Abstract

The presented dissertation thesis deals with the use of UV-photochemical generation of volatile compounds (UV-PVG) as a derivatization technique for the combination of high-performance liquid chromatography (HPLC) and atomic absorption spectrometry (AAS) detection. Two model elements arsenic and mercury and their compounds were selected for the speciation analysis. The work was divided into several parts that follow.

In the first part of the research, the apparatus for the UV-photochemical generation of the volatile mercury compounds and their detection with a new continuum source and high-resolution atomic absorption spectrometer (HR-CS AAS) with an externally heated detection tube was constructed. The analytical method was adapted for use with atomic fluorescence detection with the aim to improve sensitivity of the determination. Furthermore, apparatus for the electrochemical generation of cold mercury vapor with AAS detection was built. The construction of the apparatus was followed by optimization of the reaction conditions (concentration and flow of electrochemical reagents: sulfuric and hydrochloric acid, mobile phase, carrier medium, flow rate of the carrier gas and localization of its introduction), determination of the analytical figures of merit, and comparation of the methods. Both methods of generation were compared to each other to find a suitable method for determination of mercury species. The applicability of the proposed method (including extraction by tetramethylammonium hydroxide and HCl at 75 °C) was demonstrated by using certified reference materials DOLT-4 (dogfish liver), ERM-CE464 (tuna fish), fish tissues and by HPLC-ICP-MS and AMA 254.

The next part of work started by construction of the apparatus for the UV-photochemical generation of volatile compounds of arsenic in flow injection analysis with AAS detection in externally heated quartz tube atomizer. Emphasis was placed on the construction of the UV-photochemical generator, especially on the material of the reaction coil (Teflon or quartz). The tubes of different diameters and wall thickness were tested. The optimization of the working conditions (composition of the carrier solution and its flow rate, flow rate of carrier and reaction gas and the place of their introduction to the apparatus, reaction coil material and its length, type of UV generator) was performed. The sensitivity of the determination can be improved by

addition of a suitable reaction modifier with persistent or short-time effect (Bi(III) and Sb(III)).