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INTERFACING MICROCHIP BASED CAPILLARY ELECTROPHORESIS SYSTEM WITH A MICROWAVE INDUCED PLASMA OPTICAL EMISSION SPECTROMETER (μCE-MIP-OES)

TECHNIKA SPRZĘŻONA W UKŁADZIE MIKROCHIP – ELEKTROFOREZA KAPILARNA W OPTYCZNEJ SPEKTROMETRII EMISYJNEJ PLAZMY MIKROFALOWEJ

Abstract: A microchip based capillary electrophoresis (μCE) system was interfaced with microwave induced plasma optical emission spectrometry (MIP-OES) to provide rapid elemental separation capabilities. This system uses an extremely low flow micro-cross-flow nebulizer sited directly at the liquid exit of the chip. A supplementary flow of buffer solution at the channel exit was used to improve nebulization efficiency. A small evaporation chamber has been incorporated into the interface in order to prevent the losses associated with traditional spray chambers, allowing the entire sample aerosol to enter the plasma. Syringe pumps were used to manipulate the flow rate and flow direction of the sample, buffer, and supplementary buffer solution. Sample volumes of 40 nanolitre can be analyzed. The feasibility of this hyphenated method for elemental separation was demonstrated by the on-line electrophoretic separation of Ba^{2+} and Mg^{2+} ions within 35 s using an 8 cm long separation channel etched in a glass base. Resolution of the Ba^{2+} and Mg^{2+} peaks was 0.9 using the chip-based μCE-MIP-OES system.

Keywords: microwave induced plasma, optical emission spectrometer, capillary electrophoresis, interface, chip technology

The microwave induced plasma (MIP) is a small low power plasma that has excellent high excitation efficiency for metal and non-metal elements [1]. The technique of MIP optical emission spectrometry (OES) would be excellent for the separation of elements, however due to the small size and low thermal temperature of the plasma (compared with its high excitation capability) it cannot be easily interfaced to liquid separation techniques such as high-performance liquid chromatography (HPLC) or capillary electrophoresis (CE). This problem could be overcome by using lab on a chip

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technology for the separation as this provides rapid separation with nanolitre volumes of liquid. Laboratory on a chip devices provide an excellent opportunity for rapid on-chip pretreatment of samples, separation for speciation studies and the analysis of very small sample volumes..

The coupling of CE with analytical atomic spectrometry provides a very sensitive, element specific detection method in conjunction with high separation efficiency [2]. However, interfacing this technique remains challenging, primarily due to the flow incompability. Microfabricated analytical system using electrophoresis as a separation mechanism have been shown to reduce drastically separation times and to simplify instrumental design. Another advantage of microchip technology is that pre-etched channel networks can be used to provide several flow streams, omitting tube connectors and thus reducing dead volumes. In most microchip CE (μCE) systems, sample injection is achieved by the electrokinetic method [3]. Song et al [4,5] reported elemental speciation using μCE which was successfully interfaced with inductively coupled plasma mass spectrometry (ICP-MS) via a commercial low flow micro-nebulizer and miniaturized spray chamber. Hui et al [6] were the first to report on chip nebulizer. A chip based electrophoresis system was interfaced to ICP-OES by means of a cross-flow nebulizer.

This paper describes, for the first time, how a microchip based electrophoresis system was interfaced to an MIP-OES, incorporating a simplified small spray chamber in order to approach 100 % analyte transport efficiency. The sample and buffer solution were introduced into the separation channel of μCE chip by hydrodynamic injection with a microsyringe pumps. A voltage applied along the length of the channel separated the ions of interest, but a hydrodynamic flow was also used to shorten the overall analysis time. Barium and magnesium were used as test elements because of the strong emission of the elements in the MIP and similar ion mobilities of the ions. The analytical performance of the chip-based μCE-MIP set up was examined.

Materials and methods

An Echelle grating optical emission spectrometer (PLASMAQUANT 100, Carl Zeiss, Jena, Germany) using fibre-optical light-guides and photomultiplier tubes (PMT) and TE_{101} microwave plasma cavity assembly was used, and was essentially the same as previously described [7]. Instrument settings and operational parameters used for the experimental MIP-OES system are summarized in Table 1.

The MIP resonant cavity as an excitation source, specified previously [7], was used. The plasma is viewed axially with the axis of the plasma perpendicular to the plane of the entrance slit. Since the plasma torch, cavity, generator and gas flow have been described in detail in a previous paper [7], they will not be discussed again here, but briefly summarized only. The microwave generator is connected by means of a flexible cable to the rectangular resonant cavity of the TE_{101} design. The torch is a quartz capillary made of Suprasil (Heraeus, Hanau, Germany). Table 1 lists the MIP apparatus specifications and operating conditions for the generation of plasma.

Table 1

Instrumental parameters for the μCE-MIP-OES system

Mounting	Czerny-Turner in tetrahedral set-up
Focal length, mm	500
Spectral range, nm	193–852
Order lines	28^{th}–123^{rd}
Microwave frequency, MHz	2450
Microwave power, W	160
Microwave cavity	TE_{101} rectangular, water cooled
Microwave generator	700 W, MPC-01 (Plazmatronika Ltd., Wroclaw, Poland)
Plasma viewing mode	Axial
Plasma torch, axial position	Quartz tube, 3.0 mm i.d., air cooled
Argon flow rate, $cm^3\ min^{-1}$	700
Plasma supporting helium flow rate, $cm^3\ min^{-1}$	160
Plasma form	Annular
Supplementary buffer flow rate, $mm^3\ min^{-1}$	20
CE potential, kV	5
Read	On-peak
Integration time/s	0.1
Background correction	Fixed point
Determination	Simultaneous
Wavelength, nm (line type)	Ba 455.403 (II); Mg 285.213 (I)

Experiments were carried out on a laboratory-built μCE system (the detailed fabrication method has been reported previously [8]), which was composed of a 0–30 kV high voltage power supply (HVPS Spelman, Spisska Nova Ves, Slovakia) and two microsyringe pumps (Ascor, Warsaw, Poland) which were capable of providing 0.4–100 $mm^3\ min^{-1}$. These overcome the pulsation introduced through the use of peristaltic pumps at low flow rates. The microchip used in this μCE-MIP-OES system consisted of two (30 × 25 × 3 mm) glass plates. The design of the microchip, with the channel layout, is shown in Fig. 1 [4]. The gas flow rate was controlled by means of a mass flow controller (DHN, Warsaw, Poland). An external argon source was needed

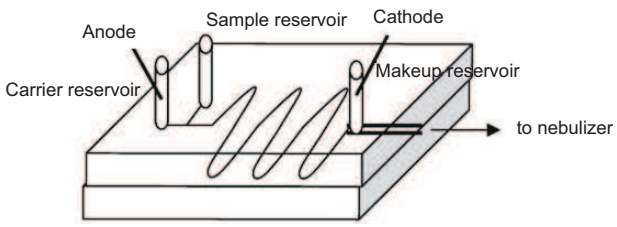

Fig. 1. Schematic diagram of the microfluidic chip

for the nebulization, as the MIP-OES is not able to provide the pressure required by this interface.

The microchip was interfaced to the MIP-OES via a commercially available, low flow rate concentric nebulizer (Micromist, Glass Expansion, Switzerland), as shown in Fig. 2 [4]. The uptake flow rate of the nebulizer was about 20 mm^3 min^{-1}. A miniature evaporation tube-shaped spray chamber (Model QuDIN, Epond, Vevey, Switzerland) fitted directly with the quartz plasma torch was used to obtain high sample introduction efficiency with the low flow rate nebulizer. The experimental conditions of the chip-based μCE system are summarized in Table 1. The instrument could be run in either a continuous flow mode to give a quick assessment of the instrument stability and the μCE separation or in time resolved acquisition mode for quantification of the peak areas.

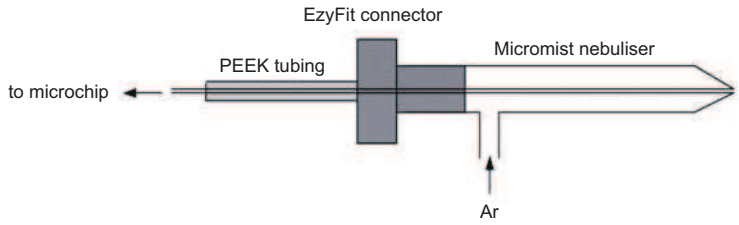

Fig. 2. Schematic diagram of the interface

A schematic diagram of the entire experimental sample introduction system set-up (μCE-MIP-OES) is shown in Fig. 3.

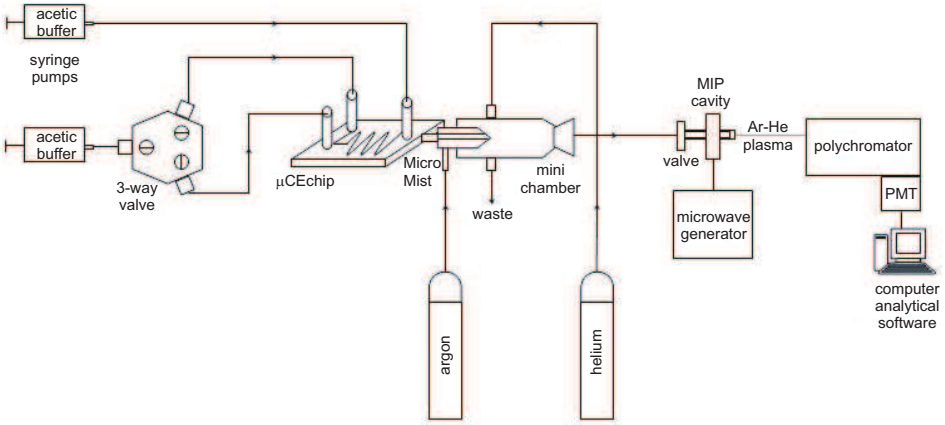

Fig. 3. Component diagram of the elaborated microchip based μCE-MIP-OES system (not to scale)

Sodium acetate buffer (60 mM) was prepared from sodium acetate for electrophoresis (≥ 99 % , Sigma-Aldrich Chemie, Steinheim, Germany) in doubly distilled water. The pH of the buffer was adjusted to 4.2 with acetic acid ((≥ 99 %,

Sigma-Aldrich Chemie, Steinheim, Germany). Stock solutions of 5000 mg dm^{-3} of Ba and Mg were prepared from barium di(acetate) and magnesium di(acetate) tetrahydrate ((≥ 99 %, Sigma-Aldrich Chemie, Steinheim, Germany) in doubly distilled water. The pH of the prepared stock solution was 6.0. The stock solution was mixed and diluted to the appropriate concentration with doubly distilled water immediately before use. The pH of the diluted solution was approximately 6.

Water was initially deionized (Model DEMIWA 5 ROSA, Watek, Czech Republic) and then doubly distilled in a quartz apparatus (Heraeus Bi18, Hanau, Germany).

Results and discussion

One of the problem with previous design of microchip sample introduction system for plasma spectrometry has been the low transport efficiency of the sample into the plasma [6]. In the experiments, a bulb-shaped spray chamber of relatively large volume was used. The large chamber may broaden the CE peak. Since the liquid flow rate in the chip is very low it should be possible to achieve 100 % transport of the sample out of the end of the chip to the microwave plasma. In order to achieve this a small cylindrical spray chamber of the volume of 10 cm^3 was used in the following study.

The optimization of wavelength was not carried out because the wavelengths used for the determination were pre-selected by the producer of the polychromator.

Preliminary analytical performance of the Ar/He-MIP was examined by measuring the S/B ratio of selected elements. However, substantial optimization of the gases parameters for the analytes was not undertaken, as this information was readily available from the literature on excitation and ionization conditions for MIP-OES with pneumatic nebulization [9] (and references cited therein). The comparison of these parameters obtained for mixed plasma with those presented for pure argon plasma and helium plasma with pneumatic nebulization shows that a mixed plasma allowed to achieve better detection limits than pure plasma gases. In addition, the mixed Ar + 20 % He MIP exhibits higher tolerance to water loading. As a result of the consideration on the above influences, an Ar/He-MIP was selected for all the subsequent experiments, for a plasma gas composition of ca 80 % Ar and 20 % He; this is in agreement with results presented earlier [9].

Two different types of experimental variables affect the method. These are as follows: first, variables controlling the emission response in the microwave plasma, that is, the microwave forward power of the microwave generator. Second, variables such as the argon carrier flow and sample uptake rate that regulate sample transport. Univariate optimization was used to establish the optimum experimental parameters. The parameters optimized are listed in Table 1.

The MIP is normally operated at low power levels in the range of 50–150 W. In this work, the stable Ar/He plasma could be maintained at a level of greater than 100 W forward power. Between 100 and 200 W, neither the intensities of spectral lines nor the S/B ratios showed such a dependence on the power that this would point to a pronounced optimum. In addition, the stability of the background and line signals did not significantly vary with power in the above-mentioned range. In general, for two

analytical lines of studied elements, S/B ratios usually tend to level off after the microwave power approaching 160 W (Fig. 4a). The intensities of spectral lines also level, but more slowly. As a result of this consideration on the above influences, an optimized power of 160 W was selected as an acceptable value and a practical working range.

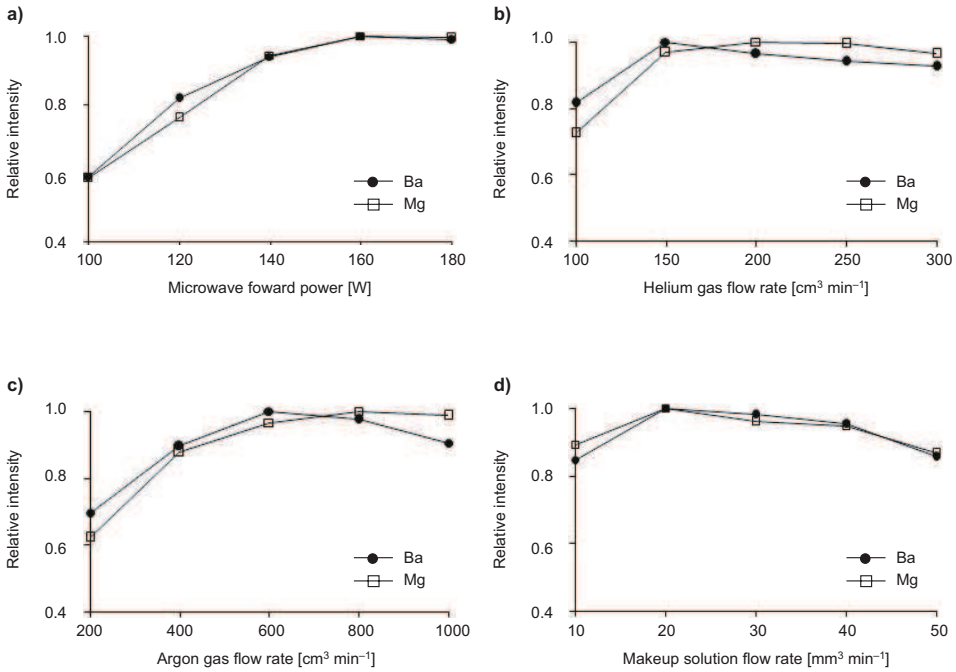

Fig. 4. Effect of the variables on the element's normalized emission intensity for microchip based μCE-MIP-OES system. Influence of (a) microwave forward power; (b) helium gas flow rate; (c) argon gas flow rate; (d) makeup solution flow rate on the emission intensity of the elements for continuous injection of 100 μg dm^{-3} Ba^{2+} and Mg^{2+} through makeup reservoir without application of voltage

The effect of plasma (support) helium gas flow rate was optimized in our experiments and was selected based upon previous experience and maintaining the plasma stability and plasma shape. Stable operation of the plasma was obtained at gas flow rates of 160 cm^3 min^{-1} (Fig. 4b).

It was also observed that the carrier Ar gas stream flow rate has a more significant influence on the emission intensities than the plasma support gas flow rate. The carrier Ar gas affects the formation of the plasma channel (an annular configuration) [10], the residence time of the analyte in the plasma, and the aerosol generation and transport efficiency [11]. To optimize the carrier (nebulizing) argon gas flow for multielement determination, the optimum flow for two elements was estimated in the total range of 200–1000 cm^3 min^{-1}. It was observed that the carrier argon stream flow rate has a significant influence on the emission intensities and thus proved to be a critical

parameter. In general, it was observed that when the flow rate was ranged between 200 and 1000 cm^3 min^{-1}, the emission intensities reached maximum at 700 cm^3 min^{-1}, and with further increase of the flow rate above these values, the emission intensities decreased for two elements (Fig. 4c). The maxima are the result of opposite effects of nebulizing gas flow on aerosol characteristics and transport and interaction of aerosol with the plasma. Increasing the nebulizing gas flow rate commonly causes a shift of both primary and tertiary drop size distributions to smaller droplet sizes. This in turn leads directly to higher analyte and solvent transport rates. However, these two transport rates exert opposite trends on net signal intensity. In addition, the higher the nebulizing-carrier gas flow, the smaller the residence time of droplets in the plasma. Therefore, the overall effect is shown as a maximum behaviour. Therefore, in this study, a 700 cm^3 min^{-1} carrier argon flow rate was chosen.

The makeup solution (buffer solution) also proved to be important for this work. When the sample pumping rate was greater than approximately 20 mm^3 min^{-1}, it was found that the signal intensities would not increase further and began to decrease (Fig. 4d). For pneumatic nebulization, the higher the liquid flow, the primary drop size distribution is shifted to bigger drop sizes. Nevertheless, the absolute amount of aerosol volume contained in smaller drop size is increased. Therefore, the higher the liquid flow, the higher the analyte and solvent transport rates, that finally show a behaviour of maximum on signal vs liquid flow. Therefore, a sample uptake rate of 20 mm^3 min^{-1} was chosen.

The analytical performance of the μCE-MIP-OES system is characterized by electrophoretic separation of a mixture of 1000 μg cm^{-3} each of Ba^{2+} and Mg^{2+}. The ion mobilities of Ba^{2+} and Mg^{2+} are similar and the ions carry the same charge. The degree of separation of the ions is an indicator of the resolving power of the μCE-ICP-OES system. Fig. 5 shows the electrophorogram of the Ba^{2+}/Mg^{2+} mixture. As can be seen in Fig. 5, the two ions are clearly beginning to separate on application of 5 000 V, and the separation was completed within 30 s. The migration times of Ba^{2+} and Mg^{2+} ions were

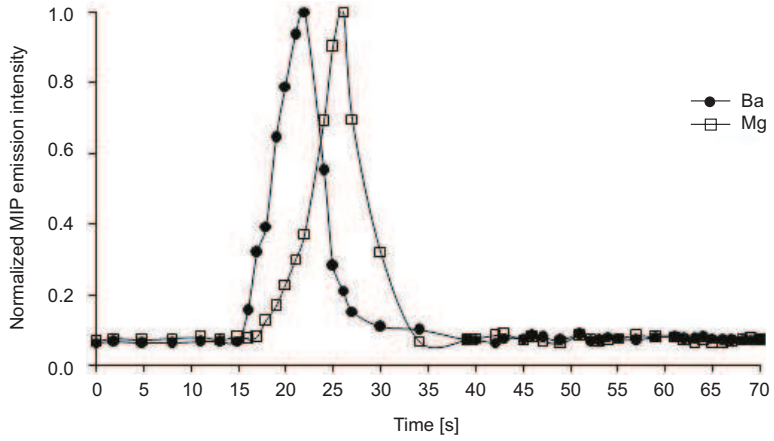

Fig. 5. Separation of Ba^{2+} and Mg^{2+} in a microchip based μCE-MIP-OES system. CE potential was 5 kV

22 s and 26 s, respectively. The half-intensity widths of the peaks were 3.7 s and 4.0 s, respectively. The resolution of the elution peaks was approximately 0.9.

Conclusions

A simple interface for chip-based μCE-MIP has been developed. The micro-concentric nebulizer converted the μCE effluent into fine aerosol for transport to the MIP. The small dimensions made it possible to place the entire device in the vicinity of the micronebulizer inlet and the makeup solution can therefore be introduced very near to the outlet of the separation channel. Sample and buffer solution flows in the μCE chip were manipulated using a pair of syringe pumps for flexible of solution flow rate and flow direction control. An evaporation tube-shaped spray chamber was used in order to facilitate the transport of the entire primary aerosol into the microwave plasma. At the moment the microchip system requires manual filling with background buffer and sample. Rapid CE separation of ions of the same charge and similar ionic mobility was demonstrated using Ba^{2+} and Mg^{2+} ions.

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Zakład Chemii Analitycznej
Politechnika Poznańska

Abstrakt: Opisano metodę rozdziału jonów Ba^{2+} od Mg^{2+} za pomocą mikrosystemu elektroforetycznego (μCE) w połączeniu z optyczną spektrometrią emisyjną (OES) plazmy indukowanej mikrofalowo (MIP). Roztwór próbki (ok. 40 nanolitrów) oraz roztwory buforowe wprowadzano do kanału separacyjnego o długości 8 cm za pomocą pomp strzykawkowych. Zaproponowany system umożliwia rozdział badanych jonów w ciągu 35 s oraz efektywne wprowadzenie próbki, w postaci aerozolu, do źródła wzbudzenia za pomocą układu mikrorozpylacz/minikomora mgielna.

Słowa kluczowe: plazma mikrofalowa, optyczna spektrometria emisyjna, elektroforeza kapilarna, aparatura, technologia chipowa