

Construction and application of new reactors for ultraviolet vapor generation coupled to atomic spectrometry

(Post-doctoral project proposal)

Introduction:

Sample introduction is the Achilles heel of the atomic spectrometric methods¹. The sample introduction system has to convert the solid or liquid sample into gaseous phase suitable for analyte atomization². The prerequisites for ideal sample introduction system are: compatibility with all atomic spectrometric methods, high analyte transport efficiency, low sample consumption, freedom from non-spectral interferences, selectivity for analyte of interest, ruggedness and reproducibility¹⁻³. However, some of the above mentioned criteria are incompatible resulting in design compromises. Volatile species generation is an advantageous way of highly efficient delivery of the analyte into the detection device and the interest in this method has been growing recently, because it can be coupled to any atomic spectrometric method^{1,3,4}. This technique offers the separation of volatile compounds from liquid matrix reducing interference⁴⁻⁵. In addition, it decreases the energy necessary for atomization or ionization of the analyte⁶⁻⁷.

The volatile species can be formed using chemical, electrochemical and photochemical reactions⁵. Chemical hydride generation using borohydrides is routinely used as a method of choice for the determination of hydride forming elements (As, Se, Sb, Bi, Pb, Sn, Te) and mercury^{1,3,6}. However, it suffers from instability of the reducing agent, high blanks due to reagent contamination and need for sample preparation in case of analytes in higher valence states^{1,3,7}. Electrochemical generation suffers from electrode passivation and resulting memory effects⁵. UV-photochemical volatile species generation (UV-PVG) is currently the most promising method due to its instrumental simplicity and possibility of using photocatalysts for the pre-reduction of analytes in higher valence states^{1,6-8}. Other advantages include broader scope of element coverage and simple hyphenation with separation techniques (HPLC, GC) for speciation analyses¹. Last but not least, photochemical methods reduce the production of toxic waste making UV-PVG an environmentally friendly method^{1,15-17}. In the last decade photochemical vapor generation has been applied for the determination of mercury as well as transition metals (Co, Fe, Ni) and hydride forming elements (As, Sb, Se, Te) in various matrices⁹⁻¹⁸.

It seems that a crucial factor for further development of UV-PVG may be the construction of photochemical reactor, because reactors of different constructions described in the literature produced contradictory results⁶. The aim of this project is to design and build new types of highly efficient flow-through UV reactors and apply them for sensitive determination of selected environmentally and toxicologically important elements (As, Hg, etc.).

Objectives:

The goal of this project is to design and test highly efficient flow-through reactors for UV-photochemical generation and develop sensitive methods for environmental analysis. The goal is divided into three steps.

Step 1: To design and build flow-through UV reactors with the quartz reaction coil located inside of the mercury lamp, where the sample will be irradiated more efficiently than in usual UV-PVG reactors. The design will be based on the reactors of Qin¹⁶ and coworkers and Zheng¹⁹ and coworkers, who proved high efficiency of such reactor on the determination of mercury, iron and nickel. At least one of the designs should be miniaturized. Recent studies using light emitting diode (LED) UV sources suggest that even low power sources can generate mercury or selenium volatile species with sufficient efficiency to achieve sensitive analysis when coupled with AFS equipment²⁰. Development of small low pressure lamps opens the field for new easy interchangeable bench peripherals that can be used with AAS, AFS, ICP OES or ICP-MS systems.

Step 2: To tune the UV lamp emission spectrum for selective and sensitive determination of different analytes. Composition of gaseous atmosphere and pressure inside the lamp affects the UV lamp

emission spectrum. Almost all works described in literature use commercial low-pressure mercury lamps filled with small drop of mercury amalgam in argon inside the discharge tube resulting in line spectrum with maximum emission at 253.7 nm. Our aim is to test different compositions of gas filling the UV lamp and, therefore, different emission profiles. Two approaches can be employed: either filling the lamp with different discharge gasses emitting in UV range (hydrogen, deuterium, helium) or filling the lamp with amalgam modifying mercury emission spectrum (e.g. CdHg) to produce more lines in UV-C region. Articles discussing the mechanism of reactions during photochemical formation of volatile species suggest that lower wavelengths could improve the efficiency of generation for some elements^{1,6,11}.

Step 3: To apply the built reactors for determination of mercury, arsenic and other elements in various matrices including environmental and biological samples to test their efficiency and applicability. Dissolution procedures for sample preparation compatible with UV-PVG will be developed to achieve this goal. This aim is consistent with extension of knowledge about applications of UV-PVG.

Risk Management:

Based on literature research, step one should be feasible leading to the construction of highly efficient flow-through reactors, which would allow sensitive determination of both intended analytes (As, Hg). Step two is a novel approach, which is, nevertheless, based on a sound principle. Even if step two does not yield the expected increased generation efficiency, the feasibility of step three is not at risk.

Outcomes:

The project will result in at least two publications dealing with very sensitive determination of environmentally interesting elements using the UV-PVG technique. The papers will be published in journals from first quartile. The developed reactors will be used in future research as well.

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