



Low power capacitively coupled plasma microtorch for simultaneous multielemental determination by atomic emission using microspectrometers

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ABSTRACT

A new, low power capacitively coupled plasma microtorch (30 W, 13.56 MHz, 0.5 Lmin⁻¹ Ar) was investigated in conjunction with commercially available microspectrometers for the simultaneous multielemental analysis by atomic emission spectrometry of liquid samples without desolvation. Emission spectrum is simpler than in ICP-AES, the resonance lines are the most intense, so that a microspectrometer with FWHM of at least 1.5 nm is satisfactory for the record. The deviation from the Boltzmann distribution for Fe I has demonstrated the departure from the LTE in plasma. The non-spectral matrix effects of Li, Na, K, Ca and Mg on analytes emission are depressive and depend on matrix volatility, ionization potential of the interferent and analyte excitation energy. The detection limits ($\mu\text{g mL}^{-1}$) are in the range 0.003 (Li) and 1.5 (Mn). The use of the standard additions method allowed the simultaneous determination of elements in environmental certified reference materials with overall recovery of $95 \pm 10\%$ and relative standard deviation of 1.7–8.2%. Compared to the traditional ICP, the microtorch has a simple construction, runs at low argon flow and can be integrated in a portable system suitable for *in-situ* simultaneous determination of elements.

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1. Introduction

Atomic emission spectrometry with inductively coupled plasma (ICP-AES) is a reference analytical technique in spectrochemistry being the most used for multielemental determination in the standardized routine laboratory analysis [1]. The ICP-AES is a mature method with excellent analytical performance for rapid trace determination when using the CCD technology and dual-viewing. The simple adjustment of different sample introduction systems to handle solids, slurries, liquids or gases increases the versatility of ICP [2–4]. The high maintenance costs of the ICP led research in atomic spectrometry toward investigation of less expensive plasma sources, such as microwave induced plasma (MIP), capacitively microwave plasma (CMP), microwave plasma torch (MPT) and radiofrequency capacitively coupled plasma (CCP), all generated at low gas flow rate ($<1 \text{ Lmin}^{-1}$) and low/medium power ($<300 \text{ W}$). Jankowski [5] showed that a low-power MIP-AES system with ultrasonic sample nebulization can meet the criteria for ISO 11885 designed for the determination of 33 dissolved or particulate elements in raw, potable and wastewater by ICP-AES. The preliminary results of Feng and

coworkers [6] have demonstrated that a miniaturized MPT-AES system with CCD detection is suitable for multielemental determination in liquid samples with pneumatic nebulization and aerosol desolvation.

In our laboratory the analytical performance of a medium power (275 W) argon CCP torch with a Mo tubular electrode and single or double ring electrodes used in the multielemental analysis by atomic emission spectrometry (CCP-AES) of pneumatically nebulized liquid samples was investigated [7–10]. The results were the basis for building a simultaneous spectrometer with photodiode array as detector for the determination of alkali and earth-alkali elements as a substitute to the old methane-air flame photometer [11,12]. A viable alternative to atomic emission spectrometry with low/medium power microwave plasma or CCPs is atomic fluorescence using commercially available microspectrometers [13–16].

Innovations in the technology of optoelectronic detection have enabled the development in the last decade of several fully miniaturized spectrometric systems with different plasma sources for the determination of Hg by the cold vapor technique, hydride generating elements and volatile organic compounds [17–23]. The miniaturized spectrometric systems provide a substantial decrease of all costs and the advantage of portability [24,25].

The aim of this work was a preliminary investigation of a new capacitively coupled plasma microtorch in conjunction with

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commercially available microspectrometers for the simultaneous multielemental analysis by atomic emission spectrometry (μ CCP-AES) of liquid samples without desolvation. The advantages and drawbacks of the μ CCP against the traditional ICP are emphasized. Excitation temperatures of Ar I and Fe I lines were calculated and based on the deviation from the straight line of the Boltzmann plot it was stated the departure from the local thermal equilibrium (LTE) in plasma. A focus of this study was also the answer to the question of whether a microspectrometer with CCD interfaced with a low power μ CCP could be an analytical tool in AES even for elements having rich spectra. Detection limits, non-spectral interferences of easily ionizable and earth-alkali elements and several spectral interferences were evaluated for the simultaneous multielemental analysis of environmental samples using such a system after acid mineralization. The study is a matter of significant relevance for analytical practice since until now low power plasmas have been used for elemental determination rather in liquid samples introduced by electrothermal vaporization than by pneumatically nebulization.

2. Materials and methods

2.1. Instrumentation

The experimental set-up (Table 1) consisted of plasma microtorch, introduction system of liquid samples, radiofrequency generator, CCD microspectrometer, fibre optic system for collecting radiation emitted by the plasma and data processing system. In order to get better sensitivity both in UV and VIS, the microtorch was interfaced to the Ocean Optics microspectrometers HR4000 (200–420 nm) and HR4000 CG-UV-NIR (200–1100 nm).

The schematic diagram of the experimental set-up is presented in Fig. 1, while constructive details about microtorch and a photograph of the resulting plasma are provided in Fig. 2.

The home-made microtorch consists of a PTFE bush in which a 5 mm i.d. and 25 mm length quartz tube is mounted. The Mo tip microelectrode is fixed in a Mo support inside the quartz tube. The rf power supply is connected to the plasma torch via a silver cable bounded on the Mo electrode. The Ar flow together with the aerosol enters the plasma sheath through four 0.75 mm diameter holes made on the support on a 3 mm diameter circumference around the microelectrode. The support gas accomplishes the cooling of the microtorch assembly so that no water recirculation system is needed. Plasma is easily ignited by touching the quartz tube with an external grounded electrode after the rf power supply is connected. Since the tip microelectrode is in contact with the plasma it participates itself in the formation of the discharge by secondary electron emission. Plasma arises as a diffuse discharge on the tip of the powered microelectrode and can be generated at atmospheric pressure at powers in the range 10–30 W, 13.56 MHz and Ar flow rates below

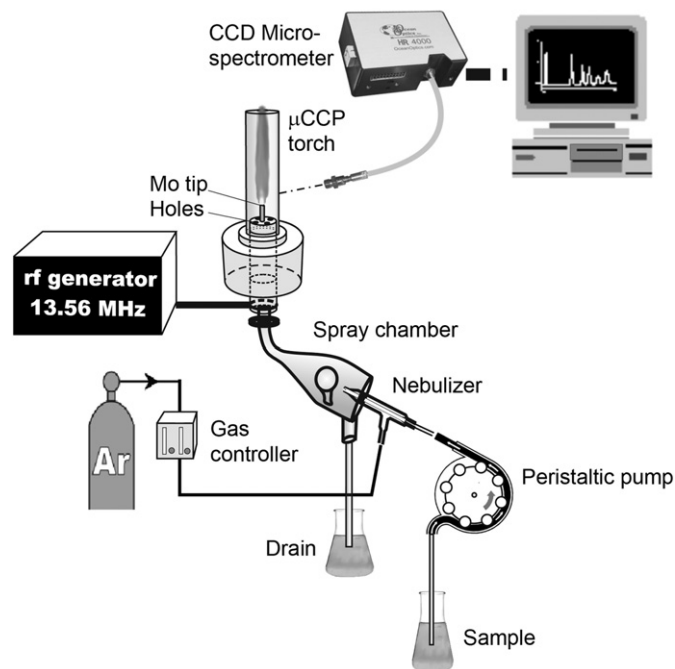


Fig. 1. Schematic diagram of the μ CCP-AES experimental set-up.

1 L min⁻¹. For analytical purposes, the CCP glow discharge is preferred to the rf arc as it is more stable and offers better excitation conditions, precision and accuracy. The fibre optic of the microspectrometer is mounted on an XYZ translator with micrometric adjustment by 0.1 mm increment that allows targeting different viewing zones in the plasma.

The miniature Ocean Optics simultaneous spectrometers are connected to the computer via a universal USB port and do not require an external power supply. The Spectrasuite soft allows the background correction.

2.2. Reagents, standard solutions and CRMs

Monoelemental stock solutions of Ca, Cd, Cu, Fe, In, Li, Mg, Mn, Na, Pb, Sr and Zn 1000 μ g mL⁻¹ as nitrate (Merck, Darmstadt, Germany) were used to prepare multielemental solutions. Dilutions were made with 1% nitric acid (v/v). The accuracy of the method was checked by analyzing soil and river sediment reference materials (CRM025-050, LGC6135, SRM 2709, NCS DC78301 purchased from LGC Promochem GmbH, Germany) mineralized in aqua regia in a high-pressure microwave system according to a procedure previously used [14].

Table 1

Characteristics of equipment used in the μ CCP-AES system.

Radiofrequency generator	Free-running oscillator, 10–30 W power level, 13.56 MHz (Technical University of Cluj-Napoca, Faculty of Electronics, Telecommunications and Information Technology); dimensions (L×W×H): 15×17×24 cm ³ .
Plasma microtorch	Capacitively coupled with central Mo tip microelectrode (1 mm-diameter); 5 mm i.d. quartz tube, 25 mm length, 160 nm cut-off; (INCDO-INOE 2000, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania); working gas: 5.0 quality argon (Linde Gas SRL, Timisoara, Romania); Ar flow rate: 0.3–0.5 Lmin ⁻¹ .
Sample introduction system	Meinhardt pneumatic nebulizer (Perkin-Elmer, Norwalk, USA) equipped with peristaltic pump and impact bead spray chamber; sample uptake in plasma (0.5 mL min ⁻¹ , 5% nebulization efficiency) through 4 holes (0.75 mm i.d.) made on a 3 mm diameter circumference around the tip microelectrode.
Detection	HR4000 Microspectrometer Ocean Optics (200–420 nm, 50 μ m entrance slit, 1200 groves mm ⁻¹ grating, Toshiba CCD with 3648 pixels, FWHM ~0.33 nm, collimating system 74-UV, fibre optic QP 600 μ m, 25 cm length) (Ocean Optics, Dunedin, USA); HR4000 Microspectrometer Ocean Optics CG-UV-NIR (200–1100 nm, 50 μ m entrance slit, Toshiba CCD with 3648 pixels 1304AP, FWHM ~1.5 nm, fibre optic QP 600 μ m, 25 cm length (Ocean Optics, Dunedin, USA) Collimating fused silica lens (5 mm diameter, 10 mm focal length; beam divergence 2° or less; 0.22 numerical aperture of spectrometer collimating mirror).
Data acquisition	Spectrasuite soft (Ocean Optics); 10 s and 30 s integration time; background correction: computer-subtracted.

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