



A novel ion selective gas sensor based on pulsed atmospheric pressure chemical ionization and ion-ion-recombination



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ABSTRACT

In a former work on the investigation of ion generation and ion-ion recombination kinetics at atmospheric pressure with an ion mobility spectrometer equipped with a pulsable electron emitter, we found that different ion species and concentrations could be distinguished by only considering the specific ion-ion recombination kinetics. In the present work, these findings are utilized for the development of a novel compact and simple gas sensor. In a first step, the gas mixture becomes ionized by atmospheric pressure chemical ionization for a defined ionization time. Subsequently the ionization source is turned off and the ion specific decay of the ion concentration as a function of the recombination time is measured. This decay depends on the generated ion species and the compounds of the gas mixture respectively. For the analysis of these decay curves and visualization of the results, we use discriminant analysis. As an exemplary target analyte, we chose dimethyl-methylphosphonate (DMMP). With the current setup we achieve a limit of detection of 8 ppb_v for the detection of DMMP in presence of significant higher ammonia and formaldehyde concentrations by only considering the recombination kinetics.

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1. Introduction

Monitoring of environments or processes is an important sector in sensor technology. Generally, the major goal is the detection and analysis of chemical warfare agents [1], toxic industrial compounds [2], explosives [3] or drugs of abuse [4]. Thus, there are numerous special requirements for the employed measurement systems and sensors respectively. First, the sensors have to be selective to secure an exact identification of the compounds. However, as even small amounts of hazardous compounds can have a high impact on the human health, additionally a very high sensitivity combined with a fast response time is essential. Furthermore, an easy interpretation of the sensor signal is beneficial. There are already various measurement systems for the quantitative analysis of gaseous mixtures on the market. Mass spectrometer (MS) [5,6] for example have a high selectivity and precision, but are expensive and require an enormous instrumental effort. An analysis with a multidimensional gas chromatograph [7] coupled to an efficient detector is very selective and sensitive but very time consuming. An ion mobility spectrometer (IMS) [8,9] is very fast and the instrumental effort is lower.

While the selectivity is limited, compared to MS, the atmospheric pressure chemical ionization process leads to a very high sensitivity. However, the interpretation of IMS or MS measurement data is complex. Common gas sensors provide an easy read-out with the drawback of lower analytical performance compared to, e.g. mass spectrometer. Among others, commonly used gas sensors are gas sensitive field effect transistors [10], surface acoustic wave (SAW) sensors [11], metal oxide sensors [12]. The novel sensor principle presented in this work is based on an atmospheric pressure chemical ionization (APCI) [13]. Depending on the detection principle, this ionization technique enables very low detection limits in the ppb_v or even ppt_v range. As separation technique we use the time dependent and ion specific ion-ion-recombination kinetics [14].

2. Sensor idea and measuring concept

To illustrate the basic idea of this novel sensor concept, the generated ions in an atmospheric pressure chemical ionization process are investigated with a drift tube ion mobility spectrometer (IMS) [8]. Here, a gas mixture is ionized and subsequently the different generated ion species are separated via their specific mobility in a neutral drift gas under influence of an electrical field. Then, the mobility separated ion species discharge at a faraday detector leading to a drift time dependent ion current, i.e. the ion mobility spectrum. The used IMS is equipped with a pulsable electron

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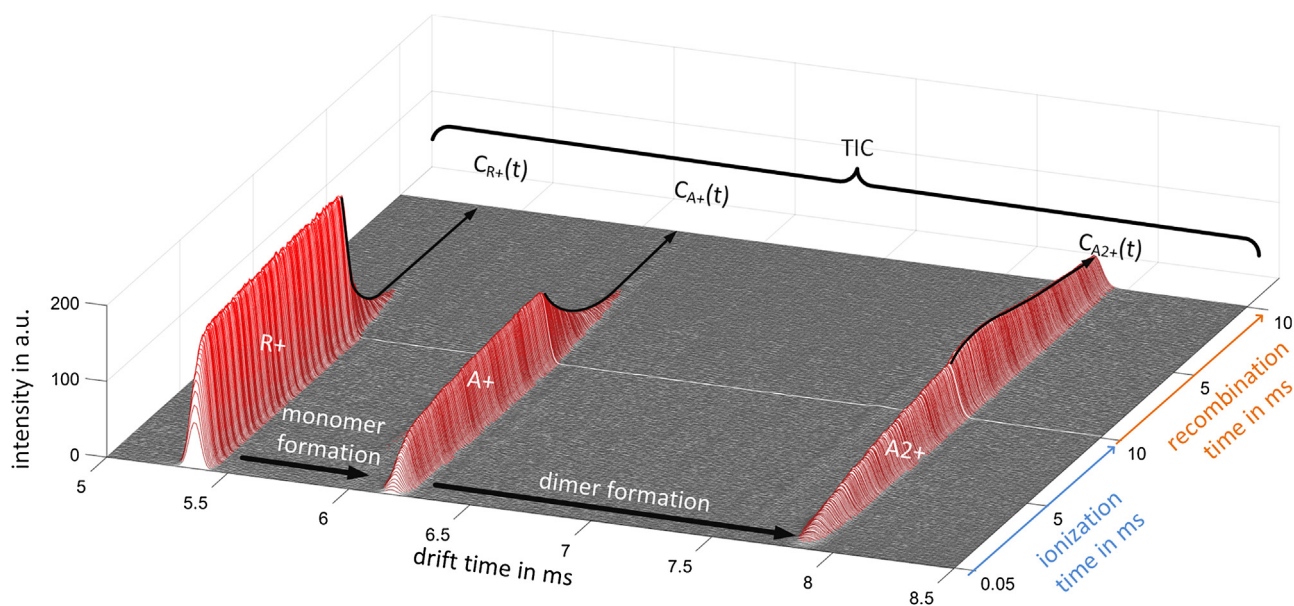


Fig. 1. Positive ion mobility spectra of clean air containing 50 ppbv DMMP at different ionization times. With increasing ionization time the ion concentrations of the positive reactant ions (R^+), the DMMP-monomer (A^+) and dimer ions (A_2^+) increases. Subsequently, the ionization source is turned off and the ion concentration decreases during the recombination time. Only DMMP-dimer ions are detected at the end of the recombination time.

emitter that allows the adjustment of the ionization time t_{ion} and furthermore, it is possible to add a recombination time t_{rec} between the end of the ionization time and the ion separation. During this recombination time the previously generated ions are kept in a field free area where the positive and negative ions recombine. With this setup, it is possible to investigate the influence of the ion generation kinetics and the ion recombination kinetics on the resulting ion mobility spectra. In a previous work we demonstrated the benefits of a pulsable electron emitter as ionization source for IMS [15]. Here, we could show that the determination of reaction rates with this setup is possible by only varying t_{ion} or t_{rec} . These ion specific reaction rates are the bases for the novel sensor concept presented in this work. Fig. 1 visualizes the varying ion concentrations of clean air containing 50 ppbv Dimethyl-methylphosphonate (DMMP) [16] during ionization and recombination time. To generate this diagram, approximately 400 ion mobility spectra are placed in succession starting with $t_{ion} = 50 \mu s$ and constant $t_{rec} = 0$ and then subsequently increasing t_{ion} to 10 ms. To visualize the ion concentration during recombination, the ionization time is kept constant at $t_{ion} = 10$ ms and spectra are measured for recombination times of $t_{rec} = 0 \mu s$ to 10 ms. Hereby, three ion species are detected: positive reactant ions, DMMP-monomer and DMMP-dimer ions. Ion species which consist of one analyte molecule are called monomer ions, while ion species consisting of two analyte molecules are named dimer ions. With increasing ionization time from 50 μs to the maximum of 10.000 μs all occurring ion concentrations increases until there is an equilibrium between ion formation and ion losses. The total ion concentration (TIC) is the integral of each spectrum and thus the TIC equals the sum of all occurring ion concentrations. It can be seen, that the positive reactant ion peak increases much faster than the DMMP-monomer ion peak and the DMMP-monomer ion peak increases much faster than the DMMP-dimer ion peak, which can be explained by the consecutive reaction chain of positive reactant ions to DMMP-monomer ions to DMMP-dimer ions. A detailed description is given in [17]. Thus, the relation between the peak intensities of the ion species changes. However, the important thing to note here is that varying the ionization time leads to different ion distributions in the reaction chamber depend-

ing on the present analytes and their concentrations. Subsequently, at the end of the ionization time of 10.000 μs the electron source is turned off and the positive ions recombine with the negative ion species. In Fig. 1 the decay of the generated ion species during the recombination time is depicted. The positive reactant ion peak decreases much faster than the DMMP-monomer ion peak. From the increasing DMMP-dimer signal, it can be seen, that due to the high proton affinity of the DMMP-dimer ions, more DMMP-dimer ions are formed although the electron emitter is turned off. However, a further increase of the recombination time also leads to recombination of DMMP-dimer ions. As for the ionization process, the recombination process of ions depends on the present analytes. In this work, we focus on the total ion concentration (TIC), which can be interpreted as the integral of one IMS spectrum, i.e. the sum of all occurring ion concentrations. Previous works [18,19] shows, that the recombination process of different ion species and concentrations can be distinguished by only considering the decay of the TIC. In this present work, we develop a sensor principle based on TIC measurements at different recombination times to distinguish different gas mixtures. This leads to a much more simple sensor setup compared to IMS.

3. Fundamentals and experimental setup

In this section, the experimental setup, the measurement procedure and the theoretical background are described. The schematic of the experimental setup is depicted in Fig. 2. It mainly consists of a pulsable electron emitter as ionization source [20], a reaction chamber including a shielding grid, a faraday detector which is connected to a transimpedance amplifier and an electronic control and processing unit. The measurement procedure can be divided into three steps: 1. ion generation, 2. ion specific ion recombination and 3. measurement of the total ion concentration (TIC).

1. The electron emitter emits high kinetic electrons of about 7.2 keV for a definable ionization time t_{ion} which initiate the atmospheric pressure chemical ionization (APCI) described by [13,21]. The ionization process starts with the ionization of nitrogen by electron impact ionization and results in the formation of protonated

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