DOI: 10.17344/acsi.2017.3137 *Acta Chim. Slov.* **2017,** *64,* 248–255

Scientific paper

Separation/preconcentration of Cr(VI) with a Modified Single-drop Microextraction Device and Determination by GFAAS

Sándor Kapitány,[1,*] Erzsébet Sóki,[1] József Posta[2] and Áron Béni[3]

[1] *Institute of Environmental Sciences, University of Nyiregyhaza, Nyiregyhaza, Hungary*

[2] *Department of Inorganic and Analytical Chemistry, University of Debrecen, Debrecen, Hungary*

[3] *Institute of Agricultural Chemistry and Soil Science, University of Debrecen, Debrecen, Hungary*

* *Corresponding author: E-mail: kapitany.sandor@nye.hu*
Tel.: +36-42-599-400; Fax: +36-42-402-485

Received: 08-03-2017

Abstract

We have developed a chromium speciation and preconcentration method with the use of the graphite furnace atomic absorption spectrometry (GFAAS) technique. This method is based on single-drop microextraction (SDME) technique. Nowadays the microextractions have become popular, because low amount of organic solvent needs to be used for the separation. The sample was introduced into the extraction cell with a single chloroform droplet. For the separation and enrichment of chromium species, an ion-pair forming compound was used. After the extraction, the chromium content of the droplet was determined by GFAAS. The analytical sensitivity of the standard SDME technique was improved by increasing the volume of organic phase and by sample recirculation. Because of the increased contact area and the developed extraction device, the stability of droplet was markedly increased. As an application we have determined the Cr(VI) content of sea water by the GFAAS technique using these separation/enrichment methods. Under the optimized extraction conditions, the linear range, detection limit ($S/N = 3$) and precision (RSD, $n = 3$) for Cr(VI) were 0.14 – 5.00 μg/L, 0.042 μg/L, and ≤ 3.0%, respectively. The advantages of this method are the following: cost efficiency, the high enrichment of chromium species and easy usage with the GFAAS technique. Therefore the concentration of the chromium species can be determined at the ng/L level.

Keywords: Chromium speciation, GFAAS, sample preparation, SDME

1. Introduction

In analytical chemistry one of the greatest challenges of the 21st century is the development of speciation analysis.[1–4] Speciation analysis means it is not enough to determine the total concentration of the desired element, as the effect of different species of an element on a living organism can be quite different. Hence it is common in speciation analysis for the species to be separated from each other before the quantitative determination of the separated fractions takes place.

Speciation can be divided into two groups: on-line and off-line methods. On-line methods often require expensive chromatographic instruments.[3] They are faster than off-line methods, where the separation and detection is divided in time, although off-line techniques (non-chromatographic methods) are still much cheaper.[4] This is the reason of their popularity even nowadays. Another major challenge of speciation analysis is that some trace elements are below the detection limit of the instruments, thus the enrichment of the species is needed. Enrichment can be carried out easily using extraction techniques.[4,5] Needless to say, the transformation of the different species must be avoided during sample handling.[4,6]

Chromium has two stable valencies in nature. The two species have totally different effect on living forms. Cr(III) is an essential trace element for proper insulin activity, whereas Cr(VI) is toxic and carcinogenic to all living organisms even in trace amounts.

The separation of chromium species can be performed using various separation-enrichment procedures including liquid-liquid extraction[7–12] and solid-phase extraction[13–17]. Pure chromatographic methods involve using liquid extraction for sample preparation to separate and preconcentrate chromium species,[18,19] but oftentimes this results in inadequate sensitivity for the trace concentration of chromium in real samples. These separation techniques combined with flame or graphite furnace atomic absorption spectrometry can be more sensitive than HPLC and UV/VIS methods.[4]

In the case of on-line chromium speciation, the flow injection system can be used for solid phase[20] or liquid extraction.[8] Expensive methods, such as flow-injection coupled to ICP-MS (FI-ICP-MS) have been developed where 74 ng/L and 18 ng/L detection limits can be achieved for Cr(III) and Cr(VI), respectively.[20] To reduce the analysis drawback and cost of the automated chromium speciation, methods were developed with the sequential injection analysis (SIA) system with UV/VIS[21,22] and FAAS[23] or GFAAS[24] detection. Further improvement of these systems was based on the miniaturization of the flow manifolds. The result was a micro sequential injection analysis Lab-On-Valve (µSI-LOV), which alleviated the majority of the drawbacks of FIA methods[25] and it had a small size with a mini spectrometer, which was developed for a field operated chromium speciation method.[26]

Nowadays the current trend is the simplification and miniaturization of sample preparation techniques.[20,27–30] The base of this concept is to preserve the advantages of the original extraction method and to reduce its drawbacks. The possible results of the miniaturized extraction techniques are increased selectivity and enrichment. The methods include reduced organic solvent consumption and waste production to achieve environmentally friendly and inexpensive processes.[27] The microextraction techniques generally are greener,[31] faster and more automatable than the original techniques.

In recent years, the liquid-liquid extraction (LLE) has become popular in miniaturization,[12,30] because it is fast, easy to use, inexpensive and compatible with many analytical instruments. There are three major categories: single-drop microextraction (SDME),[12,32,33] hollow-fiber microextraction (HF-LPME) and cloud-point extraction (CPE).[34] Major advantages of single-drop microextraction are the following: simplicity, a very limited amount of organic solvent, one-step extraction and preconcentration. Major disadvantages of the SDME are that the droplets are unstable and that their volume is limited to 5 µL. Also the reproducibility and extraction efficiency of this method are poor due to the droplet stabilization problems. There were early attempts to increase the volume and stability of the microdroplet by modifying the needle geometry by flared or oval tube.[35,36] The HF-LPME is better and more complex than the SDME, but it has similar problems except for droplet stabilisation. The CPE has overcome the above mentioned problem, but is difficult to automatize and has very limited applicability for complex samples.[30]

Good example of the automation of SDME was a sequential injection (SI) coupled to GFAAS, which was used for the determination of Cd.[37] This method used a modified FIA system with homemade extraction cell. This setup was difficult to adopt for other instruments and had a long idle time for the GFAAS instrument, because sample preparation time was 10 min and the determination approx. 2 min. The on-line speciation is better for FAAS and ICP techniques. For GFAAS exists a direct chromium speciation. The principle of these methods is using β-diketone to make complex ions of chromium species with different volatilization temperature,[38] but it has higher RSD values than other methods. The other approach is using the commercially available multi-purpose samplers (MPS by Gerstel) for determination of organic compounds by GC-MS.[39,40] These methods' advantages are readiness to use, but they are very expensive and available only for gas and liquid chromatograph. The semi-automated approach to the microextraction was suggested for GFAAS.[41]

Our choice for chromium speciation was the SDME, as it is simpler, requires no foreign material (hollow-fiber) and creates a stable redox system for Cr(VI).

Our goal was to reduce the SDME method's disadvantages and to develop a cheap and fast analytical method that would enable us to separate, enrich and determine Cr(VI) species in environmental samples such as tap water, surface water, sea water, etc. Our goal was to develop extraction method using higher volume and stability of the droplet at higher sample flowrate. Another important feature is that the volume of the sample is freely variable, if a higher enrichment needs to be achieved. Finally, there is a possibility to the automatization of the extraction.

2. Experimental

2. 1. Reagents

All solutions were prepared using ultrapure water. Chloroform was HPLC grade, 96% acetic acid and sodium acetate were analytical reagent grade. These chemicals were obtained from VWR International and methyltrioctylammonium chloride (CAS:5137-55-3, purity ≥97%) from Sigma Aldrich were used for the liquid-liquid extraction. Both Cr(III) and Cr(VI) stock standard solutions containing 1000 mg L^{-1} of Cr were obtained from Fluka.

2. 2. Apparatus

To prepare sample solutions ultra-pure water was used, which was made using a Millipore Milli-Q RG apparatus. The pH of the solutions was measured with a pH

Table 1. Heating program I for the determination of total chromium in aqueous phase with Varian AA-20 GFAAS instrument.

Step	Temperature [°C]	Time [s]		Argon flow rate [cm^3 min^{-1}]
		Ramp	Hold	
1	110	1	15	250
2	130	6	10	250
3	1500	8	10	250
4	2300	0	5	0
5	2450	1	3	250

Table 2. Heating program II for the determination of chromium(VI) in chloroform with Varian AA-20 GFAAS instrument.

Step	Temperature [°C]	Time [s]		Argon flow rate [cm^3 min^{-1}]
		Ramp	Hold	
1	45	1	5	250
2	85	6	40	250
3	1000	15	15	250
4	2300	0	5	0
5	2450	1	3	250

meter made by HANNA Instrument. For the chromium analysis a graphite furnace atomic absorption spectrometer (Varian AA-20 + GTA 96) was used. The injected volume of the samples was 20 µL. The temperature program of the furnace was customised for proper determination as seen in Table 1 and Table 2. Chromium measurements were carried out at 357.9 nm wavelength with a spectral bandwidth of 0.5 nm. Argon 99.996% (Linde Hungary) was used as protective gas and integrated absorbance (peak area) was used for the determination.

2. 2. 1. The Modified SDME Cell

The aim of the developed extraction cell was to reduce the disadvantages of the SDME. The procedure is as follows: first, the droplet is sitting, not hanging. This configuration increased the stability of the droplet. The new glass cell is hollowed for the organic droplet (Fig 1). It has two main components: an extraction cell and glass stopper. The extraction procedure is the following: the closed cell is filled with distilled water, and after that the cell is opened so that the organic droplet can be placed in it. Then it is closed. The sample solution is introduced into the extraction cell with a syringe pump. After the extraction the organic droplet can be removed with syringe or pipette. The 10 – 100 µL micropipette (Biohit) was a better solution. The Hamilton syringe for GC was problematic because it had metal parts and the extraction solvent reacted on it. The results were increased blank values for chromium.

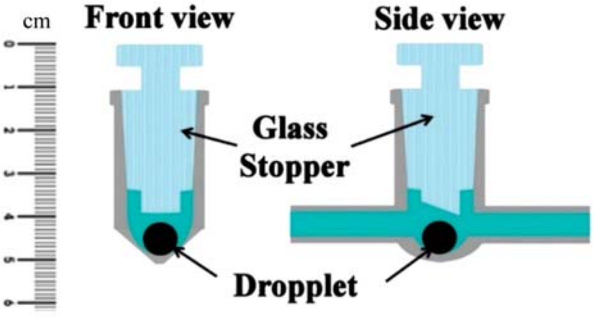

Figure 1. The new extraction cell

The advantages of this cell geometry were the following: first, it stabilised the droplet, increased robustness of the extraction and ensured a higher flow rate of the sample. Second, the droplet volume was increased to 40 µL to provide a greater contact area between the two phases and a higher extraction efficiency. On the other hand the higher droplet volume was better for GFAAS determination. The droplet could be introduced into the graphite tube or the vials of the autosampler.

At this experiment 40 µL of the chloroform droplet was used and the ion-pair agent was dissolved in chloroform to separate and enrich the Cr(VI) content of the sample.

2. 2. 2. The Recirculating Single-drop Microextraction Device

This system is an upgraded version of the above mentioned system. It is understood that extraction efficiency can be increased by repeating the procedure. Our aim was to construct an extraction system to multiply the single-drop extraction. The result was the recirculating single drop microextraction system shown in Fig. 2. This system consists of a sample reservoir (25 mL beaker), a peristaltic pump (MTA KUTESZ LS-204), an extraction cell, a Hoffmann clamp and a Tygon tube (i.d.: 0.76 mm).

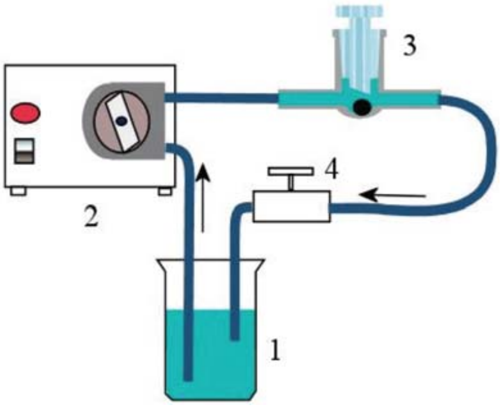

Figure 2. Recirculating single drop micro extraction device with peristaltic pump: 1 sample reservoir, 2 peristaltic pump, 3 extraction chamber, 4 Hoffmann clamp 5 Tygon tube

The Hoffmann clamp was needed to set the back pressure, as the extraction chamber could be fully loaded with the sample solution.

The procedure is as follows: first, the beaker is filled with the sample and the tubes are inserted into the sample solution. After that the whole system is filled using the peristaltic pump and finally, the droplet is ready to be inserted into the extraction cell. The additional advantages of this system over the modified SDME are increased extraction efficiency thanks to the recirculating sample and easier sample changing, as the syringe pump is replaced with peristaltic pump and during the clean-out procedure only the inlet tube has to be put into the distilled water.

3. Results and Discussion

3. 1. Method Development

The principal steps of the method are: adjusting the pH of the water sample, extraction with the new system and finally GFAAS measurement to determine the chromium concentration in the chloroform. Optimal parameters, such as pH, time, reagent concentration and GFAAS heating programme were explored for each step. The aqueous phase volume was set to 10 mL.

3. 1. 1. Optimization of the Extraction

We tested the extraction range of 1.0 – 7.0 pH with 0.5 steps. 1.0 mol/L HCl and 0.1 mol/L NaOH was used to set the pH. The optimum pH range of this extraction was found from 2.0 – 5.0 pH. Thus for all further analyses, we used 4.0 pH, and it was adjusted with acetic acid / sodium acetate buffer (10 mL sample solution + 1 mL buffer). 1 L buffer was prepared from 847 mL 0.1 mol/L acetic acid and 153 mL 0.1 mol/L sodium acetate.

Methyltrioctylammonium chloride concentrations in the chloroform were investigated in the range of 0.1 – 5 % (*w/w*) and the ideal was found at 1 % (*w/w*). Probably at the high methyltrioctylammonium chloride concentration, there is a negative effect on GFAAS determination, because too much organic material was introduced into the graphite tube and at the ashing step chromium losses occurred.

The flow rate of the sample solution was investigated. Previously with the syringe pump the optimal flow rate was 1.0 mL/min with single extraction. The peristaltic pump was used in the range of 2.5 – 14.0 mL/min and the extracted Cr(VI) linearly increased by the flow rate (Fig. 3). At the higher flow rate, the droplet immediately ran out from the extraction cell. The flow rate was reduced to 11.5 mL/min to ensure the stability and repeatability of this method. At this parameter, 10 mL of the sample circulated in the extraction cell 11.5 times in 10 min. This was a remarkable signal increase with GFAAS measurements compared to previous SDME sample preparation.

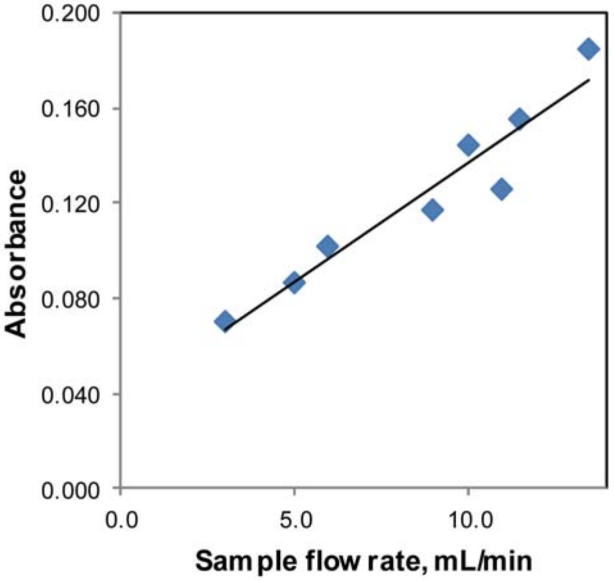

Figure 3. The effect of the flow rate of the sample solution on absorbance. Sample volume was 10 mL, Cr(VI) concentration was 1 µg/L (pH = 4) Extraction time was 10 min (GFAAS, 40 µL droplet volume was diluted to 100 µL)

The extraction time was investigated in the range of 1 – 35 min (Fig. 4). We found that the chromium concentration of the droplet linearly increased in the range of 1 – 15 min.

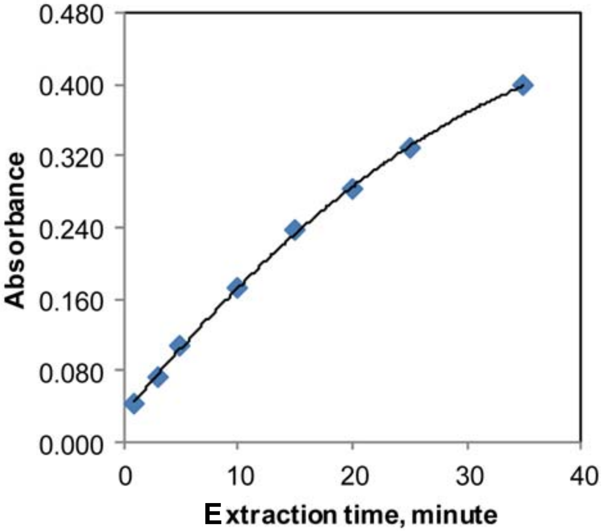

Figure 4. Extraction time effect on the absorbance at 11.5 mL/min flow rate and 10 mL sample volume, concentration of the Cr(VI) was 1 µg/L (pH = 4) (GFAAS, 40 µL droplet was diluted to volume 100 µL, 0.01 mol/L methyltrioctylammonium chloride in droplet)

We limited the extraction time to 10 min to take in account the throughput of this method, and all further measurements were carried out in 10 min.

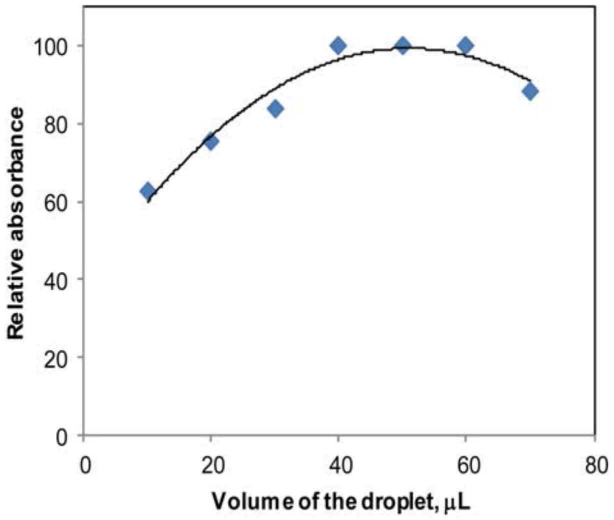

Figure 5. Effect of droplet volume on the relative absorbance (0.25 μg/L pH = 4), flow rate was 11 mL/min (GFAAS, droplet volume was diluted to 100 μL)

The volume of the droplet was investigated between from 10 – 70 μL and the ideal volume was found at 40 μL (Fig 5). At a 70 μL droplet volume, the efficiency of the extraction was decreased.

3. 1. 2. Optimisation of the Heating Programme

The graphite heating was optimized for organic media with a high-concentration of methyltrioctylammonium chloride. The right drying and ashing steps had to be used to maximise the chromium(VI) signal at GFAAS determination. The modified programme is shown in Table 2. Two kinds of calibration standards were prepared. One of them was diluted from the Cr(III) stock standard in water. The other was diluted from the Cr(VI) stock standard in water and was extracted by chloroform with methyltrioctylammonium chloride in 13 mL plastic test tube with screw cap. This liquid-liquid extractions were carried out at an optimum pH and methyltrioctylammonium chloride concentration. The ratio of the phases was 1:1 (3 + 3 mL). Heating programme I was used for the water phase and programme II was used for organic solutions. The results are shown in Fig 6.

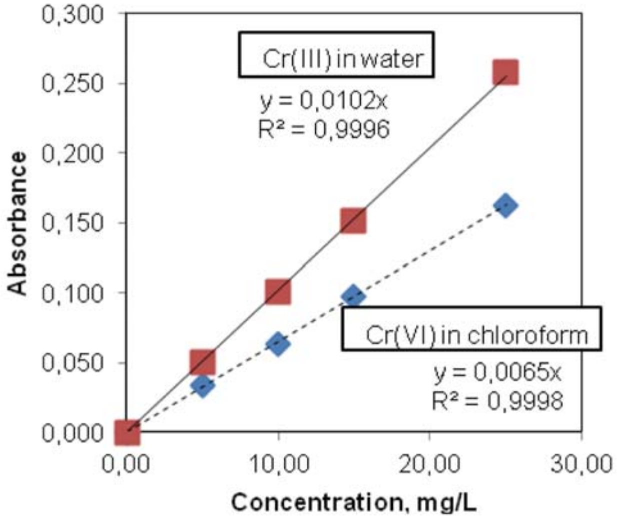

Figure 6. GFAAS calibration curve for Cr(III) in water phase and Cr(VI) in organic phase with 1 % (*w/w*) methyltrioctylammonium chloride in chloroform.

The sensitivity of the chromium determination was decreased in organic media. Therefore, the extraction calibration had to be used for Cr(VI) determination. This calibration method was used for all further measurements at Cr(VI) determination.

3. 2. Method Validation

The 1000 mg/L Cr(VI) stock standard was used and the calibration standards were established by dilution with distilled water. These prepared solutions (10 mL sample + 1 mL buffer) were extracted by this method and the chloroform phase was analysed by the GFAAS.

The recovery analysis was carried out with three different known quantities of Cr(VI). These spiked samples were processed as normal samples. The method was validated for linearity with 0.14 – 5.00 μg/L Cr(VI). The equation of the calibration curve was $y = 0.2958x + 0.0395$ ($R^2 = 0.99$), where 'y' is the peak-area and 'x' is the concentration of Cr(VI). The detection limit of the method was 42 ng/L.

The recovery of Cr(VI) in spiked tap water samples ranged from 97% to 101.1% and the precision of the measurements was from 2.38% to 2.81% (Table 3). Regarding the result for the repeatability of this method, 2.53% was observed.

Table 3. Cr(VI) recovery of the developed method (3 replicates)

Sample	Cr(VI) in aqueous phase μg L^{-1}		Recovery, %	RSD %
	Added	Determined		
1	1.00	0.97	97.0	2.53
2	3.00	2.96	98.6	2.81
3	8.00	8.09	101.1	2.38

3. 3. An optimised Method for Cr(VI) Analysis

The optimised procedure was: first, the sample pH was set to 4 with acetic acid and sodium acetate buffer. A 10 mL sample and 1 mL buffer were introduced to the beaker, the flow rate was set to 11.5 mL/min and the extraction time was 10 min. In this procedure, the methyltrioctylammonium chloride concentration in the chloroform droplet was 1 % (*w/w*). After the extraction, 40 µL of chloroform was diluted to 100 µL to ensure enough sample volume for the autosampler. Finally 40 µL of the sample was introduced into the graphite tube and the chromium content was determined with the optimized heating programme. At this method the enrichment factor (EF) was 100.

3. 4. Analysis of the Real Samples

The developed method was tested with sea water samples. The water samples were collected from same location at different time. The results were summarized in Table 4.

Table 4. Bulgarian Black Sea water samples 2016 ($n = 3$, RSD ≤ 3%)

Date	Cr(VI) (µg/L)	Total Cr (µg/L)
I.16.	0.28	0.72
III. 26.	0.24	0.97
V. 28.	0.17	0.28
VI. 29.	0.17	0.66
VII. 20.	0.17	0.45
VIII. 21.	0.21	0.41

The Cr(VI) and total chromium concentrations were determined in sea water samples and the results were in good agreement with other research.[42]

3. 5. Comparison to Other Methods

Our developed method has very good limit of detection compared to other cited methods in Table 5.

The advantage of the developed method is that the sample volume is freely variable. Large amount of water sample can be used to increase the enrichment. The higher volume of the droplet and the recirculation of the sample solution around the droplet leads to higher efficiency of extraction than possible with the normal SDME. This off-line method can be easily adapted to any GFAAS instrument and there is no need to modify the expensive instrument. This SDME technique can be applied to other analytical task, where a high enrichment of the analyte is important.

There are a number of potential drawbacks to the SDME method. Low sample throughput as it takes 10 min, but other SDME methods require the same extraction time. Highly skilled lab worker is needed to set the droplet and this device. The chloroform is volatile, therefore the temperature has to be controlled and before the GFAAS the sample vials have to be sealed to avoid evaporation of the organic solvent. This effect can cause unexpected increase of the chromium concentration. Currently, extraction cell is not commercially available, because it has to be made manually.

Table 5. Comparison of Cr(VI) determination methods for water samples

Extraction method	Analytical method	LOD (µg/L)	Automation approach	Reference
Continuous SDME	GFAAS	0.042		This research
SPE	ICP-AES	0.200	FIA	43
CME	ICP-MS	0.018	FIA	20
SPE	FAAS	0.034	FIA	44
SPE	FAAS	0.8	FIA	45
SPE	FAAS	0.3	SIA	23
SPE	GFAAS	0.02	SIA	24
SPE	FAAS	45		46
SPE	GFAAS	0.027		47
CPE	FAAS	0.18		48
CPE	GFAAS	0.01		49
–	UV/VIS	23	SIA	21
–	UV/VIS	5.6	µSIA-LOV	26
LLE	UV/VIS	7.5	FIA	50
LLME	UV/VIS	0.26	SIA	22
DLLME	FAAS	0.08		51
DLLME	TXRF	0.8		52
Thermal	GFAAS	0.7		38

CME: capillary microextraction, SDME: single drop microextraction, CPE: cloud point extraction, SPE: solid phase extraction, LLE: liquid–liquid extraction, LLME: liquid–liquid microextraction, DLLME: dispersive liquid–liquid microextraction, FAAS: flame atomic absorption spectrometry, GFAAS: graphite furnace atomic absorption spectrometry, TXRF: total reflection X-ray fluorescence spectrometry, ICP-AES, Inductively coupled plasma atomic emission spectroscopy, FIA: flow injection analysis, SIA: sequential injection analysis, LOV: Lab-On-Valve

3. 6. Automatization

Currently, the peristaltic pump had a timer to switch off after 10 min. We are planning to increase the automati-

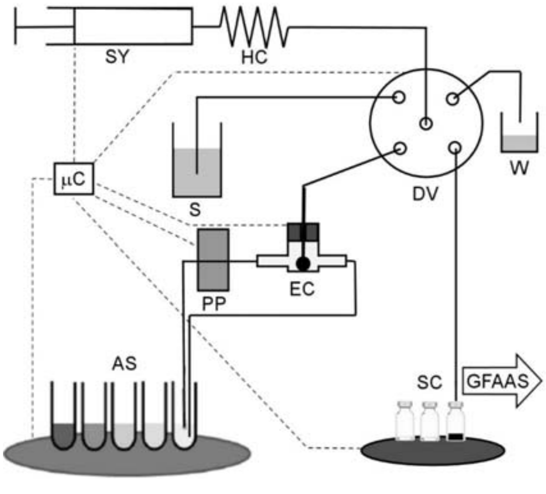

Figure 7. The proposed semi-automatic apparatus for chromium speciation method SY: syringe + steeper motor, HC: holding coil, DV: distribution valve (Hamilton), W: waste, S: organic solvent, PP: peristaltic pump, EC: extraction cell, AS: auto-sampler, SC: sample collector, µC: microcontroller (Arduino)

zation degree of this process. The notion is based on semiautomatic chromium speciation approach with µSIA technique. First, the Arduino microcontroller coordinates the syringe, distribution valve, peristaltic pump and tip of the extraction cell. The next step is to couple the developed device with an autosampler and sample collector (Fig. 7).

This system is containing new and salvaged parts to reduce the cost. The Arduino microcontroller is easily programmable, cheap and easy to connect the display, relay control and motor driver boards.

Further plan is to replace the sample collector (SC) with the autosampler of the GFAAS to achieve the full automatization.

The planned fully automated sample preparation system will be useful to determine the Cr(VI) by GFAAS.

4. Conclusions

In this study a novel single drop microextraction (SDME) technique is presented for chromium speciation. The advantages of this method are, in addition to minimal organic solvent consumption and the need for only one droplet per sample to extract, the higher stability of the drop and the possibility of high enrichment of the analysed elements. The higher volume of the droplet in a modified cell and the recirculation of the sample solution around the droplet leads to higher efficiency of the extraction than is possible with the normal SDME. This simple, easy to make, cheap, effective, rugged and safe extraction method can be used to create fully automated sample preparation system. Finally, this recirculating system can also be used for the extraction and enrichment of other analytes at the ng/L level.

5. References

1. R. Cornelis: Handbook of Elemental Speciation, Weinheim, Germany, Wiley-VCH. **2003**. https://doi.org/10.1002/0470868384
2. S. A. Katz, H. Salem: The Biological and Environmental Chemistry of Chromium, VCH, Weinheim, Germany, **1994**, pp. 155–186.
3. J. A. Caruso, M. Montes-Bayon, *Ecotoxicol. Environ. Saf.*, **2003**, *56*, 148–163. https://doi.org/10.1016/S0147-6513(03)00058-7
4. A. Gonzalvez, M. L. Cervera, S. Armenta, M. d. l. Guardia, *Anal. Chim. Acta* **2009**, *636*, 129–157. https://doi.org/10.1016/j.aca.2009.01.065
5. L. Adlnasab, H. Ebrahimzadeh, Y. Yamini, *Anal. Methods*, **2012**, *4*, 190–195. https://doi.org/10.1039/C1AY05449J
6. M. Pettine, S. Capri, *Anal. Chim. Acta* **2005**, *540*, 231–238. https://doi.org/10.1016/j.aca.2005.03.040
7. S. C. Nielsen, S. Strürup, H. Spliid, E. H. Hansen, *Talanta*, **1999**, *49*, 1027–1044. https://doi.org/10.1016/S0039-9140(99)00044-2
8. S. C. Nielsen, E. H. Hansen, *Anal. Chim. Acta*, **2000**, *422*, 47–62. https://doi.org/10.1016/S0003-2670(00)01051-5
9. A. R. Kumar, P. Riyazuddin, *Microchem. J.*, **2009**, *92*, 145–149. https://doi.org/10.1016/j.microc.2009.03.001
10. Y. Akama, A. Sali, *Talanta*, **2002**, *57*, 681–686. https://doi.org/10.1016/S0039-9140(02)00076-0
11. N. E. El-Hefny, *Separ. Purif. Techn.*, **2009**, *67*, 44–49. https://doi.org/10.1016/j.seppur.2009.03.004
12. B. Hu, M. He, B. Chen, L. Xia, *Spectrochim. Acta B*, **2013**, *86*, 14–30. https://doi.org/10.1016/j.sab.2013.05.025
13. K. O. Saygi, M. Tuzen, M. Soyak, L. Elci, *J. Hazard. Mater.*, **2008**, *153*, 1009–1014. https://doi.org/10.1016/j.jhazmat.2007.09.051
14. M. V. B. Krishna, K. Chandrasekaran, S. V. Rao, D. Karunasagar, J. Arunachalam, *Talanta*, **2005**, *65*, 135–143.
15. M. Korolczuk, M. Grabarczyk, *Talanta*, **2005**, *66*, 1320–1325. https://doi.org/10.1016/j.talanta.2005.01.047
16. S. Morales-Munoz, J. L. Luque-García, M. D. L. Castro, *Anal. Chim. Acta*, **2004**, *515*, 343–348. https://doi.org/10.1016/j.aca.2004.03.092
17. Z. Abbas, B.-M. Steenari, O. Lindqvist, *Waste Manag.*, **2001**, *21*, 725–739. https://doi.org/10.1016/S0956-053X(01)00005-8
18. A. N. Tang, D. Q. Jiang, Y. Jiang, S. W. Wang, X. P. Yan, *J. Chromatogr. A* **2004**, *1036*, 183–188. https://doi.org/10.1016/j.chroma.2004.02.065
19. L.-Y. Ying, H.-L. Jiang, S. C. Zhou, Y. Zhou, *Microchem. J.*, **2011**, *98*, 200–203. https://doi.org/10.1016/j.microc.2011.01.010
20. W. Hu, F. Zheng, B. Hu, *J. Hazard. Mater.*, **2008**, *151*, 58–64. https://doi.org/10.1016/j.jhazmat.2007.05.044
21. L. V. Mulaudzi, J. F. v. Staden, R. I. Stefan, *Anal. Chim. Acta*, **2002**, *467*, 51–60. https://doi.org/10.1016/S0003-2670(02)00188-5
22. M. Alexovič, V. Andruch, Ioseph S. Balogh, J. Šandrejová, *Anal. Methods*, **2013**, *5*, 2497–2502. https://doi.org/10.1039/C3AY40284C
23. S. Şahan, Ş. Saçmacý, Ş. Kartal, M. Saçmacý, U. Şahin, A. Ülgen, *Talanta*, **2014**, *120*, 391–397. https://doi.org/10.1016/j.talanta.2013.12.030
24. A.-M. Zou, X.-Y. Tang, M.-L. Chen, J.-H. Wang, *Spectrochim. Acta B*, **2008**, *63*, 607–611. https://doi.org/10.1016/j.sab.2008.02.008
25. M. M. Grand, P. Chocholous, J. Ruzicka, P. Solich, C. I. Measures, *Anal. Chim. Acta*, **2016**, *923*, 45–54. https://doi.org/10.1016/j.aca.2016.03.056
26. M. Yang, J.-X. Li, J.-H. Wang, *Talanta*, **2007**, *72*, 1710–1716. https://doi.org/10.1016/j.talanta.2007.01.020
27. V. Andruch, L. Kocúrová, I. S. Balogh, J. Škrlíková, *Microchem. J.*, **2012**, *102*, 1–10. https://doi.org/10.1016/j.microc.2011.10.006
28. J. M. Kokosa, *Trends Analyt. Chem.*, **2013**, *43*, 2–13. https://doi.org/10.1016/j.trac.2012.09.020
29. S. Dadfarnia, A. M. H. Shabani, *Anal. Chim. Acta*, **2010**, *658*, 107–119. https://doi.org/10.1016/j.aca.2009.11.022

30. A. Sarafraz-Yazdi, A. Amiri, *Trends Anal. Chem.*, **2010**, *29*, 1–14. https://doi.org/10.1016/j.trac.2009.10.003
31. D. L. Rocha, A. D. Batista, F. R. P. Rocha, G. L. Donati, J. A. Nóbrega, *Trends Analyt. Chem.*, **2013**, *45*, 79–92. https://doi.org/10.1016/j.trac.2012.12.015
32. M. A. Jeannot, A. Przyjazny, J. M. Kokosa, *J. Chromatogr. A*, **2010**, *1217*, 2326–2336. https://doi.org/10.1016/j.chroma.2009.10.089
33. L. Xu, C. Basheer, H. K. Lee, *J. Chromatogr. A*, **2007**, *1152*, 184–192. https://doi.org/10.1016/j.chroma.2006.10.073
34. K. Pytlakowska, V. Kozik, M. Dabioch, *Talanta*, **2013**, *110*, 202–228. https://doi.org/10.1016/j.talanta.2013.02.037
35. H. Yiping, W. Caiyun, *Anal. Chim. Acta*, **2010**, *661*, 161–166. https://doi.org/10.1016/j.aca.2009.12.018
36. X. Wang, J. Cheng, X. Wang, M. Wu, M. Cheng, *Analyst*, **2012**, *137*, 5339–5345. https://doi.org/10.1039/c2an35623f
37. A. N. Anthemidis, I. S. I. Adam, *Anal. Chim. Acta*, **2009**, *632*, 216–220. https://doi.org/10.1016/j.aca.2008.10.078
38. P. Bermejo-Barrera, M. C. Barciela-Alonso, B. Pérez-Fernández, A. Bermejo-Barrera, *Spectrochim. Acta B*, **2003**, *58*, 167–173. https://doi.org/10.1016/S0584-8547(02)00229-X
39. X. Wang, Y. Li, F. Cai, Q. Qing, K. Yuan, B. Chen, T. Luan, *Talanta*, **2017**, *164*, 727–734. https://doi.org/10.1016/j.talanta.2016.06.011
40. X. Wang, K. Yuan, H. Liu, L. Lin, T. Luan, *J. Sep. Sci.*, **2014**, *37*, 1842–1849. https://doi.org/10.1002/jssc.201400198
41. M. Alexovic, B. Horstkotte, I. Srámková, P. Solich, J. Sabo, *Trends Analyt. Chem.*, **2017**, *86*, 39–55. https://doi.org/10.1016/j.trac.2016.10.003
42. T. Shigematsu, S. Gohda, H. Yamazaki, Y. Nishikaw, *Bull. Inst. Chem. Res.*, **1977**, *55*, 429–440.
43. A. G. Cox, I. G. Cook, C. W. McLeod, *Analyst*, **1985**, *110*, 331–333. https://doi.org/10.1039/an9851000331
44. E. Rossi, M. I. Errea, M. M. F. d. Cortalezzi, J. Stripeikis, *Microchem. J.*, **2017**, *130*, 88–92. https://doi.org/10.1016/j.microc.2016.08.004
45. M. Sperling, S. Xu, B. Welz, *Anal. Chem.*, **1992**, *64*, 3101–3108. https://doi.org/10.1021/ac00048a007
46. A. Tunceli, A. R. Türker, *Talanta*, **2002**, *57*, 1199–1204. https://doi.org/10.1016/S0039-9140(02)00237-0
47. A. C. Sahayam, G. Venkateswarlu, S. C. Chaurasia, *Anal. Chim. Acta*, **2005**, *537*, 267–270. https://doi.org/10.1016/j.aca.2005.01.017
48. K. Kiran, K. S. Kumar, B. Prasad, K. Suvardhan, R. B. Lekkala, K. Janardhanam, *J. Hazard. Mater.*, **2008**, *150*, 582–586. https://doi.org/10.1016/j.jhazmat.2007.05.007
49. X. Zhu, B. Hu, Z. Jiang, M. Li, *Water Res.*, **2005**, *39*, 589–595. https://doi.org/10.1016/j.watres.2004.11.006
50. W. Chen, G. Zhong, Z. Zhou, P. Wu, X. Hou, *Anal. Sci.*, **2005**, *21*, 1189–1193. https://doi.org/10.2116/analsci.21.1189
51. P. Hemmatkhah, A. Bidari, S. Jafarvand, M. R. M. Hosseini, Y. Assadi, *Microchim. Acta*, **2009**, *166*, 69–75. https://doi.org/10.1007/s00604-009-0167-x
52. Z. Bahadir, V. N. Bulut, M. Hidalgo, M. Soylak, E. Marguí, *Spectrochim. Acta B*, **2016**, *115*, 46–51. https://doi.org/10.1016/j.sab.2015.11.001

Povzetek

Razvili smo metodo za speciacijo in predkoncentracijo kroma, ki uporablja tehniko atomske absorpcijske spektrometrije z grafitno kiveto (GFAAS). Metoda je osnovana na tehniki mikroekstrakcije v kapljico (SDME). Dandanašnji so mikroekstrakcije postale popularne, saj je za separacijo potrebna majhna količina organskega topila. Vzorec je v ekstrakcijski celici v stiku z eno samo kapljico kloroforma. Za separacijo in obogatitev kromovih zvrsti smo uporabili ionsko-parno spojino. Po ekstrakciji smo vsebnost kroma v kapljici določili z GFAAS. Analizna občutljivost se je izboljšala glede na standardno SDME tehniko zaradi večjega volumna organske faze in zaradi kroženja vzorca. Zaradi večje stične površine in razvite ekstrakcijske naprave je bila tudi stabilnost kaplice znatno večja. Kot primer uporabe smo določili vsebnost Cr(VI) v morski vodi s tehniko GFAAS in razvito separacijsko/ekstrakcijsko metodo. Pri optimiziranih ekstrakcijskih pogojih je bilo za Cr(VI) linearno območje 0,14–5,00 µg/L, meja zaznave (S/N = 3) 0,042 µg/L in natančnost (RSD, n = 3) ≤ 3,0 %. Prednosti metode so naslednje: cenovna učinkovitost, visoka obogatitev kromovih zvrsti in enostavna uporaba v povezavi z GFAAS tehniko. Koncentracijo kromovih zvrsti tako lahko določimo na ng/L nivoju.