

Element-sensitive X-ray detection for capillary electrophoresis

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Received 27 July 1995; revised 20 September 1995; accepted 3 October 1995

Abstract

The application of metal-sensitive and -specific detection systems could essentially increase the information content of the results from high-resolution separation systems used for the determination of different metal-containing species (e.g. in medicine, ecology, biochemistry). Many separations are performed in capillaries or miniaturized systems (GC, CE, microbore HPLC) which possess very low detection volumes in the nanolitre region. For the generation of detectable X-ray signals from the analytes inside the capillary PIXE (proton-induced X-ray emission) was used after the pretreatment of the capillaries by laser ablation or with etching solutions. The coupling is demonstrated by signals achieved for a pressure-driven capillary system as well as for CE using capillaries with 75–100 μm I.D. The influence of capillary pretreatment and the design of the PIXE measuring chamber on the signals is demonstrated. With the introduced experimental setup the limits of detection have been 10^{-5} M or less for various metals, e.g. As, Cu, Fe, Ni, Pb, Rb, Y and Zn. A comparison with direct and indirect UV detection modes is performed and examples for the speciation of arsenic and lead compounds are discussed as well as potentialities for the improvement of the technique and the decrease of the limit of detection of the analytes.

Keywords: X-Ray detector; Proton-induced X-ray emission; Detectors, electrophoresis; Heavy metals; Arsenic; Lead; Metal ions

1. Introduction

Capillary separation systems (CE [1–3], GC [4]) are characterized by very low detection volumes, which makes the application of highly sensitive detection systems necessary. In most cases UV–Vis or fluorescence detection is applied, using the direct or indirect detection mode. Especially when analyzing metal-containing species derivatization is often impossible and the indirect detection modes are

unable to supply satisfactory information about the separated species. No direct information about the metal in a compound is available, though this is mainly responsible for the chemical and biochemical behavior of this substance in samples of biological or ecological origin. Therefore the application of a metal-sensitive and -specific detection system could increase the information content of a separation significantly.

A metal-specific signal can be generated using X-ray excitation or atomic spectroscopy. Due to the extremely low amount of detectable volume especial-

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ly in high-resolution capillary techniques (<1 nl/s) common atomic spectroscopy and excitation by an X-ray tube are unable to provide the desired signals.

First promising results for the coupling of CE systems with miniaturized inductively coupled plasma-mass spectrometric (ICP-MS) detection systems have been published recently [5].

If the generation of the X-rays is performed using accelerated ions or synchrotron radiation a high amount of energy density is available and even with only nanolitres of sample volume detectable X-ray emission signals can be produced. Under the aspect of multielement capability and availability the application of accelerated ions provided by a PIXE system (proton-induced X-ray emission) [6,7] will be preferred, because all elements with an atomic number higher than $Z=14$ can be detected simultaneously and the signal from the capillary wall can be depressed to a large extend.

The first attempts to couple capillary systems off-line with PIXE [8–23] have been done using isotachopheresis (ITP) for the separation step, followed by an accumulation of the sample zones and the PIXE detection of the dried samples. Unfortunately, the successful separations achieved with the electrophoretic technique are partly destroyed by the fractionation step and the following transfer of the fractions to a filter system suitable as target during the PIXE analysis. Therefore, an on-line detection system should be preferred.

For the on-line generation of the X-rays during the separation experiment the ion beam has to pass the capillary wall. Therefore it must be examined, if accelerated ions after passing the capillary wall are able to generate detectable X-rays despite of the loss in energy.

The paper presents an on-line PIXE detector for capillary methods and first successful tests of this detector in combination with a capillary zone electrophoresis (CZE). Information about the process of capillary preparation and the construction of the measuring chamber are included as well as examples for the separation and speciation of metal-containing samples. For the same mixture of metals the detection power of the PIXE system is compared with direct and indirect UV detection. Critical assessments of further applications and improvements of this system are discussed.

2. Experimental

2.1. Materials

The chemicals used were of analytical grade. Only triply distilled water was added to all buffers and standard solutions.

The etching mixture HF/NH₄F, glacial acetic acid, NaAsO₂ (solution), H₃AsO₄, Pb(NO₃)₂, Cu(NO₃)₂·3H₂O, Zn(CH₃COO)₂, Ni(NO₃)₂, FeCl₃, RbCl, HCl, NaOH, Na₂HPO₄, H₃BO₃, Na₂B₄O₇·10H₂O and creatinine were purchased from Merck (Darmstadt, Germany) as well as Na₂CrO₄, hexadecyltrimethylammonium bromide (HTAB) and tris-(hydroxymethyl)aminomethane (Tris). α -Hydroxyisobutyric acid (α -HIBA), polyethylene glycol 6000 (PEG) and 8-hydroxyquinoline-5-sulfonic acid (HQS) were obtained from Fluka (Buchs, Switzerland) and Y₂O₃ from Aldrich (Steinheim, Germany).

Capillary material of 75 and 100 μ m I.D. with different outer diameters was purchased from CS Chromatographie Service (Langerwehe, Germany) and J&W (Folsom, CA, USA). The total length of the capillaries for the PIXE measurements has been set between 50 and 90 cm with the detection window at 30 to 70 cm. To perform the direct and indirect UV detection, the capillaries have been used with a total length of 57 or 67 cm. The detection window was mounted at 50 or 60 cm length, respectively.

2.2. Apparatus

The pressure-driven experiments and the electrophoretic separations with PIXE detection have been performed on a self-made apparatus. Its set-up can be properly fitted to the vacuum chamber. For the adjustment of the pressure N₂ was used. It has been applied to rinse the capillaries as well as to perform pressure injection at a constant pressure of 15 kPa with following electrophoretic separation or pressure-driven experiments. For the generation of the electric field a HCN 7E-35000 power supply (F.u.G. Elektronik, Rosenheim, Germany) was purchased. The UV detection of the CZE measurement was performed on a P/ACE 2100 from Beckman Instruments (Palo Alto, CA, USA) equipped with fixed wavelengths.

The PIXE experiments have been performed on the 2-MeV Van de Graaff accelerator at the University of Leipzig. The proton beam with an energy of 1700 keV was collimated to a diameter of 400 μm using a set of 3 diaphragms. Using etched capillaries, the proton energy inside the capillary is about 1.2 MeV. The proton-induced X-rays were detected with a low-energy Ge (LEGe) detector through the backside of the experimental chamber using two different geometric arrangements at 90° and 180° in comparison to the incident ion beam. For all parts of the apparatus material of high purity was selected.

For pressure-driven and electrophoretic experiments the X-ray signal was accumulated for 10 s or after an accumulated charge of 6 μC and stored on a hard disc drive for later evaluation. The after that calculated netto areas of the K_α - or L_α -line of the characteristic X-rays were figured as 'counts' (Fig. 3b, Fig. 4b, Fig. 5b). Because of time-depending inhomogeneities of the ion beam only the detection of the charge makes a comparison of different spectra possible. During the measuring process the proton current of 150 nA was kept as constant as possible.

3. Results and discussion

3.1. Preparation of the 'ion windows'

To guarantee the excitation of sample components inside the capillary, the wall thickness has to be lowered down below 10 μm , thus generating the so-called 'ion window'.

Two different procedures were tested. First, an ion window was produced by laser ablation using a Q-switched ruby laser. Unfortunately, a lot of negative influences on the reproducibility of the hole preparation have been observed, which were accounted to the applied laser parameters, the capillary geometry, the composition and the color of the capillary coating and even to the properties of the surface on which the capillaries were mounted during the laser experiments. Therefore the laser ablation technique under simple conditions is not suitable to prepare ion windows with desired dimensions.

Secondly, after the removal of about 5 mm of the polyimide coating of the capillary the quartz material was etched down to a wall thickness of less than 10 μm at a constant temperature of 23°C. Depending on the original wall thickness, after 30 or 60 min the remaining wall thickness was determined using a microscope. The performed experiments demonstrate convincingly that the wall thickness can be decreased very reproducibly in this way. The slope of the curve is influenced by the capillary material, due to slight differences in the production procedures of the different manufacturers or the quality of the used original quartz material. At constant temperature the wall thickness is proportional to the etching time and can therefore be prepared according to the needs. Correlation coefficients (wall thickness versus etching time) of $k=0.9999$ and etching rates between 10 and 13 $\mu\text{m}/\text{h}$ using the described etching mixture could be obtained. For all further experiments, capillary material was prepared using the etching technique.

Because the capillary with the 'ion window' is very sensitive to breakage, it has to be fixed by an adhesive on a silica slice (180° arrangement) or on a acrylic glass holder (90° arrangement) after the etching procedure. Due to the fact, that an excitation of the adhesive by the ion beam during the experiments cannot be excluded, only adhesives without any inorganic impurities could be used.

Capillaries prepared in this way possess enough mechanical stability to allow easy handling and to withstand more than 50 h real proton beam time at a current density of about 1 $\mu\text{A}/\text{mm}^2$ and an input energy of 1800 keV.

3.2. Configuration of the experimental chamber

In Fig. 1a the fundamentals of X-ray emission during bombardment with an ion beam are illustrated. For the detection of the generated element-specific X-rays the detector can be set to 45°, 90° and 180° with respect to the incident ion beam.

The different cell designs for the measurements are shown in Fig. 1b. An 180° arrangement of the incident ion beam and the LEGe detector was preferred (Fig. 1b, part A) for the determination of X-rays with energy >8 keV. The capillary has to be mounted on a silicon slice (99.9999% Si, 160 μm

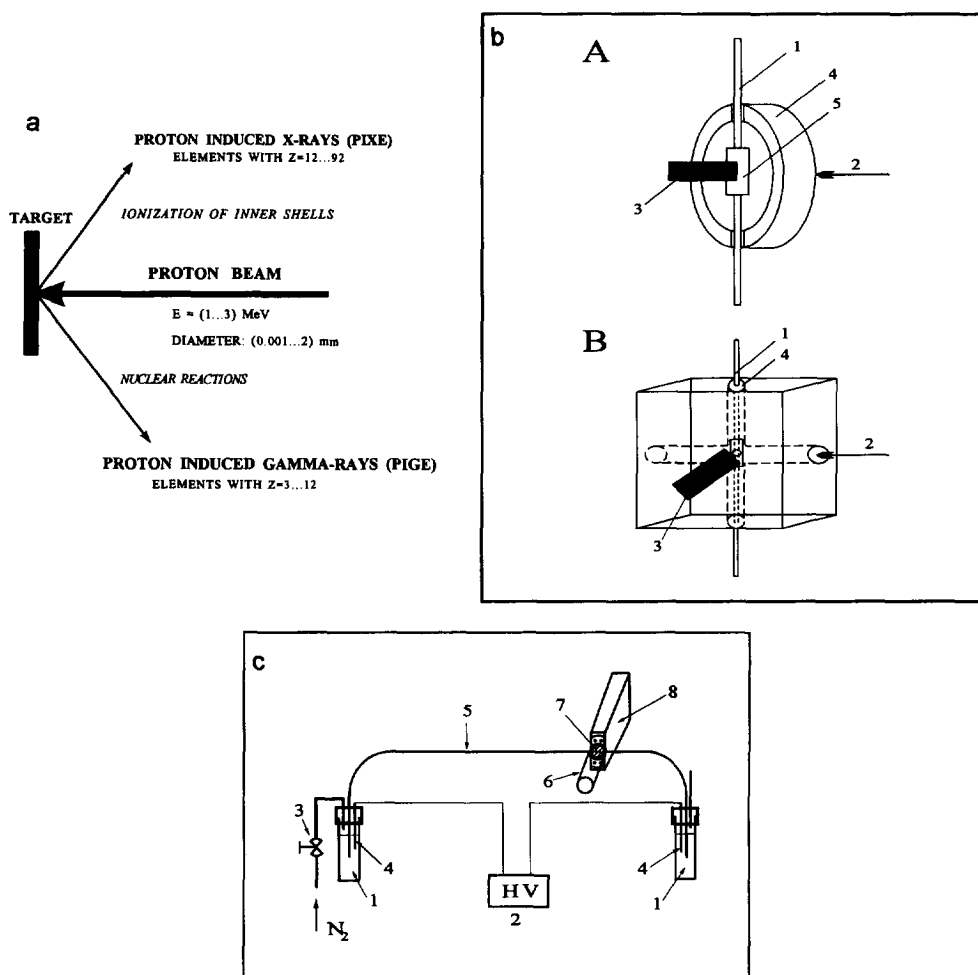


Fig. 1. (a) Fundamentals of PIXE and PIGE. (b) Detector arrangement A: 180° angle setup, B: 90° angle setup. 1=Capillary with 'ion window', 2=incident ion beam, 3=Si(Li) or Ge detector, 4A=aluminum beam tube, 4B=silicon gum, 5=160- μm silicon slice. (c) Configuration of the coupled CZE separation and PIXE detection system: 1=buffer reservoirs, 2=high-voltage power supply, 3=needle valve and pressure regulation system, 4=Pt electrodes, 5=quartz capillary with 7='ion window', 6=Si(Li) detector, 8=incident ion beam inside the beam tube.

thickness) for stabilization and sealing of the vacuum system in which the ion beam is focused on the capillary. The silicon between the capillary and the detector absorbs the X-rays with energy $<8 \text{ keV}$ to a high extent and Bremsstrahlung is generated inside by the accelerated ions, which pass the capillary without interaction. Nevertheless, because the intensity of the X-rays is decreased by the square of the distance, the very close position of the quartz capillary and the detector (5 mm) allows a sensitive detection of the generated X-rays with higher energy.

The 90° arrangement is shown in Fig. 1b, part B. At this chamber the capillary is mounted on an acrylic glass holder. Due to constructional conditions the distance between the capillary and the detector is about 4 cm. Therefore the intensity of X-rays reaching the detector is drastically reduced. On the other hand this construction offered the possibility to change the silicon slice in front of the detector entrance for a Mylar foil (8 μm thickness) thus reducing the absorption of lower-energetic X-rays. Furthermore the Bremsstrahlung generated in the

capillary holder of the 180° arrangement does not appear. The only detectable Bremsstrahlung background is produced inside the capillary material and the sample solution.

The configuration of the coupled separation and detection system is shown in Fig. 1c. Instead of an UV or fluorescence detector the vacuum system of the ion beam generator and an X-ray detector are coupled to the capillary. The N₂-pressure system with a needle valve allows to push the sample solutions or rinsing liquids through the capillary.

3.3. Pressure-driven experiments

These experiments were performed to test the quality of the prepared 'ion window', the sensitivity of the detector, the detector arrangement (90°/180°) and the possibility to get a sufficient sample signal within short analysis times, which is a requirement for the application of the PIXE detection to separation units.

Prior to each injection the capillary was rinsed with 1 M NaOH for 5 min, followed by a 10-min rinsing step with 10 mM EDTA. Next the capillary was filled with the sample using a constant pressure of 20 kPa. The system was allowed to equilibrate and not later than after 2 min the spectrum of the sample components was recorded.

In Fig. 2 the PIXE spectrum of a sample containing a 0.5 mM concentration of Cu, Fe, Ni, Pb and Zn ions is shown. On the abscissa the number of detected X-rays is expressed as counts. On the axis of ordinates the detector channels, each of which is correlated with a fixed energy value of the generated X-rays, are printed. The Bremsstrahlung background in the region of lower energy (channel 50–110) is generated inside the capillary wall (3 μm thickness) and the buffer solution in the capillary and must be accepted during each measurement. Nevertheless, under the given measuring conditions (90° arrangement of the measuring chamber) elements with a characteristic X-ray energy below 8 keV, like Cu, Fe, Ni and Zn, could be detected down to 0.01 mM concentrations, which was impossible using the 180° arrangement of incident ion beam and detector.

The pressure-driven experiments have confirmed the possibility to obtain element-specific signals

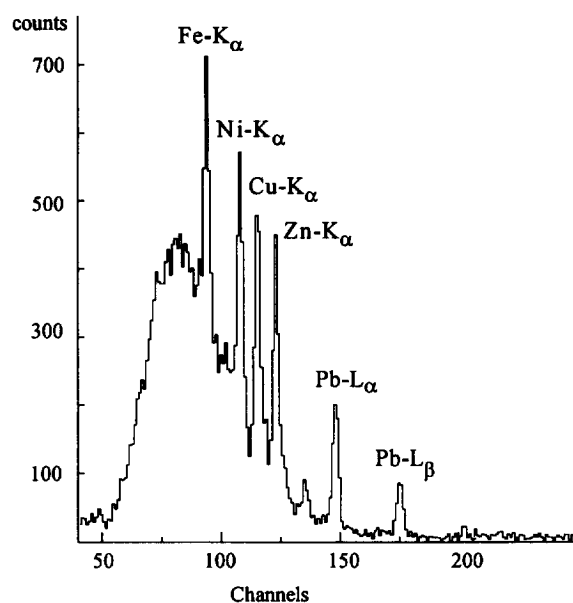


Fig. 2. X-ray spectrum of a pressure-driven sample passing the 'ion window' capillary parameter: $l=70$ cm, $100\ \mu\text{m}$ I.D., $106\ \mu\text{m}$ O.D. ('ion window'), $p=20$ kPa, detector arrangement 90° , $6\ \mu\text{C}$, sample concentration $5 \cdot 10^{-4}$ M each metal (Cu, Fe, Ni, Pb, Zn).

within short analysis times; this makes the system suitable to couple it to capillary separation units.

3.4. CZE with X-ray detection

The incident ion beam hits not only the sample components inside the capillary but also the solvent, e.g. water and buffering ions. In addition to the insignificant heating of the solvent by the ion beam the high inherent energy of the accelerated ions results in a decomposition of the water molecules (radiolysis), thus generating oxygen and hydrogen. The small bubbles formed interrupt the charge transport inside the electrophoretic separation unit. Therefore a real on-line separation and detection using the introduced construction is impossible. The electrophoretic separation of the samples was performed until the first sample zone was near the PIXE detector. After the switch off of the high voltage, a constant pressure of 10 kPa was used to move the separated zones through the PIXE detector. All separations have been performed with voltages <10 kV to avoid a voltage breakthrough between the

capillary and the Si and Al slice (likely only in the 180° arrangement) and to guarantee the comparability of the results measured with both detection chambers.

3.4.1. Detection at the 180° arrangement

For the first CZE–PIXE experiments a simple sample composition of three metal ions with differences in charge and the complexing behaviour have been selected. From Rb, Pb and Y characteristic X-rays with an energy >8 keV can be generated thus making them suitable for the detection under the above-mentioned conditions. The separation was optimized using an UV detector of a commercial instrument. The metal cations form complexes with the buffer components acetate and α -hydroxyisobutyrate. Depending on the complexing properties, an average number of ligands is bonded [13] to the complex, thereby decreasing the positive charge of the central ion to a magnitude between zero and one. Indirect UV detection has to be performed, since uncomplexed and complexed ions do not possess sufficient absorption properties for a direct detection in the UV–Vis region. From the UV signals obtained during the separation (Fig. 3a) in the commercial apparatus the migration times of the separated ions have been determined. The expected migration times in the home-made system, which was coupled to the PIXE detector, were calculated for each ion using Eq. (1) and Eq. (2),

$$v = \mu E = \mu \frac{U}{L} = \frac{l}{t} \quad (1)$$

$$\frac{U_1 t_1}{L_1 l_1} = \frac{U_2 t_2}{L_2 l_2} \quad (2)$$

where v is the velocity of the separated ions, μ is the electrophoretic mobility, E is the field strength, U is the applied voltage, l is the capillary length to the detector, L is the capillary length of the whole capillary and t is the migration time of the ion to the detector. The subscripts 1 and 2 are related to both different capillaries used for UV and PIXE detection. The separation was stopped some seconds before the first signal reaches the detector. After the switch off of the high voltage the separated sample components

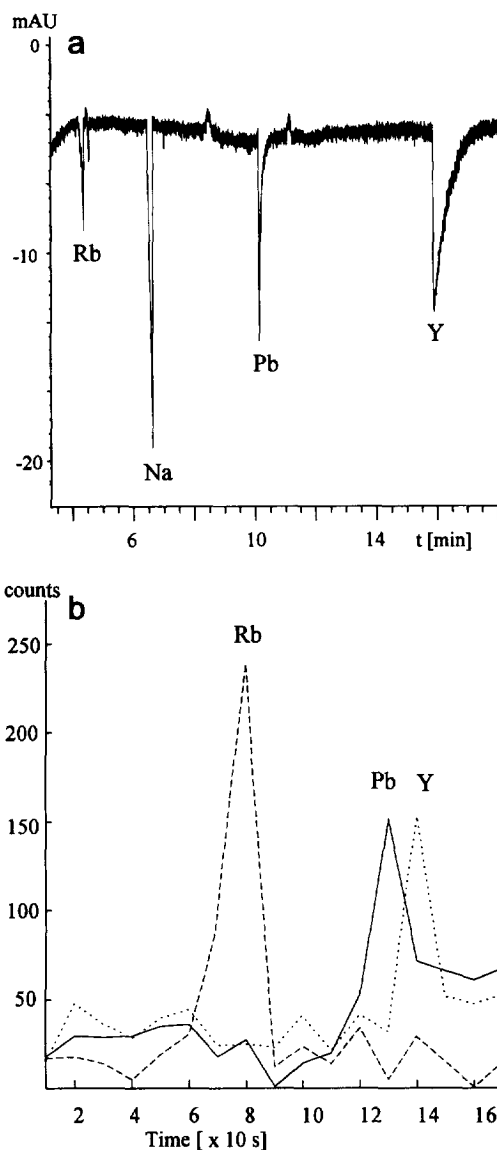


Fig. 3. (a) CZE with indirect UV detection buffer: 30 mM creatinine, 5 mM α -HIBA, 30 mM acetic acid, pH 4.50; sample concentration 0.5 mM for Rb⁺, Pb²⁺ and Y³⁺; $l=60$ –67 cm, 100 μ m I.D., $\lambda=214$ nm, separation voltage 29 kV, 10-s pressure injection. (b) CZE with PIXE detection buffer: 30 mM creatinine, 5 mM α -HIBA, 30 mM acetic acid, pH 4.50; sample concentration 0.05 mM for Rb⁺, Pb²⁺ and Y³⁺; $l=50$ –70 cm, 100 μ m I.D., 106 μ m O.D. ('ion window'), electrokinetic injection at 3.5 kV for 87 s; separation voltage 3.5 kV for 15 min; $p=10$ kPa.

were pushed through the detection window by a pressure of 10 kPa. In Fig. 3b the simultaneously collected PIXE spectra from the Rb, Pb and Y channels are shown. The X-ray spectra were accumulated for 10 s and stored on a hard disc. Despite of the loss in resolution all three components are well separated. The high peak width of all three peaks results from the lower applied voltage for the separation and the superimposed hydrodynamic flow profile due to the detection of the pressure-driven sample zones. In addition the worse resolution for Pb and Y could be reduced to the transient state of separation for both elements due to the shorter separation time in comparison with the separation detected by UV. Consequently, a loss in resolution for the longer migrating sample components was observed for all analyzed samples.

The different sample concentrations applied do not influence the peak resolution, because the original distance between the individual peaks are relatively high and the complexing ligands are present in high excess.

3.4.2. Detection at the 90° arrangement

To demonstrate the better detection abilities for elements with characteristic X-ray below 8 keV a mixture of 5 elements including lead, which was measured even with the 180° arrangement was selected. The metals form strong complexes with 8-hydroxyquinoline-5-sulfonic acid (HQS), thus making a detection at the maximum absorbance at 254 or 375 nm possible. Using UV detection at 254 nm the described separation [14] was optimized by changing the buffer composition. In Fig. 4a the separation of the five metal ions as their complexes under optimized conditions are shown. The signals marked with the letter 'R' can be related to the complexing agent. In the case of the lead complex no adequate increase of the peak area was observed after the addition of supplementary lead to the sample. Due to the ability to form stable complexes even with the buffer anions phosphate or borate [15], the formation of a second, UV-invisible complex must be taken into account. The PIXE spectra of the sample mixture (Fig. 4b) received in the same buffer but with a higher sample concentration show clearly separated peaks for lead, zinc and copper, an unre-

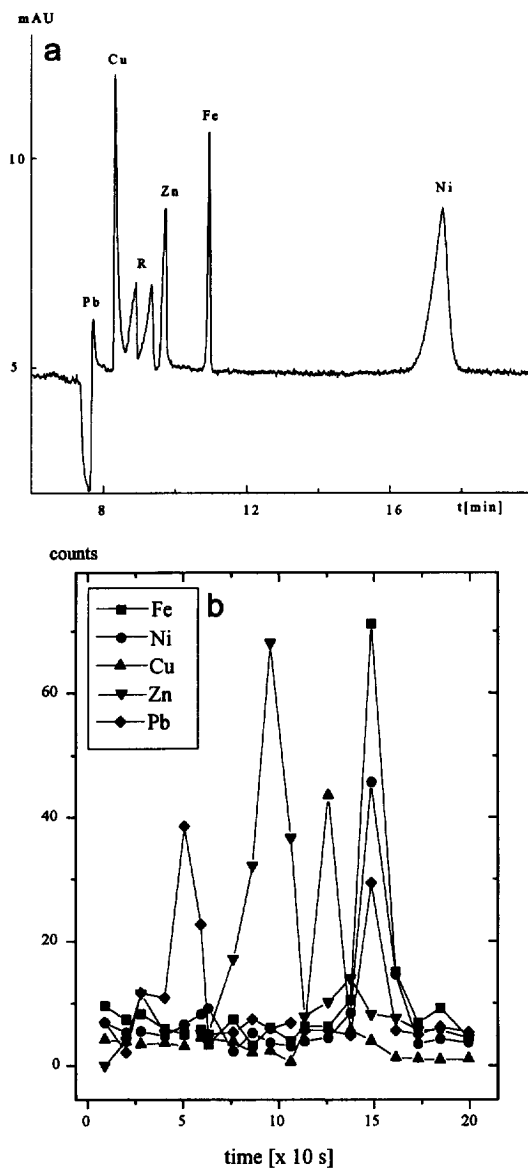


Fig. 4. (a) CZE with direct UV detection buffer: 10 mM phosphate, 6 mM borate pH 8.00, 0.1 mM 8-hydroxyquinoline-5-sulfonic acid, 0.1% polyethylene glycol; sample concentration 0.02 mM for Cu^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} and Fe^{3+} ; $\lambda=214$ nm, $l=50\text{--}57$ cm, 75 μm I.D., 5-s pressure injection, separation voltage 15 kV. (b) CZE with PIXE detection buffer: 10 mM phosphate, 6 mM borate pH 8.00, 0.1 mM 8-hydroxyquinoline-5-sulfonic acid, 0.1% polyethylene glycol; sample concentration 0.1 mM for Cu^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} and Fe^{3+} ; $l=50\text{--}70$ cm, 100 μm I.D., 106 μm O.D. ('ion window'), pressure injection 10 s at 20 kPa, separation voltage 7 kV for 12 min, $p=10$ kPa.

solved peak for iron and nickel and two clearly visible peaks for the lead ion. Variations of the buffer composition showed the existence of an additional Pb–phosphate complex, which is migrating behind the lead complex formed with HQS. The reversal of the migration order of the copper and zinc complexes has been attributed to the different sample concentrations applied for the detection with UV and PIXE systems and the resulting differences in the complex composition. The injection of a sample with higher concentration reduces the excess of the organic ligand HQS. By this way the probability for the formation of complexes with other ligands or other composition is increased. As discussed above the loss in resolution for the latter peaks is caused by the hydrodynamic flow applied for the detection procedure, the lower high-voltage and the achieved transient state of separation due to shorter separation time.

3.4.3. Speciation of arsenic compounds using the 180° arrangement

To demonstrate the potentials of the CZE–PIXE coupling for rapid and sensitive metal speciation, an earlier optimized separation of arsenic and selenic compounds [16] was applied. In Fig. 5a the fast separation of arsenite and arsenate in a chromate-containing buffer is shown using indirect UV detection. Due to the differences in their charge and absorption coefficients the detectable signal for both arsenic species is quite different. By this way the detection limit of the arsenite ion is obviously lower as for the higher oxidation state due to the drastic lower charge and the slightly higher individual absorbance at the detection wavelength. The PIXE spectrum (Fig. 5b) of the arsenic channel shows well separated peaks. In contrast to the indirect UV detection the peak areas above the average background signal are equal for both arsenic species within the statistical variation. Charge and UV absorbance of the separated species does not influence the measured signals.

3.4.4. Comparison of the detection limits of UV and PIXE detection

In Table 1 detection limits for the complexed metal ions using different detection modes are given. With the introduced PIXE detection system detection

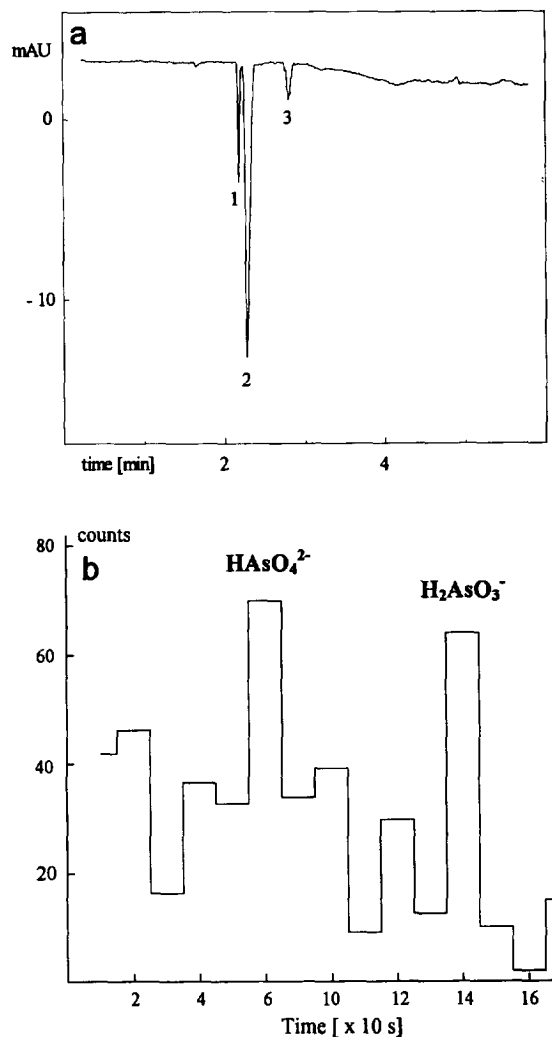


Fig. 5. (a) Speciation of arsenic compounds by CZE with indirect UV detection. Buffer: 5 mM CrO_4^{2-} (adjusted with Tris to pH 10.0), 0.25 mM HTAB; $l=50\text{--}57$ cm, 75 μm I.D., separation voltage -15 kV, $\lambda=254$ nm, 5-s pressure injection, sample concentration 0.1 mM, 1= Cl^- , 2= HAsO_4^{2-} , 3= H_2AsO_3^- . (b) Speciation of arsenic compounds by CZE with PIXE detection. Buffer: 5 mM CrO_4^{2-} (adjusted with Tris to pH 10.0), 0.25 mM HTAB; sample concentration 0.1 mM HAsO_4^{2-} and H_2AsO_3^- , $l=50\text{--}70$ cm, 100 μm I.D., 106 μm O.D. ('ion window'), electrokinetic injection at -3.5 kV for 87 s, separation voltage -3.5 kV for 8 min, $p=10$ kPa.

limits at the 10^{-5} M range could be achieved for most of the elements, which is only comparable with the results achieved with the indirect UV detection mode after pressure injection. For all elements

Table 1
Comparison of detection limits using different kinds of detection modes

Element	Injection mode	Detection mode		
		UV	Indirect UV	PIXE
Rb	Pressure		$5 \cdot 10^{-5} M$	(180°)
	Electrokinetic		$1 \cdot 10^{-6} M$	$1 \cdot 10^{-5} M$
Pb	Pressure		$2.5 \cdot 10^{-5} M$	(180°)/(90°)
	Electrokinetic		$7.5 \cdot 10^{-7} M$	$< 1 \cdot 10^{-5} M / 2 \cdot 10^{-5} M$
Y	Pressure		$2.5 \cdot 10^{-5} M$	(180°)
	Electrokinetic		$5 \cdot 10^{-7} M$	$< 1 \cdot 10^{-5} M$
Cu	Pressure	$5 \cdot 10^{-7} M$		$7.5 \cdot 10^{-5} M / 1 \cdot 10^{-5} M$
	Electrokinetic			(180°)/(90°)
Zn	Pressure	$5 \cdot 10^{-7} M$		$1 \cdot 10^{-5} M$
	Electrokinetic			(90°)
Fe	Pressure	$2.5 \cdot 10^{-7} M$		$1 \cdot 10^{-5} M$
	Electrokinetic			(90°)
Ni	Pressure	$7.5 \cdot 10^{-7} M$		$1 \cdot 10^{-5} M$
	Electrokinetic			(90°)

The determination of the detection limits for each metal ion was performed under the conditions described in the text.

analysed lower detection limits could be achieved using the electrokinetic injection followed by indirect UV detection or the pressure injection followed by direct UV detection.

The electrokinetic sample injection leads to an enrichment of the higher charged metal cations inside the capillary, thus lowering the detection limit of Pb and Y in comparison to Rb. The different concentrations for Cu and Pb detectable with the two measuring chambers (90°/180°) confirm the expected differences in sensitivity to X-rays with energies below or above 8 keV.

4. Conclusions

With the introduced PIXE detection system an element-specific detection after electrophoretic separation is possible. The applicability to speciation analysis of elements with $Z > 12$ is the main advantage of this technique. Depending on the energy of the generated characteristic X-rays of the sample components two different measurement chambers can be used for the detection of the elements under optimum conditions. The high detection limits of $10^{-5} M$ are insufficient, but could be further decreased down to $10^{-7} M$ by the utilization of different effects, as the reduction of the distance between the capillary and the detector in the 90°

arrangement and the separation at higher voltages. Furthermore, the application of longer capillaries and higher separation voltages should improve the resolution of the detected PIXE signals. The elimination of the influence of the gas-forming process on the electrophoretic separation would make the detection of separated zones under pressure-driven conditions unnecessary, those improving peak profiles, resolution and detection limits. This effect could be achieved by separating the electrophoretic high-voltage part from the detection part of the capillary in a similar way as it was demonstrated for electrochemical detection [17] some years ago. Using buffers with $\text{pH} > 4$ the interruption of the separation process caused by the isolating properties of the generated gas bubbles is avoided. The bubbles then would be transported outside the capillary by the electroosmotic flow.

Although the sensitivity of an CZE-ICP-MS system could not be achieved, performing the detection without an influence of the buffer ions is an advantage. The energy of the X-rays generated from the common buffer components (phosphate, borate, organic solvents and modifiers) is too low to get detected, thus making the detection step uninfluenced from the used buffers and their concentration. Even a metal-containing buffer system like chromate does not lead to significant problems concerning the detection.

While at the moment only few experiences are published about the CE–ICP–MS system further experiments with both element-sensitive detection systems are necessary to consider the advantages and disadvantages of both systems more in detail.

Acknowledgments

Dr. Volker Gottschalch is acknowledged for providing the microscopes for the control of the etching parameters. We thank Gunar Liebergeld for supporting the laser ablation studies.

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