions, the calibration graph was linear from 0.03 to 0.13 μg l^{-1}. The equation of calibration graph was $A = 6.815C + 0.006$ (where A is the absorbance and C is the concentration of Cr(III) in μg l^{-1}.) with the correlation coefficient of 0.9982. It should be noted that the linear range can be extended by varying

Table 3
Analytical characteristic of the method.

Parameter	Value
Dynamic range	0.03–0.13 (μg l^{-1})
Correlation coefficient (R^2)	0.9982
Limit of detection	0.006 (μg l^{-1})
Limit of quantification	0.020 (μg l^{-1})
R.S.D. (%) ($n = 6$)	5.1% (at 0.1 μg l^{-1})
Preconcentration factor	333
Enhancement factor	327

Table 4
Determination and speciation of chromium in real samples.

Sample	Added (ng l^{-1})		Found[a] (ng l^{-1})		Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Tap water	–	–	570 ± 25	320 ± 19	–	–
	400	–	961 ± 43	–	97.8	–
	–	400	–	704 ± 36	–	96.0
	150	200	713 ± 38	528 ± 34	95.3	104.0
Mineral water	–	–	682 ± 28	Not detected	–	–
	500	–	1196 ± 51	–	102.8	–
	–	400	–	419 ± 21	–	104.7
	200	300	874 ± 44	310 ± 21	96.0	103.3
Urine	–	–	155 ± 8	320 ± 25	–	–
	150	–	313 ± 19	–	105.3	–
	–	170	–	482 ± 31	–	95.2

[a] The results are mean of three measurements ± standard deviation.

Table 5
Comparison of analytical characteristic of the proposed method with some published method for speciation of chromium.

Separation/preconcentration technique	Detection technique	Dynamic range (μg l^{-1})	LOD[a] (μg l^{-1})	R.S.D. (%)	PF[b]	EF[c]	Ref.
SFODME	GFAAS	0.03–0.13	0.006	5.1	333	327	This work
SPE[d]	GFAAS	–	0.0061	6.1	18	–	[44]
DLLME[e]	GFAAS	0.5–8.0	0.07	9.2	–	300	[45]
SPE	GFAAS	<50	0.003	4.0	–	35	[46]
Direct speciation	GFAAS	<20	0.7	<10	–	–	[42]
SPE	FAAS	<50	0.3	4.3	32	–	[7]
DLLME	FAAS	0.3–20	0.08	2.6–4.0	–	262	[31]
CPE[f]	FAAS	2.5–80	0.7	2.0–5.5	–	48	[47]
SPE	ICP-MS	0.3–5	0.025	0.6–3	10	–	[48]
SPE	ICP-MS	0.1–100	0.01	<5.0	–	63	[49]
CPE	ETV-ICP-OES[d]	–	0.22	3.8	50	–	[16]

[a] Limit of detection.
[b] Preconcentration factor.
[c] Enhancement factor.
[d] Solid phase extraction.
[e] Dispersive liquid–liquid microextraction.
[f] Cloud-point extraction.

the preconcentration factor. The limit of detection and quantification defined as $3S_b/m$ and $10S_b/m$ (where S_b is standard deviation of the blank and m is the slope of the calibration graph) were 0.006 and 0.020 μg l^{-1} respectively. The relative standard deviation (RSD) for six replicate measurements at 0.1 μg l^{-1} of Cr(III) was 5.1%.

3.10. Application

To examine the reliability of the recommended procedure, the method was applied for the determination of chromium species in tap water, well water, mineral water and urine samples. The water samples were filtered through a Millipore 0.45 μm pore-size membrane. In the case of urine, the sample (ca. 50 ml) was first centrifuged at 3000 rpm and then was filtered through a Millipore 0.45 μm pore-size membrane. 1 ml of the water and 2 ml of the urine samples were diluted to 10 ml and were treated according to the given procedure. The accuracy of the method was verified by the analysis of the samples spiked with the known amounts of Cr(III) and Cr(VI) at different levels. As demonstrated in Table 4, the recoveries of added chromium species are good. The accuracy of the method was further checked by applying the procedure for the determination of chromium in certified reference river water sample SLRS-1. The concentration of chromium in this sample was found to be 0.35 ± 0.03 μg l^{-1}. Thus, at the 95% confidence limit it is in agreement with the accepted value of 0.36 ± 0.03 μg l^{-1}. These results indicate that the matrices of the tap, mineral water and urine samples have no effect on the SFODME-GFAAS method for determining the species of the chromium.

3.11. Comparison with other methods

The figures of merit of the determination of chromium species by developed solidified floating organic drop microextration was compared with some of the previously reported methods [7,16,31,42,44–49] and the results are shown in Table 5. As illustrated, the enrichment factor of SFODME is higher and consequently, its detection limit is lower than most of the other reported methods.

4. Conclusion

It has been demonstrated that solidified floating organic drop microextraction (SFODME) combined with GFAAS, can be used as a powerful tool for the speciation of ultra trace amount of chromium ions in water and urine samples. The main benefits of the proposed method are rejection of matrix constituent in GFAAS analysis, enhancement of sensitivity, minimum organic solvent consumption, low cost, as well as a high enrichment factor.

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