Abstract

This thesis encompasses a development of innovative methodologies based on atomic fluorescence spectrometry, offering precise and sensitive determination of ultra-trace elements, such as bismuth, cadmium, and nickel. The common denominator of all parts of this work is the use of a research-grade non-dispersive atomic fluorescence spectrometer (AFS).

First part of this work is dedicated to the development of a highly sensitive methodology for bismuth determination based on hydride generation (HG) coupled with AFS. Bismuthane was generated by the reaction with $NaBH_4$ in HCl medium in a flow injection arrangement and directed by a stream of carrier argon and hydrogen to an atomizer. A detailed optimization of the optical path of the spectrometer (electrodeless discharge lamp, lenses and interference filter) and atomization parameters in two flame atomizers – miniature diffusion flame (MDF) and flame-in-gas-shield atomizer (FIGS) – was performed. An excellent repeatability and extremely low limits of detection were achieved, namely 1.8 ng L^{-1} with the MDF and 0.9 ng L^{-1} with the FIGS.

Subsequently, a photochemical vapour generation (PVG) of bismuth was coupled to AFS, employing a flow injection arrangement of the generator, a standard mercury low-pressure UV lamp and a coiled Teflon reactor. A flow rate of 3 mL min^{-1}, corresponding to an irradiation time of 90 s, and a combination of acetic acid and formic acid as the photochemical medium in the presence of Co^{2+} as a sensitizer were found optimal for PVG. The atomization conditions using FIGS atomizer were optimized and they did not differ significantly from HG-AFS, except for the significantly higher flow rate of oxygen. A limit of detection of 12 ng L^{-1} was achieved.

A methodology for cadmium determination based on chemical vapour generation (CVG) coupled with AFS using an electrodeless discharge lamp as the excitation source was also developed. Cd volatile species were generated in a four-channel flow injection CVG system by the reaction of the analyte with $NaBH_4$ in a HCl medium in the presence of Cr^{3+}/KCN as modifiers enhancing the CVG efficiency. The atomization conditions were optimized for both MDF and FIGS atomizers. The sensitivity obtained with the FIGS atomizer was approximately twofold higher compared to that with the MDF atomizer; therefore, the FIGS atomizer was selected for further analytical applications, providing an excellent limit of detection of 0.42 ng L^{-1}.

To expand the applicability in terms of number of analyte elements, the spectrometer was modified to be operated with boosted discharge hollow cathode lamps also called

Superlamps. The operational parameters of the Superlamp were optimized using bismuth as the model analyte with respect to the intensity of the emitted radiation and the resulting fluorescence radiation. The achieved analytical characteristics were compared for both excitation sources - electrodeless discharge lamp and Superlamp.

Last part of this thesis is dedicated to the development of a method for nickel determination based on PVG and AFS using the Superlamp as the excitation source. The PVG was conducted with a high-efficiency flow-through photoreactor from the photochemical medium containing formic acid at the flow rate of 1.5 mL min^{-1} through the photoreactor, which corresponds to an irradiation time of 29 s. The atomization conditions in both MDF and FIGS atomizers were optimized and a limit of detection of 5.3 ng L^{-1} was achieved with the FIGS atomizer.

Last but not least, all the developed methodologies were verified by the determination of Bi, Cd and Ni in certified reference materials of water, hair, and blood (Bi) and real samples of water (Ni) and rice samples (Cd).