

DEVELOPMENT OF CHROMIUM SPECIATION METHODS FOR ENVIRONMENTAL SAMPLES

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ABSTRACT. We have worked out several chromium speciation and pre-concentration methods with the use of the GFAAS technique. These methods were based on classical and continuous liquid-liquid extraction techniques using a patented continuous extraction device. For the separations and enrichments of chromium species was used ion-pair compound. As an application we have determined the Cr(III) and Cr(VI) content of water using these separation/enrichment methods and the GFAAS technique. The advantage of these methods is the cost effectiveness, high chromium species enrichment and easy use with GFAAS technique, therefore the concentration of the chromium species can be determined at the ng/L level.

Keywords: liquid-liquid extraction, pre-concentration, chromium speciation, FAAS, GFAAS

INTRODUCTION

Liquid-liquid extraction is used in both analytical and preparative chemistry and also in the industry for a long time for separating dissolved components. The method is based on the fact that the components or their derivatives in the solution distributed in different ratios between the two liquid-phases that are immiscible (Sekine et al., 1977). The liquid-liquid extraction is carried out with a simple glass tool, the separating funnel, which has stood the test of time. However, with this method we get only gross information about the transport-process between the phases. Thus, we can observe only the final state of the extraction.

In the case of the so called continuous extracting device developed a long time ago, one phase was introduced in form of little droplets to the other phase to carry out the extraction (Wehrli, 1937). Although the sampling and the analysis happened not at the same time, but after the separation and homogenization of the phases. The disadvantage of the previously mentioned methods and tools is that we do not get a whole picture about the kinetics of extraction.

In analytical chemistry one of the greatest challenges of the 21st century is the appearance of speciation analysis. Speciation analysis means that it is not enough to determine the total concentration of the desired element, since the effect of an element on a living organism can be quite different. Hence it is a common way in speciation analysis that the species are first separated from each other than the quantitative determination of the separated fractions follows. Speciation can be divided into two groups: on-line and off-line methods. On-line methods require expensive chromatographic instruments. They are faster than off-line methods, where the separation and detection is divided in time, but off-line techniques are still much cheaper. This is the reason why they are still popular even nowadays. Another great challenge of speciation analysis is that some trace elements are below the

detection limit of the instruments, thus enrichment of the species is needed. Enrichment can easily carry out by extraction techniques (Posta, 2006).

At the University of Debrecen such experiments have been conducted for a long time which is resulted in development of the continuous extraction device which is a simple glass tool connected to the nebuliser of FAAS instrument (Gambasidze, et al., Posta et al., 1988). This device can perfectly used for the separation and enrichment of Cr(III) and Cr(VI).

Chromium has two stable valency form in nature. The two species have totally different effect on living form. Cr(III) is an essential trace element for the proper insuline activity, while Cr(IV) is toxic, carcinogenic to all living organisms even in trace amount. This is the reason why we have to develop such analytical methods that make possible to separate, enrich and determine these two valency form of chromium in environmental samples such as tap water, surface water and sea water, etc.

MATERIALS AND METHODS

Reagents

All solutions were prepared using ultrapure water. Chloroform from Spektrum 3D and Aliquat 336 from Sigma Aldrich were used for the liquid-liquid extraction. A chromium(VI) stock standard solution containing 1000 mg of Cr(VI) per liter was obtained from Fluka and 1000 mg per liter chromium(III) stock standard was made by Merck. All chemicals and solvents used were of analytical grade.

Apparatus

To prepare sample solutions ultra pure water was used, which was made by a Millipore Milli-Q RG apparatus. The pH of the solutions were adjusted with an ISFET pH Meter made by Shindengen. For the chromium analysis a graphite furnace atomic absorption spectrometer (Perkin Elmer AAnalyst type 600 apparatus with Zeemann background correction)

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was used. The injected volume of the samples was 30 μL . The temperature program of the furnace was made by the manufacturer. We performed the flame atomic absorption spectrometric determinations by UNICAM SP 1900 spectrometer. Chromium measurements were done at 357.9 nm wavelength.

The continuous extraction device

The continuous extraction device is shown in Fig. 1. This device was based on formerly developed continuous titration device, which was developed at the University of Debrecen (Posta, et al., 1980).

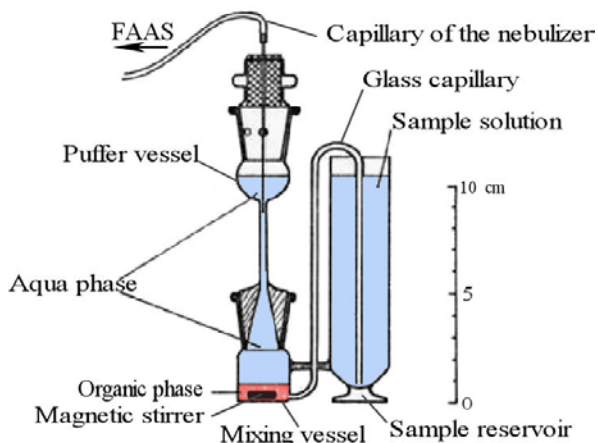


Fig. 1. Continuous extraction device

The sample was introduced into 100 mL volume sample reservoir, which was connected with mixing vessel by 1 mm diameter glass capillary. Magnetic stirrer was used in the mixing chamber to help the liquid-liquid extraction. Chloroform with complexing agent was used for the liquid-liquid extraction. Before start the continuous extraction was filled with distilled water the mixing and buffer vessel. After that was sealed the glass stopper with metal capillary and connected this device with flame atomic absorption spectrometer's nebulizer via teflon capillary. To maximize the extraction efficiency the magnetic stirrer rotation speed was optimised. In this case very small chloroform droplets exist in the mixing chamber. At the system installation the glass stopper's hole was uncovered and the nebuliser was feed with distilled water from buffer vessel. To start of the extraction and measurement the glass stopper was rotated by 90 degree and these's hole was get closed. After that this device completely sealed and the nebuliser had sucking effect on sample liquid and this flowed trough at mixing vessel, where started the extraction. The liquid's flow rate was determined by the AAS's nebulising rate (F). During the extraction the volume of the liquid in the buffer and mixing vessel was constant. Due to the difference of density between water and chloroform and geometry of mixing vessel the chloroform droplets cannot leave the mixing vessel and only extracted water flow into the AAS instrument,

where the element concentration of aqueous phase was followed.

The element concentration in organic phase at any time can be calculated by the following equation (1). The element concentration depends on rate of nebulising and volume of mixing vessel.

$$c_t = c_0 \times \left(1 - e^{-\frac{F \times t}{V}} \right) \quad (1)$$

C_t : analyt concentration in the mixing vessel

C_0 : initial concentration

F : nebulizing rate

T : time

V : volume of the mixing vessel

RESULTS AND DISCUSSION

Separation and enrichment of chromium(VI)

Numerous methods can be used for separation and enrichment of essential Cr(III) and toxic Cr(VI), but applying the liquid-liquid extraction is very useful (Hála, et al., 1966, Adam, 1971, Irving, et al., 1973). Our developed method based on ion-pair complex formation of Cr(VI) with quaternary ammonium salts (Nagy, et al., 2007). The solubility of this ion-pair complex is good in chloroform. Tridecyl-methyl-ammonium chloride (Aliquat 336) was used as quaternary ammonium salt. The structural formula of Aliquat 336 is shown in Fig 2.

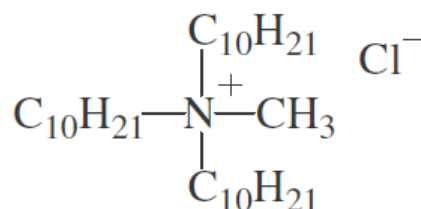
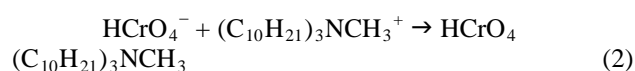


Fig. 2 Structure of the tridecyl-methyl-ammonium-chloride (aliquat 336)

Aliquat 336 was dissolved in chloroform. The formation of the ion-pair complex is shown in equation (2).



To demonstrate the principle of the device we extracted the chromium (VI) with Aliquat-336 in chloroform. The water phase's pH was 4, the extraction processes was followed by FAAS. The measurement's parameters were: acetylene: 1.8 L/min, air: 4.5 L/min, observation high: 14 mm and nebulising rate: 5.6 mL/min.

In Fig. 3.1 reference curve represented absence of Aliquat, accordingly was no extraction and in water

phase concentration of chromium changed as equation 1. The 2-7 curves represent increasing concentration of Aliquat in organic phase and the absorption signal of unextracted chromium is plotted. These curves show that the extraction has three steps, the first the nearly flat part of the curve was represented high efficiency extraction. Second part of the curves indicates, by the time the free complexing agent in organic phase was decreasing thus the amount of none extracted chromium was increasing in aqueous phase and this resulted the steeply raising of the curves. At step three, the curves hardly was raised, which is the result of the absence of the free complexing agent. The 7th curve

shows full efficiency of extraction, but in this case 4 % of chromium ions was leaked through the mixing vessel without extraction. This extraction efficiency depends on the environment of extraction, even as on device parameters (device's geometry, phase ratio, nebulising rate, etc.), on concentration of complexing agent, on stability of complexes and on speed of complex formation. To optimise these parameters we should decrease the amount of unextracted ions, hereby to improve the extraction efficiency. Area between the first and the last curve represents the amount of extracted chromium (VI).

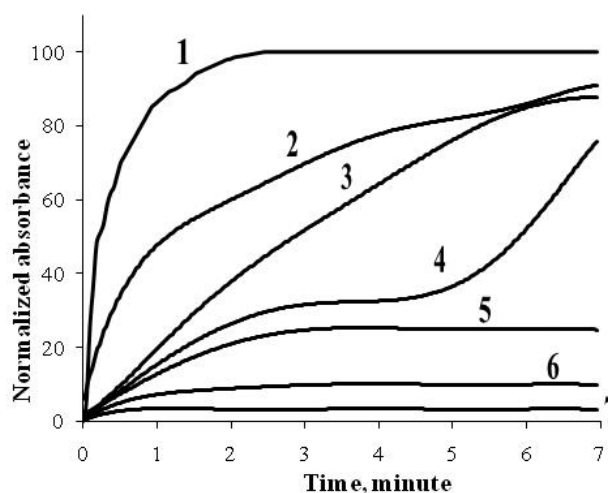


Fig. 3. Extraction process of 40 mg/L chromium(VI):
1. without Aliquat, 2. 1:4; 3. 3:10; 4. 1:2; 5. 1:1, 6. 3:2, 7. 2:1 Aliquat 336/chromium(VI) ratio

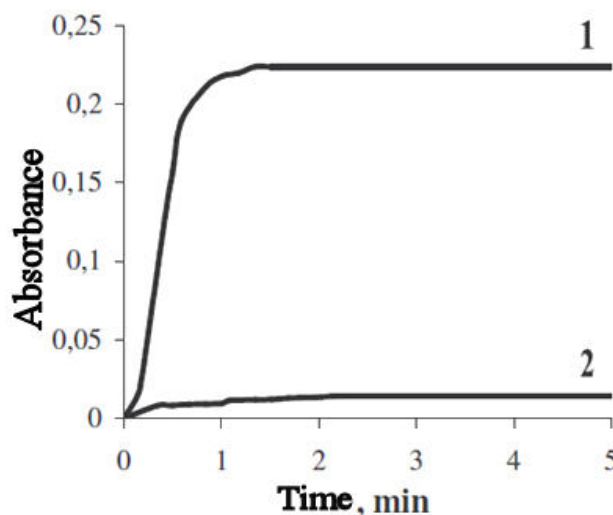


Fig. 4. Change of chromium during continuous extraction detected by atomic absorption. 1. without Aliquat 336, 2. with chloroform containing 1% (m/m) Aliquat 336, chromium content: 3 mg/L Cr(VI), pH=4. (Parameters of the AAS: acetylene 2 L/min, air 5 L/min, detection height 10 mm, rate of nebulization 7.5 mL/min, recording speed 6 cm/min)

Chromium content of the chloroform phase was determined by a high sensitive atomic absorption spectrometry method (GFAAS). To check the efficiency of the extraction and the enrichment we used continuous extraction device (Fig. 1.). Our results can be seen in Fig 4.

In the absence of complexing agent in organic phase, total Cr(VI) content was passed through the extraction device (curve 1). In the presence of Aliquat 336 in chloroform (1% (w/w)), absorbance curve was hardly raised (curve 2). We can conclude that the extraction was of high efficiency and Cr(VI) was

enriched in organic phase. In measurements the efficiency of extraction was reached 96 %, which was determined by graphite furnace atomic spectrometer (GFAAS). 100 mL volume Cr(VI) sample was extracted to 2 mL chloroform with the continuous extraction device, which is a 50 fold enrichment factor. In this case the detection limit of Cr(VI) with GFAAS was 1.00 ng/L (1 ppt). The developed method was able to determine Cr(VI) in samples with low total chromium content (fresh water, surface water, spring water, rain water, etc.). If the volume of sample

increases, the enrichment of Cr(VI) increases as well and the detection limit improves.

Analysis of water samples

The results of the water analysis are given in Table 1. We prepared solutions with known Cr(VI) concentrations and determined them with the extraction, and we found total recovery. The method for the analysis of water samples was well applicable. The determined Cr(VI) content of sea water samples agreed with literature data (Issihiki et al., 1989).

Table 1.

Determination of total Cr and Cr(VI) in samples with continuous extraction with GFAAS detection				
Sample	Cr(VI) [µg/L]	RSD [%]	Total Cr [µg/L]	RSD [%]
River Gyöngyös	0.895	1.3	7.03	1.1
River Répce	0.054	2.7	0.93	1.4
River Tisa	0.712	1.6	1.90	1.1
Adriatic Sea	0.086	2.5	0.50	1.9
Egean Sea	0.087	2.9	0.37	2.1
Tapwater, Debrecen	0.278	2.0	0.50	2.0
Rainwater, Debrecen	1.380	1.3	2.21	1.1

CONCLUSIONS

Continuous extraction device was developed, which was connected to flame atomic absorption spectrometer (FAAS). By this method we can follow the processes of extraction, we can determine the capacity of the organic solvent and numerous extraction methods can be planned. The methods were applied for chromium speciation. The Cr(VI) species can be extracted from water into chloroform with tridecyl-methyl-ammonium chloride at high efficiency (96%) and high pre-concentration (50-100 fold) can be reached. The Cr(VI) concentration in the organic phase was determined with graphite furnace atomic absorption (GFAAS) method. The limit of detection of the method after pre-concentration was 1 ng/L (1 ppt).

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