MASARYK UNIVERSITY

Faculty of Science
Department of Chemistry

Separation Methods and Mass Spectrometry Applications

Ph.D. THESIS

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Introduction

Mass spectrometry is now used across a broad range of disciplines and settings, including academic research, biotechnological development, pharmaceutical discovery, clinical testing, environmental analysis and geological testing. Several analytical methods have been developed for the determination of antibiotics in various environmental matrices (e.g. wastewater, soil, sludge, and manure) can be found in the literature. The analytical procedures consisted of the extraction of the compounds from sludge, clean-up of the extracts and analysis by chromatographic techniques (liquid or gas chromatography coupled with mass spectrometry). The extraction of antibiotics from sludge is affected by the various adsorption mechanisms, such as hydrogen bonding, cation exchange, hydrophobic interactions and complexation involved in their retention in the solid phase. For the determination of antibiotics, liquid chromatography (LC) with both diode-array (DAD) and mass spectrometry detection (MS) or tandem MS have been used. LC-MS/MS is the most widely employed in the determination of antibiotics in complex matrices due to its high sensitivity, selectivity and its ability to provide compound information.

Nanoparticles form aggregates which refer the accumulation of several nanoparticles. The aggregation of nanoclusters is well known and several papers have been reported on this issue. Mass spectrometry is considered as one of the significant analytical tools in analytical chemistry as it is employed to analyze organic, inorganic and biological molecules such as proteins, oligonucleotides, carbohydrates, and lipids.

In this work, the formation of various nanoclusters via Laser Desorption and Ionization (LDI), Matrix Assisted Laser Desorption and Ionization (MALDI) and/or Laser Ablation (LA) was studied using Time Of Flight Mass Spectrometry (TOF MS) and Quadrupole Ion Trap Time-Of-Flight Mass Spectrometry (QIT-TOF-MS). Also the aim was to contribute towards the understanding of processes which could take place in the plasma plume formed during the ionization. The knowledge about the clusters formation is essential for nano-technology and it might also be useful to study nanoparticles interactions with biomolecules.

Abstract (in English)

Mass spectrometry is a sensitive technique used to detect, identify and quantitate molecules based on their mass and charge (*m/z*).The Thesis deals with the applications of Laser Desorption and Ionization (LDI) and/or Matrix-Assisted Laser Desorption and Ionization (MALDI) Time of Flight Mass Spectrometry (TOF MS)/Quadrupole Ion Trap Time-Of-Flight Mass Spectrometry (QIT-TOF-MS) analysis of various nano-materials or nano-layers and with laser ablation synthesis of arsenic phosphides, piperazine and it's derivatives.

Several different chemical materials including nano-materials like gold nano particles (GNPs), nano-diamonds, pre cursors of arsenic phosphides, Si wafers, piperazine and it's derivatives, etc. were analyzed using either LDI or MALDI TOF MS or QIT-TOF-MS. The stoichiometry of the clusters was determined via isotopic envelope analysis and

computer modelling. Primarily, in all studies the optimal laser power conditions for the cluster generation under applied experimental set up were always searched for and the formation of various clusters in the plasma plume during the LDI and/or MALDI ionization of used nano materials was examined also with respect to understand processes during the pulsed laser deposition of nano-materials (like Si wafers). The results contribute to the understanding of chemical bonding in studied materials. Original results concerning the laser ablation synthesis of arsenic phosphides from nano – precursors were obtained.

Abstrakt (in Czech)

Hmotnostní spektrometrie je citlivá metoda, užívaná k detekci, identifikaci a kvantifikaci molekul využitím rozdílů v poměru hmotnosti a náboje (*m/z*). Předkládaná disertační práce se zabývá aplikacemi ionizace laserovou desorpcí (Laser Desorption and Ionization, LDI), resp. ionizace laserovou desorpcí s použitím matrice (Matrix-Assisted Laser Desorption and Ionization, MALDI) ve spojení s Time of Flight (TOF) hmotnostní spektrometrií (TOF-MS) nebo TOF hmotnostní spektrometrií s kvadrupólovou iontovou pastí (QIT-TOF-MS) k analýze různých druhů nanomateriálů a nanovrstev a laserovou ablační syntézou fosfidů arsenu a derivátů piperazinu.
Studované materiály, jako jsou např. nanomateriály (nanočástice zlata, nanodiamanty), prekurzory pro přípravu fosfidů arsenu, Si wafery, piperazin a jeho deriváty, aj., byly analyzovány buď LDI nebo MALDI s TOF-MS nebo QIT-TOF-MS. Stechiometrie získaných klastrů byla určena metodou analýzy izotopových "obalových křivek" (isotopic envelope analysis) a pomocí počítačového modelování. Pro všechny studované materiály byla určena energie laseru, optimální pro tvorbu klastrů za daných experimentálních podmínek. Tvorba klastrů v plazmovém výboji během LDI a/nebo MALDI ionizace analyzovaných materiálů byla studována také ohledem na objasnění procesů k nimž dochází během depozice nanomateriálů pomocí pulsního laseru (např. na Si wafery). Získané výsledky umožňují porozumět chemickým vazbám ve studovaných materiálech. Originální výsledky byly získány studiem laserové ablační syntézy fosfidů arsenu z příslušných prekurzorů.

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