



Detection of some industrially relevant elements in water by electrolyte cathode atmospheric glow discharge optical emission spectrometry



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ABSTRACT

An electrolyte cathode atmospheric glow discharge optical emission spectrometry (ELCAD-OES) method was developed for the detection of the industrially relevant In, Rh and Te in water samples. Acid/additive type, sample pH and flow rate were optimized. The UV–Vis spectrum was scanned for analytical lines, free from spectral overlap interferences, and sensitive enough for quantifying the analytes at mg L^{-1} or lower levels. In several cases, the background spectrum of the ELCAD hindered the use of conventional, resonant analytical lines in the UV due to overlaps with bands of molecular species (e.g., OH, NO, N_2). Te and Rh showed lower emission intensities than In (determined at In I 451.1 nm), even using the most sensitive, interference-free transitions (i.e., Te I 214.3 nm, Te I 238.6 nm and Rh I 437.5 nm). The emission intensities were highly sample pH dependent, i.e., analytical signals could only be detected at pH levels lower than 2. Conversely, the use of acidity lower than pH 1 caused lower plasma volume, due to its contraction into the sample introduction capillary, and discharge instability in terms of its frequent self-extinction. The detection limits for In, Rh and Te were 0.01, 0.5 and 2.4 mg L^{-1} , respectively. Calibration curves were linear up to $100\text{--}150 \text{ mg L}^{-1}$. The precision for In, Rh and Te in aqueous standards, expressed as relative standard deviation (RSD), was not higher than 4.6%, 6.4% and 7.4%, respectively. Samples with high salt content (e.g., well water) caused positive matrix effects (i.e., 2.0- to 3.6-fold signal enhancements), but also ~ 1.5 times higher RSDs.

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1. Introduction

Alternative means of solution sample introduction to that of conventional sample dispersion by nebulization is an attractive research topic in spectrochemistry. This is due largely to certain shortcomings of conventional nebulization techniques, for instance, the usually low-sample conversion/transport to the spectrochemical source [1,2]. Lately developed glow discharge (GD) plasmas, utilizing the sample solution (electrolyte) itself as one of the discharge electrodes, can overcome this drawback since they offer a direct and continuous sample introduction into the vaporization-excitation source, which is an important advantage over nebulization-based techniques [3]. Analytical systems based on this concept markedly differ from conventional, laboratory-based spectrochemical techniques. Their most important and outstanding feature is to provide the possibility for the continuous, real-time monitoring of the toxic element content of natural and waste waters [4].

Solution electrode GDs were first reported in electrochemistry and used in the so-called GD electrolysis in 1887 by Gubkin [5]. After many decades of silence in this field, they were studied further in the 1950s and 1960s [6–8]. Although the phenomenon of ordinary GDs to

emit spectra of elemental components from the nebulized/vaporized/excited sample solutions was well-known in those times, the utilization of a solution cathode GD for spectrochemical analysis was first reported in 1993, which is named as the electrolyte cathode atmospheric glow discharge (ELCAD) [9]. Since its appearance, the solution cathode concept has triggered a fairly wide interest and increase in development of ELCAD-like plasmas, combined with optical emission spectrometry (OES) detection, e.g., the liquid sampling atmospheric pressure glow discharge [10], the liquid electrode spectral emission chip [11], the drop spark discharge [12], the electrolyte jet cathode discharge [13], the solution cathode glow discharge [14–16] and the liquid electrode dielectric barrier discharge [17]. Recently, the ELCAD was demonstrated with atomic absorption spectrometry (AAS) detection, which has been proven to be rather a diagnostic tool, due to the low sensitivity [18]. The currently growing interest in the research of the solution electrode-based plasmas is also manifest in reviews, giving details on differences in physical, chemical and analytical features of various GDs, as well as the plasma excitation mechanisms [3,4,19–21].

For ELCAD-type plasmas, the limitations in sensitive detection of certain elements arise from the condition that these GDs work with a solution cathode. Therefore, they are saturated with water vapor in particularly dissociated form, which corresponds to a high concentration of hydroxyl (OH) radicals inside the plasma. The OH-radicals

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cause recombination of the analytes as hydroxides, which deteriorate or even fully depress their OES/AAS signals [18]. Moreover, due to the operation of ELCAD in ambient atmosphere, the ingress of N_2 from air into the outer core of the plasma occurs [19]. Because of these operating conditions, intense bands of excited plasma molecular species are present in the UV spectrum, which may overlap with the most sensitive resonant lines of certain elements, situated mostly over the same spectral range.

In this study, an attempt is made to find out the detection possibilities of a couple of toxic, industrially relevant elements (i.e., In, Rh and Te), which have not yet been studied in ELCAD-type or similar atmospheric plasmas. These elements have very low crustal abundance, including natural waters (some $ng\ L^{-1}$) [22–24]. However, they are relevant in a series of present day's industrial productions: for instance, indium for thin films, especially, corrosion shielding of hard alloys, and for electronic devices [25,26], such as LCD-monitors, TV and touch screens [25], solar cells [26] and light emitting diodes [27], rhodium in fabrication of automotive catalytic converters [28] and tellurium in semiconductor and electronic devices, such as solar panels [29], X-ray detectors [30], also in research, for fabrication of advanced optical materials [31]. Waste disposal and material processing raise the levels of these elements in the environment [28,32,33], which demand their detection/monitoring in various environmental compartments, including natural and waste waters.

The specific aims of the present work is (i) to check/select sensitive analytical lines of the analytes in the UV–Vis emission spectrum of ELCAD, (ii) to identify the possible interfering plasma (molecular) species and (iii) to study alternative acidic media/additives in order to find optimal conditions for the detection of the concerned analytes in different water samples by means of ELCAD-OES.

2. Experimental

2.1. Instrumentation

All experiments were performed with the application of a capillary ELCAD cell. This design possesses more focused plasma input power, which corresponds to higher energy in the discharge to affect vaporization, dissociation and excitation than regular ELCADs with wide-bore sample injector-tube [34]. If not stated otherwise, the GD was operated at an optimal discharge current of 70 mA and a discharge voltage of 950 V by a homelabmade (Aqua-Concorde), 1.2 kV high voltage power supply, providing a constant electric current for sustaining the plasma. The electrolyte cathode was coupled to the negative pole of the power supply through a Pt electrode and an ionic conductor (wool fiber) fabricated into the wall of the capillary but electrically insulated from the waste reservoir. A tungsten rod of 1 mm diameter with a sharp-tipped end was applied as anode, which was connected to the positive pole of the power supply through a 1.41 k Ω ballast resistor ($3 \times 470\ \Omega$, 8 W, $\pm 10\%$ connected in series) for assuring good plasma stability. The anode-to-cathode distance was positioned to ~ 3.25 mm by means of adjusting the screwable holder of the anode. The built-in voltmeter of the power supply was connected directly to the anode and cathode contact cables of the plasma, in order to display the real discharge voltage. The emission of the ELCAD plasma was viewed by UV–Vis monochromator optics, dismantled from a Varian AA-6 spectrometer. This optics was equipped with a stepper motor and mechanics for exhibiting fast/slow wavelength change/adjustment of the monochromator. The plasma observation length and height were precisely positioned in the optical path by micrometer screws. The original detector of the spectrometer was replaced with a Hamamatsu Model H11462-021 (Hamamatsu Photonics, Heersing, Germany) photosensor module, which incorporates a 28 mm diameter side-on photomultiplier tube (PMT), a high voltage power supply circuit and a low-noise amplifier. The voltage response of the PMT was registered by a Kipp&Zonen Model BD11E flatbed x-t recorder (Delft, The Netherlands). The operating

point voltage of the PMT was adjusted to 825 V, which setting provided high sensitivity and low background (dark current) noise. The entrance slit-width of the monochromator was adjusted to a spectral band-pass of 0.1 nm over the whole UV-visible spectral range. The schematic of the ELCAD–OES experimental arrangement is depicted on Fig. 1.

In order to maintain a smooth and continuous uptake of either the plasma blank electrolyte or the sample/standard solutions, a Cole-Parmer Model 74900-00 single-syringe infusion pump (Vernon Hills, IL, USA) was programmed to operate a 50 mL volume Hamilton syringe. The syringe was connected to the sample introduction capillary of the ELCAD unit through a three-way valve, which could also be switched to syringe loading position from a sample/standard container. Digital images of the glow discharge were taken with a Panasonic Model GP-MF622 CCD camera (Kadoma-shi, Osaka, Japan), fitted with a Biotar 1.5/75 (Carl Zeiss, Jena, Germany) telephoto lens.

2.2. Materials and sample preparation

All chemicals were of analytical grade, or better quality. De-ionized, ultrapure water (Milli-Q RG, Millipore, Billerica, MA, USA) having a resistivity of 18 M Ω cm was applied for dissolution of chemicals (powders) and standard/sample dilutions. Stock solutions of the analytes were prepared by weighing appropriate amounts of their corresponding powders (i.e., $InCl_3$, $RhCl_3$ and TeO_2) and then dissolving them in ultrapure water and/or acids (HCl, HNO_3). The chemicals were weighed on a Kern&Sohn Model 770-14 electronic analytical balance (Kern&Sohn GmbH, Balingen, Germany). Single-element standard solutions were diluted from the stock solution of each analyte. The pH of each standard/sample was adjusted with inorganic acids (HCl, HNO_3) by using a Voltcraft Model PHT-01 ATC pH meter (Conrad Electronic GmbH, Hirschau, Germany), which was calibrated on daily base against pH 7.00, 2.90 and 1.68 buffer solutions. The pH determinations in the standard/sample solutions were performed in ~ 10 min measurement cycles with an accuracy of $pH \pm 0.01$ at 25 $^\circ C$.

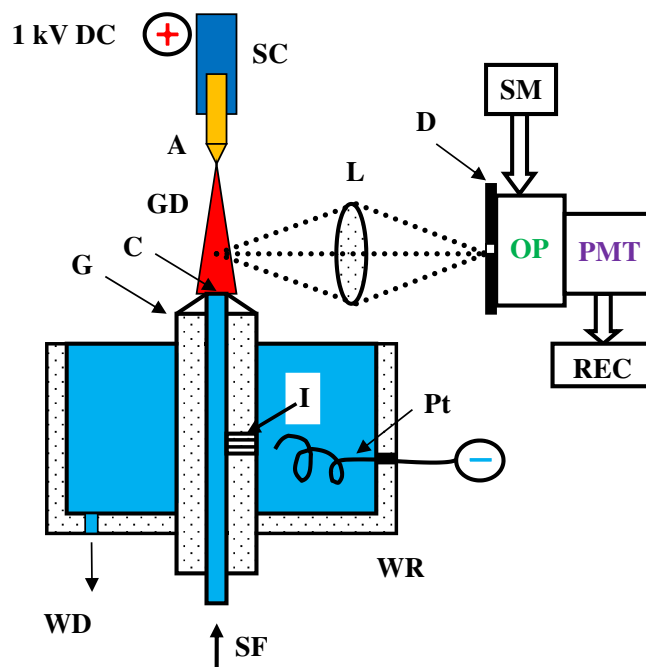


Fig. 1. Scheme of the ELCAD–OES measurement set-up; A—anode (W-rod), C—cathode (electrolyte solution), D—diaphragm, G—glass capillary, GD—glow discharge, I—ionic conductor (wool fiber), L—quartz lens ($f = 75$ mm), OP—optics, PMT—photomultiplier and amplifier, Pt—platinum contact wire for the ionic conductor (insulated from waste reservoir), REC—flatbed recorder, SC—stainless steel cooler, SM—stepper motor and mechanics, SF—sample flow, WD—sample waste drainage, WR—sample waste reservoir.

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