Bojidarka Ivanova / Michael Spiteller

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QUANTIFICATION BY MATRIX–ASSISTED LASER DESORPTION IONIZATION MASS SPECTROMETRY USING AN APPROACH BASED ON STOCHASTIC DYNAMICS – EXPERIMENTAL AND THEORETICAL CORRESPONDENCES

By Bojidarka Ivanova[*] and Michael Spiteller

PREFACE

The goal of this work is to describe more recent developments in the quantitative mass spectrometry and to illustrate how our new model equations based on the stochastic dynamics relate to the determining the 3D molecular and electronic structures of analytes. It is aimed at researchers in Chemistry who would like to find out about what is going on in mass spectrometric methodological contributions more recently. The work could also be used to MSc and PhD students in the field of Chemistry, in particular, highlighting the 'Analytical chemistry', 'Physico–chemistry' and/or 'Computational and theoretical chemistry', respectively.

ABSTRACT

In the present work we argue for that the temporal behaviour of the analyte MS intensity under matrix–assisted laser desorption/ionization (MALDI) and electrospray ionization (ESI) mass spectrometric (MS) experimental conditions can be expressed quantitatively by means of stochastic dynamics. We explore the Box–Müller's method with an implication to an approximation to the Maxwell–Boltzmann distribution of the intensity of analyte MS peaks as a random variable for the thermodynamic equilibrium. The description of the MS intensity as a stochastic variable has led to exact model equations valid to any MS peak intensity of any MS analyte ion within the framework of series of independent measurements and sample techniques for MALDI– or ESI–MS analyses over a random scan time. The model equations are obtained from a representative statistically study. In total, intensities of ninety MS peaks of molecular and fragment ions of (4-diethylamino-benzylidene)-pyridin-4-yl-amine **(1)** are examined. There are used two sample preparation techniques and two matrix components: *(i)* an analysis of single crystal; and *(ii)* an analysis polycrystalline analyte–matrix compositions in presence of matrixes 2,5–dihydroxybenzoic acid (DHB) or 4–hydroxy–α–cyanocynnamic acid (CHCA) within the $t \in$ 0.009–114.51 mins. The employment of the Ornstein–Uhlenbeck' and Einstein's approximations to the stochastic variance parameter (σ^2) as '*diffusion parameter*' leads to a significant statistical correspondence between MALDI–MS and ESI–MS diffusion parameters showing a correlation coefficient $r = 0.995$. The theoretical quantum chemical modeling of the molecular and electronic structures of the analyte MS ions and the employment of high accuracy *ab initio* and methods based on the density functional theory (DFT) including both static and molecular dynamic computations as well as adiabatic and diabatic method of the diffusion coefficients result to a correlation between theory and experiment $r = 0.7732–1$. The capability of MALDI–MS to elicit 3D structural information about the analytes is highlighted explicitly and quantitatively discussing the relations between the temporal behavior of the analyte MS intensity–experimental 'diffusion' parameter–theoretical 'diffusion' parameter–molecular/electronic structure of analyte MS ion. The theoretical modeling of the diffusion parameters is based on the Arrhenius' approximation, which becomes valid to both ESI– and MALDI–MS methods. The experimental diffusions are correlated independently with the corresponding data obtained on the base on *'current monitoring method*'. The work therefore is intended as a bridge between theory and experiment drawing upon the mass spectrometric capability of an exact 3D structural determination based on a stochastic dynamic approach. The empirical adequacy of our theoretical concept is tested by chemometrics. The statistical analysis shows that it is really

empirically testable. Moreover, it is applicable to atmospheric pressure chemical ionization mass spectrometric data, as well.