# How Operating Pressure and Electric Field Strength Affect Sensitivity in High Kinetic Energy Ion Mobility Spectrometry

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**Summary:**

Currently, High Kinetic Energy Ion Mobility Spectrometers (HiKE-IMS) are under investigation regarding trace gas detection in field applications. Despite their low operating pressures between 20 and 60 mbar, previously reported limits of detection for compounds like benzene are in the single digit $ppb_V$-range [1]. However, even lower detection limits for a broad range of substances are required. To achieve this objective, we experiment with operating pressure and electric field strength to further improve the limits of detection of HiKE-IMS.

**Keywords:** trace gas detection, ion mobility spectrometry, low pressure, field-deployable HiKE-IMS, mass spectrometry

## Introduction – Ion Mobility Spectrometers

Ion Mobility Spectrometers (IMS) are powerful tools for trace gas analysis in field applications capable of detecting hazardous substances in low concentrations of few parts-per-trillion ($ppt_V$) in mediums such as ambient air. Compared to large and heavy laboratory instruments like most mass spectrometers, IMS are available in small size and can be carried by a single person even wearing a hazmat suit. For most portable IMS systems, the gaseous samples are ionized via reactant ions, in most cases protonated ammonia or water clusters. Then, reactant and product ions are injected into a drift region where they are separated in an electric field. The degree of separation depends on the substance specific ion mobility, which is dependent on multiple properties including charge, mass, and ion-neutral collisional cross-section. At the end of the drift region, the separated ions reach a Faraday plate where they discharge and the current over time is recorded. The ion current is amplified with a transimpedance amplifier and the ion mobility spectrum results [2].

The previously described conventional ion mobility spectrometers have outstanding sensitivity and decent selectivity, but have three main issues: 1.) Non-polar, low proton affine substances, e.g. benzene, cannot be ionized through proton transfer reactions via water clusters or via adduct formation/ligand switching. Therefore, these substances are difficult or impossible to detect. 2) Quantitative analysis is difficult due to competing ionization reactions that can even lead to full discrimination of certain compounds in the presence of other compounds 3.) Different substances can have similar ion mobilities, resulting in overlapping peaks.

## High Kinetic Energy IMS

In an effort to overcome the above mentioned issues of conventional IMS, the High Kinetic Energy Ion Mobility Spectrometer (HiKE-IMS) was developed [3]. The HiKE-IMS is operated at an absolute pressure of 20 - 60 mbar, which enables operation at high reduced electric field strengths $\varepsilon$ of up to 120 Td where $\varepsilon$ is defined as the electric field strength E divided through neutral gas density N. When operated at high reduced electric field strengths, protonated water cluster size can be reduced down to bare $H_3O^+$, which enables protonation of substances with low proton affinity like benzene, achieving limits of detection in the region of single digit $ppb_V$ [1]. Furthermore, ionization is also possible with $O_2^+$, which enables charge transfer reactions with many substances. In order to further increase separation power the reduced electric field strength can be varied in both the reaction region and the drift region enabling (de)clustering of ions and/or exploring the field depended ion mobility.

Thus, we propose a new IMS design that can be switched from ambient pressure to low pressure to either have lowest limits of detection with decent resolving power (IMS mode) or less sensitivity but a broader spectrum of detectable substances, less chemical cross sensitivities and improved identification capabilities (HiKE-IMS mode).

## Theoretical

A theoretical, and experimentally validated description of the sensitivity of HiKE-IMS was given in [1]. It was shown that the product ion concentration [S] depends on the square of the neutral gas density N and linearly on the reduced electric field strength ε. In this work, this relation is rearranged according to Equation (1), showing a linear dependence on the electric field strength E multiplied by the neutral gas density N. Thus, by increasing the pressure or electric field strength the sensitivity can be increased to significantly improve the limits of detection.

$$[S] \sim \varepsilon N^2 \sim E N \qquad (1)$$

Therefore, we propose the above mentioned concept of varying operating pressure to operate the device in either IMS or HiKE-IMS mode.

## Preliminary Data

Dimethyl methylphosphonate (DMMP) was used as a first test substance at constant concentration of 40 ppb$_V$ in the clean, dry air (1.4 ppm$_V$ water). The operating pressure and the reduced electric field strength were changed in factors of 2 at constant electric field strength, i.e. when operating at half the reduced electric field strength, pressure was doubled. First, reduced electric drift field strengths of 25, 50 and 100 Td were applied at a constant pressure of 50 mbar corresponding to electric field strengths of 33, 66 and 132 V/mm. The same electric field strengths were applied at 100, 200 and 400 mbar leading to reduced electric field strength of 12.5, 25 and 50 Td at 100 mbar, 6.25, 12.5 and 25 Td at 200 mbar and 3.125, 6.25 and 12.5 Td at 400 mbar. The resulting amplitudes of the DMMP product ion peak are shown in Figure 1. The expected linear relation between the amplitude and the electric field strength E is clearly visible for pressures 100, 200 and 400 mbar. However, the data set for 50 mbar shows a different behavior: At the highest electric field strength of 132 V/mm (100 Td) the signal amplitude decreases, which is caused by fragmentation of DMMP occurring for this substance at reduced electric field strengths above 90 Td. It should be noted that Equation 1 does not account for additional effects like fragmentation. If now looking at the

slopes in Figure 1, the expected linear increase with increasing pressure is not visible. Since one pair of inlet capillaries was used as flow restrictions, changing the pressure also changes the sample flow rate into the (HiKE-)IMS and thus changes dilution of analytes. Hence, the measurements presented in Figure 1 need to be repeated with adjusted capillaries and also with other substances like benzene (non-polar) or methyl salicylate, to further validate the relationship between pressure and peak amplitude as a function of analyte class.
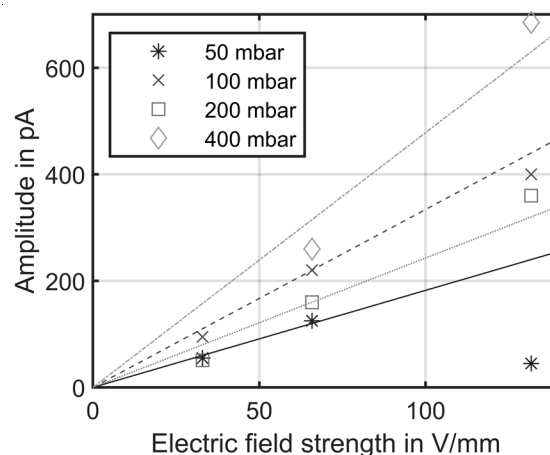


Fig. 1. Amplitude of the DMMP product ion peak (40 ppb$_V$ DMMP in clean, dry air with 1.4 ppm$_V$ water) in a (HiKE-)IMS operated at different pressures and electric drift field strengths. The (HiKE-)IMS temperature was constant at 40 °C.

## Conclusion

As expected, the number of generated product ions and thus the sensitivity depends on the pressure and electric field strength, which explains the lower limits of detection in IMS compared to HiKE-IMS. Therefore, pressure should be variable according to the application to take advantage of either a HiKE-IMS or an IMS. This concept will be further investigated and presented at the SMSI in more detail.

## Acknowledgements

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