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ELEMENTAL SPECIATION BY CAPILLARY ELECTROPHORESIS WITH INDUCTIVELY COUPLED PLASMA SPECTROMETRY: A NEW APPROACH BY FLOW FOCUSING® NEBULIZATION

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Abstract

A novel system for Capillary Electrophoresis (CE) and Inductively Coupled Plasma (ICP) sample introduction that incorporates a dedicated Flow-Focusing® based nebulizer as aerosol generation unit is presented, aiming to provide high signal sensitivity and low detection limits for element speciation at short analysis times. To prove its viability, the system prototype constructed has been coupled to an inductively coupled plasma - optical emission spectrometer (ICP-OES) and an inductively coupled plasma - mass spectrometer (ICP-MS) for Cr(III) and Cr(VI) speciation. Separation - nebulization system and operation parameters (i.e., capillary length, nebulizer geometry, carrier flow, carrier ionic strength, separation potential and sample injection volume) have been considered and studied, and the analytical figures of merit obtained for model samples in ICP-MS are presented. The results obtained show that the developed instrumental system permits Cr speciation in less than two minutes with detection limits of 0.1, 0.2 and 0.03 µg/L for Cr(III), Cr(VI) and total Cr, respectively.

Keywords

Hyphenation, Capillary Electrophoresis, ICP-OES, ICP-MS, Chromium speciation, Flow-Focusing® nebulization

1. Introduction

Trace elements toxicity often depends on their chemical form. Therefore, there is ever growing need of analytical methodologies for determination of different chemical forms of the same element – speciation analysis [1]. Chromatographic techniques coupled to element detectors are often the tools of choice for this kind of analysis. However, Capillary Electrophoresis (CE) is a powerful tool in element speciation because of its high separation capabilities and its environmentally friendly nature, which is due to the use of aqueous buffer solutions with moderate pH levels and its extremely low reagent/sample consumption [2-4]. The latter, however, presents an important problem when CE is coupled to Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS) due to liquid flow incompatibility (typically one order of magnitude lower in CE than in ICP sample introduction systems nebulizers). In the last 20 years, numerous approaches for overcoming this incompatibility have been proposed, applied to model and real samples. Most of these rely on addition of a make-up flow prior the nebulizer, aiming to deliver enough liquid for the nebulizer to function correctly and to compensate the suction effect of the nebulizer on the separation capillary, which disturbs the electro-osmotic flow [5-7]. Micronebulizers [8-10] are often applied and direct injection nebulizers applications have also been reported [11]. Another approach consists in the generation of volatile forms by derivatization of the analytes [12-14]. Hyphenations of ICP-MS with CE microfluidic devices have also been reported [15, 16]. Most of the published reports have been recently reviewed by Álvarez-Llamas et al. [4] and Michalke [17]. Commercial systems based on some of the abovementioned approached are nowadays offered by various leading manufacturers [18, 19].

Despite these advances in CE-ICP coupling, the analyte quantities introduced in the plasma after CE separation are still much lower than the ones achieved by using other separation techniques (e.g., chromatography, on-line solid phase extraction, etc.). Therefore, the analytical sensitivities with this combination tend to be lower and the obtained detection limits tend to be higher [2, 4]. Together with the relatively long analysis times, this makes CE-ICP combination unattractive for routine element speciation analysis. In order to overcome the sensitivity drawback, different preconcentration techniques have been proposed. These techniques (recently reviewed by A. Timerbaev [2]) include off-line (such as solid or liquid phase microextraction) and in-line (such as sample stacking in different modes) preconcentration. However this additional step could increase further the analysis time and could be a source of errors from contamination, analytes form transformation, etc.

In this work, a novel system for electrophoretic separation and ICP sample introduction is presented. The proposed system uses pneumatically generated liquid flow for carrier transport and sample injection, which provides higher carrier/sample flows (in comparison with typical CE systems that rely mainly on electroosmosis). Moreover, the system incorporates a dedicated Flow-Focusing® (FF) based micronebulization unit for improving nebulization efficiency at low (for ICP based spectrometers) sample uptakes. Thus, the system proposed aims to increase the amount of sample injected, separated

and transported to the plasma and, therefore, to provide high signal sensitivity and low detection limits at short analysis times.

Flow Focusing® [20] nebulization principle has already been applied to the construction of conventional and micro nebulizers that have shown excellent nebulization efficiency, especially at low sample uptakes [21, 22].

Therefore, the purpose of this work was to study the viability of the proposed approach as a first step to a future development of a dedicated device for routine sample speciation analysis. To this end, a prototype of Capillary Electrophoresis Flow Focusing® Nebulization System (CEFFS) has been constructed and optimised for separation of Cr(III) and Cr(VI) in model samples and detection in ICP-OES and ICP-MS.

2. Material and methods

2.1. Instrumentation

A scheme of the system prototype used in this work, including some component photographs, is presented in Fig. 1. It consists of the following main components: home-made carrier electrolyte module (a), 10 port selection valve (model 7610-600, Rheodyne Rohnert Park, CA, USA) (b), 0.75 mm i.d. fused silica separation capillary (Supelco Analytical, Bellefonte, PA, USA) (c), dedicated Flow Focussing® nebulizer (home-made prototype) (d) and a high voltage power supply (model Brandenburg 707R, Applied Kilovolts Ltd., Worthing, UK) (e).

The home-made carrier electrolyte module (a) (component photograph on Fig. 1) is built around a PEEK cross connector. On one side of this connector a 1.5 mL conical vial (agglutinated to an appropriate fitting) is screwed; it contains the carrier electrolyte. On the opposite side another fitting is screwed, that holds a fused silica capillary which extends through the cross connector and enters until the bottom of the vial. A third cross connection is used to fit a gas inlet for carrier electrolyte driving. To the fourth one (i.e., the opposite to the gas inlet) a fitting that holds a Pt wire is screwed. This Pt wire also extends through the cross connector and enters to the bottom of the conical vial; it serves as an electrode for the CE separation. As already mentioned, the system prototype constructed in this study uses pressure to generate the carrier electrolyte flow, in contrast to the conventional CE systems, which use electroosmosis (however, pressure accompanied electroosmotic flow in CE is nowadays used for shortening separation times where possible). Pressurized argon (1.5 bar) is supplied by the gas inlet of the cross connection to push the carrier electrolyte through the fused silica capillary all the way to the dedicated FF nebulizer.

The sample is injected in the carrier stream by a selection valve (b). It is first introduced in a loop by a syringe and then, by rotating the valve, into the separation capillary. The amount of injected sample is not controlled by the loop volume, but by the time the valve was in injection position and hence, not all the loop volume is injected. The loop

serves only as a simple mean for performing consecutive injections of samples and standards with different concentrations (further explanation is given in the discussion below).

The home-made FF nebulizer (d) (component photograph in Fig. 1) serves as both a mean to close the CE electric circuit and to nebulize the sample after analytes separation. It is built around a cross connector (the same type as the one used for the carrier electrolyte module construction). On one of its sides, a glass tube is fastened by an appropriate fitting. The other end of this glass tube was previously flame shaped in order to obtain a 100 µm diameter nebulizer exit orifice (component photograph in Fig. 1). The end of the CE separation fused silica capillary is connected to a 75 µm i.d. Pt tube using a shrink tubing (the ends of the Pt tube and the capillary tube were previously polished in order to obtain minimum dead volume). This assembly is fixed to the cross connector by a fitting on the opposite side to the glass tube. The Pt tube extends through the connector, and enters into the glass tube on the other side. Through the third side of the cross connector a Pt wire (connected to the high voltage power supply) is passed, entering also into the glass tube. This Pt wire is coiled around the Pt tube at the end of the CE capillary. It serves as an electrode for CE separation and also to fix axially the Pt tube relative to the moulded orifice at the end of the glass tube. The Pt tube is then positioned at 60 µm distance from the glass tube orifice, forming this way the FF nebulization nozzle (component photograph in Fig. 1). The distance between the Pt tube exit and the nebulizer's orifice is regulated with the two screw fittings supporting the glass tube and the CE capillary, respectively, to the cross fitting. A gas fitting is connected to the last side of the cross connector in order to provide the Ar nebulizer gas flow inside the glass tube, to the nebulizer nozzle. Glass tubes have already been used for construction nebulization nozzles based on the Flow Focusing® principle [23]. However, to the authors' knowledge, this is the first time such procedure and material are applied for the construction of a FF nebulizer for sample introduction in ICP based spectrometers.

The electophoretic separation through the CE capillary was driven by a Brandenburg 707R high-voltage dc power supply which can be operated in a voltage-controlled (15 kV maximum) mode. Electrical connections between the power supply and the electrolytes were maintained using platinum electrodes. The electrode at the carrier electrolyte module (a) was held at a positive potential while the one at the nebulizer tip end (d) was grounded.

A dual-view ICP-OES model Optima 4300DV (Perkin-Elmer, Norwalk, CT, USA) was used for system development and optimisation. The spectrometer's software does not allow sampling of transient signals. Therefore, for acquisition of each electropherogram, a single run of 300 replicates was measured at 0.1 sec integration time (0.4 sec read time). These signal acquisition parameters, limited by the ICP-OES instrumentation used, were not the optimal for this kind of measurements and thus led to high baseline noise, which was unfavorable for the detection limits. Therefore in addition to the ICP-OES test, the CEFF system was also evaluated with an ICP-MS model 7700 (Agilent Inc., Tokyo, Japan) allowing for better transient signals measurements. Both

spectrometers' operating conditions, optimised for working with the CEFF system, are shown in Table 1.

The CEFF prototype tested in this research works at very low liquid flows (around 7 ± 1 µL/min). In order to ensure maximum emission signal, and to minimise the aerosol transport time for decreasing peaks' diffusion caused by mixing of slow moving aerosols a spray chamber that provides high aerosol transport values and has a low internal volume is needed. Therefore, a dedicated single pass spray chamber was constructed and used with the ICP-OES spectrometer. Its characteristics were as follows: approximately 50 mm length, 10 mm and 4 mm i.d. at the nebulizer and the exit sides, respectively, and approximately 3.5 mL volume. During operation, no need for liquid draining from the chamber was observed indicating that high aerosol transport rate has indeed been achieved, which could be also due to both the high quality of the aerosols produced with the Flow Focussing® nebulizer and the low liquid flow rate. With the ICP-MS, the spectrometer's commercial double pass Scott type spray chamber was used, due to the impossibility to fit the dedicated spray chamber into the spectrometer's Peltier cooling jacket.

2.2. Reagents

Ultrapure water (18.3 MΩ cm) and appropriately diluted high-pure nitric acid (65% Suprapur®, Merck, Darmstadt, Germany) were used for preparing all the reagents. Stock solutions of Cr(III) and C(VI) were prepared by diluting analytical-grade $Cr_2(SO_4)_3$ and $K_2Cr_2O_7$, respectively (Panreac, Barcelona, Spain), in order to obtain standard solutions containing two Cr species: Cr(III) as a cation (Cr^{3+}) and Cr(VI) as an anion ($HCrO_4^-$) (more information is included in the discussion below).

2.3. Procedure

Optimised electrophoretic separation conditions used with CEFFS are listed in Table 2. The following protocol was established for Cr speciation:

(i) A controlled pressure (1.5 bar) is applied to the gas inlet of the carrier electrolyte module in order to obtain a stable flow through the separation capillary to the nebulizer.

(ii) The sample is introduced into the sample loop of the injection valve by means of a plastic syringe.

(iii) The valve is rotated to "inject" position for an optimised period of time (3 sec). At this point, a portion of the sample is injected into the separation capillary.

(iv) The valve is rotated back to "load" position and the separation potential (15 kV) is applied between the injection module and the nebulizer nozzle.

(v) The signal from Cr is registered with the relevant ICP spectrometer in a continuous mode (acquisition conditions in Table 1).

(vi) After the separation takes place, the high voltage power supply is turned off, the valve is rotated to "inject" position and rinsed with 0.5 mL of electrolyte in order to prevent occurrence of memory effect between samples.

(vii) After the electrolyte inside the carrier module is consumed, the module is unscrewed, refilled and screwed back. This can be done with the plasma ignited or extinguished, depending on the spectrometer used.

3. Safety Considerations

The high-voltage could provoke electrical shock. In this research, prototypes with open electrodes and circuits have been used. Such open experimental setups should be, and have been, handled with extreme care in order to avoid high-voltage electrical shock hazards.

4. Results and discussion

4.1. Proof of concept

Fig. 2A shows the ICP-OES signals obtained for various consecutive injections of a standard solution containing equal concentration (i.e.,10 mg/L) of Cr(III) and Cr(VI), when increasing the applied separation potential from 0 (electropherogram 1 in the figure) to 15 kV (electropherogram 6). As can be observed, two peaks start to appear at a separation potential of 12 kV (electropherogram 4) indicating a possible separation of the two Cr species. When further increasing the separation potential, the resolution is improved (electropherograms 5 and 6).

In order to prove the origin of the two peaks, three samples with different Cr(III)/Cr(VI) concentration ratios were analysed. The results of this test, shown in Fig. 2B, suggest that the first peak corresponds to Cr(III) and the second one corresponds to the Cr(VI) specie. This was the expected result, taking into account the polarities of the species (i.e., cation for Cr(III) and anion for Cr(VI)) and the separation potential applied (i.e., anode to the carrier electrolyte module and ground to the nebulization nozzle).

Fig. 2C presents two consecutive sample injections of a standard solution having equal concentrations (10 µg/L) of Cr(III) and Cr(VI) in ICP-MS. The first injection (electropherogram 1) was performed without separation potential application and the second one (electropherogram 2) with 15 kV separation potential application. As in the case of ICP-OES, two separate peaks corresponding to Cr(III) and Cr(VI), respectively, were registered when 15 kV voltage was applied, while only one peak corresponding to total Cr content was recorded when no separation voltage is applied. This test proved the concept's viability in another ICP-based spectrometric technique. Moreover, in this case the analytes' concentration in the model sample was three orders of magnitude lower than in ICP-OES (i.e., 10 µg/L vs. 10 mg/L) showing, as expected, the clear sensitivity advantage of ICP-MS against ICP-OES experiments.

4.2. Pressure-induced and electroosmotic carrier electrolyte flow

The Flow Focussing® nebulization principle is known to cause high pressure at the exit of the liquid capillary, in contrary to most of the conventional nebulizers used for liquid sample introduction in ICP, which have low pressure at this point due to Venturi effect. This is why, with the prototype described, low carrier electrolyte flows are obtained using relatively high carrier flow generation gas pressures (around 1.5 bar for obtaining approximately 7 µL/min). The high pressure at the exit of the liquid capillary of the FF nebulizer cannot be efficiently compensated by solely the electroosmotic flow, and therefore it pushes the carrier electrolyte upstream (i.e., in the direction opposite to the nebulizer nozzle) and drains the system. For this reason, the CEFF system design was based on a pressure driven carrier flow to compensate for the FF nebulizer high pressure. However, that this approach has some inherent advantages, such as the possibility to use higher flows than the purely electroosmotically generated ones, which is beneficial for the analytical sensitivity, and the possibility to determine total analyte content by simply not applying separation potential to the system.

A decrease in the peaks' migration times is observed when increasing the separation potential (see electropherograms in Fig. 2A). This behaviour is typical for the conventional CE systems based on electroosmotic flow. Therefore, it can be inferred that even if this research prototype uses pressure for inducing the carrier flow, electroosmotic flow probably occurs also when high voltage is applied in the separation capillary, which could explain migration times' behaviour.

4.3. Electrophoretic separation parameters study and optimisation

The choice of the CEFFS configuration and its operation conditions was done after some theoretical considerations and optimisation studies. The following parameters were taken into account: separation capillary length, carrier flow generation pressure, carrier electrolyte concentration, sample injection time and separation potential. The optimised operation conditions used in this work are listed in Table 2.

4.3.1. Separation capillary length

Three different separation capillary lengths (from 1 m to 3 m) were tested, and the results obtained are shown in Fig. 3. Increasing the capillary length leads to a decrease in the peaks' resolution. This is probably due to the lower electrical current (because of the higher electrical resistance) and to the higher diffusion grade due to the parabolic front shape of the pressure-driven carrier flow. Capillary lengths shorter than 1 m were not tested due to need of a certain minimum distance between the nebulization unit and the selection valve when fitting the CEFFS to the spectrometer.

4.3.2. Carrier flow generation pressure

As already mentioned above, with the Flow Focussing® (FF) nebulization principle, there is a zone of high pressure at the tip of the liquid flow capillary of the nebulizer. This pressure extends further upstream through the liquid flow capillary (in the case of CEFFS – the separation capillary). With the conventional FF-based nebulizers for liquid sample introduction in ICP, external pumping system is mandatory in order to provide constant liquid flow to the nebulization nozzle. Usually, a peristaltic pump is used; however it generates pulsations in nebulization, especially at the low revolutions needed to obtain low liquid flows. In the CEFF prototype, the carrier electrolyte flow is generated by high gas pressure applied in the headspace inside the carrier electrolyte module to overcome the FF nebulizer pressure. This pressure was optimised in order to achieve a stable flow during sample injection and separation, at a rate that provides enough time for the analyte species to separate in the electric field. It was observed that this flow was most stable when the pressure applied is the same as the nebulization gas pressure provided at the nebulization module. Therefore, and in order to maintain the system as simple as possible, a T cross split mounted on the nebulisation gas tube of the spectrometer has been used to divide the flow in two streams for nebulization and carrier flow generation. The nebulization gas flow of 0.7 L/min was chosen according to the authors experience with the Optima 4300 spectrometer as an optimum for maximum aerosol transport rate and plasma stability. The nebulizer geometry was tuned up in order to obtain a nebulization gas flow of 0.7 L/min with a pressure of around 1.5 bar. This pressure has also been found to be sufficient to push the carrier electrolyte through the separation capillary and to obtain Cr species separation when high voltage is applied.

4.3.3. Carrier electrolyte concentration

15 mM HNO_3 solution was used in this work as carrier electrolyte, and the same was also used for preparing standard solutions. It was selected in order to provide a pH around 2.5 that will ensure the presence of Cr(III) as Cr^{3+} cation and of Cr(VI) as $HCrO_4^-$ anion [24]. In real samples analysis, however, the actual pH value of the sample should be taken into account and the carrier electrolyte acidity should be adjusted accordingly in order to prevent changes by oxidation or reduction. Additional ionic strength adjustment might be needed after some optimization studies.

4.3.4. Sample injection time

In CEFFS, the sample is injected into the carrier flow stream by means of an injection valve. The sample is first introduced into a loop, by a syringe, and then into the carrier flow stream by rotating the selection valve. Initially, a loop of a fused silica capillary

with the same internal diameter (i.d., 75 µm) as the separation capillary and a length as short as possible was fitted to the selection valve (approximately 10 cm), and all the loop volume was injected. However, this sample volume was found to be too large for efficient separation. Consequently, loops of lower i.d. (50 µm) were fitted and tested. These also proved to be inefficient, provoking a decrease in the carrier electrolyte flow because of the smaller section of the loop capillary. Therefore, it was decided to introduce only a portion of the initially tested loop volume, controlling the exact amount of sample injected by the time the valve is set in "inject" position. This approach gave better results in terms of resolution, even if leading to a slight degradation in precision due to manual operation. Further, the effect of the injection time was studied and results are presented in Fig. 4. On one hand, increasing the injection time from 3 to 5 sec resulted in an increase in the peak high for Cr(III) and Cr(VI), which is a natural consequence of the higher amount of analyte injected. However, the resolution of the two peaks was found to decrease due to incomplete separation of the analytes. On the other hand, injection times lower than 3 sec resulted in a high decrease in signal precision, since injection time is manually controlled. Therefore, an injection time of 3 sec was chosen as a compromise between signal sensitivity, peaks' resolution and signal precision.

It is worth mentioning that, according to the authors' experience, this approach to sample injection is the highest source of uncertainty with this system prototype, and proper modifications, such as the use of a more sophisticated automatic injection valve.

4.3.5. Separation potential

The influence of the high potential application on the Cr separation is shown in Fig. 2A. The studies have shown that separation improves when increasing the potential applied. Therefore, the maximum voltage of the power supply (i.e., 15 kV) has been used. The use of even higher separation potential could probably result in better separation, which is why a more powerful power supply should be used in future prototypes construction.

4.4. System performance characteristics

System performance was evaluated in both ICP-OES and ICP-MS. However, unsatisfactory high detection limits were obtained with ICP-OES. This could be attributed, on one hand, to the sub-optimal signal acquisition conditions allowed by the spectrometer acquisition software, which lead to very high baseline noise levels (see explanation in *Instrumentation* section) and, on the other hand, to the inherent low sensitivity obtained with the instrument used in this work, even if working at optimal sample introduction conditions.

The analytical figures of merit obtained with ICP-MS (*i.e.*, peak migration times, separation resolution, sensitivity, precision and detection limits) are shown in Table 3. As observed in Fig. 2 and Table 3, no baseline separation was achieved with the CEFFS prototype. This can be a consequence of the pressure driven carrier flow. On one hand,

this flow is higher than the electroosmotic flows obtained in conventional CE, thus decreasing the time for separation and, consequently, the resolution. On the other hand, the pressure driven laminar flow has a parabolic profile, which increases diffusion and decreases resolution. Separation resolution could probably be improved by increasing the applied separation potential, as the results shown on Fig. 2A suggest. In this research, however, the applied separation potential was limited by the maximum voltage delivered by the available power supply. Nevertheless, at the optimum working conditions for Cr separation with the available instrumentation, the two peaks could be considered resolved enough to be used for quantification of the two species [25] if peak height is used. The positive side of using pressure driven carrier flow and large sample injection volume can be observed in the sensitivities and, especially, in the excellent detection limits obtained with ICP-MS (see Table 3). Peak heights were used for sensitivity and LOD calculations when the system was operated in separation mode, while peak area was used for calculating the analytical figures of merit when determining total Cr concentration (without separation).

Precision (RSD%) values between 11% and 13% were observed. No significant differences in precision were observed between total Cr determination (without separation potential) and Cr speciation determination (with 15 kV applied). This leads to the conclusion that the separation procedure by itself does not influence precision. Based on the daily work experience, the authors consider the major source of uncertainty to be the manual sample injection (see discussion above).

A comparison with other recently published CE-ICP methods for Cr speciation is given in Table 4. As already mentioned, the inherent benefits of the approach described in this work leads to lower detection limits, without the need of a preconcentration step, and thus, to shorter analysis time in comparison with the conventional CE techniques.

5. Conclusions

A new system for element species separation based on capillary electrophoresis and Flow Focusing® nebulization has been developed. The prototype constructed has been successfully applied for Cr separation in liquid model samples with ICP-OES and ICP-MS detection. The association of CEFFS-ICP-MS provides excellent analytical sensitivity and detection limits, and shorter analysis times in comparison with other recently proposed methods. The results obtained in this feasibility study should be seen as a first step to a possible development of dedicated equipment for routine speciation of metal species by plasma-based spectrometric techniques. To this end, however, the prototype used in this work should be further improved in order to obtain better analytical performance, especially regarding peak resolution capability, and precision.

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Figures

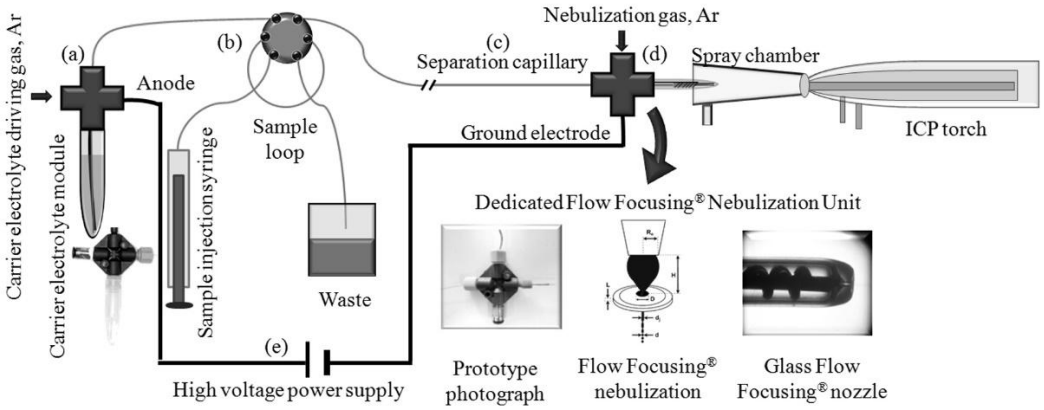

Figure. 1. Scheme of the system prototype and photographs of some system components.

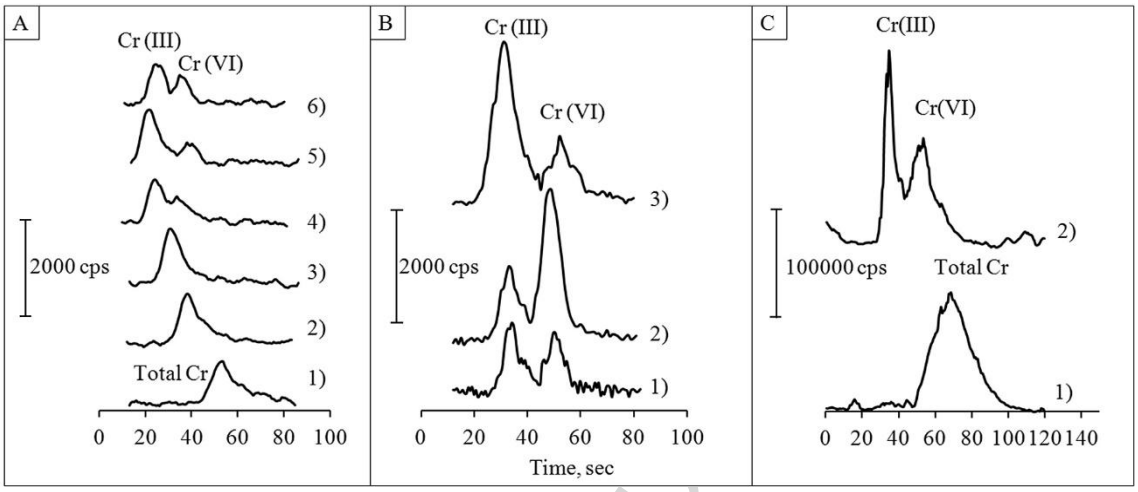

Figure 2. Proof of concept for the strategy applied in this study. A: Injections in ICP-OES; sample Cr(III) and Cr(VI) 10 mg/L each; carrier electrolyte 15 mM HNO_3; injection time 3 sec; separation potential 1) 0 V, 2) 4 kV, 3) 8 kV, 4) 12 kV, 5) 14 kV, 6) 15 kV. B: Injections in ICP-OES; carrier electrolyte 15 mM HNO_3; injection time 3 sec; separation potential 15 kV; samples 1) Cr(III):Cr(VI) = 1:1, 2) Cr(III):Cr(VI) = 1:3, 3) Cr(III):Cr(VI) = 3:1. C: Injections in ICP-MS; sample Cr(III) and Cr(VI) 10 µg/L each; carrier electrolyte 15 mM HNO_3; injection time 3 sec; separation potential 1) 0 V, 2) 15 kV.

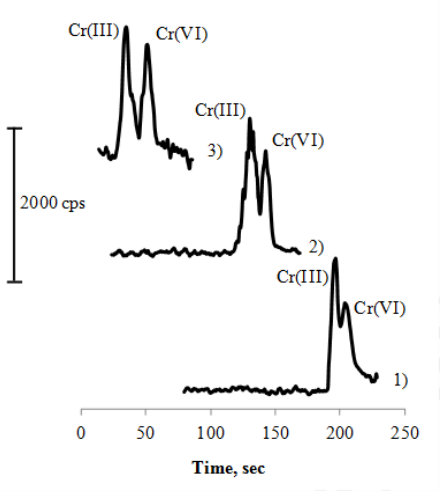

Figure 3. Influence of the separation capillary length on the Cr species separation. Sample Cr(III) and Cr(VI) 10 mg/L each; carrier electrolyte 15 mM HNO_3; flow generating pressure: 1.5 bar; injection time 3 sec; separation potential 15 kV; separation capillary length: 1) 3 m, 2) 2.5 m), 3) 1 m.

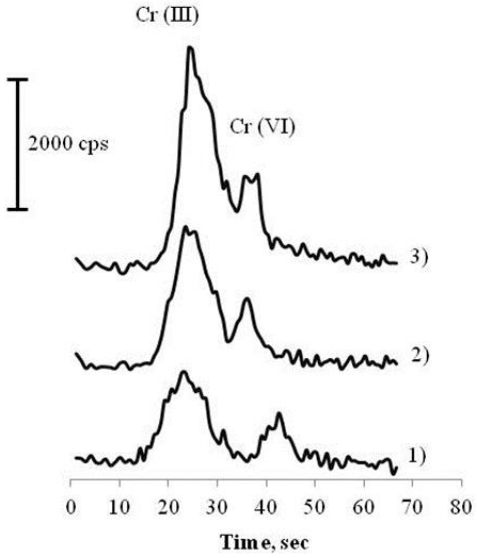

Figure 4. Influence of sample injection time on the Cr species separation. Sample Cr(III) and Cr(VI) 10 mg/L each; carrier electrolyte 15 mM HNO_3; flow generating pressure: 1.5 bar; separation potential 14 kV; injection time:1) 3 sec, 2) 4 sec, 3) 5 sec.

Tables

Table 1. ICP-OES and ICP-MS working conditions, optimized for use with CEFFS.

ICP OES (Perkin-Elmer 4300DV)		**ICP-MS (Agilent 7700)**	
Ar flows	Plasma: 15 L/min Auxiliary: 0.2 L/min Nebulizer: 0.7 L/min	Ar flows	Plasma: 15 L/min Auxiliary: 0.2 L/min Nebulizer: 0.7 L/min Carrier: 0.2 L/min
RF power	1300 W		
Viewing mode	Axial	RF power	1250 W
Integration time /Read time	0.1 sec / 0.4 sec	Dwell time	0.2 sec
Points acquired	300	Run time	300 sec
Emission line	Cr II (267.716 nm)	Isotopes	^{52}Cr, ^{53}Cr

Table 2. Optimum electrophoretic separation conditions used with CEFFS.

Parameter	Value
Separation capillary length	1 m
Carrier flow generation pressure	1.5 bar
Carrier flow	7 ± 1 µL/min
Carrier electrolyte concentration	15 mM, HNO_3
Sample injection time	3 sec
Separation potential	15 kV

Table 3. Analytical figures of merit obtained with the CEFFS in ICP-MS.

Figure	Cr (III)	Cr(VI)	Total Cr
Migration time, sec[1]	34 ± 2	55 ± 2	67 ± 2
Resolution	0.9		--
Sensitivity, cps/ppb[2]	18374	10338	224608
Precision, %[3]	13	12	11
LOD, µg/L[4]	0.1	0.2	0.03

[1]Mean ± standard deviation, n = 3; [2]Calculated using peak height for Cr (III) and Cr (VI) peaks and as peak area for total Cr peak; [3]Expressed as relative standard deviation %, n = 5 (at 10 µg/L for each analyte); [4]Limit of detection, based on 3σ of the baseline signal of 10 points.

Table 4. Comparison of the approach described in this work with other CE-ICP spectrometry couplings reported.

Description	Total run time, sec	LOD, µg/L			Reference
		Cr(III)	Cr(VI)	Total Cr	
CEFFS-ICP-MS	≈ 120	0.1	0.2	0.03	This work
Short column CE-ICP-MS	≈ 60	1.8	1.9	-	[26]
CE–DRC-ICP-MS; derivatization of Cr(III) to Cr(III)-DTPA^{2-}	≈ 140	1.3	0.4	-	[27]
Flow injection with CE-ICP-MS; derivatization of Cr(III) to Cr(III)-DTPA^{2-}	≈ 140	8	6	-	[7]
CE-ICP-OES with home-made prototype interface	≈ 500	1.5	1.8	-	[28]

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Highlights

- A new approach for hyphening capillary electrophoresis with plasma based spectrometry;
- Approach viability for element speciation demonstrated by Cr(III)/Cr(VI) separation;
- Separations in less than 100 sec with excellent detection limits in ICP-MS;
- Potential for development of dedicated devices for routine sample speciation analysis.