

Aim of the project and description of researches: This project is to develop completely novel, effective, and universal sample introduction systems based on operation of dielectric barrier discharge (DBD) in modified spray chambers with micronebulizers for simultaneous pneumatic nebulization (PN) of sample solutions, *in situ* pre-evaporation of resulting primary sample aerosol and plasma-assisted chemical vapor generation. These systems will be combined with an inductively coupled plasma mass spectrometry (ICP-MS) instrument for simultaneous and efficient introduction of volatile and non-volatile species forming elements, and their sensitive and free from severe matrix effects determinations. The new method will be fully optimized and validated. Its reliability and applicability in multi-element analysis will be illustrated by element analysis of several relevant certified reference materials of environmental and food samples. Furthermore, mechanisms responsible for pre-evaporation of sample aerosol and plasma-assisted chemical vapor generation (PA-CVG) will be evaluated to increase effectiveness and reliability of the new sample introduction systems.

Reasons why this research topic was taken: Despite a high number of applications in element analysis of sample solutions, PN with different pneumatic nebulizers and spray chambers is still considered as the Achilles' heel of ICP-MS. This is because sensitivity of measurements and detection limits of elements achievable with ICP-MS are restricted by PN efficiency, which is commonly <5-10%. In case of non-volatile species forming elements, introduced *via* PN, a common way to improve analytical figures of merit for them is pre-evaporation of resulting primary sample aerosol by means of conventionally heated spray chambers or pre-evaporation tubes placed after spray chambers. In this case, complete or partial sample aerosol evaporation takes place, resulting in enhancing the sample aerosol transport rate and analytes introduction efficiency. Unfortunately, convective heating used in these systems makes that walls of spray chambers or pre-evaporation tubes are ineffectively heated, while common temperature drifts are responsible for instability of analyte signals and relatively long washout times during routine ICP-MS operation. To improve transport efficiency of elements that form vapors (like Hg) or covalent hydrides (like As, Bi, Ge, Pb, Sb, Se, Sn and Te), chemical vapor generation (CVG) is used as an alternative to PN. However, it involves chemical reaction in acidic solutions (commonly HCl) with a reducing agent (overwhelmingly NaBH₄), and then, separation of evolved volatile element species from post-reaction solutions prior to their transport to ICP. This enables to increase sensitivity of measurements of volatile species forming elements and eliminate common matrix effects in ICP-MS. Nevertheless, vast interferences coming from concomitant transition metals, primarily of Co, Cu, Ni, commonly occur at the stage of CVG. Reduced forms and/or borides of these metals are formed and adsorb volatile element species before their evolution and separation from post-reaction solutions.

Expected effects: To overcome drawbacks of sample introduction to ICP-MS by PN and CVG, this project proposes completely novel and universal sample introduction systems based on DBD in modified spray chambers with a micronebulizers. The new concept assumes that *in situ* pre-evaporation of sample aerosol and PA-CVG processes will take place inside modified spray chambers by interaction of solution droplets with the DBD phase. The innovative concept of the DBD-based system will bring several benefits over previously reported sample introduction systems: **1.** homogenous and efficient heating of sample aerosol by DBD generated inside the spray chamber to produce pre-evaporated and pre-heated tertiary aerosol that introduced into ICP-MS will be responsible for much enhanced transport of non-volatile species forming elements, improved analytical performance due to superior atomization conditions, and efficient evaporation of total dissolved solids responsible for matrix effects, and **2.** effective and massive interaction of solution droplets with reactive species of DBD that will be responsible for efficient production of volatile species of certain elements inside the spray chamber without need to carry out chemical reaction using a certain reducing agent. Considering simplicity of novel systems for combined sample introduction *via* PN with simultaneous *in situ* aerosol pre-evaporation and PA-CVG by DBD action, it can be expected that they will find application in routine analyses of samples containing ultratrace levels of selected elements, and such that require high dilutions due to presence of matrix components (environmental and food samples, pharmaceuticals). The new sample introduction systems will bring much more benefits to ICP-MS and other spectrometric methods, *e.g.*, inductively coupled plasma optical emission spectrometry (ICP-OES), than custom and overwhelmingly applied PN, CVG, or dual PN with CVG systems. Their potential (boosted analytical performance) and universality (multi-element capability) will significantly improve quality of sensitive and interference-free measurements of non-volatile and volatile species forming elements by ICP-MS and ICP-OES.