Element sensor based on microplasma generators

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Abstract

Purpose – The purpose of this paper is to present a study on miniaturized instruments for analytical chemistry with a microplasma as the excitation source.

Design/methodology/approach – The atmospheric pressure glow microdischarge could be ignited inside a ceramic structure between a solid anode and a liquid cathode. As a result of the cathode sputtering of the solution, it was possible to determine its chemical composition by analyzing the emission spectra of the discharge. Cathodes with microfluidic channels and two types of anodes were constructed. Both types were tested through experimentation. Impact of the electrodes geometry on the discharge was established. A cathode aperture of various sizes and anodes made from different materials were used.

Findings – The spectroscopic properties of the discharge and its usefulness in the analysis depended on the ceramic structure. The surface area of the cathode aperture and the flow rate of the solution influence on the detection limits (DLs) of Zn and Cd.

Originality/value – Constructed ceramic structures were able to excite elements and their laboratory-size systems. During the experiments, Zn and Cd were detected with DLs 0.024 and 0.053 mg/L, respectively.

Keywords LTCC, Environmental sensors, Spectral analysis, Microplasma, Microchip, Optical emission spectroscopy

Paper type Research paper

1. Introduction

Increasing environmental pollution highlights challenges for new solutions for its protection by monitoring contamination in real time and directly in the place where it occurs. Usefulness of the present measuring systems satisfies the needs of laboratory facilities but due to their dimensions, it cannot be used *in situ* or their use may be difficult. Miniaturization of systems to the lab-on-chip level can serve as one of the solutions to this problem. Lab-on-chip systems are currently based on silicon, glass and ceramic substrates, using various microelectronic techniques for their processing. Especially, ceramic systems are suitable to be used in aggressive environments, for example, during plasma generation in various discharge gases. Atmospheric

pressure plasmas are efficient excitation sources for analytical optical emission spectrometry (OES). However, the most commonly used inductively coupled plasma (ICP) is a bulky excitation source that needs to be cooled and consumes a lot of energy and gas. Atmospheric pressure glow discharge (APGD) can be used instead of ICP due to lower operational and
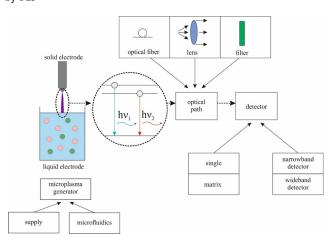
maintenance costs, but there is still the problem of a destructive impact of the discharge on metallic electrodes. One or both electrodes in APGD can be replaced by liquids, thereby enabling to stably generate the discharge in contact with them (Webb et al., 2005). The first of such discharge systems described in the literature by Cserfalvi and Mezei was electrolyte cathode atmospheric discharge (Cserfalvi and Mezei, 1994). APGD sustained and operated in contact with a flowing liquid electrode (FLE) has many advantages over other plasma-based excitation sources such as low power and gas consumption. Moreover, there is a significant reduction in the sample volume required for OES analysis (Cserfalvi and Mezei, 1994; Jamroz et al., 2017). The concept, which uses discharges generated in contact with liquids for elements sensing is presented in Figure 1.

The most important components in such system are: a supply and microfluidic introduction unit of samples to the microplasma based excitation source. During microplasma generation, emitted spectrum is characteristic for contaminants present in the liquid electrode. The microplasma can be driven by DC, AC, microwaves or by impulses (Bruggeman and Brandenburg, 2013). Applied power supplies mostly depend on construction of the microplasma generators. DC- and AC-driven discharges are typically used under atmospheric pressure for analytical chemistry purposes.

So far, various microsystems were proposed to sustain APGD generated in contact with analyzed sample solutions and determine in them different elements using this excitation source (Franzke and Miclea, 2006; Mitra et al., 2008; Jamroz et al., 2012; Schwartz et al., 2016). Miniaturization of these systems can significantly reduce costs of element analysis and amounts of samples required for this. Jamroz et al. (2017) presented a non-flowing and stationary setup, which required 50 μL of a sample for one measurement.

This work presents a ceramic chip for sustaining microAPGD, which can be a part of a measuring shunt and does not require any special introduction unit of sample solutions to the microchip. This microAPGD can be implemented, for example, in real-time characterization of water pipes. So far, microAPGDs were generated in systems fabricated with the use of various micromechanical technologies (Franzke et al., 2003;

Figure 1 Components of the whole system based on the microplasma excitation source generated in contact with liquids for element analysis by OES

Gianchandani et al., 2009). In addition, Hopwood et al. (2000) and Bass et al. (2001) presented miniature ICP and capacitively coupled microplasma (CCμP), respectively, also fabricated in typical microelectronics technology. Materials used in low temperature co-fired ceramics (LTCC) technology work very well in extreme conditions of electric discharges, especially, under high temperatures and high voltages (Kita et al., 2015; Dabrowski et al., 2018). Examples of microplasma systems fabricated in LTCC technology are given in Table 1.

The aim of the present work was to:
- miniaturize a typical laboratory discharge setup,
- improve ceramic chips lately reported by Macioszczyk et al. (2016a, 2017a) and
- fabricate a ceramic structure for stable operation of He microAPGD between a solid anode and a flowing liquid cathode (FLC).

Macioszczyk et al. (2016a, 2017a) presented structures with a drop outlet of wastes and with completely evaporating solutions, respectively. Here, He microAPGD between a solid anode and a FLC solution inside a ceramic chip was developed and studied. Cathodes with microfluidic channels and two types of anodes were constructed. Both devices were tested as excitation sources prior to analytical OES and determination of traces of Cd and Zn in solutions. Although analytical performance of the proposed microAPGD excitation sources was fair, the microplasma sustained in developed ceramic chips degraded with time the surface of the LTCC substrates and electrodes.

2. Materials and methods

The concept of a microAPGD device proposed and developed in this paper is shown in Figure 2(a). Acidified solutions containing Cd and Zn were pumped into a microfluidic channel of a ceramic chip via a fluid inlet. Then, they filled the microfluidic channel until the inner cathode was touched and electrical connection was closed. The microplasma was sustained between the solid anode and the FLC formed. Due to sputtering of the solution surface, analytes were transported to the microAPGD column, where they were excited. Radiation emitted by microAPGD was focused onto the entrance slit of a spectrometer, using a collimating lens. The ceramic structure was placed inside a polymer housing to facilitate its operation and correct its position [Figure 2(b)].

A Du Pont GreenTape951 LTCC system (Du Pont, Wilmington, DE, USA) was used to fabricate the chip in LTCC technology. Successive layers of the cathode and both anodes are shown in Figure 3. All patterns were laser-cut (LPKF ProtoLaser U, Nd: YAG 355 nm, LPKF Laser & Electronics AG, Garbsen, Germany) on Du Pont 951PX green sheets (thickness of 254 μm).

The cathode consisted of eight layers. An external Au electrode (a Du Pont 5742 paste for an Au cofireable conductor), placed at the bottom of the Layer 8, was deposited by a 325 M screen using a screen-printer (Aurel VS1520A, Aurel Automation S.P.A., Modigliana, Italy). The internal cathode was made of a Pt paste (a Du Pont 9141 Pt conductor) and connected to the external electrode by two vias filled with an Au paste (a Du Pont 5738 Au via fill). The microfluidic channel was located in Layers 3-6. The structure was covered by two additional layers (1-2) with a cathode aperture, where the plasma had contact with the solution, acting as the FLC.

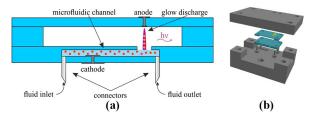**Table 1** Plasma chips fabricated in ceramic technology

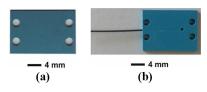| Description	Application	References
APGD and a gas flowing through chamber	Technology presentation	Yamamoto *et al.* (2008)
Dielectric barrier discharge (DBD) and a gas flowing through chamber inside a ceramic chip with open electrodes	Gas spectroscopy	Macioszczyk *et al.* (2016b)
BDB with a gas flowing through chamber	Gas excitation	Vojak *et al.* (2001)
RF microplasma-generating discharge	Technology presentation	Baker *et al.* (2006)
DBD between buried electrodes in a ceramic chip	Selective treatment of cell cultures	Fischer *et al.* (2017)
APGD between a liquid cathode and a solid anode inside a ceramic chip; discharge wastes are freely dropped out from a chip	Analytical atomic spectrometry	Macioszczyk *et al.* (2016a)
APGD between a liquid cathode and a solid anode inside a ceramic chip; the cathode evaporates in a chamber	Analytical atomic spectrometry	Macioszczyk *et al.* (2017a)
DBD between ceramic electrodes	Production of plasma activated water	Macioszczyk *et al.* (2017b)

Figure 2 A cross-section of a ceramic structure in which He microAPGD was sustained in contact with a flowing liquid cathode (a) and a view of a modular ceramic – polymeric device for OES analysis of liquids (b)

(a)   **(b)**

In the ceramic chip "Type 1" [Figure 4(a)], one of the anodes consisted of two layers with a screen-printed internal Pt electrode (Du Pont 9141), Au vias (Du Pont, 5738) and the external Au electrode (Du Pont 5742). In the second ceramic chip ["Type 2", Figure 4(b)], the electrode was made of a W wire placed inside the ceramic structure. Both ceramic structures were fabricated in the standard LTCC process. Only the lamination process was modified a little bit just to prevent microfluidic channels inside both chips from sagging. In this case, pressure was reduced from 20 MPa to 5 MPa. After firing in standard conditions, ceramic structures were placed in the polymeric housing (Z-ABS material, Zortrax, Poland) that was made-up by fused deposition modeling (FDM) using a three-dimensional printer (M200, Zortrax, Poland). Dimensions of both ceramic chip structures were 21 × 40 × 2.6 mm. As can be seen in Figure 3, 0.7 mm spacers were placed between the cathode and the anode. In the cathode, fluid connectors were glued.

Figure 3 Successive layers of ceramic cathode, spacers and anodes

Figure 4 Ceramic chips with anodes with a screen-printed Au electrode ("Type 1") (a) and a solid W electrode ("Type 2") (b)
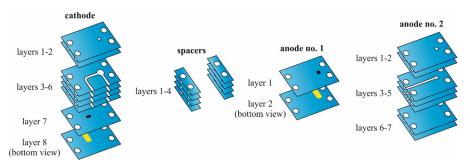

(a)   **(b)**

3. Results

The analytical performance of both modular ceramic – polymeric structures, used for sustaining He microAPGD and analysis of solutions containing Cd and Zn by OES, was examined. The measurement setup (Figure 5) consisted of a

Figure 5 The measurement setup

peristaltic pump (Reglo Ismatec ICC, Wertheim, Germany) with three independent pump channels, a pressurized container with He as working gas, power supplies for operation of high-voltage DC- or AC-driven microAPGDs (Dora Laboratory Equipment, Wroclaw, Poland) and a Shamrock SR500i imagining spectrometer (Andor, Oxford Instruments, Abingdon-on-Thames, GB) with a Newton DU-920-OE CCD detector. The spectrometer had two diffraction gratings: 1,800 lines/mm for the 200-400 nm spectral range and 1,200 lines/mm for the 400-900 nm range. The analyzed liquid samples were 0.1 mol/L HNO_3 solutions containing Cd(II) and Zn(II) ions at concentrations of 2, 5 and 10 mg/L. Both DC- and AC-driven He microAPGDs were ignited and stably operated inside fabricated ceramic structures.

The ceramic chip "Type 1" for DC-driven He microAPGD operation is presented in Figure 6. In this case, the anode was connected into a circuit through a ballast resistor (2 kΩ, 250 W). The DC-driven microAPGD device was run using the following parameters: a FLC solution flow rate of 0.5 mL/min, a He flow rate of 5 L/min, a discharge voltage of 1.7 kV and a discharge current of 40 mA (68 W of power).

The plasma (Figure 6) was stable and homogeneous, but after 1 h of uninterrupted work, both electrodes started degrading and got destroyed. Relatively intensive Cd (213.9 nm) and Zn (228.8 nm) atomic emission lines were observed in the spectrum of this He microAPGD. Additionally, OH, NO, OH and N_2 molecular bands were identified (Table 2).

The device with the ceramic chip "Type 2" was used to sustain AC-driven microAPGD and was run without any significant deterioration of electrodes. Emission spectra of this microAPGD were acquired using the following operating parameters: a FLC flow rate of 1-4 mL/min, depending on

cathode aperture diameter, a He flow rate of 5 L/min, a peak-to-peak voltage of 7.5 kV, a mean current of 4 mA and a frequency of carrier wave of 1.37 kHz. The current value confirmed that it was the glow discharge (Roth *et al.*, 2005). The voltage waveform during the AC-driven discharge are presented in Figure 7.
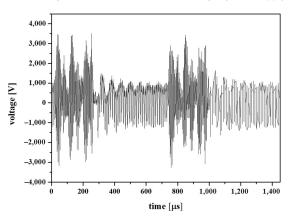
As before, intensive atomic emission lines of Zn and Cd were identified at 213.9 nm and 228.8 nm, respectively (Figure 8). Intensities of band heads of other molecular species identified in these spectra are given in Table 2. As AC-driven microAPGD sustained in the ceramic chip "type 2" was more stable than DC-driven microdischarge sustained in the ceramic chip "type 1", it was used in all subsequent experiments.

Detection limits (DLs) of Cd and Zn achievable with DC- and AC-driven He microAPGD were assessed on the following equation (Armbruster and Pry, 2008; Belter *et al.*, 2014):

$$DL = \frac{3\sigma}{a} \qquad (1)$$
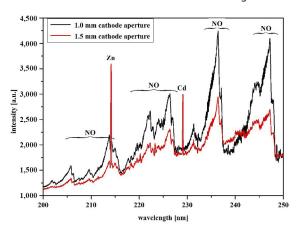
where σ is the standard deviation of the repeatedly measured intensity of the background for a blank solution (0.1 mol/L HNO_3) and a is the slope of the calibration curve (sensitivity) with the upper linearity range at 10 mg/L (the highest concentrated solution measured in this work). DLs of Cd and Zn achievable using the DC-driven microdischarge were determined to be 0.082 mg/L and 0.24 mg/L, respectively.

Figure 7 Voltage waveform of AC-driven discharge by Dora supply

Figure 6 The DC-driven He microAPGD device

Table 2 Intensities of atomic lines and molecular bandheads

| Wavelength [nm] | Atom/molecule transitions | Intensity [a. u.] | |
		AC-driven microAPGD	DC-driven microAPGD
213.9	Zn I	2.70×10^3	1.70×10^3
228.8	Cd I	2.22×10^3	5.44×10^3
247.9	NO (A-X)	4.20×10^3	7.36×10^3
282.9	OH (A-X)	7.07×10^3	4.21×10^3
308.9	OH (A-X)	6.43×10^3	5.70×10^4
337.2	N_2 (C-B)	1.15×10^5	5.40×10^3
357.7	N_2 (C-B)	5.20×10^4	4.70×10^3
375.5	N_2 (C-B)	1.06×10^4	3.60×10^3
380.2	N_2 (C-B)	9.38×10^3	4.50×10^3
589.0	Na I	9.98×10^3	not detected

Figure 8 Emission spectra of AC-driven He microAPGD sustained in the ceramic structure "Type 2 anode" – the effect of the cathode aperture diameter. The concentration of Cd and Zn – 2 mg/L

Figure 9 Intensity responses of for three concentrations of Cd and Zn

Nevertheless, due to rapid degradation of anodes in ceramic chips "Type 1" and "Type 2"), the DC-driven He microAPGD was not further investigated. In this case, the lifespan of mentioned above ceramic chips, used for DC-driven He microAPGD operation, was 1 h and 2 h, respectively. Therefore, AC-driven He microAPGD was used in further experiments. In this case, DLsof Cd and Zn were established to be dependent on the FLC solution flow rate (from 1 to 4 mL/min) and the cathode aperture diameter (1.0 mm and 1.5 mm). Respective results are given in Table 3.

As Table 3 demonstrates, different values of DLs of Cd and Zn were obtained for each cathode aperture and FLC solution flow rate. The lowest DLs of Cd (0.053 mg/L) and Zn (0.14 mg/L) were established when using a cathode aperture diameter of 1.5 mm and a FLC solution flow rate of 1 mL/min. In these conditions, background intensity fluctuation in vicinity of atomic emission lines of Cd and Zn for the measured blank solution, expressed as σ, was the lowest and equaled 39.2 and 126, respectively.

Intensity responses for three concentrations are presented in Figure 9.

4. Discussion

DC-driven He microAPGD sustained and operated in the ceramic chip "Type 1" was unstable; the lifespan of the mentioned chip structure was relatively short (about 1 h). Surfaces of both electrodes (anode and cathode, Figure 10)
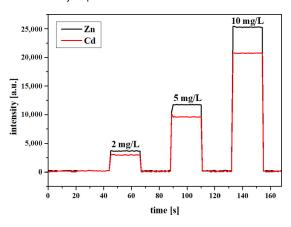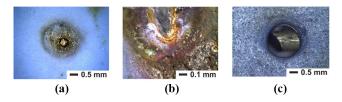
Figure 10 Electrodes degraded in ceramic chips used for sustaining DC-driven microAPGD

Notes: (a) Anode in chip "type 1" and; (b) cathode in chip "type 1", and non-degraded AC-driven microAPGD; (c) anode in chip "type 2" after use with AC-driven microAPGD with any damage

included in this chip were imaged with the aid of a Leica DM4000 M LED microscope (Leica Microsystems, Wetzlar, Germany).

Pt metallization of the anode (thickness 10 μm) in the ceramic chip "Type 1" was almost completely etched by the plasma up to the via. On the bottom of the cathode, some cracks were observed in the ceramic, in addition to a partially melted glass phase and some metallic contamination on the surface. Screen-printed metallization was no longer present in these conditions. To reduce the impact of the constant electrical field on the anode and the cathode in the ceramic chip "Type 1", the power supply was changed from DC to AC. In addition, the anode in the device was replaced with a W wire (the ceramic chip "Type 2"). Hence, the W anode had a higher melting point and was more reliable than the thin Pt electrode.

Table 3 Comparison of DLs of cd and Zn obtained for AC-driven microAPGD operated in the ceramic chip "Type 2" under different experimental conditions related to the FLC solution flow rate and the cathode aperture diameter

	DLs [mg/L]			
	Cd		Zn	
	Cathode aperture diameter [mm]			
FLC solution flow rate [mL/min]	1.0	1.5	1.0	1.5
1	0.14	0.053	0.42	0.14
2	0.094	0.16	0.30	0.25
3	0.073	0.097	0.25	0.26
4	0.069	0.053	0.16	0.22

Table 4 Comparison of DLs of cd and Zn reported in literature with those obtained in the present study for DC-driven microAPGD (sustained in the ceramic chip "Type 1") and AC-driven microAPGD (sustained in the ceramic chip "Type 2")

Source	DLs [mg/L]	
	Cd	Zn
Cserfalvi and Mezei (1994)	0.10	0.10
Jamróz *et al.* **(2012)**	0.20	0.14
Schwartz *et al.* **(2016)**	0.053	0.20
Kim *et al.* **(2000)**	–	0.60
Jamróz *et al.* **(2012)**	0.05	0.10
Macioszczyk *et al.* **(2016a)**	0.14	0.20
This work (ceramic chip "Type 1" for DC-driven microAPGD)	0.082	0.024
This work (ceramic chip "Type 2" for AC-driven microAPGD)	0.053	0.14

Certainly, this construction solved the problem of the short lifespan of the ceramic structure. In addition, microAPGD was more stable.

Molecular bands of the OH (A-X) system were observed in emission spectra of both DC- and AC-driven microAPGDs, which resulted from dissociation of water vapor. Based on these OH molecular emission spectra, it was possible to determine rotational temperature (T_{rot}) of the plasma (Jamroz *et al.*, 2012). Lifbase software (version: 2.1, SRI International, Menlo Park, CA, USA) was used to assess this value. In this case, the empirical OH molecular emission spectrum was compared with those simulated at different T_{rot} values. In case of AD-driven He microAPGD, it was established that the highest correlation (R = 0.93) between modeled and measured spectra was for T_{rot} = 3,000 K. For the DC-driven discharge, the T_{rot} value was established to be 4,500 K with the correlation coefficient of 0.91. Intensive emission from N_2 molecules was likely related to diffusion of N_2 from the surrounding air into the microAPGD column.

When a smaller cathode aperture (1.0 mm) was used, higher power density was achieved, hence, higher amounts of analytes were likely sputtered into the microAPGD phase in these conditions. As a result, it was possible to introduce higher amounts of solutions at increased flow rates, i.e. up to 4 mL/min. Therefore, intensities of atomic emission lines of Cd and Zn were higher and subsequently higher slopes of calibration curves were established, giving rise to lower DLs of Cd and Zn. When a higher cathode aperture (1.5 mm) was used, available power density was lower. In these conditions, the system was cooled at higher FLC solution flow rates due to higher amounts of water vapor in the microAPGD phase. As a result, the highest intensities of atomic emission lines of Cd and Zn were obtained at the lowest flow rate, i.e. 1 mL/min. Detectability of Zn was weaker than this for Cd because the analytical line of this element interfered with the NO molecular band in this spectral range. Hence, the standard deviation of the background in vicinity of the Zn atomic emission line was deteriorated. Its higher values obtained in these conditions resulted in worsening the DL of Zn. It was not the case of Cd, which atomic emission line was not interfered by any molecular spectra. Therefore, it was concluded that the ceramic chip "Type 2" with both apertures could be used for measurements of this element. DLs of Cd and Zn obtained in this study with the developed AC-driven He microAPGD system are compared with those reported in other works in Table 4.

5. Conclusion

The present work brings a completely new miniature device for determination of Cd and Zn in solutions by analytical OES. The device was based on the He microAPGD excitation source, microAPGD was ignited between the solid anode and the FLC solution. Anodes and the microfluidic compartment within the cathode were entirely fabricated using LTCC technology. Developed ceramic structures were placed inside a polymeric housing made in three-dimensional printing technology. The AC-driven microAPGD system appeared to have better performance than the DC-driven system; it uninterruptedly run for a few hours during OES measurements. Under optimal experimental conditions, DLs of Cd and Zn obtained with AC-driven microAPGD were 0.053 and 0.14 mg/L, respectively, which was comparable or better than DLs reported by other researchers for similar microplasma excitation sources (Table 4). DLs of elements were, in general, better than these in the earlier work (Macioszczyk *et al.*, 2016a). During all experiments, cathodes within ceramic chips used for sustaining the AC-driven discharge demonstrated very good reliability. Screen-printed anodes (thickness 10 μm) were etched by the microplasma, but the solid W anode (50 μm wire diameter) exhibited better durability (W has higher melting point than Pt). A higher T_{rot} value for the DC-driven discharge as compared to this for the AC-driven discharge was likely the reason why the cathode and the anode in the ceramic chip "Type 1", used for operation of the DC-driven discharge, had poorer durability Figure 10(a) and 10(b).

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