

Time of Flight Mass Spectrometry for analysis of nano- and plasma modified materials

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More than 100 years passed since the construction of the first mass spectrometer (Thomson in 1906) and now this instrumentation belongs to the most important analytical techniques in all branches of chemistry, science and technology. The discovery of Matrix Assisted Laser Desorption Ionization (MALDI) with Time Of Flight (TOF) detector – MALDI TOF MS enabled to ionize biomolecules without their fragmentation and importance of such invention was evaluated by giving Nobel Prize (1/4) to Koichi Tanaka (in 2002). MALDI TOF MS is now the leading analytical instrumentation for studying biomolecules, pharmaceuticals products, peptides, proteins, polymers, and any kind of molecules with masses even exceeding 1 000 000 Daltons. Applications include first of all genomics and proteomics.

Instrumentation of Time Of Flight Mass Spectrometry (TOF MS) with ionization either using matrices (MALDI) or applying just Laser Desorption and Ionization (LDI) represents suitable instrumental technique also for MS analysis of nano-materials. Still it is perhaps not realized fully that TOF MS can also be applied with advantage to analyze inorganic compounds, adsorbed organic and/or inorganic compounds on various surfaces, to study chemical structure of the inorganic polymers, plasma modified surfaces of inorganic, organic and hyphenated materials and also of nano-materials and nano-layers.

In this work basic principles of TOF MS will be elucidated and the possibilities of TOF MS illustrated by extensive applications and examples of bulk, nano-materials and plasma modified surfaces, while the advantages but also the limitations and future trends will be mentioned and discussed.

As for the instrumentation is concern, most often a nitrogen UV laser (337 nm) is applied to generate ions and under the use of a suitable matrix like e.g. alpha-cyano-4-hydroxy cinnamic acid (CHC), or 2,5-dihydroxy benzoic acid, etc. even large molecular weight compounds like proteins can be ionized without any strong fragmentation. The mechanism of ionization remains still not completely resolved but it is sure it may involve absorption of UV light pulse by the matrix with consecutive transfer of energy to the analyzed molecule - which then undergoes ionization in plasma phase as a result of the relatively large amount of energy absorbed. In order to move resulting ions down the flight tube in the mass spectrometer the ions are accelerated in an electric field (up to 25 kV). The analysis can be done either in positive or negative ion modes and in linear or reflectron arrangements. Simplified scheme of TOF MS and experimental set up is given in Figure 1.

Various applications of TOF MS to analyze the surfaces of organic or inorganic materials, bulk, nano-materials, clusters etc. will be demonstrated and discussed.

- TOF MS can be used, for example to detect and/or analyze adsorbed molecules on various surfaces. To clean e.g. chip surface is not an easy task. Chemical methods of cleaning might be substituted by plasma treatment. Plasma treated surfaces are finding extensive applications in technology, industry and medicine etc, as we have reviewed recently [1]. Chemical changes on various surfaces like glass [2], silicon [3], mica and also polymers and natural materials due to application of diffuse coplanar barrier discharge has been studied recently. The surface is cleaned and adsorbed organic compounds removed but also activated Deposition of e.g. gold nano-particles on such cleaned surface is then facilitated.
- Advantages in using TOF MS for analysis of nano-materials have been demonstrated in literature and also in several our papers. Most of the nano-materials especially carbon nano tubes, but also nano-silver [4] are toxic. The exception seems to be nano-gold [5] which is now extensively used in nano-medicine. Formation of nano-gold clusters in plasma via MS analysis was studied in [6]. Nano-gold is now extensively studied for photo-thermal therapy of cancer.
- Another class of nano-materials finding applications in medicine are nano-diamonds. We have recently analyzed and characterized them [7]; some other details of TOF MS analysis will be given.
- Extensive applications are those concerning the determination of structure of chalcogenide glasses as demonstrated in [7-10] and will be discussed.

- Instrumentation of TOF MS can also be used as a synthesizer. Laser ablation synthesis from various precursors has been shown in several papers, i.e. clusters were generated by laser ablation from AgSbS₂ nano-material or from pulsed laser deposited layer of this material as it was demonstrated in [12]. The synthesis of new phosphorus-nitride clusters from α -P₃N₅ [11], or e.g. laser ablation synthesis of selenium tetroxide, SeO₄, was shown in [13].
- Several other examples (non published data) will be also shown and discussed.

Concluding, TOF MS instrumentation can be used to analyze adsorbed chemical compounds on various surfaces, to study chemical changes of polymers or inorganic materials due to modification by plasma, to perform analysis of nano-layers, glasses, modified carbon nanotubes, nano-diamonds and/or also to perform structural analysis of nano-layers or bulk materials.

Perspectives and future trends of TOF MS applications in nano-science and nano-technology are elucidated while problems and limitations are discussed, as well.

Acknowledgement

Support from Ministry of Education, Youth and Sports of the Czech Republic (Projects MSM, 0021622411, 0021627501, and CZ.1.05/2.1.00/03.0086), and Czech Science Foundation (Projects No. 104/08/0229, 202/07/1669) are greatly acknowledged.

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Figures

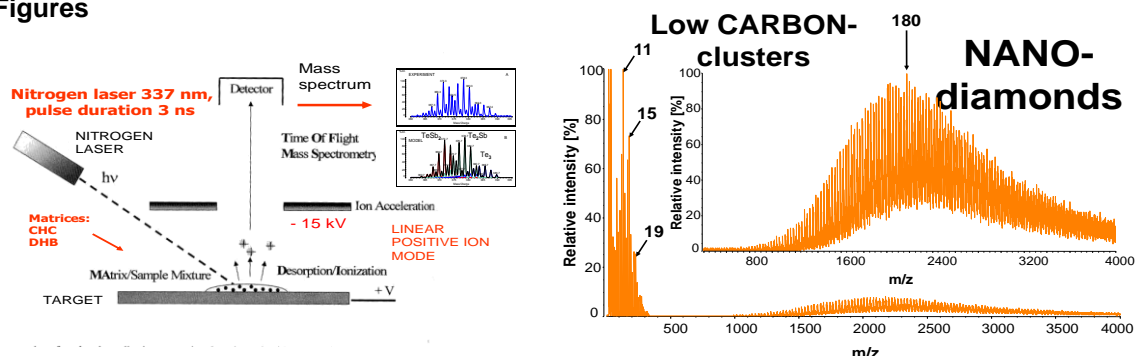


Fig. 1: Scheme of TOF MS (left) and experimental set up for nano-materials analysis. TOF MS spectrum of nano-diamonds (right).