

Abstract

Various possibilities for the use of electrochemical generation of volatile compounds for the determination of trace and ultratrace quantities of elements using atomic absorption spectrometry and optical emission spectrometry, respectively, were studied in this work. The Thesis is divided into four thematic sections. Electrochemical cold mercury vapor generation is common to the first two parts. The third part is devoted to electrochemical generation of the volatile form of cadmium and the last part deals with the use of the electrochemical hydride generator as a derivatization unit for speciation analysis of arsenic compounds.

The optimization of each individual determination was carried out including, for example, various designs of the generator of volatile compounds (forms) of the analyte, the changes in the design of the gas-liquid separator, optimization of the concentration and the flow rate of all the solutions and the carrier gas. However, the value of the electric current employed was the most important parameter.

In the first section, the in-situ trapping system of the cold mercury vapor generated in the graphite furnace (with the inner surface covered with a gold foil) of the atomic absorption spectrometer was also designed and optimized. The absolute limit of detection, 80 pg, was attained under the optimum conditions after a 60 s collection. This value is significantly lower than that of 124 pg, attained using chemical mercury cold vapor generation as the comparative technique. The accuracy of the method was verified by analyzing the certified reference material NIST 1641d.

The same mercury cold vapor generator was used in the second part, but a miniature microwave micro-strip plasma was used as the exciting source for the detection by an optical emission spectrometer. The detection limit for the mercury determination, $1.1 \text{ ng}\cdot\text{mL}^{-1}$, was attained using this original arrangement of the experiment and it was nine times better than that obtained for the chemical generation with NaBH_4 .

The third topic of this work was focused on the electrochemical generation of the volatile form of cadmium. The limit of detection, 830 pg, was attained for the determination of cadmium in the solution using a more sensitive flow injection arrangement coupled with AAS detection. In comparison, a value about ten times better was obtained using the chemical generation. On the other hand, the limits of detection for the chemical and the electrochemical generation of the volatile form of cadmium were comparable ($\sim 2.5 \text{ ng}\cdot\text{mL}^{-1}$) in the continuous flow analysis mode. Based on the evidence obtained, the question of what actually is the volatile form of cadmium was discussed.

In the fourth part, an electrochemical hydride generator was used as the derivatization unit for the on-line speciation analysis of selected arsenic compounds after their HPLC separation. Compared with the chemical generation, the connection of the techniques discussed provides an advantage in the obtaining comparable sensitivities for all the four substances analyzed. The limits of detection for the proposed determination of arsenite, arsenate, dimethylarsinate and monomethylarsonate were in the range from 0.8 to $1.9 \text{ ng}\cdot\text{mL}^{-1}$.