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Hyphenation of capillary electrophoresis to inductively coupled plasma mass spectrometry as an element-specific detection method for metal speciation

Bernhard Michalke*, Peter Schramel

GSF Forschungszentrum für Umwelt und Gesundheit GmbH, Institut für Ökologische Chemie, Neuherberg, 85758 Oberschleißheim, Germany

Abstract

A stepwise development for the use of capillary electrophoresis and inductively coupled plasma mass spectrometry (ICP-MS) for speciation investigations is presented. The high resolution power of CE is used for the separation of metal species, whereas ICP-MS is taken for element-specific detection with low detection limits. This contribution starts with an off-line combination of both instruments. Separation and identification of species in model solutions and real samples are shown by scanning UV detection at the CE unit with subsequent metal quantification in peak related fractions, applying electrothermal vaporization ICP-MS. Finally, first separations are demonstrated, using the on-line hyphenation with a laboratory-made nebulizer. Here, standard solutions are separated and monitored by UV and ICP-MS. Stability of electrical current during nebulization was checked and a possibly interfering suction flow was estimated. After optimization sufficient electropherograms were obtained. Advantages and problems are discussed for both modes.

Keywords: Speciation; Detection, electrophoresis; Platinum; Selenium; Metals; Gluthathione; Inorganic ions

1. Introduction

The high separation potential of capillary electrophoresis (CE) makes CE techniques valuable for separations of metal species. The separation of metal ions, of metals with different oxidation states or of organometallic compounds are possible with CE [1–5].

On the other hand, inductively coupled plasma mass spectrometry (ICP-MS) is an element specific multi-element detection method, providing extremely low detection limits. Therefore, the combination of CE with ICP-MS promises a powerful tool for metal speciation [1,2,4].

When using CE for species separation, several conditions are required: (a) The species must not be altered by CE conditions like buffer pH, salt concentrations, complexing agents or high voltage etc. [1,4]; (b) the metal concentration per species must be fairly high, as the total sample intake by CE is usually extremely low (about 5 nl [4], 1–30 nl [6]) without sample preconcentration like stacking. On the other hand [1] describes the possibility of a nebulization efficiency up to (nearly) 100% for a CE–ICP-MS hyphenation. This is contradictory to the "normal" nebulization efficiency of about 2%. The high efficiency results in low detection limits even at low CE sampling volumes.

Detection is carried out by UV [2] (in this work often by a fast scanning UV detector) preferably in addition to subsequent metal detection, e.g. by ICP-MS. The latter can be done "on-line" [1] or "off-

*Corresponding author.

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line", especially when using a graphite furnace for electrothermal vaporization (ETV) at the ICP-MS inlet [4,5]. Peak identification methods are applied additionally as detailed in [3,7].

This contribution describes the stepwise development for the combination of CE with ICP-MS.

1.1. Step 1

Species are separated and differentiated in standard solutions by migration time (t_m) and UV spectra at the CE.

Identification and characterization of species prior to connection to a metal detector are considered to be important and useful for method development [2,8,9].

1.2. Step 2

Peak fractionation at the CE system with subsequent metal quantification by ETV-ICP-MS.

Metal concentrations can be clearly attributed to peak fractions, related directly to UV signals and spectra.

1.3. Step 3

Peak fractionation and element quantification after separation of the species in a real sample, as well as after peak identification [7] and sample stacking [6,10,11]. Separations of molecules (species) in real samples are considered to be more complicated [7,12]. Further, analytes of interest are often present only in low concentrations. Therefore, an on-column preconcentration step (stacking) was applied in analogy to [11,13]. Stacking with discontinuous buffer systems are working in the isotachophoresis (ITP) mode, which is a most promising preconcentration method and effective tool when the analyte is not dissolved in pure water [10,14]. Major compounds are diluted by ITP, whereas trace compounds get enriched by a factor up to two orders of magnitude [6,10,11,13] (e.g: ×200 [9]). But the intactness of the species during the procedure must be given [1] (and was known from primary experiments).

1.4. Step 4

Speciation, using the hyphenation and a laboratory-made nebulizer. Detection is still carried out by UV. Controlling the stability of the electrical circuit during nebulization. A constant current (without breakdowns or too high values etc.) is necessary for an adequate CE performance and is sometimes difficult to achieve ([9], own experiments).

1.5. Step 5

On-line coupling of CE with ICP-MS, using a laboratory-made, modified Meinhard nebulizer. Detection is performed by UV and by the ICP-mass spectrometer. The on-line combination of CE and ICP-MS offers very short analysis times, high species resolution and prompt element detection. The key to a successful coupling of CE with ICP-MS is the interface [1]. Therefore, our nebulizer provides for an exact and optimized positioning of the capillary end to the Ar gas stream, resulting in a minimized dead volume and a high nebulization efficiency.

1.6. Step 6. Optimization of the hyphenation

Although a successful hyphenation and an ICP-MS signal was achieved in our first experiments, the whole system needed further optimization. Solutions had to be found for the (initially) low nebulization efficiency, resulting in a poor signal-to-noise ratio and peak broadening. Further, long migration times had to be shortened.

Off-line combinations of standard solutions and real samples as well as first species separations, using the on-line mode, will be shown.

Se speciation is carried out because Se is essential for humans. Sufficient Se supplementation can protect against several heart diseases and possibly against cancer [15,16]. The bioavailability of Se is dependent on its binding form (species).

Pt is emitted increasingly into the environment. Elevated Pt levels have already been seen in some plants, proving that the path into food chain is possible. This transformation of Pt into bioavailable Pt complexes recommends for a Pt speciation.

2. Experimental

2.1. Sample preparation

Pt–methionine was prepared by mixing $[PtCl_6]^{2-}$ with methionine. The compounds react easily to a Pt–methionine complex [17]. Se(IV) and Se(VI) stock solutions (final concentrations 1 g Se/l) were prepared by dissolving Na_2SeO_3 in doubly distilled water or $Na_2SeO_4 \cdot 10H_20$ in doubly distilled water. Pt standard solution ($[PtCl_6]^{2-}$) was prepared by dissolving 5 mg of the salt in 100 ml double distilled water.

The preparation of the gluthathione (GSH)-containing size-exclusion chromatography (SEC) fraction of human milk followed the descriptions in [7]: Sampling of the human milk was carried out as described in [18]. Pooled human milk was defatted, and milk proteins were precipitated by centrifugation (25 840 *g*, 30 min, 8°C). The supernatant was used for SEC fractionation. The GSH-containing fraction was picked out according to the M_r calibration of the SEC column [3,7].

2.2. Capillary zone electrophoresis (CZE)

A Biofocus 3000 CE system (Bio-Rad, Munich, Germany) was used for the CE experiments. The temperature for carousel and capillary was 20°C, using air cooling for the carousel compartment, but liquid cooling for the total capillary length up to the nebulizer. For this purpose the CE–MS interface from Bio-Rad (slightly adapted to the nebulizer) was used.

The CZE methods for all analytes were derived from [4]: Table 1 gives an overview of the methods. A standard addition of the analytes improved analyte identifications as outlined in [7].

2.2.1. Determination of the CE sampling volume

All instrumental and methodical parameters were set identically to the parameters of the experiments, where the defined injection volume was necessary (same capillary, same temperatures, identical flushing before injection and the same injection mode and time). After injection the capillary was immediately purged with nitrogen into a freshly prepared outlet buffer (400 μl). The additional liquid volume from capillary was negligible (max. 120 cm×50 μm: volume=2.35 μl, <1% of total outlet buffer volume). Then the capillary was flushed with buffer into an empty vial, which was filled up to 100 μl with buffer afterwards. Finally, both vials were transferred to ETV-ICP-MS for element determination. The injection volume was calculated due to the measured Pt or Se concentration, found in the vials (usually no

Table 1
Conditions of the CE separation methods

Sample	Capillary (cm×μm I.D.) c=coated	Injection p.s.i.×s[a]	Stacking yes/no	Leading electrolyte for stacking	Buffers	Polarity
Pt–methionine	36×50/c	25	No	No	Bio-Rad 148-5010, phosphate buffer pH 2.5	+/−
SEC fraction from human milk/GSH	50×50	25	No	No	Bio-Rad 148-5023, borate buffer, pH 8.3	−/+
	50×50	electrokinetic, 120 s	Yes	$HPO_4^{2-}/H_2PO_4^-$, 200 m*M* pH 6, injection 5 s, 8 bar	Bio-Rad 148-5023, borate buffer, pH 8.3	−/+
Se(IV) and Se(VI)	120×50	30	No	No	Bio-Rad 148-5010, phosphate buffer pH 2.5	−/+
Na_2PtCl_6	100×50/c	30	No	No	$HPO_4^{2-}/H_2PO_4^-$, 100 m*M*, pH 6	−/+

Common parameters: Temperature=20°C for carousels (air cooling) and capillary (liquid cooling). Purging before each run: (1) 120 s water; (2) 120 s buffer.

[a] 1 p.s.i.=6894.76 Pa.

Pt or Se was seen in the second vial), according to the given buffer volume and the known concentration in the sample.

2.2.2. Estimation of the preconcentration factor (stacking)

GSH standard solutions (0.3 mg/l and 1 mg/l) were analyzed by CE using the determination method especially developed for GSH [7] and the new developed stacking method for GSH (in analogy to [13]). Peak areas and peak heights of GSH peaks from both methods were compared. The linearity of the UV response was checked by performing a 6 point calibration curve between 0.3 and 300 mg/l, showing a coefficient of 0.997. The preconcentration factor was estimated as 250 ± 11 ($n=4$). These results were considered to be sufficient for the given purpose.

2.2.3. Estimation of a possible suction driven flow by nebulization gas stream

A liquid flow through the capillary, produced by a suction from the nebulization gas stream would be very undesirable. The performance of CE separations could be decreased drastically. For estimation of this possible flow, two experiments were carried out:

1. The capillary was filled with buffer and the inlet tipped into the inlet buffer vial. Then the electrical circuit was checked by measuring the current (19 μA). Then nebulization gas was turned on, while the capillary inlet was kept open in the air. If there was a suction flow, air should enter the capillary. After 60 min the capillary inlet was tipped again into the inlet buffer and the electrical current was measured. In case of a suction flow, an air bubble would be in the capillary and interrupt the electrical circuit. The actual current then would be 0.

2. The second experiment was similar, but instead of keeping the capillary inlet in the air it was tipped into a Se standard solution (1 g/l). After 60 min the capillary was flushed with bidistilled water during nebulization and ICP-MS detection. In case of a suction flow Se standard solution would enter the capillary and Se would be flushed afterwards with the water to ICP-MS.

2.3. Fractionation (off-line mode)

Peak-related fractions were collected into vials at the capillary outlet by the CE device. The vials were filled with 100 μl buffer. The fractions were transferred to the ETV unit of ICP-MS and were measured directly [7,19].

2.4. Hyphenation and nebulization

For hyphenation experiments an "user assembled cartridge" (Bio-Rad), equipped with a capillary, was used. The capillaries used in these experiments were 120 cm×50 μm I.D. (inlet/UV detection: 40 cm, UV detection/nebulizer: 80 cm), uncoated and UV transparent for Se speciation or 100 cm×50 μm I.D. (inlet/UV detection: 39 cm, UV detection/nebulizer: 61 cm) for Pt investigations.

This cartridge is specially designed for CE–MS coupling: The liquid coolant bypasses the UV detection window and leaves the cartridge at the capillary outlet. There the MS interface (predominantly cartridge adapter and tubing for capillary coolant and coolant backflow) fits tightly and leads the capillary and liquid coolant to the nebulizer. Thus, a temperature control along the whole capillary is possible.

The modified Meinhard nebulizer was laboratory-made and specially designed for the requirements of CE–ICP-MS hyphenation. Special care was focused on the possibility of an exact and optimized positioning of the capillary end by a micro screw and on a reliable closing of the electrical circuit of CE during nebulization. A coaxial sheath flow [4 μl/h buffer (cf. Table 1)] round the CE capillary provides the electrical connection from the capillary outlet to the outlet electrode in a buffer reservoir at the end of the nebulizer.

2.5. Se and Pt determination

Off-line mode: Se and Pt determinations have been done by ICP-MS (ELAN 5000, Perkin-Elmer, Sciex, Canada), coupled with a graphite furnace HGA 600 (Perkin–Elmer, Germany) using standard addition method for the quantification [7,19]. ETV was chosen to overcome the well known polyatomic

interferences (Se) and for adaption of the sample intake to the low sample volumes from CE fractions.

On-line (hyphenation) mode: ICP-MS was used with the laboratory-made nebulizer fitting into a zyclon nebulization chamber (Perkin–Elmer) in the graphic mode. Se was determined at $m/z=77$ and 78, Pt at $m/z=195$ and 196. Further instrumental parameters are detailed in [19].

2.6. Chemicals

Na_2SeO_3, $Na_2SeO_4 \cdot 10H_2O$, GSH and methionine were purchased from Sigma (Munich, Germany). The capillaries as well as phosphate buffer (pH 2.5) were bought from Bio-Rad, whereas $H_2PO_4^-/HPO_4^{2-}$ were delivered from Merck (Darmstadt, Germany). The Se and Pt standards as well as $Na_2PtCl_6 \cdot 6H_2O$ were purchased from Aldrich (Steinheim, Germany). The TSK-gel (ToyoPearl HW 40 S) for SEC fractionation was from Toso Haas (Stuttgart, Germany).

3. Results

3.1. Steps 1 and 2

Species are separated and differentiated in standard solutions by t_m and UV spectra at the CE and the peaks are fractionated at the CE system with subsequent metal quantification by ETV-ICP-MS.

Primary experiments showed a total Pt load of 5 ng Pt from the $Na_2PtCl_6 \cdot 6H_2O$ stock solution according to the determination of sampling volume (cf. Section 2.2.1, $n=8$). For Pt quantification, the inlet buffer, peak fractions and outlet buffer were monitored by ETV-ICP-MS.

Fig. 1A shows a successful separation and differentiation of $PtCl_6^{2-}$ (peak 2) from Pt–methionine (peak 1) and of Pt–methionine from methionine (peak 3). The peak identification is successfully carried out by standard additions (not shown) and UV spectra (Fig. 1C–E). After peak fractionation the total Pt intake (5 ng) is recovered, when summing up all fractions. 95% are detected in the Pt–methionine fraction, 5% at $PtCl_6^{2-}$. No platinum was seen in the methionine fraction or in the inlet or outlet buffer vial (Fig. 1F, freshly prepared). After 5 days aging at 4°C in the refrigerator, the solution shows a changed electropherogram (Fig. 1B). The baseline is noisy, the peaks 1–3 are disturbed and new peaks are seen. When peak fractions and buffer vials (in, out) are transferred again to ETV-ICP-MS, the concentration pattern of Pt is different (Fig. 1G): The total sum of platinum remains 5 ng (=100%) but only 20% are attached to Pt–methionine and 2% to $PtCl_6^{2-}$. No Pt is detected in the inlet buffer and at the methionine peak, but 78% were found in the outlet buffer. New Pt species, generated by species transformations during aging of the solution, are separated from peaks 1–3 and therefore are not collected into fractions. They appear in the outlet vial.

3.2. Step 3

Peak fractionation and element quantification after separation of the species in a real sample, as well as after peak identification and sample stacking.

For elucidating whether the off-line combination of CE–ETV-ICP-MS is working successfully even for real samples, we chose a well characterized Se and GSH-containing SEC fraction from human milk (out of the frame work of another speciation project). The Se amount of the total SEC fraction was determined as 0.14 ng (before CE separation). Primary experiments investigated the injection volume and the preconcentration factor according to Sections 2.2.1 and 2.2.2, both necessary for subsequent Se quantification: The injection volume was 5 nl±0.09 nl ($n=8$) in this case and the factor was 250±11 ($n=4$). Fig. 2A shows an electropherogram of this Se and GSH-containing fraction. Peak 5 is identified as GSH by GSH standard addition before stacking (Fig. 2B) and after stacking, too (not shown). After sample stacking (without GSH addition!) peaks are drastically increased in height, whereas the resolution is decreased (Fig. 2C). However, peak 5 (=GSH) remains well separated. After peak fractionation Se was monitored exclusively in peak fraction 5. Quantification and calculation due to the CE sampling volume and preconcentration results in a Se content of 0.12 ng. This Se amount of peak fraction 5 corresponds well to 0.14 ng, which is the Se

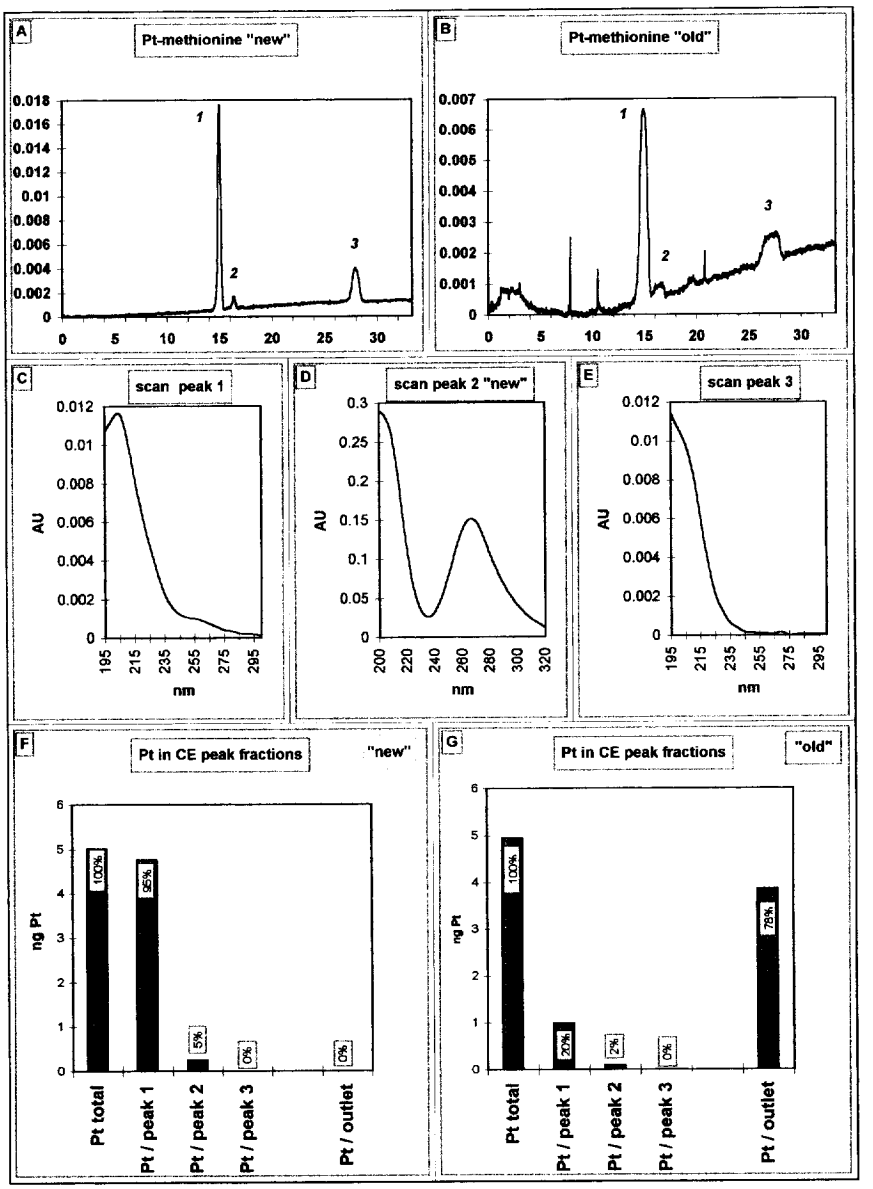

Fig. 1. Electropherograms of a new (freshly prepared) and 5-day-old solution of Pt–methionine (peak 1), Na_2PtCl_6 (peak 2) and methionine (peak 3) are shown in (A) and (B). The peaks were identified by standard addition and by characteristic UV spectra (C–E). Total sample intake was 5 ng Pt ($n=8$); 4.75 ng Pt were found in the peak fraction 1; 0.26 ng Pt in fraction 2 and no Pt was seen in peak 3 (new). After 5 days, several UV peaks were seen. Only 1.1 ng Pt were detected in peaks 1 (1 ng) and 2 (0.1 ng), 3.86 ng Pt were not peak fractionated and reached the outlet buffer. In total, the mass balances added up to 100% (new and old).

amount of the total SEC fraction. Thus, the off-line combination of CE–ETV-ICP-MS shows impressively that Se is quantitatively associated with GSH in this real sample.

3.3. Steps 4 and 5

Speciation, using the hyphenation and a laboratory-made nebulizer. Detection is still carried out by

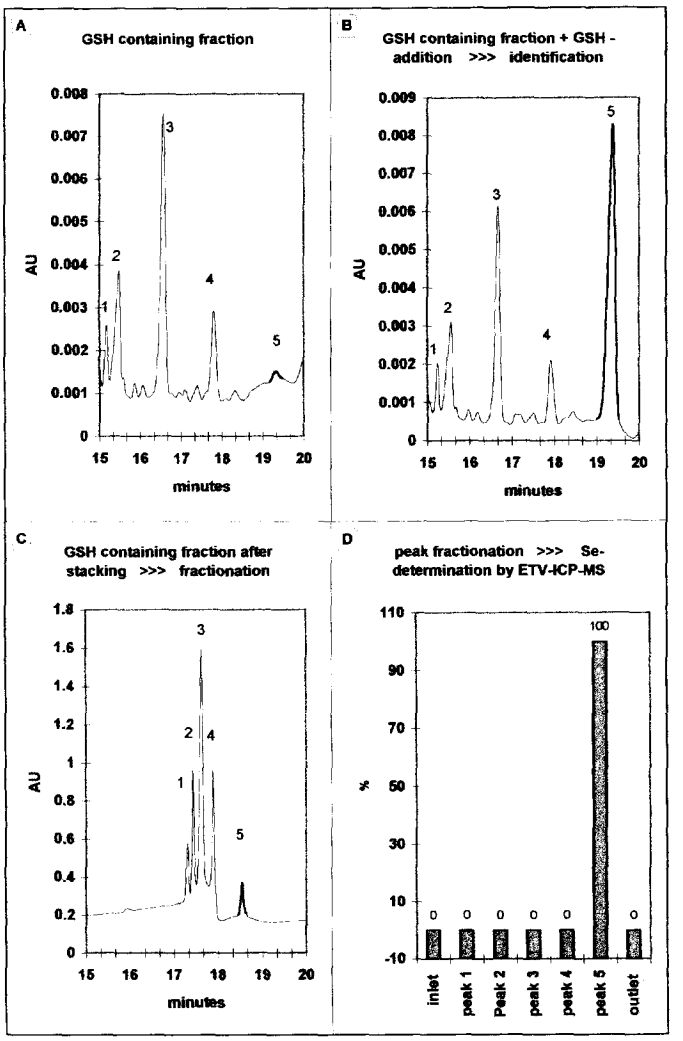

Fig. 2. An electropherogram is shown from a human milk fraction (A). Total Se in the fraction is 0.14 ng. The marked peak increased in height after the addition of GSH (B), identifying this peak by the method of GSH standard addition. (C) Electropherogram of the human milk fraction after sample stacking. Fractions were collected from peaks 1–5 ($n=5$). Se was determined by ETV-ICP-MS in the five peak fractions and in the inlet and outlet buffers. Se was found only in fraction 5 (D). The Se content of peak 5 was calculated due to the CE sampling volume and the preconcentration factor from stacking as 0.12 ng.

UV. Controlling the stability of the electric circuit during nebulization. On-line coupling of CE with ICP-MS, using a laboratory-made, modified Meinhard nebulizer. Detection is performed by UV and by the ICP-mass spectrometer.

A necessary precondition is a minimized suction flow. The two experiments (see Section 2.2.3: measuring electrical current and possible Pt intrusion into the capillary) indicated that there was no detectable suction flow. Electrical current again was about 20 μA after keeping the capillary inlet into air and no Se was detected when finally flushing the capillary after the second experiment.

Current stability: After an optimized positioning of the capillary end, the electrical current was nearly constant during nebulization. Fig. 3 shows the very first hyphenation experiment. The upper part demonstrates the separation of Se(VI) and Se(IV) (UV

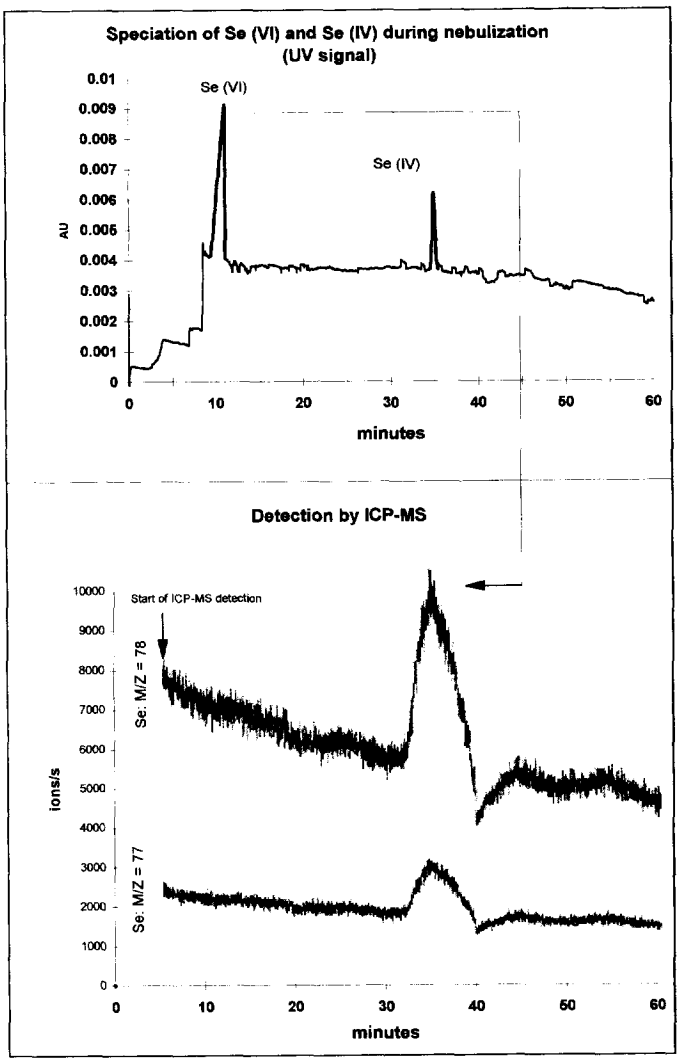

Fig. 3. The very first hyphenation is shown, separating Se(VI) and Se(IV). The UV signal demonstrates two peaks at 12 and 35 min. Se(IV) (50 mg/l) is known to show a 10 times higher UV response than Se(VI) (1 g/l). Therefore, the Se concentration of the latter is 20 times higher than that of Se(IV). The lower part shows the ICP-MS signal. According to capillary length (inlet/UV=40 cm, UV/nebulizer=80 cm), the time difference between UV detector and elemental detector is bigger than expected before the first experiment. Unfortunately, the run was terminated automatically after 60 min before Se(IV) reached the nebulizer. The peak width at ICP-MS is still unsufficient, probably due to a sub-optimized positioning of the capillary end during this first hyphenation attempt.

signal), using the laboratory-made nebulizer at the capillary outlet. The electrical current was stable at 21 μA, drifting to 23 μA within 60 min.

Fig. 3 (bottom) shows the Se signals from ICP-MS of the upper run. Due to hyphenation, there is a time difference between UV detector and elemental detector. The run was terminated automatically after 60 min, as the time delay between UV and ICP-MS was not expected to be so long before the first experiment.

Fig. 4 shows the electropherogram of Na_2PtCl_6 with UV and element-specific detection. The marked UV peak of Na_2PtCl_6 and the marked peak from ICP-MS are well corresponding, showing that the hyphenation is working well in this case. Peak width of both UV and ICP-MS are sufficient. In addition,

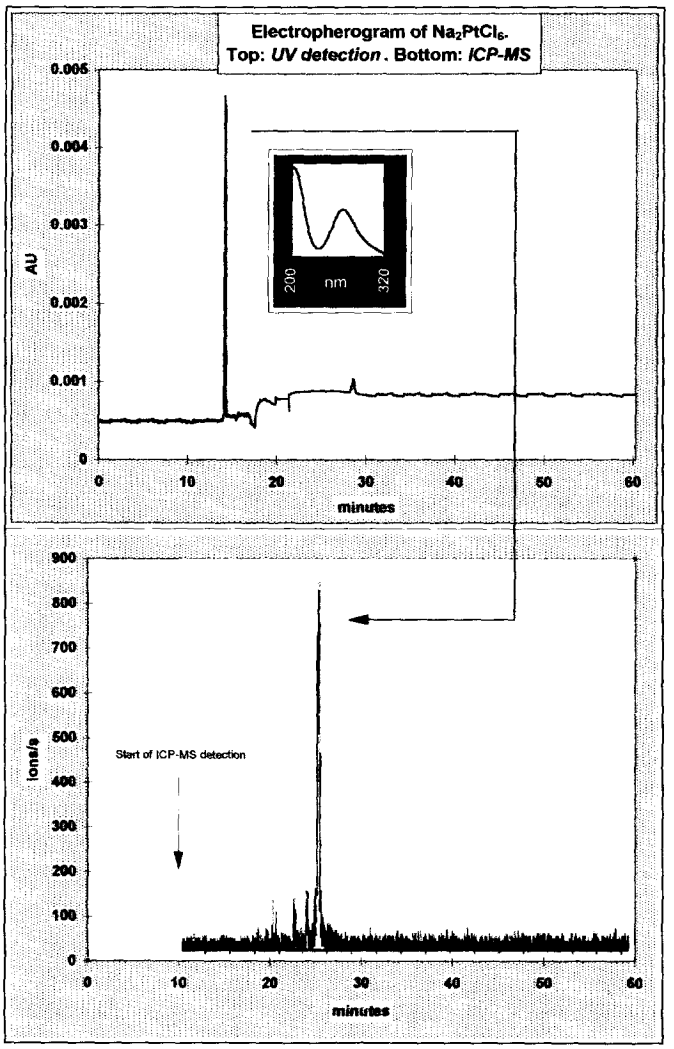

Fig. 4. An electropherogram of Na_2PtCl_6 (100 mg/l) is shown. Top: the UV detector monitors the peak at 14 min with a UV spectrum known for Na_2PtCl_6 (window in Top). ICP-MS shows Pt around 25 min. This delay is due to the additional capillary (61 cm) from the UV detector to ICP-MS. Because of a better positioning of the capillary end, the peak width at ICP-MS is now sufficient.

the UV spectrum of the peak shows the characteristic course of Na_2PtCl_6 indicated in the "window" in Fig. 4 (top).

3.4. Step 6. Optimization of the hyphenation

Fig. 5 demonstrates an optimized attempt for the on-line combination, using Se(VI) as a sample. Although the sample has the same concentration as Se(VI) from Fig. 3, the peak width and signal-to-noise ratio looks well now. The time delay between UV detection and ICP-MS is again around 25 min.

4. Discussion

4.1. Off-line combination

The off-line mode has shown to be a useful tool for easy species separation and quantification. Espe-

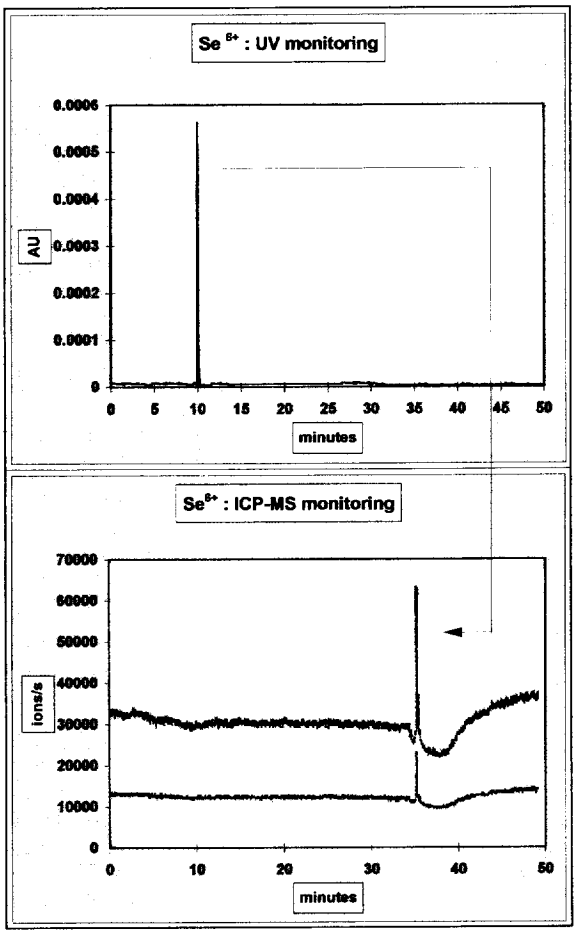

Fig. 5. A repetition of the hyphenation for Se(VI) is shown. The UV-detected electropherogram now shows a clear course without alteration of the baseline or (slight) peak fronting. The ICP-MS signal demonstrates a sufficient signal-to-noise ratio and a very small peak width. These improvements are due to an optimized position of the capillary end to the nebulizer as well as to a better position of the nebulizer to the cyclon chamber.

cially, when analyzing only few (stable) substances in a sample, this method can easily be applied. Molecules are separated and identified by t_m, UV spectra and by their metal content. This procedure is a valuable advanced development of the works of [2,4,7]. Many problems like current stability, suction flow or capillary cooling to the nebulizer can be avoided in contrast to an on-line hyphenation. Further, species transfers, that are slow compared to analysis time, can be monitored easily as demonstrated in Fig. 1. After 5 days aging, the sample shows new peaks and Pt has turned almost quantitatively to peaks other than 1–3. When looking at the analysis of a real sample (Fig. 2), the results look very promising. Although the total Se content of the sample is low (0.14 ng), fractionation still gives positive Se results. They are in good accordance with the total Se amount. Here, absolute evidence was possible for the quantitative association of Se with GSH in this sample. Sample stacking by on-line ITP–CZE [9,13,14] was absolutely necessary for a quantitative analysis. The preconcentration factor of about 250 is in the same range as [9]. But there are some drawbacks: When there is a multitude of peaks, fractionation gets increasingly difficult and a fraction change between two molecules, which are just or nearly baseline separated, is hardly performed [13]. Here, Fig. 2C gives an example. In this case no Se was seen in any of the close migrating peaks 1–4 and peak 5 was at a clear distance. Therefore, Se was attributed to peak 5 without doubt. Further, species transformations will not always result in new UV-responding molecules. Therefore these substances will not be fractionated and quantified, appearing with other UV transparent species in the outlet buffer.

For quantitative aspects a lot of primary results have to be obtained, such as a definite sampling volume and the determination of the preconcentration factor.

4.2. On-line mode

The more elegant, but complicated way, is the on-line hyphenation of CE with ICP-MS. But here problems arise, concerning the CE part as well as the nebulization/ICP-MS part. A stable and reliable electrical current along the capillary is necessary for separations. On the other hand, the current must not increase too much, because this results in heat production and band broadening [1,2,8]. During nebulization experiments the current remained below 25 μA and the capillary was actively liquid cooled. To avoid interferences to the experiment, current should be below 18 μA, capillary not cooled([8]). In contrast to [1] we could apply higher voltage (and achieved higher V/cm) for better separations, according to the liquid cooling of the capillary.

The capillary end is positioned at the Ar-nebulizer

gas stream, which makes the closing of the electrical circuit difficult. Further, the separation may be disturbed drastically by a suction flow. On the other hand, nebulization is most effective, when the capillary end stands far into the nebulization gas stream. But this position negatively affects the reliability and stability of the electrical current. Fig. 3 shows an example for a de-optimized position of the capillary end to the Ar gas stream. Obviously, the position of the capillary end and the flow rate of nebulization gas stream result in a poor nebulization efficiency [1] and in an alteration of the separation (UV: fronting of Se(VI) and the UV signal in total. The signal height is low for the high Se concentration. However, Se is an element, which is less optimal for detection with ICP-MS, as the most abundant isotope ^{80}Se interferes with the ^{40}Ar–^{40}Ar cluster and the isotopes ^{77}Se and ^{78}Se show relative abundances of only 7.9% or 23.6%. Further, the well known polyatomic interferences ($^{77}Se<<>>^{40}Ar^{36}Cl^{1}H$ and $^{78}Se<<>>^{40}Ar^{36}Cl^{1}H^{1}H$) for Se [7] cannot be excluded, as the on-line mode works without ETV. The peak width in Fig. 3 is huge, demonstrating that there is still a dead volume [1] and the aerosol remains for a long time in the cyclon nebulization chamber.

It should be noted, that Fig. 3 shows the very first performance of an hyphenation. Taking this into consideration, Fig. 3 looks promising.

After a more optimized positioning of the capillary end, detection quality increases, as shown in Fig. 4. The marked UV peak as well as the Pt peak at ICP-MS show very small peak widths. UV and ICP-MS detection correspond well. A first estimation of detection limits (3 σ) comes to about 5 mg Pt/l. This does not look spectacular, but reasons for the relatively high detection limit are given by a small injection volume and bad nebulization, due to damage to the nebulizer after the first experiment. The repetition of the Se(VI) electropherogram leads to an acceptable UV and m/z signal after an optimized positioning of (1) the capillary to the nebulizer and (2) the nebulizer to the cyclon chamber. Fig. 5 demonstrates that there is still a big potential for decreasing the detection limits. Latest experiments with a new nebulizer point to (preliminary) detection limits in the middle μg/l range (100–500 μg/l). Comparing the detection limits with those of [1] they are still higher. [1] gives ranges 60 to 200 times worse than with normal nebulization (without CE speciation, probably up to 100 μg/l). This can be due partly to the sampling volume being 8–10 times higher [1] than we used in our experiments. The differences in time delay between Figs. 3 and 4 are explained by the different capillary lengths from UV to the nebulizer and by the coating of the capillary, used in Fig. 4. Further developments concerning the shortening of analysis times point to a time reduction up to a factor ≈6. (e.g. Se(VI): UV/ICP-MS>>10 min/36 min, now: 1.6 min/5.9 min and Se(IV): UV/ICP-MS>>34 min/119 min, now: 5.6 min/19.7 min; not shown). Future optimizations will improve low detection limits valuable for real samples as well as reduced migration times. At last, the analytical power of this hyphenation will be tested on real samples.

5. Conclusions

The stepwise development of the combination of CE and ICP-MS leads to a successful off-line mode as well as to a successful hyphenation and on-line coupling. The results shown are still absolutely preliminary. Extensive optimizations and further developments will follow, aiming at more resolution, better nebulization and lower detection limits as well as shorter analysis times. Finally, applications of real samples will be carried out in future.

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