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Analytical advantages of using electrochemistry for atomic spectrometry*

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Abstract: Atomic spectrometry and electrochemistry are usually recognized as independent analytical tools used for different purposes. Here, a brief review is given of the advantages of using electrochemistry in the various fields of atomic spectrometry techniques. In the first part, the application of electrochemical preconcentration before the atomic spectrometry will be addressed and exemplified. Electrochemical preconcentration could be used with flame atomic absorption spectrometry (AAS) or graphite furnace AAS as well as with atomic emission plasma sources. The second area of the applications of electrochemistry will be directly focused on the graphite furnace AAS where the electrodeposition onto the graphite surface of the atomizer could be used for both *in situ* analyte preconcentration or modification of the surface by noble metals.

INTRODUCTION

Atomic absorption spectrometry (AAS) is generally recognized as a powerful technique with low detection limits in the range of μg/ml for flame AAS and ng/ml for graphite furnace (GF) AAS [1]. For a number of elements it is comparable to inductively coupled plasma optical emission spectrometry (ICP-OES), in the case of flame AAS, or ICP mass spectrometry (ICP-MS), in the case of GFAAS, both having the advantage of being multielemental techniques [2]. The disadvantage of ICP-OES and ICP-MS is, however, a relatively high cost, both in instrumentation and exploitation, unless a large number of routine analyses are performed daily. Therefore, research is still going on for improvement of the detection limit of AAS techniques.

The most common ways for improving the detection limit are based on preliminary preconcentration by chemical or physical procedures. The most suitable techniques of the preconcentration are solvent extraction [3–7], sorption on solid sorbents [8,9], coprecipitation [10], and electrodeposition [11]. In all cases, the *on-line* connection with flame AAS could be performed. In the case of graphite furnace AAS, the electrolytic deposition of metals could be performed either *off-line* in an outside electrolytic cell, or directly onto the graphite platform or furnace surface.

REQUIREMENTS FOR ELECTRODEPOSITION

Electrochemical preconcentration is used as a preliminary step in anodic stripping voltametry [12,13] or potentiometric stripping analysis [14,15]. During this step analyte ions are separated from the sample matrix and deposited on the electrode. The analytical signal is then obtained during the dissolution of the metal from the electrode. However, the efficiency of preconcentration and dissolution steps could be influenced by oxygen, surface-active compounds, and inert salts present in a sample. Atomic spectrometry may employ electrochemical preconcentration without facing problems typical of electrochemical methods used for final determination.

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There are several important requirements for effective electrochemical preconcentration of analyte ions on the electrode surface. As an electrodeposition of many heavy metals competes with the reduction of hydrogen ions, an electrode with high hydrogen overvoltage should be used in order to avoid extensive hydrogen ion reduction. Significantly high hydrogen overvoltage was found for mercury [12], glassy carbon [16], or glassy carbon covered by a mercury film [17]. As a consequence of the reduction of hydrogen ions, together with metal ions, the efficiency of the preconcentration is small, but electrodeposition is still possible. This is all that is needed for the subsequent determination by atomic spectrometry methods.

An important factor in electrochemical preconcentration is a ratio of the working electrode surface area to the volume of the electrolyzed sample. For these purposes, the maximal area of the electrode should interact with the minimal volume of the sample. This requirement could be achieved by the use of a flow-through cell with a thin channel between two-electrode [18] or a large surface area of working electrode [19]. Three types of flow-through, three-electrode cells with porous working electrodes made of crushed vitreous carbon were tested for copper determination by Beinrohr *et al.* [19]. The very effective cell is based on the use of a flow-through working electrode with a mercury film deposited on crushed graphite. However, one of the drawbacks of such a cell with porous electrode is a large volume of the solution required to wash out the preconcentrated metals.

ELECTROCHEMICAL PROCESSES FOR ATOMIC SPECTROMETRY

On-line electrochemical preconcentration for flame AAS

In all *on-line* preconcentration techniques a preconcentration cell is directly coupled by tubing with the nebulizer of an AAS instrument. The analytical procedure consists of two steps: (i) preconcentration of the analyte during the flow of the sample solution through the cell; (ii) dissolution of the analyte element in the carrier solution, transport of the solution into the flame, and measurement of the atomic absorption signal.

When electrochemical reactions are involved in the analytical procedure, the potential of deposition as well as the flow rate of the solution are critical in respect of preconcentration efficiency. It should be also mentioned that the effective volume of the eluent defines the lowest detection limit of the determination and, therefore, have to be as small as possible. Those parameters have to be taken into account to evaluate the analytical performance of the methods described in the literature.

The electrolytic microcell with a total volume of only 3 µl was developed in our laboratory [20]. Lead and cadmium were deposited on the glassy-carbon electrode. The designed cell exhibited good electrodeposition performance with an enhancement factor of more than 20, which offers a detection limit of 1 µg/l for Pb and 0.08 µg/l for Cd, respectively with 3 min deposition. Lower detection limit could be achieved with a longer preconcentration time, which results in a larger volume. The described cell consisted of two electrodes sealed in epoxy resin, one of glassy carbon (cathode) and one of platinum (anode). Both electrodes were positioned at a distance of about 0.1 mm, which means that a thin layer of the solution flowing between the electrodes allows to achieve a high preconcentration efficiency. Since the selectivity is not a problem in AAS, the deposition was performed in a simple two-electrode cell under galvanostatic control at a current of about 1 mA, and the dissolution of the analyte was achieved after short-circuiting of both electrodes. The developed design of the cell was used later on in the *off-line* system for GF AAS (see next paragraph) [21].

The electrochemical reaction was also used to carry out a reduction of Cr(VI) to Cr(III) followed by the sorption on alumina sorbent with flame AAS determination of speciation of chromium [22]. In the described procedure, chromium present in water was determined by flame AAS after the preconcentration of Cr(III) species on activated alumina at pH 7 in a flow system. The total chromium was determined after the electrochemical reduction of chromate ions to Cr(III), which are preconcentrate together with the original Cr(III) species in the sample. Both reduction and sorption are carried out in a combined cell containing a porous electrode, a layer of the sorbent, and the counter electrodes in series. The porous electrode was made of glassy-carbon particles coated with gold. The detection limits are 0.5 ng/ml and 250 ng/ml for 500 ml and 1 ml sample solution, respectively. Developed by Beinrohr *et al.* [22], electrochemical flow-through cells offer an elegant way to perform redox pretreatment of the sample solution directly in the flow system.

Off-line electrochemical preconcentration for graphite furnace AAS

An *off-line* preconcentration before GFAAS measurements was used by several authors. For these purposes, various materials of the electrode (metals, graphite), as well as several approaches were described. The first application of the use of electrochemical preconcentration followed by electrothermal atomization was described in 1967 [23]. The copper wire was used for deposition of mercury from urine samples. The copper electrode was inserted into the atomizer, and the atomic absorption signal of evaporated mercury was subsequently measured. Later on, the mercury drop electrode was used for electrodeposition of several metals [24]. The efficiency of preconcentration was very good, but the drawback of this procedure comes from the difficulties in handling the mercury electrode, as well as in its positioning in the atomizer. This was overcome when tungsten wire electrode was used successfully for the deposition of lead [25]. After the preconcentration step, the wire electrode was inserted vertically into the center of a graphite furnace for atomization.

The second group of the approach in electrodeposition was performed with the use of graphite as an electrode material. In this way, the analyte could be deposited onto the graphite electrode, and there are several ways to achieve the atomization of the deposited metal. The electrode can be powdered and the powder inserted into the atomizer [26]; carbon disc with the deposit could be cut off from the working electrode and transfered in the atomizer [27]; or the deposit can be stripped off by acids and the resulting solution analyzed [28].

Thomassen *et al.* [26] separated several elements from concentrated salt solutions by employing electrodeposition on a graphite rod. The electrode was subsequently ground, and the graphite powder was analyzed directly in the graphite furnace.

The possibility of using electrochemical deposition on various types of graphite electrodes with subsequent AAS determination was demonstrated and discussed by Komarek *et al.* [27]. The most promising results were obtained with a graphite disk electrode in combination with an atomizer, similar to the graphite probe, which was introduced in GFAAS to attain isothermal atomization. The example element was copper, which was deposited from the solution of pH 2 at a cathode potential of –0.7 V. The deposition was performed in 1–5 min, depending on metal concentration.

Platinum in the sample solutions of tobacco, beans, slag, and dust was electrochemically deposited at –0.9 to –1.2 V in a flow system incorporating a 3-electrode flow-through cell with a graphite counter and Ag/AgCl reference electrode [29]. After the electrodeposition the tube was placed into the graphite furnace, and an atomization temperature of 2700 °C was applied.

The outside cell described before [20,21] with two-electrode was used in off-line procedure for Pb determination in analytical-grade reagents (NaCl, Na_2SO_4) [30]. The design of the cell was as simple as possible with minimum dead volume to achieve complete elution of the deposited element with 40 µl of the eluent. The distance between the electrodes of 0.2 mm results in a cell volume of about 3 µl. The detection limit for lead was 0.2–1.2 ng/l range depending on the volume of the sample used for preconcentration. In comparison with the direct injection of 40 µl of aqueous solution, the efficiency of electrodeposition was 78%.

Another approach was based on the fact that some metal ions can be deposited electrolytically on the inner surface of a graphite tube and determined after evaporation and atomization of the deposit simply by heating the tube. This procedure was proposed by Batley and Matousek [31,32]. They deposited Co, Ni, and Cr in the presence of mercury(II) directly onto the inner surface of pyrolytically coated graphite tube used as the cathode at a controlled potential. However, an efficiency of the electrodepositon was low. As mentioned before, to achieve higher efficiency, the cell should ensure a high mass transfer rate of the electroactive species to the electrode surface. This can be achieved by using a thin-layer cell having a high electrode surface to electrolyte layer thickness ratio or by using porous electrodes. The efficiency of deposition in the graphite tube was improved when a nylon insert installed centrally inside the tube was used to produced a thin-layer flow-through cell [33]. In another approach, the porous electrodes made from graphite tubes packed with reticulated vitreous carbon (RVC) were used for effective preconcentration of Pb [34] and Pt [29].

In the work described in [34], traces of Pb were preconcentrated electrochemically in the flow system, incorporating a flow-through cell with graphite tube packed with RVC serving as the working electrode. The deposition potential of –3V was set to the graphite tube, and the sample solution with pH was adjusted to 4.8 with acetate buffer was injected into the water flow. After washing the cell with water, the tube was placed into the graphite furnace. The evaporated deposit was transported by argon gas into the plasma for excitation. A detection limit of 0.2 ng/ml of Pb in 1 ml of preconcentrated sample solution was achieved.

Electrodeposition on the graphite platform was reported in several works [35,36]. Matousek *et al*. [35] reported the possibility of *in situ* electrodeposition of lead from 0.1 mol/l KCl media directly on the graphite platform after injection of 25–50 µl of the sample solution. However, the drawback of such an approach was a rapid evolution of H_2 at the cathode (graphite platform) and Cl_2 and O_2 at the anode. As a consequence, the relative long time of preconcentration (4–5 min) was required. The further improvement of the *in situ* deposition was achieved when the analyte was electrodeposited from microliter sample volume injected directly in the graphite tube [37,38]. In subsequent work of Matousek's group [37], the electrodeposition from 0.5 mol/l NaCl medium has been studied. For this purpose, the deposition was performed directly inside the graphite tube with the aid of platinum anode wire. The quantitative separation from 50 µl volume of the solution was obtained within 120 s. However, due to the exfoliation of the pyrolytic graphite coating, the life-time of the tube was limited to about 70 cycles.

This drawback was partially eliminated by preliminary electrodeposition of palladium, which serves in a reduced form as a modifier with subsequent deposition of analyte onto the modified surface [38]. The autosampler can be programmed in a way to remove the solution after electrodeposition. Deposition of Pd was achieved within 40 s at a cell voltage of 3.0 V (5–10 mA) from 40 µl of 10 µg/ml Pd in 0.5% HNO_3. This approach provides quantitative deposition of metal within 40–60 s. The evolution of hydrogen ensures adequate stirring of the sample. This was successfully used for the determination of Pb in biological materials [39].

Recently, an interesting approach was proposed by Matousek *et al*. [40]. *In situ* electrodeposition onto the graphite tube was applied to the speciation of Bi, Pb, Ni, and Cu, in respect to differentiate between electrochemically labile and inert species. By varying the cell potential, selective reduction of free-metal ions could be achieved in the presence of the EDTA complexes. The work was tested only for model samples as the application to natural water is complicated by adsorption of natural organic matter onto the surface of the graphite which serves as an electrode.

Modification of the graphite surface in GF AAS

One of the important aspects of the analytical procedure in graphite furnace AAS is the use of chemical modification of the sample in order to modify the termochemical behavior of both the analyte and the matrix. The literature on the modifiers used for this purpose, as well as on the modification procedures, is ample [41]. Palladium and platinum chlorides were first used as modifiers in 1979 by Shan and Ni [42]. Grobenski *et al*. [43] showed that prereduction of palladium to its elemental form in a graphite atomizer significantly enhances its efficiency toward mercury. Presently, platinum group metals are recognized as the most effective and universal chemical modifiers [44]. The deposition of noble metals in their elemental form by electrolytic reduction was developed in our laboratory [45]. Before electrodeposition, tubes were cleaned by heating at 2500 °C for 5 s in the atomizer while purging argon gas through it. After cooling, each tube was wrapped with a Teflon band, the appropriate solution containing palladium, iridium, or rhodium chlorides was poured into the graphite tube (cathode), and the platinum wire (anode) was inserted inside. Conditions for electrodeposition: (i) electrolytic bath composition; (ii) current density; (iii) time of deposition, were optimized in order to find the best analytical conditions [46]. The most important advantages of the electrodeposition of noble metals is that they are deposited in elemental forms. This reduced significantly the amount of oxygen, which is present when thermal reduction is performed. As a consequence, the corrosion of the graphite is less pronounced with an electrodeposition procedure. Another advantage of using electrolytic reduction of noble metals on the graphite surface is permanent performance of modification, which means that once deposited can serve for several atomization cycles. The described procedure resulted in long-term performance (up to 100 atomization cycles) for Si [47], Hg [48], and Se [49] determination even when the atomizer was heated above 2400 °C. A similar approach was described by Matousek and Powell [38]. However, in our procedure, the modifier was deposited onto the whole inner surface of the tube, while Matousek and Powell deposited palladium on the small area covered by 40 μl droplet injected into the tube. The electrodeposition of palladium was performed before with each sample, without testing the long-term performance of such modification [39]. This procedure was successfully applied for the determination of Pb in biological material [39] as well as for the *in situ* speciation of various metals [40].

The advantages of electrodeposited noble metals were proved to work not only for standard solution but what is more critical also for real samples with complex matrix. It was shown that electrodeposited iridium can be used for the determination of selenium in the presence of a chloride-containing matrix [50], as well as for the determination of antimony in the solution containing proteins and sodium chloride [51]. The specific behavior of noble metals after electrolytic reduction was investigated [52], and the observed phenomena were explained by the formation of intercalation compounds of graphite with noble metals [53].

The electrodeposited palladium was also tested for the preconcentration of the hydride-forming elements. The first experiments were performed by Hilligsøe *et al.* [54] for the determination of germanium. The tubes with electrodeposited palladium, prepared in our laboratory, were tested for this purpose. It was found that the stabilization effect was similar to that observed when palladium was thermally reduced, however, the efficiency of trapping was lower. This was explained by the fact that palladium migrates into the subsurface layer of the graphite [52] and is not effective for the trapping of germanium hydride. We tested the performance of electrodeposited palladium for the determination of antimony after its hydride trapping [55]. Similar to the observation made for germanium, we found that the efficiency of antimony hydride trapping is lower for electrodeposited palladium when compared with thermally reduced palladium. However, thermally reduced palladium has to be introduced before each measurement; as in case of electrolytic reduction, the performance of modification is stable for at least 75 determination cycles without any significant change in the efficiency of preconcentration. This improved the sample throughput and allows reduction of the blank level.

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