

Workshop on Ion Chemistry and Plasmas

Book of Abstracts

Bratislava, Slovakia
30-31 August, 2022

Edited by Š. Matejčík, J. Országh, P. Papp



COMENIUS
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FACULTY OF MATHEMATICS,
PHYSICS AND INFORMATICS
Comenius University
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ONE-DIMENSIONAL REACTION-TRANSPORT SIMULATION OF CHEMICAL REACTIONS IN A PBS-LIKE SOLUTION IRRADIATED BY ATMOSPHERIC-PRESSURE PULSED HELIUM PLASMAS

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We present the simulation results of a one-dimensional (1D) reaction-transport simulation of chemical species in phosphate-buffered saline (PBS)-like solution irradiated by atmospheric pressure pulsed helium (He) plasmas. For the sake of simplicity, only electrons and He ions are taken as input species to the solution, the time-dependent fluxes of these species are obtained from particle-in-cell/Monte Carlo collision (PIC/MCC) simulation. It is found that the primary pathways for reactions involve the splitting of H₂O into H and OH⁻ by solvated electrons (e⁻), which produces OH and H₂ through the reactions e⁻ + H₂O → H + OH⁻, and H + H₂O → OH + H₂. The reactions eventually lead to the generation of stable species such as H₂O₂ and HOCl in the solution.

1. Background

Atmospheric-pressure plasmas have been widely used in various applications, including medical/biological applications. For most medical/biological applications, plasma-liquid interactions play an important role in delivering specific chemical species to living cells because most living cells are immersed in a saline fluid. In a recent study [1], the authors focused on the effects of charge-neutral reactive species generated in a plasma that penetrated a phosphate-buffered saline (PBS)-like solution. In this study, we only consider the effects of positive helium ions (He⁺) and electrons that are generated in pure He plasmas. We conducted one-dimensional (1D) particle-in-cell/Monte Carlo collision (PIC/MCC) simulation of a He plasma at atmospheric pressure with an applied high voltage of 1.5 KV and a frequency of 10 kHz to determine the time-dependent gas-phase fluxes of He⁺ and electrons e⁻.

2. Result and Discussion

We first performed the time-dependent 1D reaction-transport simulation of chemical species in a PBS-like solution whose surface was exposed to the electron and He⁺ ion fluxes calculated by the PIC/MCC simulation. The transport simulation demonstrated that the exposure of the solution to the electron and He⁺ ion fluxes resulted in the generation of highly reactive species such as H, OH, and H₂ in the solution. The primary pathways for reactions involve the splitting of H₂O into H and OH⁻ by solvated electrons (e⁻), which produces OH and H₂ through the reactions e⁻ + H₂O → H + OH⁻ and H + H₂O → OH + H₂. Chlorine ions (Cl⁻) from NaCl forms HOCl⁻ by the reaction OH + Cl⁻ → HOCl⁻. The HOCl⁻ reacts with Cl to produce Cl₂⁻. The simulation showed that most such reactions took place in the reaction boundary layer of the solution, i.e. within a thin 10 μm liquid layer at the gas-solution boundary, only in which highly reactive species such as solvated electrons exist. All these reactions eventually generate stable species such as H₂O₂ and HOCl in the solution. We then performed the simulation with time-independent (constant) fluxes of electrons and He⁺ ions with the same fluxes as the time-averaged fluxes of the pulsed discharges. The simulation shows results similar to those with the pulsed discharges.

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2D SPECTRAL MAP OF PYRIDINE MEASURED BY ELECTRON INDUCED FLUORESCENCE

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The pyridine was found, for example, in nicotine or in B vitamins and it is used as a solvent or precursor for agrochemicals in fertilizers [1,2]. Pyridine in B vitamins has also been found on the surface of meteorites [3]. The aim of this work is the experimental study of low electron-induced processes such as ionization and dissociative ionization, dissociative excitation, and ionization excitation of pyridine.

The experiment is based on binary electron – molecule collision conditions. The electrons were produced by trochoidal electron monochromator generating an electron beam with a well specified energy with an energy resolution 300 meV FWHM. The photons emitted during the deexcitation of the excited reaction products pass through the optical system from the vacuum chamber to the optical monochromator and they are detected by a photomultiplier operating in the photon counting mode or by CCD cam. In Fig. 1. we present an illustrative example of a 2D spectral map of the fluorescence cross section. The 2D map is made by measuring spectra in the range from 200 to 700 nm in steps of 0.1 nm for a constant energy of interacting electrons per measurement. The measurements are repeated in 5 eV steps ranging from 15 eV up to 100 eV. The spectral map of pyridine is emission spectra in x – way and cross section of the transitions in y – way. In the emission spectrum the Douglas - Herzberg system of CH^+ , CH^+ (B-A), C^+ , the hydrogen Balmer series, Deslanders - d'Azambuja system of C_2 , Swann system of C_2 and CH (A-X), CH (B-X), CH (C-X), CN (B-X), NH (A-X) transitions are observed.

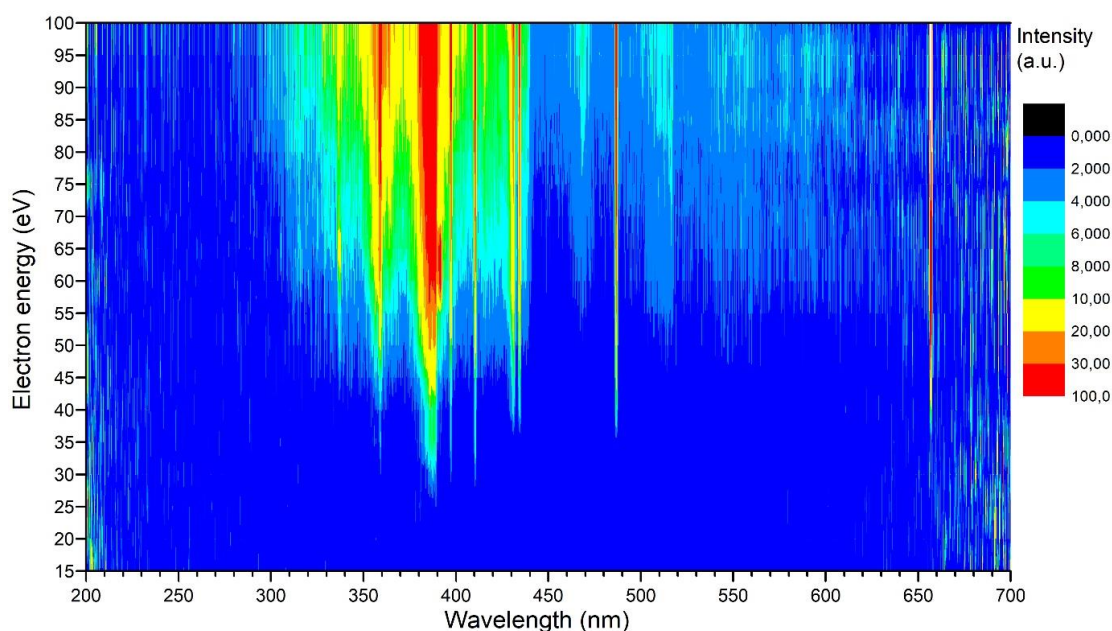


Fig. 1. 2D spectral map.

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CHARACTERIZATION OF MICROGAP VACUUM BREAKDOWN GENERATED BY PULSED ELECTRIC FIELD

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This paper reports on the study of microdischarge vacuum breakdown and its phenomena generated between sphere-plane electrodes made from palladium. The conditioning process and the saturated breakdown voltages were investigated for different electrode separations from 0,5 μm up to 10 μm . The measurements were provided in the pulse regime with the voltage ramp speed from 10 kV/s up to 10^7 kV/s.

1. Introduction

Non-thermal plasma (NTP) generated by electric discharges at atmospheric pressure has been studied for years in many areas such as industrial, biological, medical, and environmental for numerous applications [1,2]. Generation of plasma at atmospheric pressure supports fast chemical reactions which are important for many processes. However, with increasing pressure, discharge contractions occur, resulting in discharge inhomogeneities. One of the ways how to ensure the homogeneity of the discharge is to generate it at the size of the gap between electrodes at a micrometric scale near the minimum of the Paschen curve. The main objective of our work is the characterization of microdischarge breakdown and their phenomena at very high electric field. However, it is not possible to measure the pure emission current directly at high pressure due to the fast ionization processes that occur immediately after electron field emission. For this reason, our measurements were performed at low pressures, where the impact of gas on the electric breakdown can be neglected.

Several papers were focused on the characterization of microgap discharges at vacuum pressure but even though the origin of the breakdown and a lot of phenomena connected with it are still unclear [3,4]. The presented work follows the investigation of our previous study [5], where breakdown and pre-breakdown stages of vacuum microdischarge for stainless-steel electrodes were studied. In this work, we focused on the investigation of the breakdowns generated between the palladium electrodes. Palladium is a noble metal with high thermal conductivity and good resistance in oxidizing atmospheres. It is used mostly in industry, specifically as the catalytically active coats in the catalysts or in the spark-ignition engines [7]. Despite of many application of the noble metals in industry, there are no available studies about the breakdown processes and the phenomena connected with them. For this reason, in this study we focused on the characterization of the electrical breakdowns between palladium electrodes to represent the unknown properties of noble metal metal group.

2. Experimental apparatus and results

The experimental equipment for the investigation of the microgap vacuum breakdown is shown in Fig. 1. The vacuum system consisted of the vacuum chamber with the achieved pressure $\sim 2 \cdot 10^{-4}$ Pa ensured by turbopump and dry forepump. The high voltage pulse generator circuit consisted of high voltage sources switched with the *Behlke* switch controlled by function generator. The sphere cathode with a size of diameter 5 mm was grounded through the series of resistance whereas the plane anode was connected to the pulse signal. The 0 μm separation between electrodes was established by measuring electric contact by an ohmmeter.

The measurement of conditioning (cleaning the surface of an electrode from the impurities by successive discharge breakdown pulses) is the key to the investigation of vacuum microdischarge. It was reported that an unconditioned electrode surface can cause a decrease in the values of breakdown voltage [4-6]. For illustration, the conditioning process in the regime of fast pulses (10^7 kV/s) with a microgap size of 10 μm can be seen in Fig. 2. The saturation of breakdown voltage occurs after 6000 breakdowns, where its value settled at 3,4 kV with a standard deviation of 0,6 kV. When saturation occurs, the electrodes are considered to be conditioned. Based on the Fowler-Nordheim theory, the investigation of emission current, the radius of emitting surface, and enhancement factor β for various

microgap distances and pulse electric field rates based on the Fowler-Nordheim theory would be the point of interest. The measured values will provide us with better knowledge about the primary mechanism of microdischarge breakdown processes and an explanation of the processes taking place in the discharge area at higher pressures.

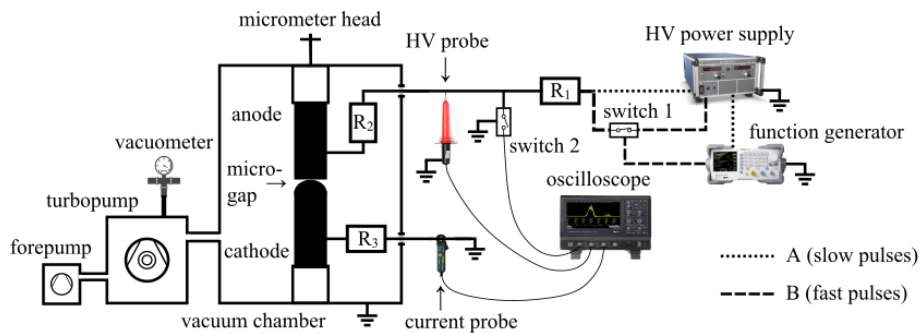


Fig. 1. The experimental apparatus for studying the microgap vacuum breakdown and its phenomena.

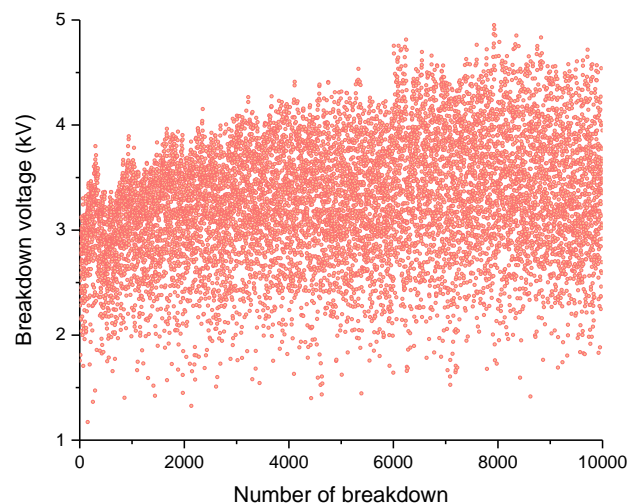


Fig. 2. The conditioning of virgin palladium electrodes (the regime of 10^7 kV/s, the microgap size of 10 μ m).

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AMINE FORMATION ON ARTIFICIAL BONE BY LOW-PRESSURE PLASMA POLYMER DEPOSITION

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Amine-rich plasma polymerization was performed on the surface of porous calcium-phosphate (hydroxyapatite [HA] or beta tricalcium phosphate [β -TCP]) artificial bone with a low-pressure plasma system. The aim of this study is to form amine groups on the surface of HA or β -TCP based porous artificial bone to improve its biocompatibility and osteogenic abilities.

1. Introduction

Regeneration of bones in large bone defects continues to be one of the most challenging tasks in orthopedic surgery. However, currently available artificial bone typically lacks osteogenic ability. The goal of this study is to form functional thin films over artificial bones to add the osteogenic ability to artificial bones.[1]

2. Experiments and Numerical simulation

Experiments were performed with a bipolar pulsed plasma system [2-4] with a CH₄/N₂/He mixed gas at a pressure of 70 Pa [5]. The applied bipolar voltage was about ± 1.2 kV and the pulse duration was about 1 μ s for each positive or negative pulse. The pulse frequency was 5 kHz, so the time elapsed between a positive pulse and the subsequent negative pulse was 100 μ s. Calcium-phosphate artificial bone samples were placed on the grounded metal electrode and exposed to the plasma for 30 min. The porous artificial bone samples used in this study had interconnected pores with a porosity of 72%-78%. The average pore diameter was 150 μ m and the average diameter of a circular passage connecting two adjacent pores was 40 μ m. X-ray Photoelectron Spectroscopy (XPS), Fourier-transform infrared (FTIR), and Ellipsometry measurements showed that polymer deposition successfully took place on the artificial bone surface and the thickness of the film deposited on a Si substrate under the same conditions was about 40 nm. It was found that polymer deposition took place even on the inner surfaces of pores at least down to the depth of 2 mm from the sample surface. The elemental composition of N atoms of the deposited film was 10 ~ 15 % and found to be stable at least over a couple of months when the plasma-treated artificial bone was kept in a desiccator. The derivatization using 4(trifluoromethyl)benzaldehyde (TFBA) showed that the surface concentration of primary amine groups over nitrogen atoms was 20 %. Effects of sterilization on plasma-treated artificial bone by autoclave, ethylene oxide gas (EOG), and gamma-ray radiation were examined.

Molecular dynamics simulation was also performed to characterize the amine-containing polymer deposition process.

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“TRUE NANO-ELECTROSPRAY” WITHOUT NARROW CAPILLARY BY GENERATION OF IONS FROM AQUEOUS TAYLOR CONES NEAR THE MINIMUM FLOW RATE

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1. Introduction

Generating ultra-fine charged droplets using electro spray is crucial for attaining high ionization efficiency for mass spectrometry. The size of the precursor charged droplets depends on the spray flow rate and the conventional wisdom holds that the electro spray of nanoliter per min flow rate (nanoelectrospray) is only possible using narrow capillaries with an inner diameter of ~ 1 micrometer or smaller. Here, the electro spray of aqueous solutions with high electric conductivities generated from a large off-line capillary of 0.4 mm i.d. has been performed using a high-pressure ion source [1]. The electric discharge is avoided by operating the ion source at high pressure. The highly stable Taylor cone can be tuned to a near-hydrostatic state that exhibits the “true nanoelectrospray” properties, i.e. high salt tolerance and minimal ion suppression.

2. Preliminary results

The $Q^{1/2}$ scaling law [2-3] describing the electro spray current I and flow rate Q is found to be valid down to the nanoflow regime under a condition that is free of electric discharge. For a given solution, the flow rate and the size of the initial droplets and ionization species can be controlled with the spray current as the indicator for the instantaneous flow rate without changing the emitter capillary of different sizes. Application-wise, the nanoelectrospray with a large micropipette tip is easy to use, free of clogging when dealing with viscous and high salt buffer solutions, and with reduced surface interaction with the emitter inner surface. Here we will introduce the operation of high pressure ion sources, flow rate control and its applications to the detection of proteins from concentrated solutions of non-volatile salts.

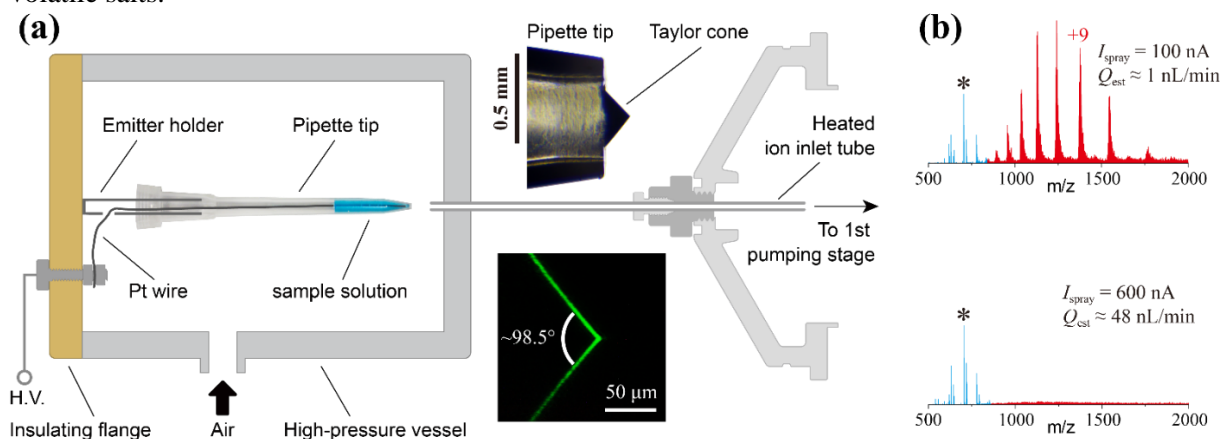


Fig. a) Schematic of the high-pressure nanoESI ion source and the connection to a mass spectrometer. Insets show the Taylor cone near the minimum spray current (Apex angle = 98.5°). b) Mass spectra of 2.5×10^{-5} M cytochrome c in PBS solution acquired at different spray currents.

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RECENT DEVELOPMENT ON THE ELECTROSPRAY IONIZATION AND ITS APPLICATION TO THE IN-VIVO ENDOSCOPIC MASS SPECTROMETRY

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A moving string sampling probe and a new ESI-based ionization source that can be readily incorporated into the existing endoscopes are developed for performing in-vivo mass spectrometry during the endoscopic procedure.

1. Ambient ionization MS

Mass spectrometry (MS) is an established and reliable method to determine the chemical compound and has long been used in a variety of clinical applications. With a direct and ambient ionization method, MS has been proven to be applicable to medical diagnosis with accelerated speed and accuracy. Ambient MS or ambient ionization MS can be performed by replacing the original ion source of a commercial mass spectrometer with a custom-made electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) variant. To maximize the ion transmission to the vacuum of the mass spectrometer, ionization is usually performed close to the ion inlet. To handle a large size sample such as living animals, the ionization has to be performed, say, at more than 1 m away from the MS instrument, and the remotely generated ions have to be transported back to the ion inlet using extended ion transported tube. Instead of sampling the ion, it is also possible to sample the neutral remotely and transport the sample to an ion source in an online fashion (see the comparison in Figure 1).

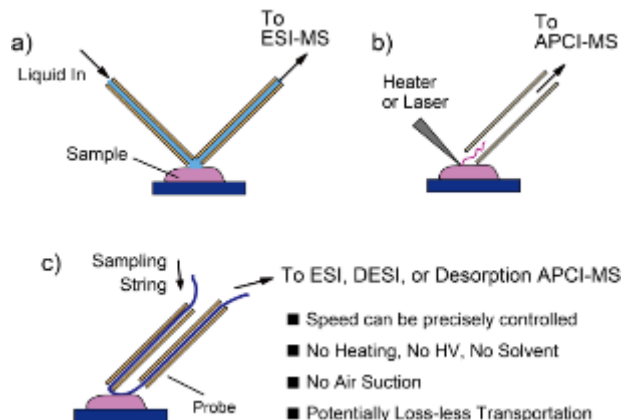


Fig. 1. Comparison of different remote sampling and transportation methods. a) Liquid phase extraction method. b) Vapor phase sampling. c) Sampling using moving sampling string such as cotton thread (Reproduced with permission from ref 2).

2. Endoscopic MS using string sampling probe

Endoscopes are indispensable medical tools for the diagnosis and treatment of diseases such as those involving the gastrointestinal tract. To make clinical decisions, the current practice requires a cut of tissue specimen by biopsy forceps for ex-vivo histopathological or other biochemical analyses, which results in a delay and increases the cost of the procedure. Therefore, there is a need for an in-vivo tissue analysis that offers histopathological equivalent assessment on-the-spot during the endoscopic procedure.

A moving string sampling probe and a new ESI-based ionization source that can be readily incorporated into the existing endoscopes are developed for performing in-vivo mass spectrometry during the endoscopic procedure (Figure 2). The medical-grade silk suture driven by a stepping motor

is used to perform the sampling on the region of interest when the probe head is brought gently into contact with the surface of the gastrointestinal tissue. The tissues and the compounds adhered to the sampling string are transported to an ionization region inside the ion inlet tube in which they are extracted and ionized by the charging droplets generated from an electrospray outside the ion inlet. Since the extraction/ionization and sampling processes are isolated, organic solvents, HV, and heating can be used for the optimization of ionization without compromising the biocompatibility of the sampling probe. The demonstration of the *in-vivo* analysis of the gastric mucosa of a mouse is performed using a 2-meter-long gastrointestinal endoscope (Figure 3).

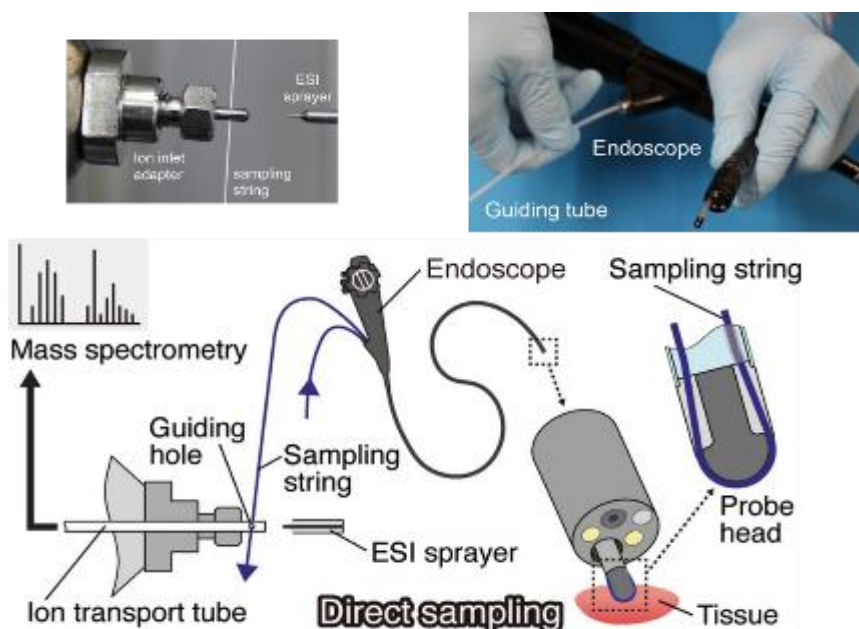


Fig. 2. Endoscope incorporated with the string sampling probe for *in-situ* mass spectrometry. The adhered analytes are extracted and ionized using an ESI base ionization confined within the ion inlet tube (Reproduced with permission from ref 3).

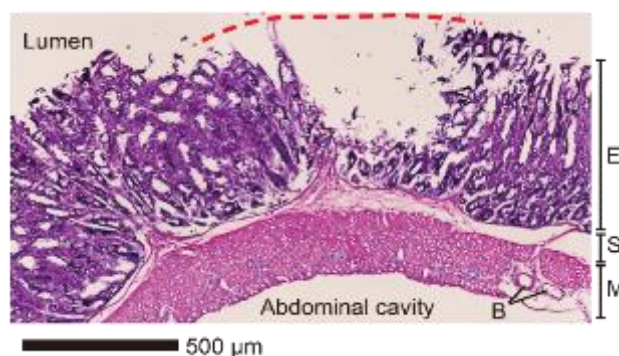


Fig. 3. H&E stained image of the region sampled by the silk sampling string after the *in-situ* MS on the gastric mucosa of a living mouse using the present string sampling probe (Reproduced with permission from ref 3).

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PTR-TOF MASS SPECTROMETRY OF EXHAUST GAS OF ATMOSPHERIC PRESSURE OPERATED GLOW DISCHARGE CREATED IN PREBIOTIC ATMOSPHERES

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The search of life precursors became hot topic mainly during the last two decades because of discovery many exoplanets, some of them should be also suitable for the life formation. One of the life precursors' synthesis ways is operation of electrical discharges in so called prebiotic atmospheres. The presented contribution gives results obtained using glow discharge operating in Titan and Mars related atmospheres with common trace gasses. Many discharge created species were determined using *in situ* PTR-TOF mass spectrometry.

1. Brief summary

Besides processes initiated by cosmic radiation and particle fluxes (like Solar wind) the processes initiated by electrical discharges in prebiotic atmospheres are possible [1, 2]. The best mimic systems relates to the atmospheres of Mars (mainly CO₂) and Titan (mainly N₂ with CH₄) where is also possible to compare laboratory obtained data with *in situ* observations from space missions [3, 4]. The discharge formed products can be analysed by different techniques, mainly gas chromatography with mass spectrometry detection. The *ex situ* use is a common application, partially with sampling by different traps. Other way is FTIR and of course some insight is possible by OES of discharge itself. Problem of all these techniques is rather complicated sampling and additionally long time needed for the analyses (about 1 hour for GC-MS) or limited number of identified species (FTIR and OES). A new way is the *in situ* analysis using a time of flight mass spectrometer with proton transfer ionization (PTR-MS) [5].

PTR-MS based on its analyte ionization way is suitable for all compounds with proton affinity higher than proton affinity of water. This is very important future for studies in prebiotic atmospheres because main components of reacting gas mixtures like nitrogen, methane, carbon dioxide, hydrogen or oxygen could not be ionized by proton transfer and thus we are able to detect the more complex products, only. Their total concentration is not so high (typically up to ppm level in the flowing regime) and thus the proton transfer reaction is running close to zero order kinetics, i.e. more or less or ionisable discharge products are ionized during reaction with hydronium ions. Thus their absolute concentrations are directly measured. The sampling frequency of PTR-MS with ToF mass filter is in order of tens kHz and thus time dependences of products concentrations can be simply measured.

The presented contribution shows couple of results obtained in gaseous mixtures related to both Mars and Titan atmospheres with some additions of other gases. All experiments were carried out at atmospheric pressure using DC glow discharge. Systems were operating at ambient temperature, in case of Titan also at liquid nitrogen temperature that is more related to the Titan surface conditions.

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ANALYTICAL CHEMISTRY OF ENGINEERED NANOMATERIALS IN THE ENVIRONMENT

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Engineered nanomaterials (ENMs) incorporated in various products are released into the environment. The major limitations of existing analytical techniques applied to environmental samples as well as to monitoring the fate of ENMs are in relatively high detection limits and the difficulty to distinguish ENMs from other chemical forms or natural colloids. A combination of analytical methods with a modeling approach has the potential to improve understanding of the behavior of ENMs and be useful for risk assessment purposes [1]. Parameters of ENMs need to be monitored by controls using suitable nanoscale reference materials [1, 2].

In air and aerosols, single-particle aerosol mass spectroscopy has the advantage due to its continuous real-time detection of single particles. In water samples and spiked waters, the ENMs analyses are performed directly or after a suitable dilution. Physicochemical and chemical properties of nanomaterials in water depend on the surrounding media and may change during any handling process. Therefore, tests of the effect of sample transport, storage, and preparation by control experiments with known quantities of defined particles are important. The nanoplastics as engineered nanoparticles are delivered through their commercial sources as well and retained in wastewater even after the wastewater treatment plant. Together with FTIR and Raman spectroscopy, the pyrolytic gas chromatography-mass spectrometry and thermal extraction desorption gas chromatography-mass spectrometry are used for their detection. In soil and sediments, isolation and pre-concentration of metal nanoparticles by extraction methods and *in situ* complementary and hyphenated analytical techniques are effective. Examples of the combination of separation and detection (FFF and HDC with ICP-MS, UV-vis, light scattering, and fluorescence detectors) with microscopic techniques and DLS will be presented to demonstrate the state of knowledge at analyses and understanding ENMs behavior in complex matrices.

Acknowledgements

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ION MOBILITY SPECTROMETRY POSSIBLE METHOD FOR NO₂ DIAGNOSTICS

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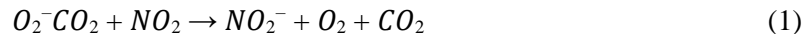
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In this paper, ion mobility spectrometry (IMS) is presented as a new method of NO₂ detection from discharges. The reactive oxygen and nitrogen species are efficiently generated in atmospheric pressure discharges and are involved in various biological and chemical processes. The efficient detection of these species is of great importance for many fields of science and applications.

1. NO₂ diagnostics

Reactive oxygen or nitrogen species (RONS) like O₂⁻, O₃, OH radicals, NO₂, H₂O₂, and others play an important role in many pathological, physiological, and biochemical processes. The RONS can be also generated by a cold atmospheric plasma jet (CAPJ) in Argon. The production of controlled RONS by the CAPJ is frequently used for biological applications such as wound healing, cancer treatment, immune cell activation, and sterilization of surfaces [1]. Therefore, is very important to monitor the production of these reactive species. There are some standard methods for their diagnosis such as gas sensors based on semiconductors, FTIR spectroscopy, and chemical gas sensors [1 – 4].

Ion mobility spectrometry (IMS) is a rapid and powerful analytical method with high sensitivity (ppb – ppt level) [5]. The RONS can be detected in negative IMS mode. The electron affinity of NO₂ is 2.273 eV and exceeding the bond energy of the electron in the reactant ions (RI) generated in ionisation source of IMS O₂-CO₂ is ~ 1.2 eV [6, 7]. Thus, the ionization of neutral NO₂ species could be ensured by a negative electron transfer reaction of the O₂⁻CO₂.



The intensity of the NO₂⁻ peaks is proportional to the concentration of NO₂. For the measurements of NO₂ substances, calibration of the IMS response to the precursor molecules must be carried out. In the Figure 1. the IMS spectra for different NO₂ concentrations are presented. Peak with the reduced mobility 2.5 cm².V⁻¹.s⁻¹ belongs to the NO₂⁻ and its intensity increased with the increasing neutral NO₂ concentration. The limit of detection was determined at 0.2 ppm (200 ppb) and the linear scale response was in the range of 0 – 5 ppm. At high NO₂ concentration above 5 ppm, the intensity of RI was decreasing rapidly and it resulted in nonlinear response to NO₂.

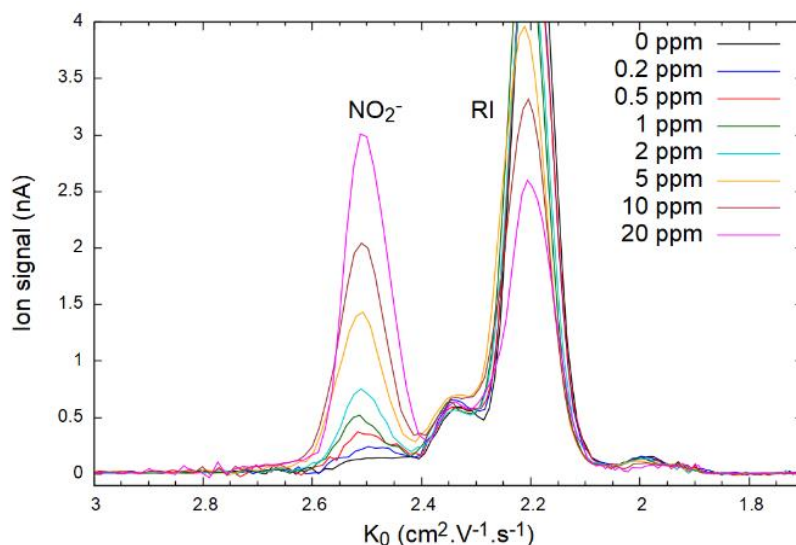


Fig. 1. IMS spectra for different NO₂ concentrations.

The present results indicate a suitability of the IMS method for NO₂ detection. The sensitivity is comparable with the most sensitive methods and the response is very fast, at the level of 1 s.

Acknowledgments

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DETECTIONS OF SELECTED PLANT HORMONES USING METHODS BASED ON IMS TECHNIQUE

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Using Atmospheric Pressure Chemical Ionisation (APCI) combined with Ion Mobility Spectrometry (IMS) and additional sampling (Solid Phase Micro Extraction -SPME) and pre-separation methods (multicolumn capillary gas chromatography – MCC GC), detection of plant hormones Auxine and Methyl Salicylate was achieved from standards and from real sample. The effect of ion polarities and APCI dopants was studied regarding the separation and detection efficiency.

1. Introduction

Plant hormones (PHs), are signaling molecules influencing the plant growth, seed germination, fruit maturation and fruit ripening and control the physiological processes such as regulation of the organ size, pathogen defense, and reproductive developments and many others [1,2]. Hence, a quantitative analysis of the PHs and determination of their concentrations in different tissues is important to understand the role of these molecules in the plants.

2. Experiment

The Ion mobility spectrometry (IMS) is a fast, inexpensive, and sensitive technique with growing application in analysis of various classes of analytes [3]. Over the past few years, SPME coupled to IMS has been used for collection and preconcentration of analytes in both gas phase and from solution for analysis by IMS [4]. The multi-capillary column gas chromatography (MCC GC), as a fast separation technique, in combination with IMS has found application mainly in the field of breath analysis [5]. In this work, an IMS-based method to exploit advantages of both SMPE, MCC and IMC for fast and sensitive analysis of real samples in complex matrix.

3. Results

In present work, detection of two plant hormones, Auxine and Methyl Salicylate from standards and from real samples is demonstrated, using the methods based on the IMS techniques. Detection of the hormones was performed both in positive and negative polarities, in addition, the influence of additives on the detection sensitivity was studied. For real samples, advanced pre-separation methods based on Multi Column Capillary Gas Chromatography (MCC GC) and SPME sampling methods were applied. High sensitivities and fast analysis were achieved for both hormones.

Acknowledgments

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THE EFFECT OF LOW-TEMPERATURE PLASMA ON DECONTAMINATION AND QUALITATIVE CHARACTERISTICS OF NUTS

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Nuts are important part of human nutrition due to the high content of healthy fats, low carbohydrates and source of several phytochemicals and micronutrients. Dried food products intended for direct consumption required special strategies to ensure microbial safety and appropriate quality of food for consumers. To prevent degradation of healthy oils, or chemical residues, the alternative method to conventional high temperature or chemical treatment is the aim of research. One of the prospective approaches is application of low-temperature plasma generated at atmospheric pressure presented in this work.

The low-temperature (LT) non-equilibrium plasma is the prospective alternative to high temperature or chemical processes for application in medicine, biotechnology, food industry and agriculture for bio-decontamination, increase of biocompatibility or other surface modification of biological and non-biological material [1–3]. Nuts are important commodity in human nutrition. Since the effect of plasma on the decontamination of surface of various kind of nuts is widely studied issue [4,5], the impact of plasma on the quality, surface properties, biological compounds and ageing effect of nuts has not been studied in details.

In our work, we analyzed the influence of cold atmospheric pressure plasma generated by Diffuse Coplanar Surface Barrier Discharge (DCSBD) [6] on the properties of hazelnuts (*Corylus avellana*) and peanuts (*Arachis hypogaea*) depending on exposure time of samples in plasma. DCSBD generates non-thermal macroscopically homogeneous diffuse plasma in ambient air and it was successfully used for decontamination of wheat, black peppercorn or almonds [7–9].

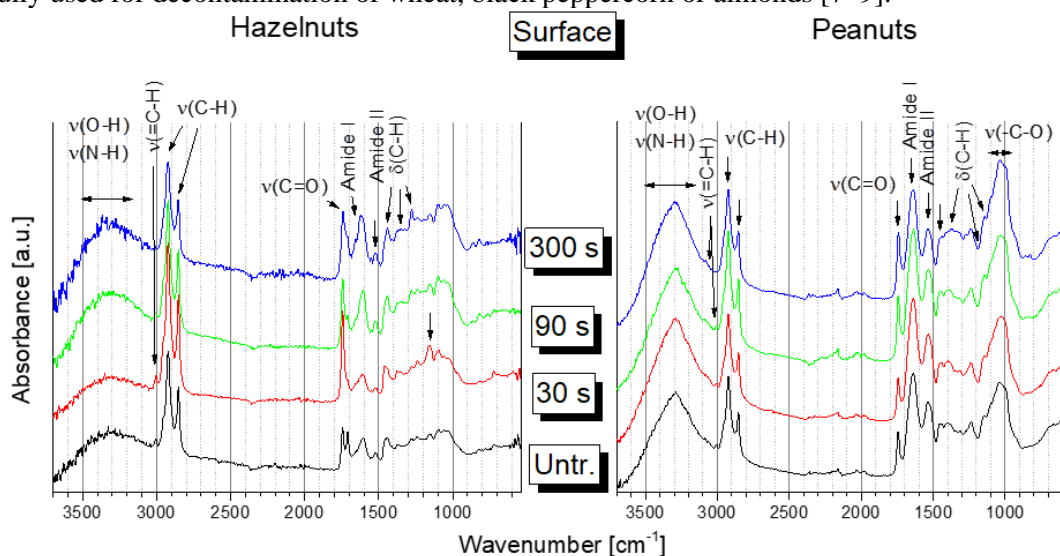


Fig. 1. ATR-FTIR spectra measured on the surface of hazelnuts and peanuts samples at different exposure time immediately after plasma treatment

The changes in chemical bonds on the surface and inside the samples were measured by Attenuated Total Reflectance Fourier Transform Spectroscopy (ATR-FTIR) immediately after plasma treatment (Fig. 1) and after 1 and 3 months after storage. The influence of plasma on morphology of nuts was observed by Scanning Electron Microscope (SEM). The antioxidant effect was evaluated by different assays for the analysis of antiradical activity and reducing ability of antioxidants presented in nuts. Since hazelnuts and peanuts are food with high content of fat qualitative parameters of oil were also studied.

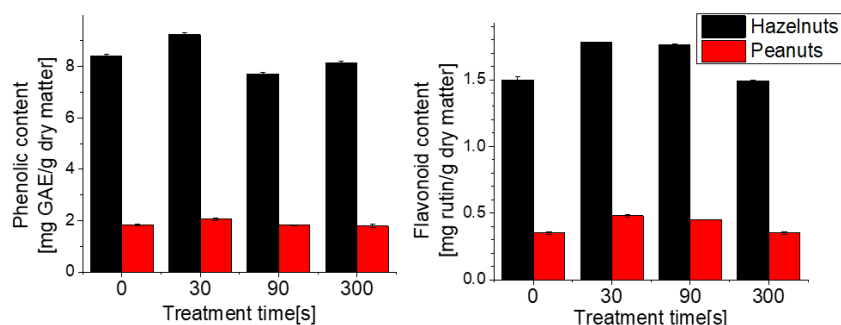


Fig. 1. Phenolic (left) and flavonoid (right) content in hazelnuts and peanuts before and after plasma treatment (30, 90 and 300 s).

Acknowledgements

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EXPERIMENTAL STUDY OF ELECTRON ATTACHMENT TO COBALT TRICARBONYL NITROSYL CLUSTERS

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In our study we are focusing on electron attachment (EA) and dissociative electron attachment (DEA) on cobalt tricarbonyl nitrosyl ($\text{Co}(\text{CO})_3\text{NO}$). $\text{Co}(\text{CO})_3\text{NO}$ is used as a precursor gas for deposition of Co in Focused Electron Beam Induced Deposition (FEBID) and following Electron Beam Induced Surface Activation (EBISA) [1].

DEA to $\text{Co}(\text{CO})_3\text{NO}$ clusters

Ion yields from our cluster measurements (created by co-expansion with Ar gas) will be compared to previous EA and DEA gas phase $\text{Co}(\text{CO})_3\text{NO}$ studies [2] and He nanodroplet cluster studies [3]. The gas phase DEA products from Ar clusters agree well with previous works [2,3], comparison with existing gas phase data [2] is shown in Fig. 1 (Left). However, formation of cluster products in He nanodroplets [3] and our co-expansion with Ar reveal some differences mostly the shape of the ion yield curves due to the higher energy resolution of the electron beam used in our experiment. The exclusive formation of the molecular ion of $\text{Co}(\text{CO})_3\text{NO}$ in clusters was confirmed in our measurements but we have detected the ~ 0 eV resonance for this ion contrary to previous work [3], similarly to other cluster fragments shown in Fig. 1 (Right).

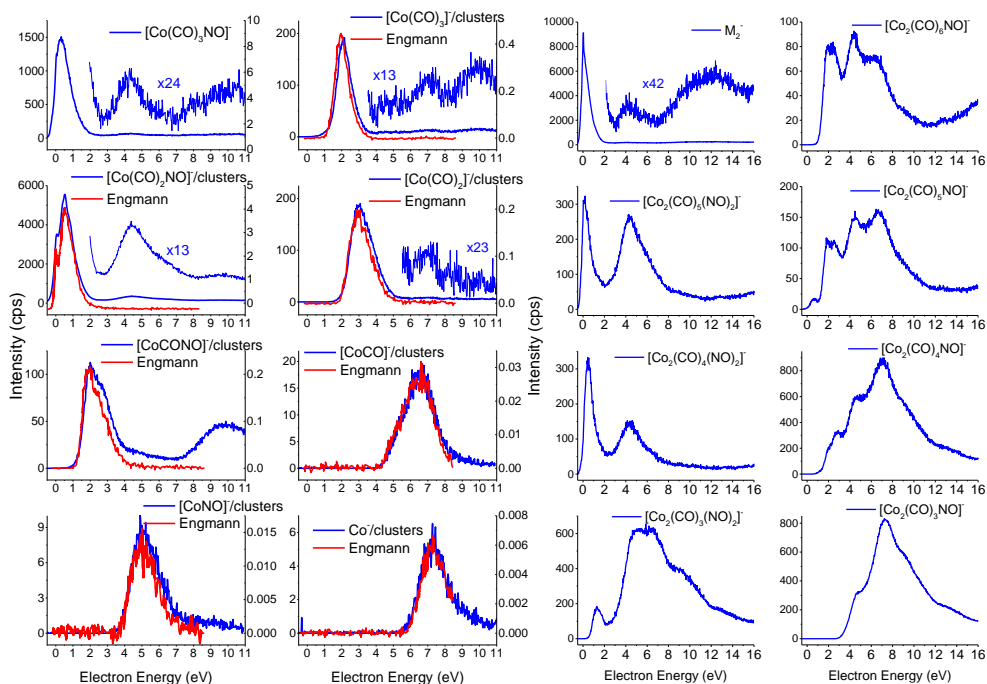


Fig. 1. (Left) Comparison of gas phase products from our Ar cluster measurements (blue) with pure gas phase products (red) [2]; (Right) Selected cluster fragments from our Ar cluster measurements

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CHARACTERIZATION OF SULPHUR-CONTAINING COMPOUNDS BY ION MOBILITY SPECTROMETRY AND MASS-SPECTROMETRY

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Positive polarity atmospheric pressure chemical ionization of selected sulphur-containing hydrocarbons (Thiophene C₄H₄S, 2-Methyl thiophene C₅H₆S, 2,5-Dimethyl thiophene C₆H₈S, Benzothiophene C₈H₆S and 2-Methyl benzothiophene C₉H₈S) was studied using ion mobility spectrometry (IMS) and IMS combined with time-of-flight mass spectrometer (IMS-TOF MS) techniques, in the dry air at 373 K drift gas temperature. The ionization was performed using the H₃O⁺(H₂O)_{3,4} reactant ions (RIs), and the dominant ionization reaction was the direct proton transfer. The ionization resulted in the appearance of M.H⁺ ions for all substances except for Thiophene which forms M⁺ and M.NO⁺ ions. The quantum-chemical calculations at the DFT method were performed to calculate the thermochemical data.

1. Introduction

Petroleum oils from fossil-based materials are currently considered to be affordable and reliable energy resources [1]. The molecular mixture in petroleum is mostly comprised of different categories of hydrocarbons (alkanes, naphthenes, and aromatic compounds) with five- or six-carbon member rings and polar compounds. Polar compounds containing hetero-atoms in petroleum are mostly composed of nitrogen, oxygen, and sulphur-containing species that must be removed, or their quantities reduced [2-4]. Sulphur-containing compounds (thiols and heterocyclic compounds) in crude oil are one of the most abundant constituents, and their so detailed structural characterization is of particular interest. In some cases, the content of sulphur in crude oil can be as high as 10% [5]. Sulphur-containing compounds exhibit high reactivity, absorptivity, and adsorptivity which make petroleum analysis difficult, and also, these components are mainly responsible for catalyst poisoning and the corrosion of petroleum pipelines [6]. Their better identification and reduction could be helpful in the oil industry for their cheaper transportation processes, cost reduction achieved for refining, and achieved a higher quality of the oil. Besides that, sulphur-containing compounds have implications regarding environmental and human health presenting high exposure risk factors [4]. The aim of this present work is the detection and identification of five selected sulphur-containing hydrocarbons at sub-atmospheric pressure by IMS-MS at positive polarity. We are focusing on to identify the nature of positive ions. The possibility to convert the measured drift times of ions in IMS to experimental collision cross-section values that can be used for structural assignments is another advantage of IMS against other methods.

2. Experimental part

In this work, the homemade ion mobility spectrometer (IMS) (Figure 1) with an atmospheric pressure chemical ionisation (APCI) source based on corona discharge (CD) has been used. The technical properties of the IMS are presented in Table 1. During measurements, the IMS was operated in the positive polarity mode at sub-atmospheric pressure (680 mbar) due to simple sampling of volatile organic compounds by the capillary inlet. The sample flow rate was controlled by a micro-splitter valve (Supelco) and adjusted by a gas flow meter (Platon). As a drift gas in IMS, a laboratory air cleaned by our self-designed circulation vacuum system with additional moisture traps (Agilent) and containers

filled with activated carbon and potassium permanganate impregnated activated alumina spheres (Alphasorb) was used.

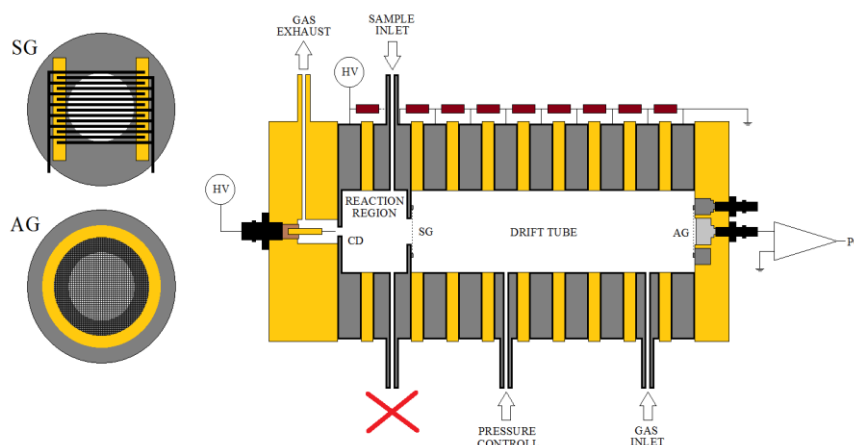


Fig. 1. Scheme of the IMS spectrometer: CD – Corona discharge, SG – Shutter grid, AG – Aperture grid, HV – High voltage.

Tab. 1. Parameters of IMS used in the experiment.

Operating Parameters	Unit
IMS drift tube length	11.9 cm
Electric field intensity	672 V.cm ⁻¹
IMS operating pressure	680 mbar
IMS operating temperature	373 K
Drift gas flow	800 mL.min ⁻¹
Sample gas flow	10 mL.min ⁻¹
CD current	10 μA
Shutter grid pulse width	80 μs
Shutter grid frequency	50 Hz

The vapours of the investigated compounds were introduced into the reaction region of the IMS through a sample inlet. The thiophenes were placed in a glass syringe (about 3 mg, 1 drop) to determine the LOD value. To achieve an equilibrium between the gas and the liquid phase we waited at least 20 minutes. Afterward, the syringe was connected via a capillary with the sample inlet, and using a syringe pump (Kent Scientific), the sample was introduced into the reaction region of the IMS with a pre-set flow rate. The reactant ions (RI) generated in CD were H₃O⁺(H₂O)_n (n=2,3) and in a very low concentration of NO⁺(H₂O)_n (n=2,3). The IMS has been operated in reverse gas flow mode.

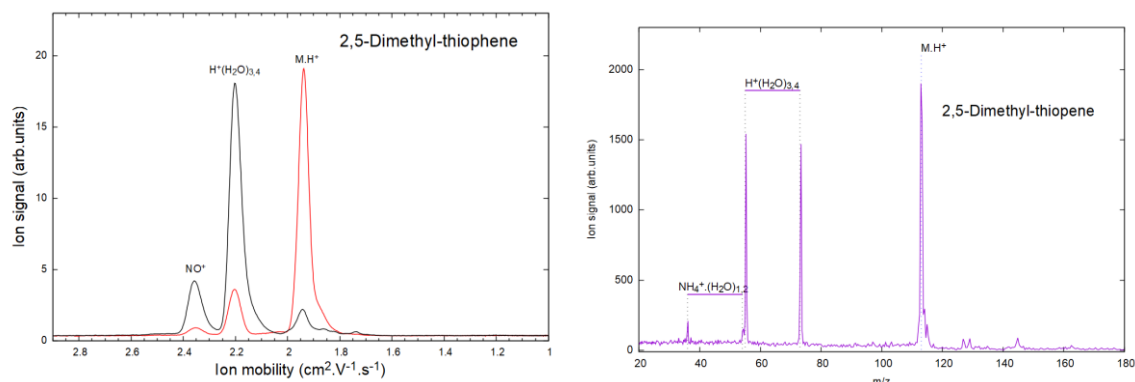


Fig. 2.: The positive IMS and the MS spectrum of 2,5 – Dimethyl-thiophene at 373K.

Figure 2 shows the positive IMS and MS spectra of the ambient air with 2,5- Dimethyl-thiophene at 373K. In the IMS spectrum 2,5- Dimethyl-thiophene has one strong peak at $K_0 = 1.94 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ which corresponds to monomer ions of sample M.H^+ confirmed by MS spectrum with ion mass $m/z = 113$. No other peaks have been observed in IMS spectra which confirms that the concentration of 2,5-dimethyl thiophene was not enough to detect their dimer ions. The other investigated compounds have similar properties and form mainly ions with H^+ . The quantum-chemical calculations at the DFT method were performed to calculate the thermochemical data for all studied sulphur-containing hydrocarbons.

Acknowledgments

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HEAT PULSE DESORPTION MASS SPECTROMETRY

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Mass spectrometry using a novel thermal desorption method using a heated gas pulse was studied for the rapid analysis of various samples such as narcotics, explosives, and amino acids. 1 picogram cocaine on a substrate was detected by 50 ms blow of heated N₂ gas at 350°C. The optimum conditions with high sensitivity and little thermal decomposition could be controlled by changing the N₂ gas temperature and pulse width.

1. Introduction

Heating is frequently used for the desorption of low-volatility compounds in mass spectrometry. The desorption efficiencies are much improved by increasing the sample temperature. Cody *et al.* developed direct analysis in real time (DART) using He Penning ionization as an ambient mass spectrometry technique [1]. They succeeded in analyzing a wide variety of compounds such as pharmaceuticals, insecticides, metabolites, drugs, and explosives by using heated (~250°C) He gas. DART ion sources that can be installed in various mass spectrometers are commercially available and are widely used as a simple and high-throughput method.

In the previous study, we developed flash desorption/mass spectrometry using a linearly driven preheated (100-750°C) stainless steel wire filament [2]. At the lowest position, the tip of the filament touched the sample surface with a contact time of around 50 ms. After touching the sample, the filament was lifted up within 50 ms. The sample components were desorbed with minimum decomposition by the momentary contact (flash heating) and fast moving up (rapid cooling) of the heated filament. In this study, another flash desorption method using a heated N₂ gas pulse (50~1000 ms), referred to a heat pulse desorption (HPD), was examined.

2. Experimental

A copper tube with an inner diameter (i.d.) of 1.6 mm and an outer diameter (o.d.) of 3.2 mm was coiled with 13 turns around a cartridge heater (16 mm o.d., 51 mm long). After a thermocouple was placed on the copper coil, the heater was wrapped by 3 layers of insulators: aluminum foil, alumina tape, and finally aluminum foil. A small pinch valve (min. opening time: 5 ms) installed between the heater and a nitrogen gas cylinder was used for the generation of the heated gas pulse. The heater temperature was controlled in the range of 25°C (RT) to 400°C. Standard samples such as narcotics, explosives, and amino acids were deposited/dried on the PTFE substrate. Real-world samples such as human sebum were captured on cotton buds. Each sample was positioned midway between the ion transfer capillary of a mass spectrometer and the exit of the heated gas. The desorbed sample components were ionized by DC corona discharge and mass analyzed by an Orbitrap mass spectrometer.

3. Results

Thermal desorption by HPD depended on various factors such as N₂ gas temperature and pulse width. By selecting the optimum pulse width (50–1000 ms) and gas temperature (200–400°C), almost all the tested compounds were desorbed with little thermal decomposition. For example, in case of cocaine, the protonated cocaine signals started to be detected at ~150°C with a pulse width of 50 ms and showed a steep increase with an increase in temperature up to 350°C, after which the intensities reached a plateau in the temperature range of 350–400°C. In these HPD conditions, cocaine was desorbed and ionized with little thermal decomposition. The HPD method would be highly beneficial for quick and high-throughput analysis.

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ELECTRON IMPACT EXCITATION OF CH₃NO₂

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Nitromethane (CH₃NO₂) is an important propellant and prototypic molecule for large class of explosives. It has been investigated by electron impact and subsequent emission of photons in the spectral region between 300 nm and 670 nm. Emission spectrum of nitromethane was recorded at an electron energy of 50 eV. New dissociative excitation channels were discovered through the appearance of different CH, CN, NH, OH and NO bands, and the Balmer series of atomic hydrogen. In addition, relative emission cross sections were recorded for the transitions of selected fragments.

Electron-molecule interactions play an important role in plasma. Some of these reactions lead to generation of excited particles which can subsequently emit photons. The emission is often used to analyse properties of the plasmas by spectrometric methods. For this type of analysis, the availability of reliable reference data is crucial. The investigation of individual electron-molecule collisions at well-defined conditions, such as collision energy or temperature, can provide great reference spectra and provide further information on process such as cross sections. Nitromethane (CH₃NO₂) and other nitroalkanes are essential compounds in various explosives and propellants. Nitrogen oxides are among the gaseous products of detonation, so called blasting gases. These are toxic and in some applications of explosives, such as mining, they can cause increased health risks. Explosion residues detection techniques are important to investigation the cause of explosions and are based on optical detection methods, especially in the mid-infrared spectral region, or on chemiluminescence.

The measurements were performed on the electron induced fluorescence apparatus at Comenius University Bratislava, previously described in [1]. The emission spectrum consists of atomic emission lines and molecular band structures originating from neutral hydrogen atoms and functional groups formed via process of dissociative excitation and dissociative ionisation and excitation of the nitromethane molecule by electrons. No indication of other atomic emission lines is present in the obtained spectrum. The dominant feature of the nitromethane emission spectrum at 50 eV is fluorescence of different of CH group transitions. Envelope of the rotational structure of CH (A²Δ→X²Π) (0, 0) with the tail overlapping with CH⁺ (A¹Π→X¹Σ) (0, 0) is very prominent. Second prominent feature lays in the violet region. It is composed of CH (B²Σ⁻→X²Π) vibrational transitions – band head of (0,0) Q branch at 388.9 nm is detected between the emission lines of Balmer series, H_ε and H_η at 388.9 nm and 383.5 nm, respectively. The CN (B²Σ⁺→X²Π) has a strong overlap with CH (B²Σ⁻→X²Π) in 383 nm – 389 nm region and also in 362 nm – 368 nm region, thus further investigation is needed in order to determine relative intensity contribution of the two to the overall signal recorded in our experiment. Further relatively intensive band detected corresponds to the transition of NH (A³Π→X³Σ⁻) between 335.5 nm and 345.5 nm. The Q branch band heads (0,0) and (1,1) are clearly visible and the vibration modes of the P branch in the range 337.5 nm – 345.5 nm are very weak and more or less blended in the background noise.

Acknowledgments

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DEVELOPMENT OF SCANNING PROBE ELECTROSPRAY IONIZATION FOR MASS SPECTROMETRY IMAGING OF TISSUES

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The development of extraction-ionization technique using picoliters of solvent and its application for visualizing the distribution of components in diseased tissues will be presented.

1. Introduction

Cellular metabolic reactions necessary for maintaining biological activities proceed with high efficiency in multimolecular crowding biosystems, and the chemical conditions change according to the health status. Thus, analytical technologies for obtaining characteristic features from the various chemical information of cells/tissues and correlating them with disease states are important to understand the mechanisms of disease and to future diagnostic technologies. Mass spectrometry imaging (MSI) is an application of mass spectrometry to obtain multidimensional chemical distribution information which contains m/z value, signal intensity and the position of sample. MSI is expected to provide rich information for understanding biological activity toward disease diagnosis.

2. Development of t-SPESI

Tapping mode scanning probe electro spray ionization (t-SPESI) is a technique that combines the elements of atomic force microscopy (AFM) and electro spray ionization mass spectrometry (ESI-MS) [1-3]. The schematic illustration of t-SPESI is shown in Fig. 1. The silica capillary probe is vibrated at its resonance frequency to force the probe end to move up and down. The charged solvent by high voltage is flowing through the probe at the same time. The extraction of sample components into the picolitres of solvent and the ESI of them are performed in a few milliseconds, alternately. The sample analytes are converted into gas phase ions and introduced into the mass spectrometer. The feedback control system was developed to improve the stability of the probe scanning over the uneven sample. The multimodal imaging with a spatial resolution of 6.5 μm was reported [4].

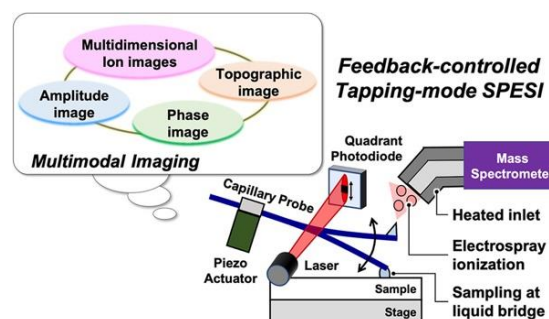


Fig. 1 Schematic diagram of the t-SPESI.

The sample analytes are converted into gas phase ions and introduced into the mass spectrometer. The feedback control system was developed to improve the stability of the probe scanning over the uneven sample. The multimodal imaging with a spatial resolution of 6.5 μm was reported [4].

3. Mass spectrometry imaging of tissues

The MSI of human cardiac tissue with dilated cardiomyopathy (DCM), an intractable disease, is studied. The tissues were obtained from the patients undergoing the ventricular assist device (VAD) implantation and the heart transplantation. The fresh frozen tissue blocks were sectioned into 8 μm thickness and mounted onto glass slides. The dried tissue sections were used as it is. The binary mixture of DMF and methanol was used for extraction-ionization. For all MSI data, the regions of nonlocalized lipid distribution were selected as regions of interests, and their averaged mass spectra were obtained. Twenty lipid ions with high intensity in the averaged mass spectrum were selected and subjected to principal component analysis (PCA). The score plots showed that the results correlated with changes in cardiac function over the course of the patient's treatment.

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CLUSTER IONS IN ION MOBILITY SPECTROMETRY

thermodynamics, mobilities and the influence on resolving power

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1. Ions in detectors used in ion mobility spectrometry – the basics

Ion mobility spectrometry (IMS) is an analytical technique based on the study of the movement of ions in gases under the influence of an electric field. There are two basic varieties of IMS. The first one uses ion mobility spectrometers with a drift tube (DT IMS), which work by determining the mobility of ions on the basis of their time of flight over a certain distance. The second variant, called differential ion mobility spectrometry (DMS), is based on measuring changes in mobility under the influence of a high electric field.

Regardless of the type of IMS technique used in the analytics, the sample molecules must be converted to a characteristic ionic form. This takes place in ionic reactors that are part of IMS detectors in chemical ionization processes. The generated ions are characterized by different stability, i.e. different lifetime. After the ions are formed, they are introduced to the transducer part of the IMS detector, where different types of ions are separated and the ion current is measured. This current gives information about the amount of a given sample component. From the point of view of IMS as a measurement technique, ions can be divided into stable ions, i.e. those whose lifetime is longer than the time they stay in the transducer part of the detector, and unstable, undergoing changes in this part. The most commonly known unstable ions are clusters consisting of an ionic core and solvating molecules, the number of which is determined by thermodynamic equilibrium.

2. Methods for studying generation and stability of cluster ions

In addition to analytical applications, IMS detectors can be used for basic research, on the basis of which it is possible to determine the thermodynamic parameters and kinetics of chemical ionization processes. In our work, we used both the previously mentioned (i.e. DT IMS and DMS) types of detectors. Typical measurements with DT IMS consisted in introducing substances whose molecules solvated different types of ions into the drift region. Changes in the drift times were observed, on the basis of which the thermodynamic parameters were calculated. Our research was carried out for chloride ions solvated with benzyl chloride molecules and for halide ions (Cl, Br and I) with various degrees of hydration.

The DMS detector allows you to study the effect of energy obtained from the electric field on the average degree of ion solvation. In our research, we recorded the signal of the DMS detector (the so-called dispersion plot) and determined the changes in mobility for different contents of water vapor in the drift gas.

3. The most important research results

Our research enabled us to gain knowledge about the processes of formation and decay of cluster ions. The most interesting results concern the following issues:

(a) It has been shown that based on the measurement of changes in the drift time for chloride ions solvated with benzyl chloride molecules, it is possible to determine the equilibrium constant and enthalpy for the formation / decomposition of cluster ions.

(b) Based on the measurement of drift times for a wide range of temperatures and humidity, the mobility of $X^-(H_2O)_n$ ions was determined (where $X = Cl, Br$ or I). The calculations were based on the abundance values of the individual ion types. These values were determined on the basis of thermodynamic parameters.

(c) The results obtained with DT IMS and DMS methods were compared. It has been shown that the changes in mobility with temperature recorded with DT IMS are comparable to the changes observed in the DMS for an increasing electric field. The course of these changes can, to some extent, be explained by using the concept of effective temperature.

ATMOSPHERIC PRESSURE DARK-CURRENT ARGON DISCHARGE IONIZATION WITH COMPARABLE PERFORMANCE TO DIRECT ANALYSIS IN REAL TIME MASS SPECTROMETRY

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An atmospheric pressure dark-current discharge state, created by combining argon with a needle electrode in ambient air, was found to have an ionization efficiency and mechanism comparable of those of conventional helium DART (direct analysis in real time), without requiring the use of a dopant or DART glow discharge.

1. Introduction

Direct analysis in real time mass spectrometry (DART-MS) was first reported by Cody et al. in 2005 [1]. It is a versatile technique that operates in open air, allowing rapid, non-contact analysis of solid, liquid and gaseous materials without any pre-treatment of samples. In common DART, excited helium (mostly the metastable 2^3S state, $He(2^3S)$) is generated inside a ceramic flow chamber by an atmospheric pressure glow discharge. The dominant positive-ion formation process is protonation, which results from the Penning ionization of atmospheric water molecules by $He(2^3S)$. $He(2^3S)$ has an internal energy of 19.8 eV, which is higher than the ionization energy of water (12.6 eV). Penning ionization results in the generation of oxonium ion H_3O^+ , and its water clusters $H_3O^+(H_2O)_n$, followed by proton transfer to analytes with proton affinities greater than that of water (691 kJ/mol). In negative-ion mode, analyte ionization can be attributed to proton transfer involving superoxide anion water clusters $O_2^-(H_2O)_n$.

Although helium DART has been performed with a great amount of success, helium gas is quite difficult to obtain recently, which makes it hard to sustain its use. Argon is a possible alternative gas for DART. Several research groups have investigated how argon works for DART compared to helium [2-4]. Excited argon stably exists in discharges (including DART glow discharge) in metastable states, such as the 3P_2 and 3P_0 states, with internal energies of 11.6 and 11.7 eV, respectively [3]. These energies are lower than the ionization energy of H_2O , which results in the formation of fewer $H_3O^+(H_2O)_n$ ions and give rise to quite low analyte ionization efficiency in argon DART [3]. Thus, dopant-assisted protonation based on atmospheric pressure photoionization has been used for the effective operation of argon DART [3,4].

Herein, a novel argon discharge ionization technique under atmospheric pressure is reported in which the analyte ionization efficiency and mechanism are comparable to those of conventional helium DART.

2. Results and Discussion

The present discharge system was easily established by modifying the conventional DART source: (1) a needle, whose tip end was formed into a hyperboloid of revolution, was placed in the sampling area, (2) heated ground state argon was flowed through the sampling area and (3) low DC voltage was applied to this needle. Notably, the use of dopants and a DART glow discharge were not required. The resulting discharge state in the sampling area is referred to as a “dark current discharge (DCD)”, a very low electric current (0.2~1 micro A) compared to the DART glow discharge. Ar-DCD, i.e., argon excited by DCD, ionized polar compounds such as α -amino acids (A) to (de)protonated molecules $[A\pm H]^\pm$, molecular anions A^- , oxygenated (de)protonated molecules $[A\pm H+nO]^\pm$, dehydrogenated deprotonated molecules $[A-2H-H]^\pm$, fragment ions $[A\pm H-F]^\pm$ (F: neutral fragment) and negative ion adducts $[A+R]^-$ (R: negative background ion). The absolute intensities of the (de)protonated molecules were found to be 1.1-8.1 times higher than those observed using the helium DART technique. In contrast, using Ar-DCD, non-polar compounds (e.g., n -alkanes; Alk) were detected as $[Alk+O-3H]^+$ and $[Alk+2O-H]^+$ ions via hydride abstraction and oxidation processes. Major background ions observed using Ar-DCD were

$\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, O_2^+ , $\text{O}_2^-(\text{H}_2\text{O})_n$, and CO_3^- , while argon-related ions were not observed. These results indicate that Ar-DCD efficiently generates excited state argon with an internal energy higher than those of well-known metastable states (~ 11.6 eV), e.g., resonance states such as $5\text{S } ^3\text{P}_1$ with an internal energy of 14.1 eV and $5\text{S } ^1\text{P}_1$ at 14.3 eV. Therefore, this suggests that ionization reactions occurring in the Ar-DCD method can be attributed to the Penning ionization of atmospheric H_2O and O_2 by resonance-state argon, in a similar manner to that in the helium DART method.

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A ROBOTIC INSTRUMENT FOR AUTOMATED SAMPLING AND CONSECUTIVE MASS SPECTROMETRY

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During the COVID-19 pandemic and the post pandemic society, automation, remote control, and other useful features are crucial for advanced measurement technologies. In conventional electrospray ionization (ESI) mass spectrometry, sample preparations are essential before introduction to mass spectrometers. In our laboratory, we have been studying a robotic instrument for fully automated sampling and consecutive ESI mass spectrometry.

1. Introduction

In general, mass spectrometry (MS) using electrospray ionization requires manual and time-consuming sample pretreatment, and a number of samples are often analyzed. So, there is an increasing demand for automated measurement and remote control to reduce the burden of the routine works in the university laboratories and companies. Desorption electrospray ionization (DESI) was firstly introduced as an ambient desorption/ionization method without sample pretreatment for mass spectrometry [1]. Such mass spectrometry methods are called “ambient MS.” Even in ambient MS techniques, a sample must be located at a fixed position near the inlet of a mass spectrometer. In recent years, researches for automated sampling and consecutive mass spectrometry on samples placed remotely from the mass spectrometer inlet have been conducted. Robots are often used for remote and automated sampling [2]. In our laboratory, we have developed an instrument that can automatically extract components from a sample located remotely and ionize the components without pretreatment by combining a sheath flow probe electrospray ionization (sfPESI) method and a tabletop 3-axis robot.

2. Experimental

As a modified version of probe electrospray ionization (PESI), the sfPESI was developed [3]. While PESI is only applicable to pretreated liquid samples, sfPESI can be applied to wet and dry samples without pretreatment away from a mass spectrometer inlet. As a sfPESI probe, a metal needle is inserted in a solvent-filled geloading tip, and the components can be extracted in the solvent at the tip of the probe when the probe touches softly the sample surface. If a touch sensor for the sfPESI probe becomes available, automated sampling and consecutive mass analysis will be achieved. Therefore, we constructed a capacitance sensitive touch sensing system for the sfPESI probe, and the probe was installed on a tabletop 3-axis robot [4]. By coupling the touch sensor with a 3-axis robot, the automated sampling and consecutive mass analysis of many samples prepared in a multiwell plate were performed. After the extracted components are electrosprayed, the solvent filled in the geloading tip is also electrosprayed for a while to clean the probe tip and suppress cross-contamination between different samples.

3. Results

An example of the total ion chromatogram (TIC) and extracted ion chromatogram (EIC) obtained by the automated sampling and consecutive analysis is shown in Fig. 1. The ion signals at m/z 571 derived from Gramicidin S were not detected, when solvent (0.9 min and 1.9 min) and cytochrome c (1.3 min) were sampled. This indicates that automated sampling and consecutive mass spectrometry without cross-contamination can be achieved.

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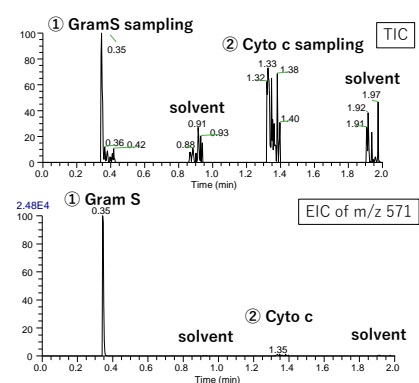


Fig. 1. TIC and EIC obtained by the automated sampling and consecutive analysis.

ELECTRON IMPACT EXCITATION OF NEUTRAL FRAGMENTS OF ACETONE

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The emission spectrum following electron impact on acetone [(CH₃)₂CO] was studied in a crossed-beam experiment and measured at several electron energies in range from 10 to 100 eV within the wavelengths of 280 - 950 nm. The emission bands of CH (A-X), CH (B-X) and CH (C-X) along with emission lines of hydrogen Balmer series were detected. Relative emission cross sections of several emission lines and bands were measured as well and dissociative excitation channels were estimated.

Acetone [(CH₃)₂CO] is the simplest ketone and it is an abundant compound of the interstellar medium. The detection of acetone in the interstellar space was first reported by Combes et al. [1]. It has been proven to be abundant in the mass spectra from 67P/Churyumov Gerasimenko, detected by the COSAC mass spectrometer at the comet's surface [2], and in the protoplanetary disk around V883 Ori [3].

The emission spectrum of acetone was measured in a crossed-beam experiment within the wavelengths of 280 – 950 nm at 50 eV electron energy and corrected for apparatus sensitivity. There were no detected transitions in the region below 380 nm and wavelength region of 445 – 900 nm consists of the lines of hydrogen's Balmer series H_α at 656.3 nm, H_β at 486 nm, and the Swan system of C₂ (d³Π_g–a³Π_u) within 460 – 472 nm. The emission spectrum within the wavelengths of 380 - 445 nm is shown in the Figure 1. The emission bands of CH (A²Δ–X²Π) (v,v) and CH (B²Σ⁻–X²Π) (0,0) fragments were identified within 415 – 445 nm and 386 – 402 nm respectively. Emission lines of hydrogen Balmer series H_γ – H_η were detected as well. Individual rotational transitions from P, Q, R branches of both CH fragments were identified according to LIFBASE 2.1.1 spectroscopy tool [4].

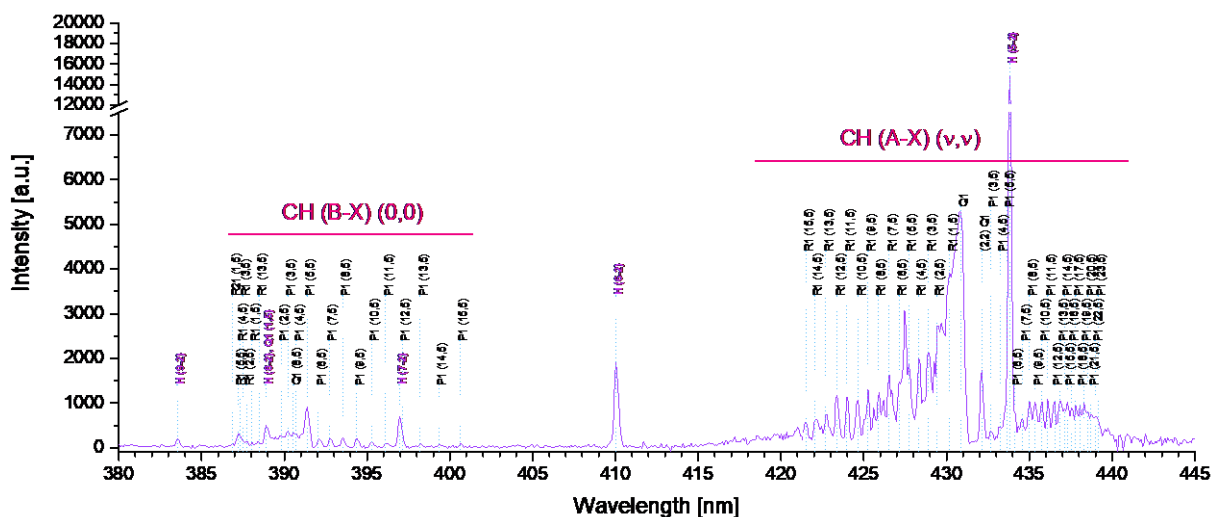


Fig. 1. The emission spectrum of (CH₃)₂CO measured by CCD camera at 50 eV electron energy.

Relative emission cross sections of selected transitions were measured as well within electron energy range of 7 – 102 eV and provide information about the threshold energies of detected transitions. Emission cross sections and their threshold energies reveal the probability of occurrence and active channels of given processes. This work is a part of more extensive study of the acetone fluorescence, which is focused on creating reference data on emission cross sections of all identified features of the spectrum.

Acknowledgments

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DEVELOPMENT OF AN AMBIENT ION MOBILITY SPECTROMETER FOR ON-SITE ANALYSIS OF EXHALED AIR AND MICROBIAL VOLATILE METABOLITES: MOLECULAR STRUCTURES AND COLLISION CROSS SECTIONS OF ORGANIC IONS IN AIR

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First, our approach to the development of an ion mobility spectrometer for detecting microbial volatile metabolites of soil-derived fungi in cultural property environments will be overviewed. In the latter part of this presentation, our study on molecular structures and collision cross sections (CCS) of organic ions in air will be presented for the development of an ambient electron emission ionization-ion mobility spectrometer for exhalation.

1. Introduction

Fungal contaminations were found on the mural paintings of the Takamatsuzuka Tumulus and Kitora Tumulus in Nara, Japan. The ability to detect and control these contaminations at an early growth stage is essential in preserving such cultural properties. We developed an ion mobility spectrometer for detecting microbial volatile organic compounds (MVOC) emitted from fungi at early growth stages [1, 2]. Ion Mobility Spectrometry (IMS) is a promising method in MVOC and breath analysis because a portable ion mobility spectrometer has the ability to detect a mixture of volatile organic compounds simultaneously in tens of milliseconds with high sensitivity. However, due to sampling in air, sample ions often form water molecule-added cluster ions, making analysis difficult. The purpose of this study is to investigate the molecular structures of ions produced by ambient electron emission ionization [3], and to calculate the expected ion mobility spectra of MVOC and breath-related organic compounds in air.

2. Ambient Electron Emission Ionization Ion Mobility Spectra and Mass Spectra Measurements

Ion mobility spectra of breath-related organic compounds such as acetone, acetic acid, propionic acid and triethylamine were measured under atmospheric pressure using an ambient electron emission ionization ion mobility spectrometer [3, 4]. Certain diluted concentrations of the above compounds were obtained by mixing sample compounds and air with PD-1B-2 permeator (GASTEC Co.), Digital-Mass Flow Controller 8000 (Horiba STEC) and a static mixer. The ion mobility spectra of acetic acid, propionic acid, acetone, triethylamine and trimethylamine were investigated by varying the voltage (V_d) applied between the surface electrode and the substrate electrode, drift gas flow rate, sample concentration and humidity. The dew point temperature of humidified air passed through distilled water was measured and the relative humidity of the humidified air was calculated. It was found that an optimum humidity for each compound increases ionization efficiency.

In order to identify ions produced in the ionization chamber, ambient electron emission ionization mass spectra were also measured using a Q-micro triple quadrupole mass spectrometer (Waters Corp.).

3. Theoretical Calculations of Molecular Geometries, Collision Cross Sections and Drift Times of Ions in Air

Optimized geometries and Gibbs free energies of all possible ions which were expected to be produced in the ionization chamber of the ambient electron emission ionization ion mobility spectrometer, were calculated with the density functional theory (DFT) method at the M06-2X/6-31++G(d,p) and APFD/6-31++G(d,p) level using the Gaussian 16 [5] and GRRM 14 [6] programs. Collision Cross Sections (CCS) of the above-mentioned ions were calculated in the classical trajectory method by

improving the MOBCAL2019 program [7] which can reproduce the mobilities of molecular ions in air. The scattering angles χ in collisions between ions and neutral gases, the collision cross sections and drift times were calculated. The Monte Carlo method was used for numerical integration. The calculated CCS values of [propionic acid+O₂]⁻, [acetic acid+O₂]⁻ and [(H₂O)₃+O₂]⁻ were 109.3~114.1, 102.1~105.0 and 99.2~103.2 Å², respectively. The calculated drift times (T_d) of [propionic acid+O₂]⁻, [acetic acid+O₂]⁻ and [(H₂O)₃+O₂]⁻ were 11.6~12.1, 10.6~10.9 and 10.2~10.6 ms, respectively. These are consistent with experimental values. The consecutive reactions took place in ambient air. The major ion O₂⁻ was formed by an electron attachment reaction.

Acknowledgements

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LABOATORY VERSION OF THE ORBITRAP MASS ANALYZER WITH SEVERAL TYPES OF ION SOURCES

HANKA - SPACE INSTRUMENT

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Application of mass spectrometry for asteroid exploration has recently become a hot topic. It is interesting both in orbit and on the asteroid. It can be used for the analysis of space dust, micrometeorites and particles from larger objects.

For the Czech *SLAVIA* satellite project was designed the *HANKA* (*H*motnostný *A*nalyzér pre *K*ozmické *A*plikace) space instrument - a high-resolution Orbitrap-based electrostatic ion trap mass analyser. The instrument is based on a commercial mass analyser [1] established in biology and medicine research, the so-called Orbitrap™ and the space CosmOrbitrap prototype (developed by LPC2E Orleans [2]). *HANKA* will bring this new technology into space to combine a small CubeSat space version of this ion trap analyzer, with an innovative in-situ hypervelocity impact ionization source for micrometeoroids.

A laboratory version of this instrument (*CIARA*) is currently under construction, where ions can be generated by three different methods:

1. Photons with molecules in the liquid phase (coupled with experiment *LILBID* (Laser Induced Liquid Bead Ion Desorption))
2. Electrons with molecules in the gas phase (*EI* source)
3. Photons with solid-phase molecules (*MALDI* or Laser Ablation)

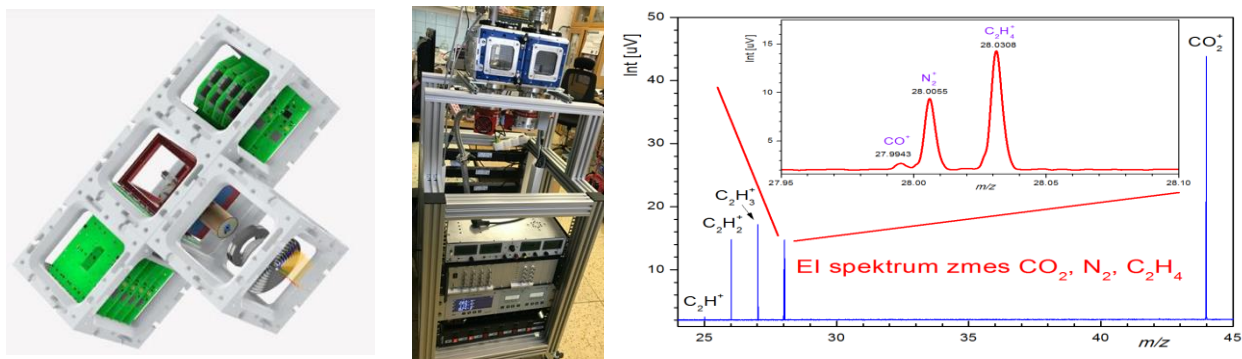


Fig. 1. *HANKA* - proposal instrument, laboratory prototyp, preliminary data from EI source

Based on the results obtained on the laboratory prototype, a miniature version of the high-resolution space mass spectrometer - *HANKA* - will be constructed.

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