VERSITA

DOI: 10.2478/s11696-007-0059-7

Coupling of Microwave Induced Plasma Optical Emission Spectrometry with HPLC Separation for Speciation Analysis of Cr(III)/Cr(VI)*

G. HELTAI**, B. FEHÉR, and M. HORVÁTH

Department of Chemistry and Biochemistry, Szent István University, Gödöllő, H-2103 Hungary
e-mail: heltai.gyorgy@mkk.szie.hu

Received 9 November 2006; Revised 10 May 2007; Accepted 6 June 2007

Feasibility and limitations of direct coupling of high performance liquid chromatographic (HPLC) separation to microwave induced plasma (MIP) – optical emission spectrometry (OES) for element-specific detection was tested and compared to inductively coupled plasma (ICP) – optical emission spectrometric detection on the basis of the Cr(III)/Cr(VI) speciation analysis of water samples. Coupling was performed by a hydraulic high pressure nebulizer (HHPN) radiative-heating/water-cooling interface which provides about 20 % and 80 % aerosol yield in the case of helium and argon carrier gases, respectively. Desolvation efficiency of aqueous solutions was approximately 80 %. Applying the ion-pair HPLC separation, the organic eluents and reagents in the MIP cause a 50—75 % signal suppression for Cr(VI) and 25—50 % for Cr(III). In a pure aqueous solution the MIP Cr(VI) signal was by 20 % lower than that of Cr(III). These effects were lower using the ICP source, but they cannot be neglected. Easily ionizable matrix elements (Na, Ca) can cause 70 % signal suppression in the MIP, and 20 % in the ICP. Therefore, species dependent calibration is required in both cases. In the case of HPLC detection by MIP-OES, the detection limit was 13 ng for Cr(III), and 18 ng for Cr(VI). Using the ICP-OES detection, the detection limit was 0.2 ng for Cr (III) and 0.4 ng for Cr (VI). The linear dynamic ranges in both cases were two orders of magnitude.

Keywords: speciation analysis, MIP-OES, ICP-OES, HPLC, Cr(III)/Cr(VI) separation

INTRODUCTION

Development of speciation analytical methods is increasingly needed in environmental and life sciences. According to recent IUPAC recommendations, the term 'chemical species' is used here to denote the specific form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure [1]. Speciation analysis in this sense requires identification and quantitation of one or more individual chemical species in the sample. These tasks can be generally solved by coupling chemical or chromatographic separation procedures with element-specific atomic spectroscopy detectors. The crucial point of this coupling is matching the mass-flow of the separation instrument (procedure) with the sample loading capacity of the spectroscopic source. Furthermore, the spectrochemical detector has to be supplied with a signal processing system suitable for the evaluation of transient (chromatographic type) signals. Chemical matrix interferences arising from the separation system (procedure) nature also have to be considered during the system calibration. Mostly ICP-OES and ICP-MS element-specific detection methods are applied in the speciation analysis due to their robustness and mass flow compatibility with chromatographic separations. In these applications the multi-element analytical capability of these expensive instruments is not utilized. That is why looking for less expensive atomic spectroscopy detectors still has importance [2].

Element-specific detection by microwave induced plasma (MIP) optical emission spectrometry (OES) in gas chromatography has been a well-established

*Presented at the XVIIIth Slovak Spectroscopic Conference, Spišská Nová Ves, 15–18 October 2006.
**The author to whom the correspondence should be addressed.

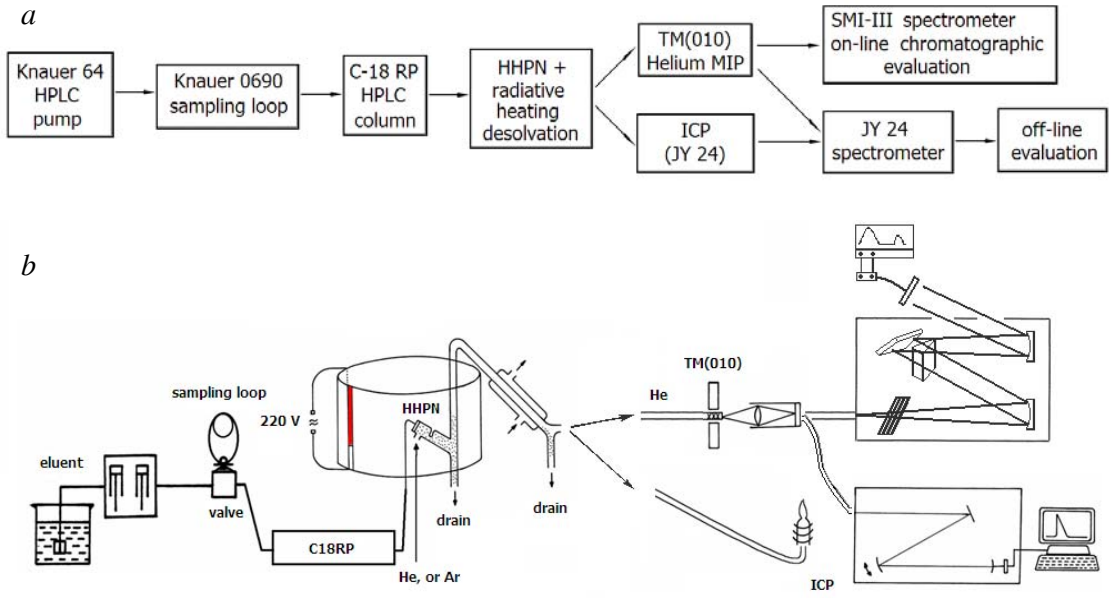

Fig. 1. Block (*a*) and instrumental (*b*) scheme of the system developed for Cr(III)/Cr(VI) analysis using MIP-OES or ICP-OES element-specific detection.

method for a long time, but its detection potential still remains a challenge when coupled with high performance liquid chromatography (HPLC) [3—5]. In this paper, the feasibility and limitations of coupling HPLC separation with element-specific detection by MIP-OES is described and compared to ICP-OES detection assuming the Cr(III)/Cr(VI) speciation analysis in aqueous media. For HPLC coupling with MIP, low-power MIP techniques were considered capable to process both wet and dry sample aerosols. Toroidal argon MIP [6] and diffuse cylindrical helium MIP [7, 8] procedures have been proved to be appropriate for this purpose as described earlier.

For the separation of Cr species present in natural water samples, ion-pair HPLC separation method was applied [9] employing FAAS or ICP-OES element specific detection. In these instruments, the typically applied solution uptake rate in pneumatic nebulizers of 1 mL min^{-1} could be easily matched to a HPLC effluent flow. A 2—5 % aerosol generation efficiency means a mass flow loading of 20—50 mg min^{-1} for the ICP radiation source. On the other hand, the sample loading tolerance of a low power atmospheric MIP is about 1 mg min^{-1}, *i.e.* direct coupling of pneumatic nebulizers to MIP requires aerosol desolvation or increase of the microwave power [10, 11]. Applying high efficiency nebulization (ultrasonic, hydraulic high-pressure nebulization (HHPN), *etc.*), both ICP and MIP sources make the desolvation of the generated aerosol unavoidable [10—13]. The matrix effects caused by organic solvents, reagents, and easily ionizable elements also have to be considered in both cases. It was generally supposed that these effects are more significant in the MIP sources where the incident power is by one order of magnitude lower, and the plasma conditions are farther from the local thermodynamical equilibrium compared to the ICP sources [14]. For coupling the MIP-OES detector to HPLC separation system, hydraulic high-pressure nebulization (HHPN) [9, 15] was selected and a radiative heating/water-cooling desolvation system was applied to the MIP-HHPN interface [16, 17].

The aim of the presented study was the testing of MIP-OES performance of element-specific detection in HPLC separations. The influence of instrumental and matrix effects on chromatographic signal intensity and calibration procedure was studied in detail.

EXPERIMENTAL

The scheme of the experimental system is shown in Fig. 1. The hyphenated system for the speciation analysis of Cr(III)/Cr(VI) was developed by coupling HPLC separation with MIP-OES detection systems [17]. Interfacing was secured by hydraulic high-pressure nebulization as developed by Berndt and coworkers [9, 15], equipped with a desolvation unit developed earlier by *Heltai et al.* [16]. The same interface system was used also with the ICP-OES detection system. Radiation of both plasma sources was detected by the spectrometric part of a Jobin Yvon 24 ICP-OES instrument which is not equipped with chromatographic signal processing. The MIP emission was optically coupled with this spectrometer by a quartz fiber. For further studies the MIP plasma was focused directly on the entrance slit of a high-resolution echelle spectrometer (Spectrametrics SMI-III) equipped with proprietary software for chromatographic signal processing.

During the studies of signal behavior, the system

Table 1. HHPN Aerosol Yield and Desolvation Efficiency at Various Carrier Gas Flows and Liquid Uptake Rates

Carrier gas	Gas flow	Liquid uptake	Aerosol yield	Desolvation efficiency
	L min^{-1}	mL min^{-1}	%	%
Helium	0.25	1.1	19	77
	0.5	1.1	23	81
Argon	0.40	1.1	88	88
	0.80	1.1	74	74

was used without the HPLC-column, whereas for chromatographic calibration and recovery studies a C18 RP column was used in a standard manner.

Cr(III)/Cr(VI) Separation Procedure

Ion-pair HPLC separation was applied in Cr(III)/Cr(VI) speciation analysis with FAAS or ICP-OES element specific detection [9]. Tetrabutylammonium cation, added to the sample in the form of acetate (TBAAc), forms selectively an ion pair with the chromate anion, leaving the Cr(III) cation free. The less polar TBA—chromate ion pair complex exhibits significant retention using the water/methanol mobile phase. The uncomplexed Cr(III) ion elutes from the column unretained. A BST Rutin C-18 type HPLC column (10 cm length, 4 mm ID) was used. The mobile phase composition was 1×10^{-4} mol L^{-1} TBAAc, 1×10^{-4} mol L^{-1} NH_4Ac, and 4×10^{-3} mol L^{-1} H_3PO_4 in 15 vol. % aqueous methanol. According to investigations of *Posta et al.* [9], the ion pair forming reaction can be reliably completed by adding TBAAc to both eluent as well as sample solution. Calibration solutions were prepared using $Cr(NO_3)_3 \cdot 9H_2O$ dissolved in 0.5 mol L^{-1} HNO_3 and from K_2CrO_4 dissolved in bidistilled water. TBAAc concentration in the calibration and sample solutions was 3×10^{-4} mol L^{-1}. All the chemicals used were of analytical grade.

Hydraulic High-Pressure Nebulization and Radiative-Heating Desolvation

The Knauer hydraulic high-pressure nebulizer was used. The C-18 HPLC column was placed between the HPLC injection valve and the nebulizer (with a 20 μm diameter slot Pt/Ir nebulizer nozzle) (Fig. 1*b*). In all experiments a 20 μl sample loop was used for injection. The HPLC eluent flow can be set in the range of 1.1—1.9 mL min^{-1}. In our experiments mostly 1.1 mL min^{-1} eluent flow was applied. The liquid flow pumped under high pressure (30—40 MPa), through the nozzle to an impact bead forms a fine aerosol in the spray chamber. The volume of the spray chamber and desolvation unit was minimized to minimize the distortion of the chromatographic signal. Therefore, the spray chamber was mounted directly to the bottom of the heated glass tube of the desolvation system and equipped with carrier gas inlets. Radiative heating of the aerosol was provided by a linear filament bulb (1500 W) placed in one focus of an elliptical mirror, whereas the aerosol carrying tube (10 mm diameter, 10 cm length) was placed in the other one. The declining part of this tube (about 15 cm length) was cooled with water. The aerosol yield and desolvation efficiency for aqueous solutions was estimated on the basis of drain flow collected under the spray chamber and the cooler (Table 1). A detailed description of the system was published earlier [16]. The achieved desolvation efficiency is significantly lower than that of membrane desolvation, however, the dead volume and the aerosol flux reduction of our system are much smaller [18, 19].

Plasma Sources and Spectrometers

MIP-OES: Cylindrical helium MIP sustained in a TM 010 resonant cavity by means of a GMW 24-DR type (Feuerbacher) generator (2.45 GHz, 0–300 W) was used in the present investigations. A Suprasil quartz tube (5 mm OD, 3 mm ID) was used as an MIP torch. In earlier studies, the optimal range of operation parameters was established as follows [14]: incident power of 180—200 W; reflected power 2.5—5 W; helium flow 0.25—0.30 L h^{-1}. Helium flow sustaining the plasma was used for transportation of the HHPN-generated aerosol from the spray chamber to the MIP unit through the desolvation unit.

Two types of spectrometers were applied in the end-on observation of MIP. In comparative studies of MIP-OES with ICP-OES detection, the spectrometric part of a Jobin Yvon 24 instrument equipped with fiber optic coupling was used. Direct focusing of the plasma spotlight on the entrance slit of a Spectrametrics SMI-III spectrometer was employed in later measurements. In both cases the wavelength of the suitable analytical line (λ(Cr) = 357.8 nm) was set on the monochromator and the blank signal was continuously recorded. The injection of the analyte solution resulted in transient signals which were stored in the spectrometer computer. The Jobin Yvon 24 spectrometer was not equipped with suitable software for transient signal processing. Therefore, off-line processing based on peak height measurement after an adequate blank correction was performed. Appropriate software was developed for on-line processing of time and wavelength resolved sig-

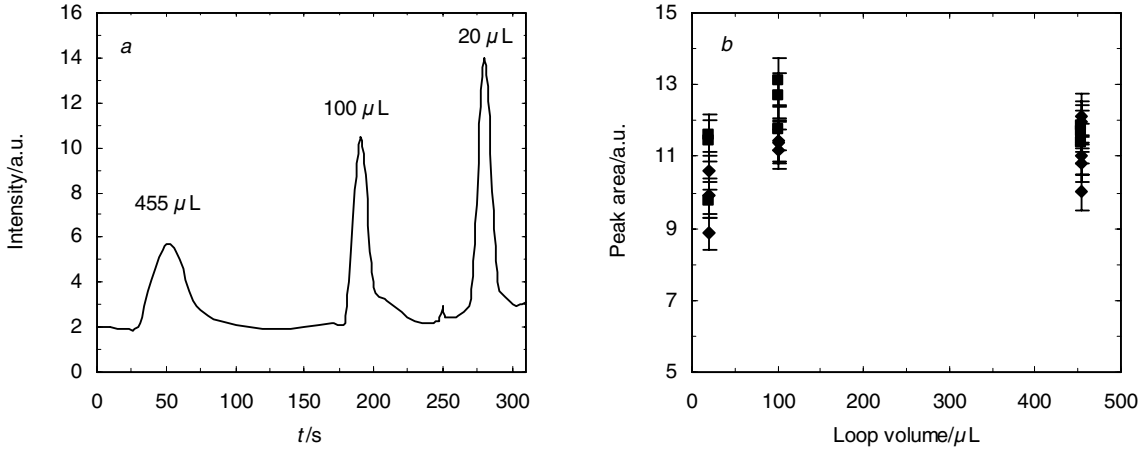

Fig. 2. MIP-OES signal obtained by applying 500 ng of Cr(VI) into the water eluent flow using sampling loops with different volumes (*a*). Variation of the MIP-OES peak areas (*b*) injecting 500 ng Cr(VI) (diamonds) or Cr(III) (squares).

nals recorded by a Spectrometrics SMI-III spectrometer.

ICP-OES: Jobin Yvon 24 sequential ICP-OES spectrometer was used. The nebulization unit was removed and the desolvated aerosol flow from HHPN was directly introduced into the sample aerosol inlet of the ICP torch. In this case the flow of aerosol carrier gas (argon) in the hydraulic high-pressure nebulizer was set to 0.6 L min^{-1}. In preliminary experiments, it was established that this is the maximum value of carrier gas flow which does not disturb the stability of the ICP. Using shield and plasma gas (Ar) flow of 0.2 L min^{-1} and 12.0 L min^{-1}, respectively, and incident power of 1125 W, stable operation conditions for the ICP experiments could be maintained when the eluent containing methanol was nebulized. The Cr emission line was recorded at $\lambda = 267.7$ nm and off-line signal processing was performed as described above for the MIP-OES measurements.

RESULTS AND DISCUSSION

Influence of the instrumental configuration and the matrix effects on the signal and calibration of Cr(III)/Cr(VI) speciation analysis was studied simultaneously with the development of the experimental system. Signal detection and processing were performed within the operating limits of the spectrometer employed. Base line correction and peak height measurement were performed using both spectrometers, whereas the peak area determination was additionally possible by processing the data obtained from the SMI-III spectrometer.

Influence of the Volume of Sampling Loop on the MIP-OES Signal

MIP-OES signals obtained after the injection of 500 ng of Cr(VI) into the distilled water eluent flow using sampling loops with the volume of 455 μl, 100 μl, and 20 μl are presented in Fig. 2*a*. Changes of the values of the peak area are plotted against the loop volume in Fig. 2*b*. These measurements were performed without changing the RP-C18 column length. It can be concluded that the 20 μl and 100 μl loops give the maximum signal for the peak height and peak area measurements, respectively. The signal duration was approximately 20 s and 60 s in both cases. The loop with the volume of 20 μl was applied in further experiments allowing both peak height and area evaluation with reasonable sensitivity and analysis time.

Influence of the Cr Ionic Form on the MIP-OES Signal

Using the same experimental setup, calibration lines for Cr(III) and Cr(VI) species were determined using the 20 μl sampling loop. In Fig. 3 sensitivity of determination of both these species is presented. Assuming both peak height and peak area, the sensitivity of Cr(III) determination is significantly higher than that of Cr(VI). It is supposed that during the sample residence within the MIP unit, the evaporation and atomization rate of the Cr(III) cations is higher compared to that of the Cr(VI) anions. Assuming the ICP-OES peak height detection for the given sample introduction setup coupled with the Jobin Yvon JY24 spectrometer, the difference between sensitivities of calibration lines of the Cr(III) and Cr(VI) species was also significant [20].

Effect of Easily Ionizable Elements Present in Aqueous Eluent on the MIP-OES Signal

Addition of Na or Ca cations into the sample solutions caused a decrease of the MIP-OES signal intensity for both Cr(III) and Cr(VI) analytes when the HHPN sample introduction setup was connected with the Jobin Yvon JY 24 spectrometer. Influence of the potassium addition was not significant [17]. Similarly

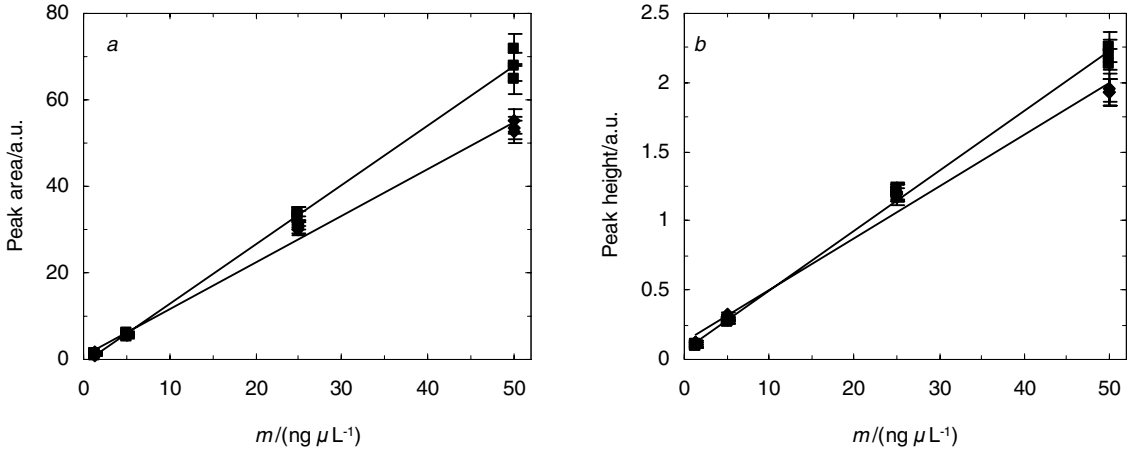

Fig. 3. Calibration lines of MIP-OES determination of Cr(VI) (diamonds) or Cr(III) (squares) species peak area (*a*) and peak height (*b*) using SMI-III spectrometer.

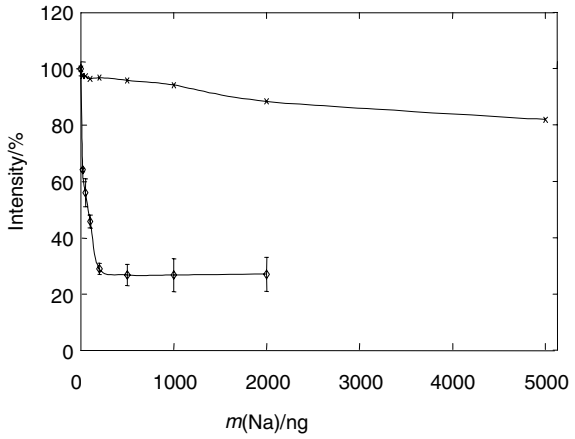

Fig. 4. MIP-OES (circles) and ICP-OES (crosses) signal suppression caused by sodium addition during the element specific detection at sampling loop volume 20 μL, injected mass 200 ng of Cr(III), JY 24 spectrometer, and peak height detection mode.

to the new detection system, the addition of sodium also causes a signal depression in ICP-OES detection as can be seen in Fig. 4. However, the extent of these signal suppression did not reach 20 % of the original value even using extremely high Na admixture. On the contrary, MIP-OES signals were reduced by 70 % of the original value already at an addition of a small amount of sodium.

Influence of Methanol Content in Eluent on the MIP-OES- and Chromatographic-Signal

The influence of increasing methanol content in eluent on the Cr(III) and Cr(VI) peak areas is presented in Fig. 5. It can be seen that the methanol vapor reaching the MIP unit causes Cr signal suppression that strongly depends on the volume of the loop employed and the oxidation state of the Cr species. In the range of 15—20 vol. % of methanol in water solution, this signal intensity decrease approaches a constant value. At methanol content in water higher than 40 vol. % the MIP discharge becomes unstable and may be extinguished.

The influence of the methanol content in eluent on the chromatographic separation is presented in Fig. 6. Given data were obtained after inserting the RP 18 column into the system and the MIP emission was detected by the JY24 spectrometer with fiber optic coupling. For efficient separation, optimal methanol concentration of 15 vol. % in water was identified. When the methanol concentration was above 20 vol. % the resolution of the Cr(III) and Cr(VI) peaks was not satisfactory and when it was below 10 vol. % the elution of the TBA—Cr(VI) complex was too slow and, therefore, also the signal to noise ratio of Cr(VI) was too low. For eluent containing 15 vol. % of methanol similar chromatograms were obtained for ICP-OES and MIP-OES (Fig. 7). However, due to the different dead volumes of both setups the chromatograms are not identical.

Recovery of TBA—Cr(VI) Ion-Pair Complex

Direct determination of recovery of the TBA—chromate ion pair complex was not possible employing the HPLC-MIP-OES system. Removal of the column from the system resulted in a significant change of the MIP operation conditions, therefore, the recovery corresponding to 100 % of the Cr(VI) could not be determined using the standard procedure. Indirect determination of recovery was carried out as follows: (*i*) 500 ng of Cr(III) not retarded within the column was injected three times in the system and the retention times of the Cr(III) peak were determined; (*ii*) using the same procedure the retention time of the Cr(VI) peak was determined by injecting 500 ng of Cr(VI); (*iii*) injection of 500 ng of Cr(VI) was repeated

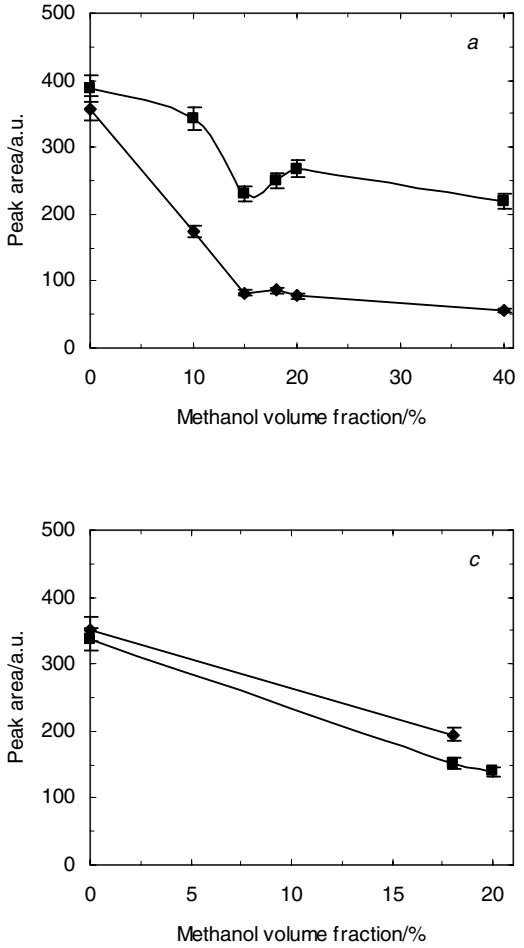

Fig. 5. Influence of methanol content in eluent on the MIP-OES peak area of 500 ng Cr(VI) (diamonds) and Cr(III) (squares) using sampling loops with the volume of 20 μL (*a*), 100 μL (*b*), and 455 μL (*c*) and SMI-III Spectrometer.

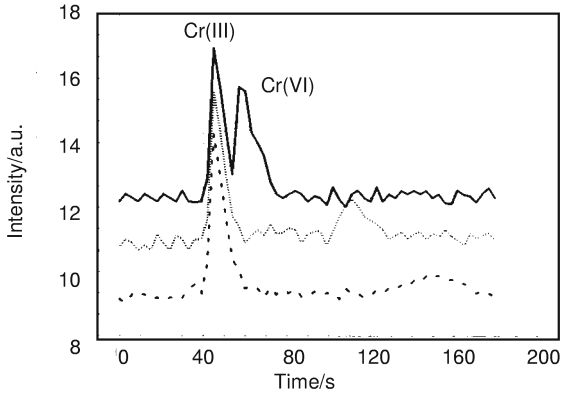

Fig. 6. Effect of methanol concentration in eluent (10 vol. % (dotted line), 15 vol. % (solid grey line), and 20 vol. % (solid line)) on chromatographic separation of 50 ng Cr(III) and Cr(VI) using MIP-OES detection (spectrometer JY 24).

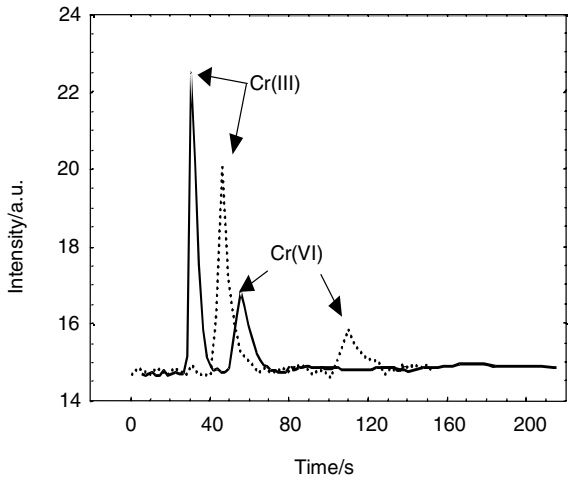

Fig. 7. HPLC-separation of Cr(III)/Cr(VI) on RP-C18 column detected by MIP-OES (dotted line) and ICP-OES (continuous line). Sampling loop volume 20 μl, injected amount 100 ng (MIP-OES) and 5 ng (ICP-OES), spectrometer JY 24.

twice, however, in the absence of TBA in eluent and the Cr(VI) sample solutions (Fig. 8).

It was observed that the residual TBAAc reagent was eluted during the analysis after the 5th injection. The next injection of 500 ng of Cr(VI) resulted in approximately the same signal intensity as in the case of the injection of 500 ng of Cr(III). The average peak area of Cr(III) is slightly higher than that of Cr(VI) (by about 4 %) but the difference is not significant (Fig. 9). Based on these observations, it can be con-

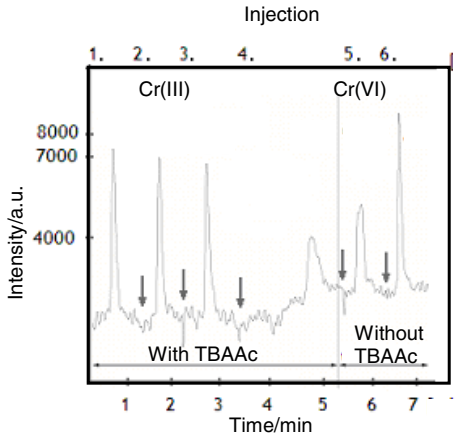

Fig. 8. Chromatographic signals corresponding to 500 ng Cr(III) and Cr(VI) in the presence and absence of ion-pair forming TBAAc reagent using MIP-OES in Cr detection by SMI-III spectrometer, (↓ denotes injection).

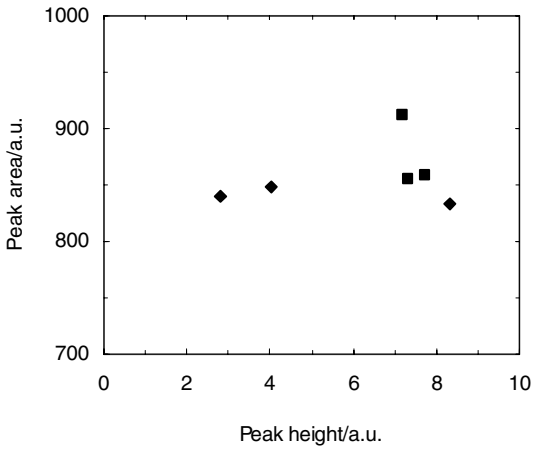

Fig. 9. Correlation of peak area with peak height for the experiments given in Fig. 8: Cr(VI) (diamonds) and Cr(III) (squares).

cluded that the recovery of the TBA—Cr(VI) complex is practically complete.

Calibration of the HPLC-HHPN-(MIP/ICP)-OES System for Cr(III)/Cr(VI) Speciation Analysis

Calibration lines of signal intensity *vs.* analyte content of Cr(III) and Cr(VI) obtained on MIP-OES and ICP-OES systems connected with JY24 spectrometer are presented in Figs. 10*a* and 10*b*, respectively. The evaluation is based on the measurement of the peak height.

With both detection methods, the linear dynamic ranges for both Cr species were equal to two orders of magnitude. The sensitivity of the Cr(III) determination was significantly higher than that of Cr(VI). The detection limits calculated on the basis of the 3σ concept were as follows: 13 ng Cr(III) and 18 ng Cr(VI) for MIP-OES detection and 200 pg Cr(III) and 400 pg Cr(VI) for ICP-OES detection. The relative standard deviation (RSD) values of the chromium determination were calculated on the basis of residual standard deviation of the calibration lines. These RSD values are very similar for Cr(III) and Cr(VI), therefore, the

Table 2. Statistical Parameters of the Cr(III) and Cr(VI) Speciation Analysis by MIP-OES and ICP-OES

Method	Cr(III) determination		Cr(VI) determination	
	RSD/%	r	RSD/%	r
MIP-OES	2.9	0.999	3.2	0.996
ICP-OES	2.1	0.999	2.3	0.967

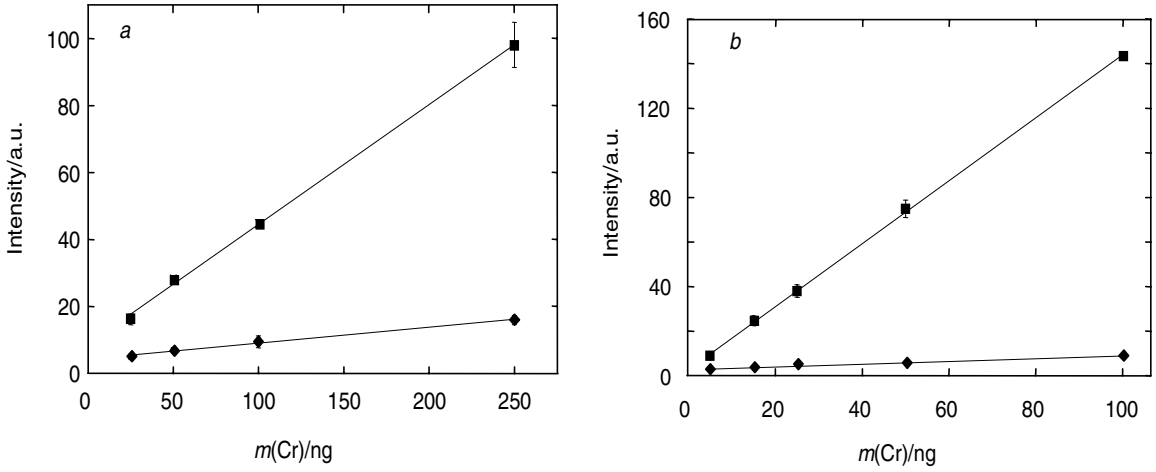

Fig. 10. Calibration lines of Cr(VI) (diamonds) and Cr(III) (squares) determined using HPLC-MIP-OES (*a*) and HPLC-ICP-OES (*b*) systems using 20 μL sampling loop and JY 24 spectrometer.

calculated detection limits are in the same order of magnitude. The RSD values and the correlation coefficients are given in Table 2.

The calibration lines of both Cr species remained different when the evaluation was performed on the basis of MIP-OES peak areas.

CONCLUSIONS

Summarizing the results of MIP-OES signal detection, it can be concluded that the speciation analysis of Cr(III) and Cr(VI) is feasible with an appropriate HPLC separation system coupled with MIP or ICP sources by hydraulic high-pressure nebulization and radiative-heating desolvation. However, sensitivity, detection strength, and linear dynamic range of these methods can be strongly reduced due to the interferences caused by organic reagents and eluents applied during the separation procedure. These effects are more significant in MIP-OES, but cannot be neglected in ICP-OES, either. Therefore, species dependent calibration is required in both cases. Easily ionizable elements also influence both detection systems when real samples are analyzed. In MIP-OES, addition of small amounts of Na or Ca cations can cause signal suppression by about 70—80 %. In ICP-OES analysis setup, the same amount of Na can cause only about 10—20 % signal decrease. The detection strength of ICP-OES was at least by one order of magnitude higher than that of MIP-OES. Further improvement of the MIP-OES performance could be achieved by increasing the desolvation efficiency (*e.g.* by Peltier cooling) and reducing the methanol vapor pressure in the plasma source.

REFERENCES

1. Templeton, D. M., Ariese, F., Cornelis, R., Danielsson, L.-G., Muntau, H., van Leeuwen, H. P., and Lobinski, R., *Pure Appl. Chem. 72*, 1453 (2000).
2. Broekaert, J. A. C. and Siemens, V., *Spectrochim. Acta B 59*, 1823 (2004).
3. Wuilloud, J. C. A., Wuilloud, R. G., Vonderheide, A. P., and Caruso, J. A., *Spectrochim. Acta B 59*, 755 (2004).
4. Matusiewicz, H., *Spectrochim. Acta B 57*, 485 (2002).
5. Ray, S. J., Andrade, F., Gamez, G., McClenathan, D., Rogers, D., Schilling, G., Wetzel, W., and Hieftje, G. M., *J. Chromatography A 1050*, 3 (2004).
6. Kollotzek, D., Tschöpel, P., and Tölg, G., *Spectrochim. Acta B 37*, 91 (1982).
7. Heltai, G., Broekaert, J. A. C., Leis, F., and Tölg, G., *Spectrochim. Acta B 45*, 301 (1990).
8. Heltai, G., Broekaert, J. A. C., Burba, P., Leis, F., Tschöpel, P., and Tölg, G., *Spectrochim. Acta B 45*, 857 (1990).
9. Posta, J., Berndt, H., Luo, S. K., and Schaldach, G., *Anal. Chem. 65*, 2590 (1993).
10. Jankowski, K., Karmasz, D., Starski, L., Ramsza, A., and Waszkiewicz, A., *Spectrochim. Acta B 52*, 1801 (1997).
11. Jankowski, K., Karmasz, D., Ramsza, A., and Reszke, E., *Spectrochim. Acta B 52*, 1813 (1997).
12. Luo, S. K. and Berndt, H., *Spectrochim. Acta B 49*, 485 (1994).
13. Jakubowski, N., Feldmann, I., and Stuewer, D., *Spectrochim. Acta B 47*, 107 (1992).
14. Broekaert, J. A. C., Bings, N., Prokisch, C., and Seelig, M., *Spectrochim. Acta B 53*, 331 (1998).
15. Ivanova, E., Schaldach, G., and Berndt, H., *Fresenius J. Anal. Chem. 342*, 47 (1992).
16. Heltai, G., Józsa, T., and Percsich, K., *Fresenius J. Anal. Chem. 355*, 638 (1996).
17. Heltai, G., Józsa, T., Percsich, K., Fekete, I., and Tarr, Z., *Fresenius J. Anal. Chem. 363*, 487 (1999).
18. Akinbo, O. T. and Carnahan, J. W., *Talanta 45*, 137 (1997).
19. Akinbo, O. T. and Carnahan, J. W., *Anal. Chim. Acta 390*, 217 (1999).
20. Heltai, G., Józsa, T., Percsich, K., and Fehér, B., *Magy. Kém. Foly. 106*, 201 (2000).