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Recent Results in the Development of Selected Ion Mobility Mass Spectrometry, SIM-MS, Technique

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Abstract. Selected ion flow tube mass spectrometry (SIFT-MS) is an analytical technique for real time qualification and quantification of a great variety of organic and inorganic volatile compounds in the range of concentrations down to the part per billion by volume. SIFT-MS technique is based on ion-molecule reactions in the flow tube between selected reagent ions and neutral analyte molecules present in the sample. Product ions of these reactions are analysed by a quadrupole mass spectrometer. However, one current shortcoming is a lack of ability to distinguish organic compounds that lead to product ions with equal mass even when their molecular structures are different. In order to separate them, an electric field could be used as the ion mobility depends on the geometry and size of the molecular ion. It is thus proposed to extend SIFT-MS with an ion mobility stage and thus to develop selected ion mobility mass spectrometry technique (SIM-MS). We present the proposed concept of this technique together with the first results obtained using a newly constructed instrument.

Introduction

Selected ion flow tube mass spectrometry has greatly contributed to the quantitative studies of concentrations of vapours of volatile compounds in air, breath or liquid headspace in the fields of food analysis [*Flores et al.*, 2013], disease diagnostics [*Dryahina et al.*, 2011], environmental science [*Sovova et al.*, 2008] and biology [*Shestivska et al.*, 2012]. Based on the ion-molecule reactions and quadrupole mass filtering this technique provides high sensitivity of detection (limit of detection down to parts per billion on volume) and real time operation. Now our group uses *Profile 3* model of SIFT-MS instrument [*Smith et al.*, 2005] to improve its application for different areas of research. But its main disadvantage is the impossibility to distinguish different compounds with the same mass-to-charge ratio, what is usually situation for organic materials. Thus we have started to construct a new instrument with the additional filtering stage based on the diverse mobility of the analysed ions in the buffer gas.

Experimental

The SIM-MS instrument has a similar construction and operation principals as the regular SIFT-MS instruments (like *Profile 3* used in our laboratory). It utilizes chemical ionization in a flow-drift tube. At the first stage of development the objective was to implement the SIFT-MS method in the new flexible format and thus a metal field-free flow tube was used. The precursor ions (H_3O^+, O_2^+, NO^+) are created in the microwave plasma discharge and after the ions of a given mass-to-charge ratio are selected by an upstream quadrupole mass filter, and then they are injected into flowing helium carrier gas through the Venturi inlet (see Figure 1) to predict the back flow of carrier gas [*Smith et al.*, 2005]. Selected precursor ions react with the trace gases in a sample introduced into the flow tube at a known flow rate during defined reaction time with known rate coefficient. A downstream quadrupole mass spectrometer detects and counts the precursor and product ions. From these data on-line computer can immediately identify and quantify the trace gases in the sample.

A detailed schematic view of SIM-MS is shown in Figure 1. The instrument consists of three vacuum chambers, where the upstream mass filter, flow/drift tube and downstream mass filter are placed. This construction differs from traditional flow tubes as the flow tube is enclosed in a chamber

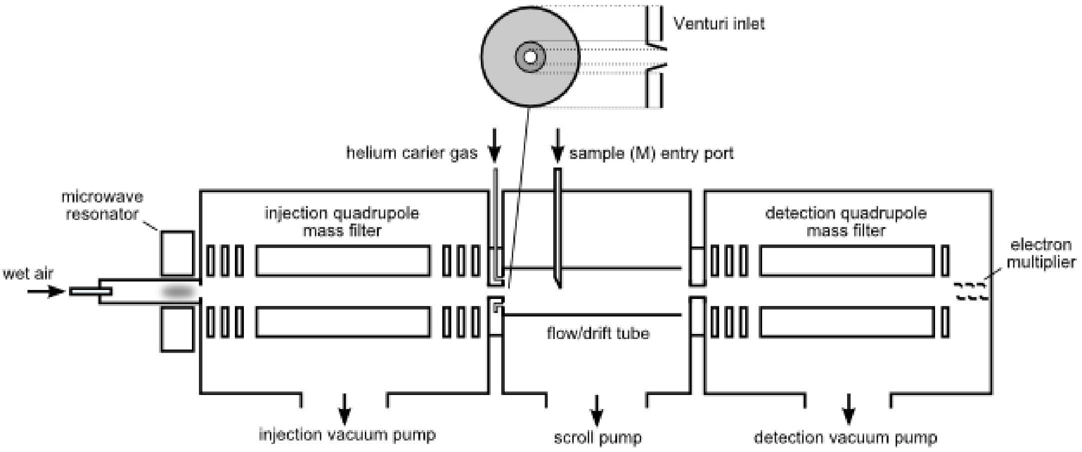

Figure 1. A schematic view of the newly constructed SIM-MS apparatus. Detailed view of the Venturi inlet is also shown.

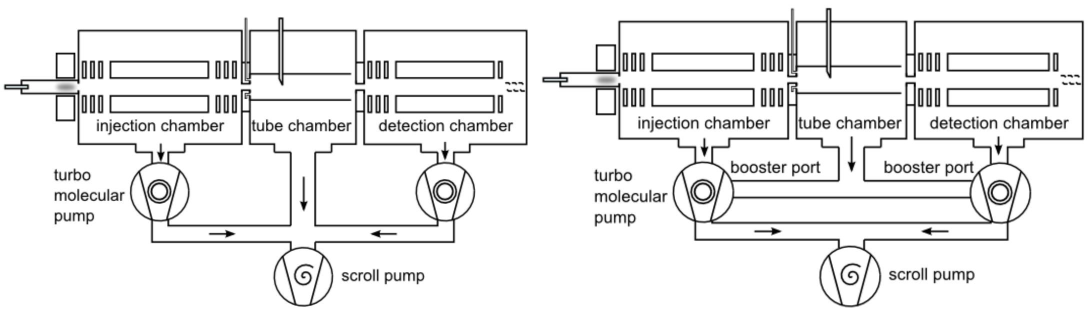

Figure 2. Vacuum systems: standard (left) and using *XDS35i* booster ports (right).

coupled to the flow tube pump, this is intended to facilitate easy modifications of the drift tube. Injection and detection chambers are pumped out to 10^{-5} mbar by *nEXT300T* turbo molecular pumps with pumping speeds 1080 m^3/h. Backing for turbo molecular pumps is provided by a scroll pump *XDS35i* (see Figure 2).

Firstly the tube chamber was pumped out to 2 mbar by the same *XDS35i* with the pumping speed 35 m^3/h. Thus the residence time of ions in the tube calculated from the pumping speed and tube geometry was *0.34 ms*, what leaded to significant diffusion loses (as will be discussed in the Results section). In order to suppress diffusion we decided to increase the pumping speed by using two booster ports of the *nEXT300T* pumps each with the pumping speed 24 m^3/h. Additional loading of these ports has not influenced the pressures in the vacuum chambers at different tube pressures (see Figure 3), but has reduced diffusion loses of ions significantly as it will be shown in the Results section. Note that pressure in the injection chamber depends on the helium pressure in the tube chamber in non-linier way due to the Venturi effect and the mixing of the backing helium with the wet air from the ion source.

To fully control and adjust the injection and detection quadrupole mass filters the custom made power supplies have been developed by our colleges Juraj Jašík and Ján Žabka. At the moment test prototype is used for detection mass filter, but the injection quadrupole mass filter is run using a legacy *Extranuclear* power supply, which does not provide perfect separation of the precursor ions and the upstream quadrupole thus works in an ion guide regime.

To validate the proper operation of SIM-MS apparatus we decided to measure the rate coefficients for the ion-molecular reactions of precursor ions with ethanol [*Michalčíková*, 2014]:

$$H_3O^+ + C_2H_5OH \longrightarrow C_2H_7O^+ + H_2O \tag{1}$$

$$O_2^+ + C_2H_5OH \xrightarrow{52\%} C_2H_5O^+ + H + O_2 \tag{2}$$

$$O_2^+ + C_2H_5OH \xrightarrow{48\%} CH_3O^+ + CH_3 + O_2 \tag{3}$$

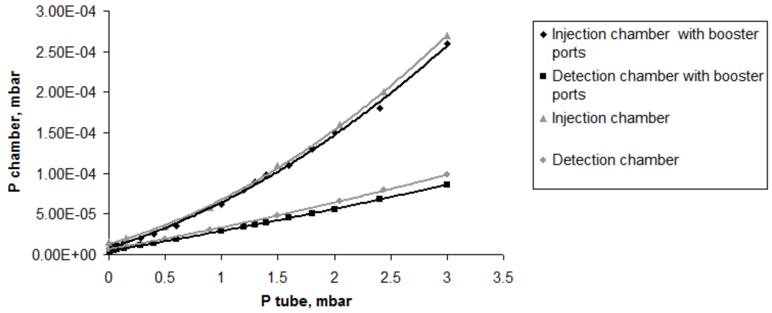

Figure 3. The dependencies of the pressures in the injection and detection chambers on the pressure of helium carrier gas in the flow tube chamber.

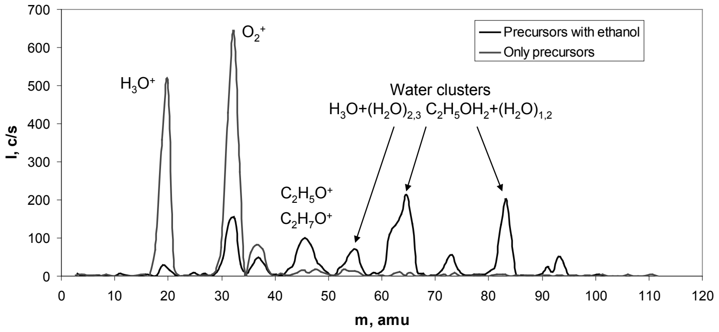

Figure 4. Mass spectra from SIM-MS with only precursor ions and with some addition of ethanol.

In order to study the rate coefficients and products of these ion-molecular reactions, it is necessary to introduce the reactant gas into the helium carrier gas or ion swarm at a measured and controlled rate, and then to acquire the count rates of the precursor ions and the product ions (see Figure 4) of the reaction as a function of the reactant gas flow rate (the introduced number density). Using these data the rate coefficients are obtained by a standard procedure [*Spanel et al.*, 1998].

Ion mobility stage

The ion mobility stage is the essential component of the SIM-MS technique. We will implement it in two phases. At the first phase the metal flow tube will be replaced by a drift tube. Traditionally, drift tubes have been designed as a stack of metal-conducting rings, which are insulated from each other with ceramic rings [*Cohen et al.*, 1970]. Metal rings were biased at different voltages to obtain an electric field of 200 to 300 V/cm along the central axis of the drift tube. But for our needs we have chosen a modern design of a drift tube using technology *FieldMaster™ Resistive Glass* manufactured by *PHOTONIS*. *FieldMaster™ Resistive Glass* is a patented process that uses lead silicate to create a resistive layer at the surface (about 10 MΩ in our case), which acts as a semiconductor as the resistive properties create uniform electric fields. By varying of the applied voltage it is possible to change the drift speed of ions in the drift tube given by

$$v_d = \mu E + 1.5 v_g \,, \tag{4}$$

where μ is the ion mobility in the given pressure and E is uniform drift field and v_g is the average gas flow velocity. Factor 1.5 accounts for the increased ion number density at the tube axis. The drift speed of ions is related to the residence time t as:

$$v_d = \frac{L}{t} \,, \tag{5}$$

where L is the length of the tube. So it is possible to write

$$t = \frac{L}{\mu E + 1.5 v_g} \,. \tag{6}$$

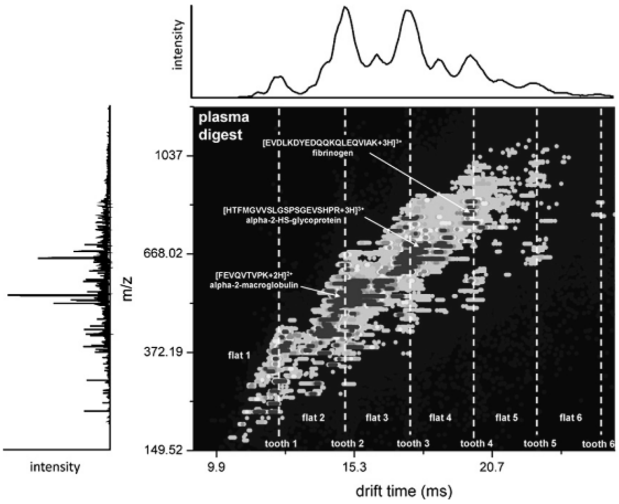

Figure 5. Ion mobility-mass map for the some peptide ions [*Valentine et al.*, 2009].

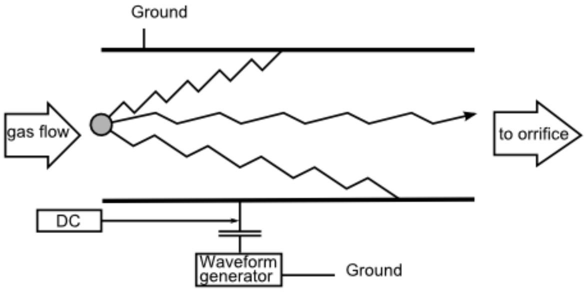

Figure 6. Schematic illustration of a differential ion mobility filter.

Using this drift tube it will be possible to obtain reduced ion mobility library for different compounds and build a mobility-mass map (see illustration in Figure 5).

At the next phase the measured data will be used to design a differential mobility filter. Its concept is based on two parallel metal plates, where one electrode is held at the ground potential, whereas a time variable voltage is applied to the other plate. Thus an electric field is applied perpendicular to the gas flow and ions are displaced toward the top plate during the high-field portion of the waveform with a velocity [*Buryakov et al.*, 1993]:

$$v_{\perp} = \mu(E)E(t)\,, \tag{7}$$

where $v_{\perp}$ is the ion velocity perpendicular to gas flow direction, $\mu(E)$ is the field-dependent mobility. During low-field portion, the ion movement is reversed and ions drift toward the lower plate. Only ions with a total displacement less than the distance to the upper plate will reach the ion sampling orifice (see Figure 6).

Results

Diffusion losses

To estimate the diffusion losses of the ions in the flow tube we have derived the dependence of the precursor ions signal at the end of the tube on the reciprocal value of the helium carrier gas pressure (see Figure 7). The ion current was collected by the ion sampling orifice disk before the downstream quadrupole. It is known that the number density of ions in the buffer gas decays in consequence of diffusion according to the expression [*Dryahina et al.*, 2005]:

$$[A^+] = [A^+]_0 \exp\left(-\frac{D(A^+)}{\Lambda^2}t\right), \tag{8}$$

where $[A^+]$ is the number density of the ions in the gas, $D(A^+)$ is the diffusion coefficient of the ions for the given pressure p and Λ is the characteristic length dependent on the tube diameter [*Adams et al.*, 1976]. Pressure variation of the diffusion coefficient is described as:

$$D(A^+) = \frac{D_0(A^+)p_0}{p}, \tag{9}$$

where $D_0(A^+)$ is the diffusion coefficient of the ions at a reference pressure p_0. From Equation 9 it follows that

$$\ln\frac{[A^+]}{[A^+]_0} = \left\{-\frac{D_0(A^+)p_0 t}{\Lambda^2}\right\}\frac{1}{p}. \tag{10}$$

From the plot in Figure 7 we can conclude that the coefficient $\left\{-\frac{D_0(A^+)p_0 t}{\Lambda^2}\right\}$ is for the vacuum system with booster ports more than a factor of two smaller than the one for the standard vacuum system. As $D_0(A^+)$, p_0, Λ are constants, it means that the residence time of ions in the tube t has become shorter and quite similar to SIFT-MS *Profile 3*, where the flow tube is 5 cm long in contrast to 14.5 cm for SIM-MS instrument.

Rate coefficients

The rate coefficients for the reactions 1–3 were measured using the dependence of the precursor ion signal decay on the number density of ethanol in the tube (see Figure 8). Obtained values are $k[H_3O^+] = 3\cdot10^{-9}cm^3s^{-1}$, $k[O_2^+] = 2\cdot10^{-9}cm^3s^{-1}$. They almost coincide with earlier results from SIFT-MS measurements: $k[H_3O^+] = 2.7\cdot10^{-9}cm^3s^{-1}$, $k[O_2^+] = 2.3\cdot10^{-9}cm^3s^{-1}$ [*Spanel et al.*, 1997].

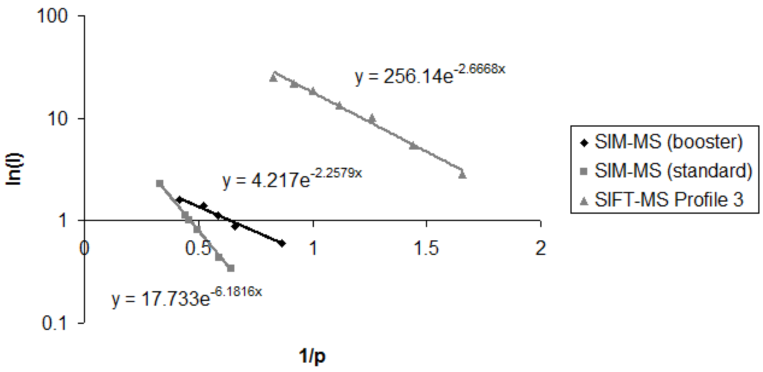

Figure 7. The dependence of the ion current at the end of the flow tube on the pressure of helium carrier gas in it.

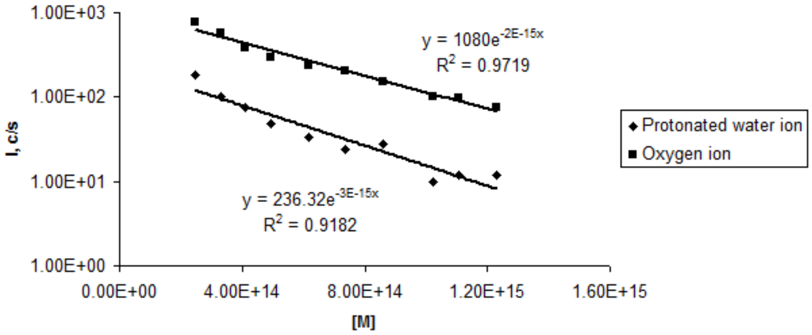

Figure 8. The dependence of the precursor ions signal on the number density of ethanol molecules in the tube.

Conclusions

The SIM-MS apparatus that is being developed has provided the first results for the rate coefficient measurement, but this is not its ultimate purpose which is development of a new method for quantification of volatile compounds with identical molecular weights. Several issues have to be studied and solved before the ion mobility stage will be functional. Diffusion loses in the tube will be moderated by the applied uniform field. The accuracy of measurements of the rate constants and concentrations of the trace gas will grow with the increasing the number of the precursor ions injected in the tube, what requires the precision work on the Venturi inlet design and ion optic systems.

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