Miniaturized Sensor for the Detection of Environmental Pollutants

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Abstract

A miniaturized ion mobility spectrometer (IMS) for the sensitive and selective detection of low concentrated substances in the ppb-range under atmospheric conditions is presented. The chip with a novel design consists of an integrated ion filter and detector and is manufactured with MEMS technologies. The implemented concept of the IMS-Chip allows an easy and flexible adaption to a broad range of target applications. Environmental analysis represents a possible field of application for the IMS-Chip. Concerning this, volatile organic compounds are substances of common interest.

First promising results are presented which demonstrate the performance of the ion detector. An outlook for further investigations and the evaluation of the integrated ion filter is given.

Key words: ion mobility spectrometer, sensitive and selective detection, MEMS technologies, volatile organic compounds, miniaturized sensor

Introduction

The fast and reliable detection of harmful substances places high demands on sensors and systems. Volatile organic compounds (VOC) are important especially in environmental analysis. Substances like benzene are very harmful to health even in low concentrations [1]. Common laboratory analysis methods are mass spectrometry and gas chromatography. Often they are also used in combination with special sample treatments to detect low concentrations of relevant substances. However, they are inconvenient for fast and portable in-situ analysis.

Ion mobility spectrometry (IMS) is an alternative method, that allows a very sensitive and selective detection of e. g. warfare agents, drugs and VOCs [2]. IMS uses electrical fields to separate ionized analyte molecules of different species. In comparison to mass spectrometry, ion mobility spectrometers can be used directly in air under atmospheric conditions without the need for vacuum. Therefore, IMS represents a suitable method for portable and miniaturized gas detection systems.

Concept of the new IMS-Chip

Common realizations of IMS are based on time-of-flight (TOF) ion filters. A drift field moves the ions in a drift tube as depicted in Fig. 1 (a). According to eq. (1) the mean drift velocity v_d of the ions depends on the electric field strength E and the specific ion mobility K.

$$v_d = K E \qquad (1)$$

The resulting drift time t_d that an ion needs to get from the ion shutter to the detector depends on the length of the drift tube L:

$$t_d = \frac{L}{K E} . \qquad (2)$$

The drift time t_d can be used to distinguish different compounds of a unknown gas mixture. These kinds of drift tubes are relatively easy to implement. However, to achieve acceptable resolutions, e. g. to separate ion with similar ion mobilities, a sufficient drift length L is required. Therefore a miniaturization of the drift tube is limited. Towards smaller geometrical dimensions, inhomogeneities of the drift field especially near the side walls and the electrodes have a detrimental effect on the functionality. Therefore the use of MEMS technologies isn't preferable.

Among other IMS realizations, like the aspiration condenser design [3], the so called differential ion mobility spectrometry (DMS) is a very promising filter technique for miniaturized ion mobility spectrometers. Fundamentals and miniaturized micromachined filters are described in Refs. [4] and [5]. DMS makes use of the field dependence of the ion mobility $K(E)$. Ions are moved along planar filter electrodes while an alternating voltage produces an asymmetric electrical field. According to Fig. 1 (b), ions oscillates between the filter electrodes. Due to different electrical field conditions, ions are deflected perpendicular to the electrodes
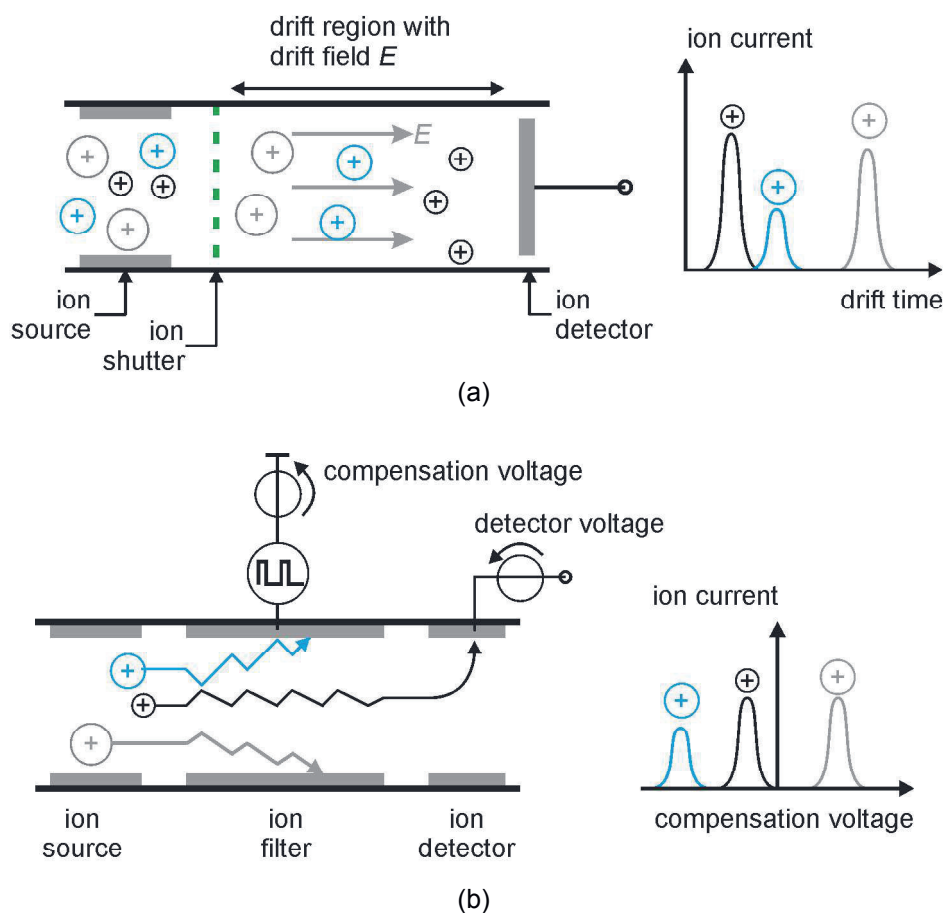
Fig. 1 Working principle of (a) time-of-flight ion mobility spectrometer TOF-IMS and (b) differential ion mobility spectrometer DMS with simplified ion trajectories.

depending on their specific change of their ion mobility $K(E)$.

An additional dc compensation voltage adjusts the filter. Only ions with a special $K(E)$ reach the ion detector behind the filter outlet. The value of the compensation voltage can be used, to distinguish different ion species.

In general electric field strengths above 15 kV/cm are required for the filter operation. With regard to a portable detector system, relatively small voltages are required. To reduce the necessary voltages to a reasonable range of 100 V, distances between the filter electrodes of a few 10 µm are necessary. Therefore, the use of MEMS technologies is one promising possibility to fabricate such filter elements.

In comparison with TOF-IMS, DMS has advantages regarding higher and continuous ion flows at the detector, as well as short measuring times. Despite that, additional load currents in the filter control are unavoidable. This is due to the needed alternating voltages and the electrical capacitance between the filter electrodes. The filter electronic have to provide this current.

A miniaturized MEMS ion filter is described in Refs. [6] and [7]. The distance between the filter electrode is 35 µm. The filter structure is etched through a silicon chip. Deep reactive ion etching (DRIE) is therefore a suitable method. Ions are entering at the topside and exiting the chip at the bottom side. The small electrode distance allows very high electric field strengths and low voltages. However, adjustments in the filter geometry, e. g. for special fields of application, require high efforts regarding the adaption of the MEMS process. Furthermore, the ion detector is an additional part and is not integrated into the silicon chip.

The IMS-Chip presented in this work (Fig. 2) is also based on DMS. In comparison to solution presented in Refs. [6] and [7], it uses a different concept for both the device and technical realization. The ion channels between the electrodes are orientated along the top side of the silicon chip. This allows the on-chip implementation of additional functional IMS parts like the ion detector. Furthermore, changes on the filter geometry towards a targeted application can be easily adapted.
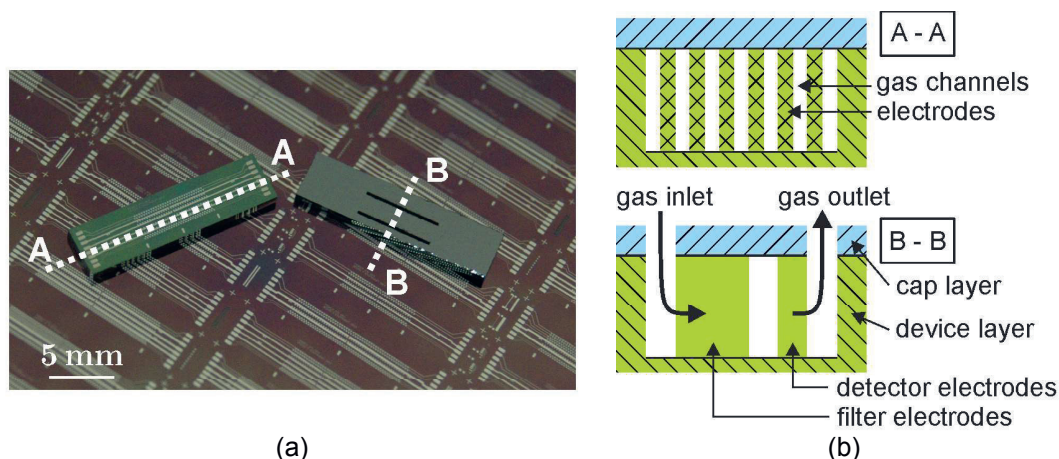
Fig. 2 Concept of the miniaturized IMS-Chip (a) the presented chip device and
(b) cross sectional view for visualization of the internal gas channels and electrodes.

The gas channels between the electrodes are covered with an additionally cap that has inlet and outlet slits for the gas transfer into the chip. The complete MEMS process takes place at wafer level. So the manufacturing process of the small devices is very cost-effective.

This approach of an integrated and miniaturized ion filter and detector for use in an ion mobility spectrometer seems to be very advantageous. The design of the IMS-Chip allows a versatile adaption of filter and detector parameters while maintaining small electrode distances in the µm-range. This presents and advantage in comparison to other miniaturized IMS designs.

Experimental

An experimental setup according to Fig. 3 for the evaluation of the developed IMS-Chip has been developed. Analytes are mixed into the carrier gas flow by using permeation devices in a temperature controlled oven. The analyte is inside this device and permeates trough a membrane into the surrounding gas flow. With the help of these commercially available devices, low concentrations of several analytes can be produced over a long period of time. Concentrations can be varied with an additional mass flow controlled gas line. For first tests, acetone filled permeation tubes and pure nitrogen as carrier gas was used.

Chemical ionization, e. g. with radioactive ^{63}Ni, and photoionization are two common methods for the ionization of the analytes. The current setup uses a discharge lamp (Heraeus Noblelight GmbH, PKS106) filled with krypton. These lamps emit photons with an energy of 10.0 eV and 10.6 eV. The ionized analytes enters the IMS-Chip and passes the ion filter and detector.

For the measurement of the ion current an electrometer (Keithley 6517B) has been used. For the generation of the filter signal an electric circuit based on presented possibilities in Ref. [8] has been developed.

Absolute analyte concentrations are measured with a photoionization detector (PID) after the IMS-Chip outlet. The PID has a separate photo discharge lamp and detects all ionized molecules in the gas stream without a filter element. The PID serves as a reference detector.

Changes in analyte concentrations are performed by either changing the ratio from permeation and carrier gas flow or the temperature of the permeation oven. Obtained concentrations of acetone in nitrogen are in the range of a few ppb to a few 10 ppm.

First Results and Discussion

The IMS-Chip includes the functional main components ion filter and detector. Important parameters of the ion detector like sensitivity, dynamic behavior and stability of the detector signal was determined. Tests of the functionality of the ion filter can be evaluated. This will be published elsewhere.

The detector converts the gas flow with the ionized analytes into an electric current. The sensitivity is defined as the change of this ion current in dependence of the analyte concentration. Therefore this value influences the absolute ion current at a given concentration. In general this value is in the nA to pA range. Fig. 4 shows an exemplary characteristic curve of the detector signal obtained with the IMS-Chip. A linear dependence of the detector current is observed in the lower ppm concentration range.
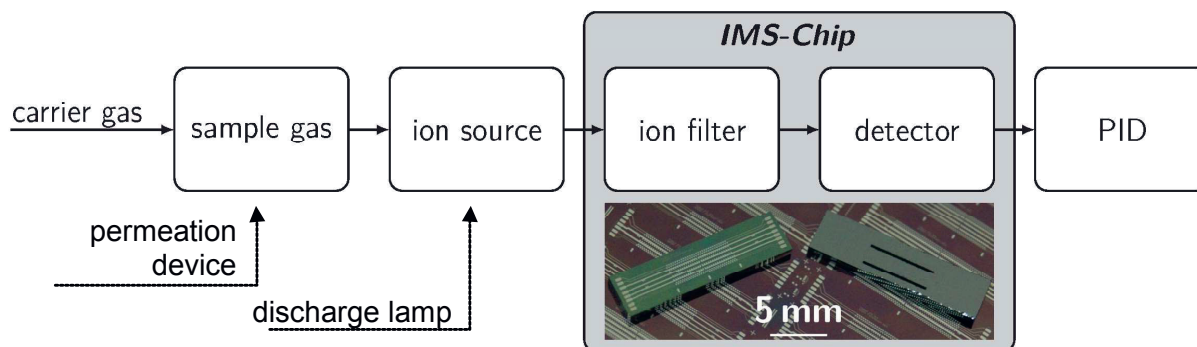
Fig. 3 The developed IMS-Chip with integrated ion filter and detector and the test setup with carrier gas, sample gas, ion source (VUV-photo discharge lamp) and a photoionization detector (PID) after the gas outlet of the IMS-Chip.
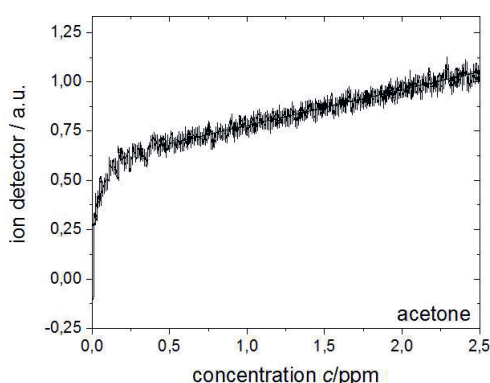

Fig. 4 Characteristic curve of the detector signal

The time that a sensor needs to respond on concentration changes is another important parameter. This dynamic behavior is evaluated by a fast change in the analyte concentration while keeping the electrical parameters of the IMS-Chip constant. In the exemplary response curve in Fig. 5, the concentration of the test gas acetone has changed from 0 to 2 ppm. The ion detector of the IMS-Chip shows a response time of a few minutes. The reference detector shows a comparable response time.
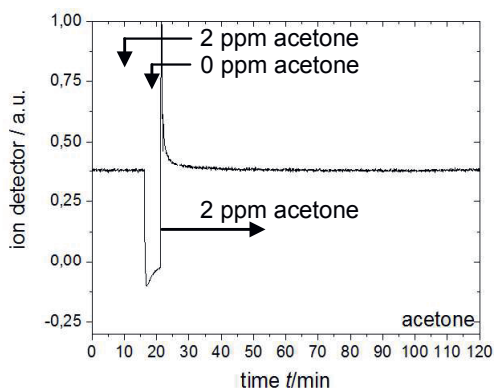

Fig. 5 Dynamic behavior and stability of the detector signal.

The measurement results show also a stable detector signal when applying a constant analyte concentration.

These first measurements indicates the basic functionality of the ion detector as a part of the IMS-Chip. There are also some effects, that cannot be explained so far. That are the change of the sensitivity towards low concentrations below 200 ppb and a overshoot of the detector signal after a change of the analyte concentration. Additional measurements and adaptions of the experimental setup have to be performed. We attribute this characteristic to an too long distance that the ions have to move from the ionization source to the IMS-Chip. The realization of an improved version of the setup is in progress.

Basing on these results and the applied corrections of the experimental setup, the evaluation of the ion filter can be performed.

Conclusion and Outlook

The presented IMS-Chip with a unique component design combines an ion filter and detector in one single miniaturized device. An experimental setup was developed to characterize the manufactured MEMS chips. First results indicate a linear response in the upper ppb range and short response times. Next steps will include further tests of the detector element and the ion filter. Afterwards the overall IMS-Chip functionality can be evaluated.

The concept of the presented IMS-Chip is a promising approach, that can be used as a part of an ion mobility spectrometer for the detection of a broad range of substances, like volatile organic compounds.

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