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An optimized GC-IMS system with significantly increased sensitivity

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Introduction

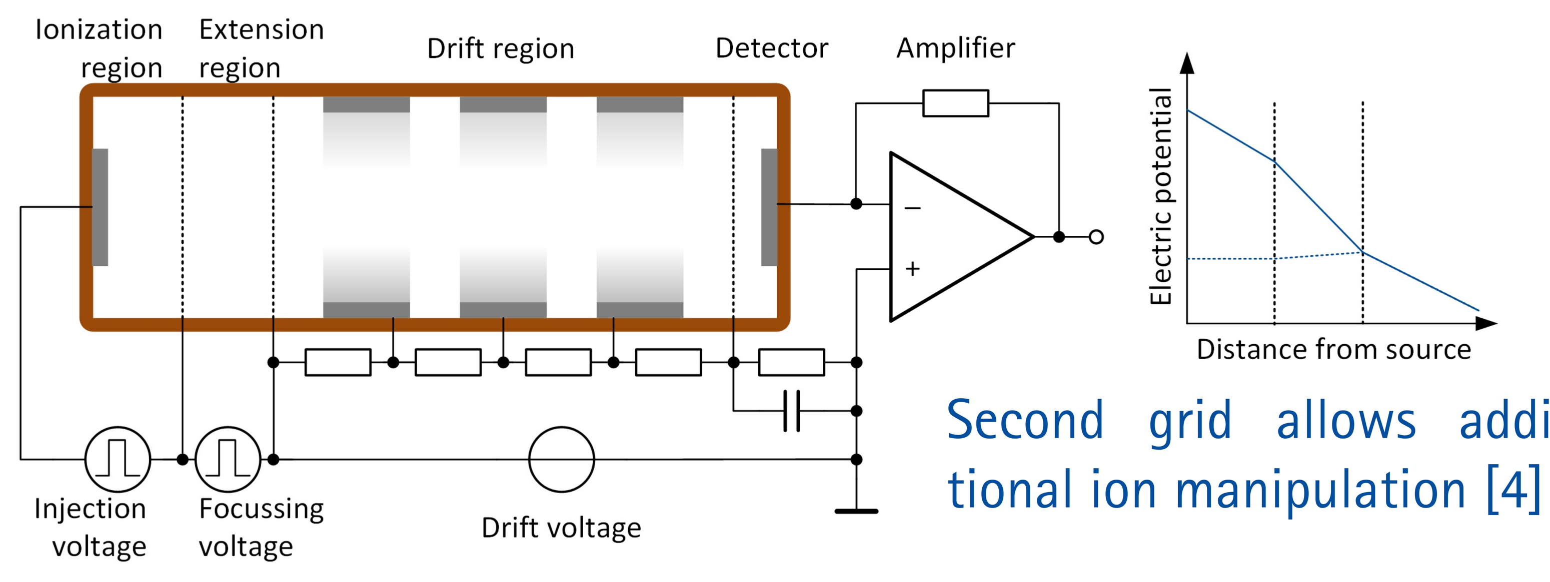
Many samples from real world applications are too complex to be analyzed by ion mobility spectrometry, let alone be ionized simultaneously by the chemical ionization enabling the excellent sensitivity of IMS. Thus, a preseperation is necessary, typically by gas chromatography. While both IMS and GC have been optimized on their own, a GC-IMS system contains additional interactions. On the one hand, assuming a peak capacity of N for the GC, each substance will enter the IMS roughly only 1/N of the measurement time, thus requiring significantly better sensitivity to achieve the same limits of detection. On the other hand, an IMS has a non-negligible volume that must be considered when optimizing the carrier gas flow and column parameters of the gas chromatograph. In this work, we present both an IMS based on an improved field-switching shutter with outstanding ppq_v limits of detection for use as a gas chromatography detector and an approach for integrating the gas flow effects of the IMS into the van Deemter equation.

Ion mobility spectrometry sensitivity

$$SNR = \underbrace{\sqrt{\frac{32\, k_B (\ln 2)^2\, T}{3\,\pi\, e\, K}}}_{constants}\; \frac{\overbrace{Q_0\, k_{shutter}}^{injected\ charge}}{\underbrace{k_{amp}}_{amplifier\ noise}}\; \underbrace{\sqrt{\frac{3\beta^6}{\beta^3+2}}}_{drift\ voltage}\; \underbrace{\frac{w_{inj} w_{amp}}{w_{inj}{}^2 + w_{amp}{}^2}}_{matching}\; \underbrace{\sqrt{t_{meas}}}_{time}$$

- Averaging time is limited by the peak width eluting from the GC
- Match between injection and amplification has to be correct, but cannot offer further improvement [1]
- Operation at $\beta = U/U_{opt} > 1$ vastly increases the SNR, but is limited by the available voltage [2]
- Reducing amplifier noise is the most direct route to improvement, but is ultimately limited by current semiconductor technology [3]
- Increasing injected charge through both a shutter with better ion transmission $k_{shutter}$ and a larger initial charge Q_0 of analyte ions
- Short IMS suffer less from coulomb repulsion [1]

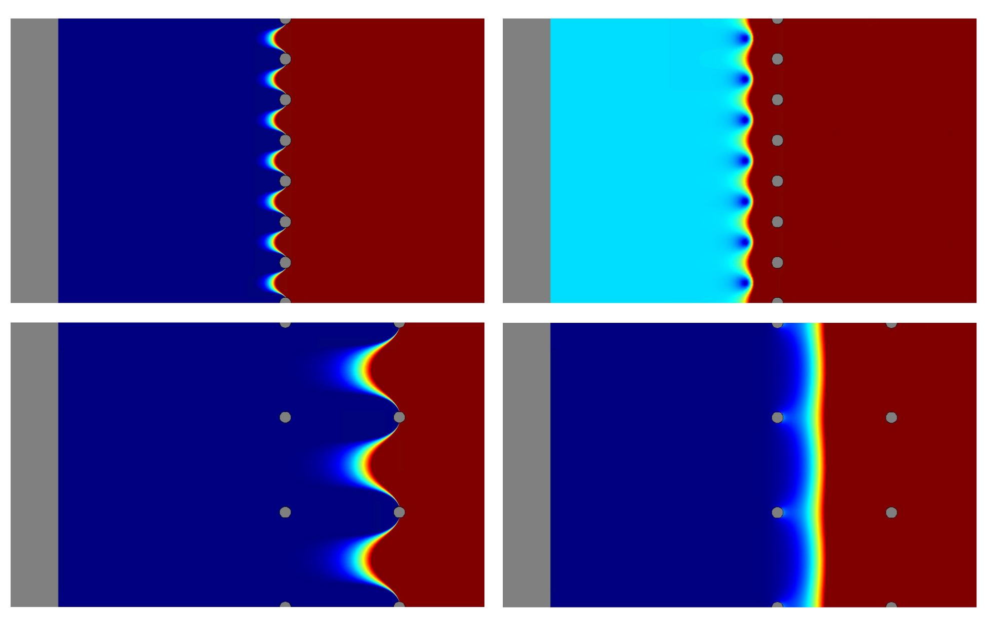
Enhanced Field Switching shutter



Second grid allows additional ion manipulation [4]

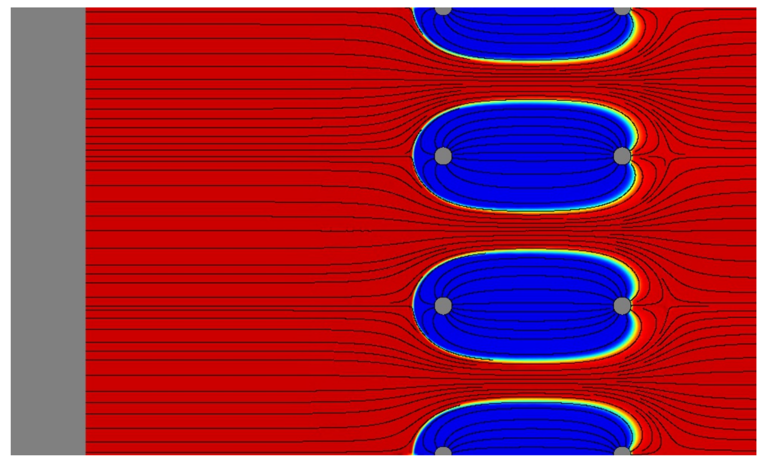
Increasing Q_0 by better ionization shielding

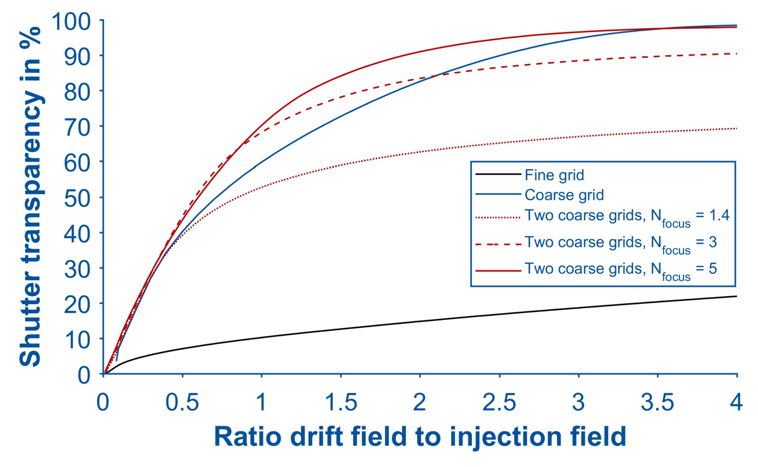
Drift direction only | Total field strength



- Opposing blocking field keeps the field in drift direction from the ionization region (left)
- Blocking field creates an unwanted opposite field (top right)
- Even with coarse grids, a dual grid is field-free (bottom right)

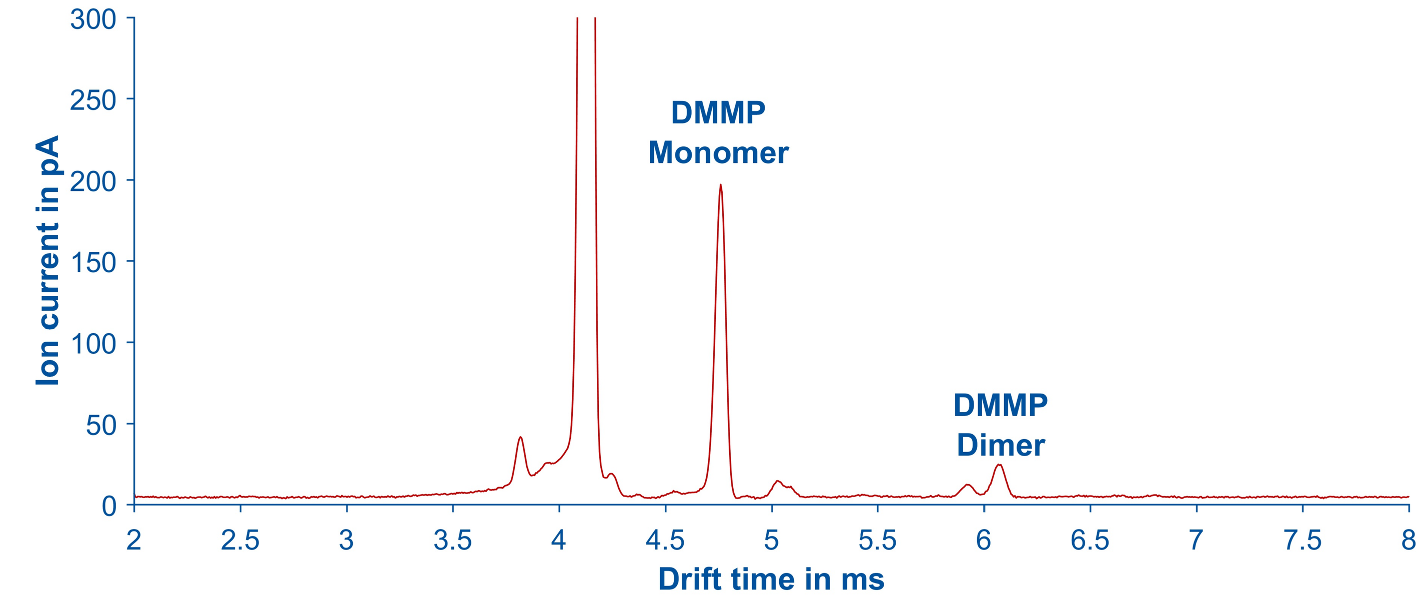
Increasing $k_{shutter}$ by better injection geometry





- Now usable coarse grids vastly increase ion transmission
- Due to ion focussing effects, ion transmission through two closely spaced grids can exceed the ion transmission through a single grid

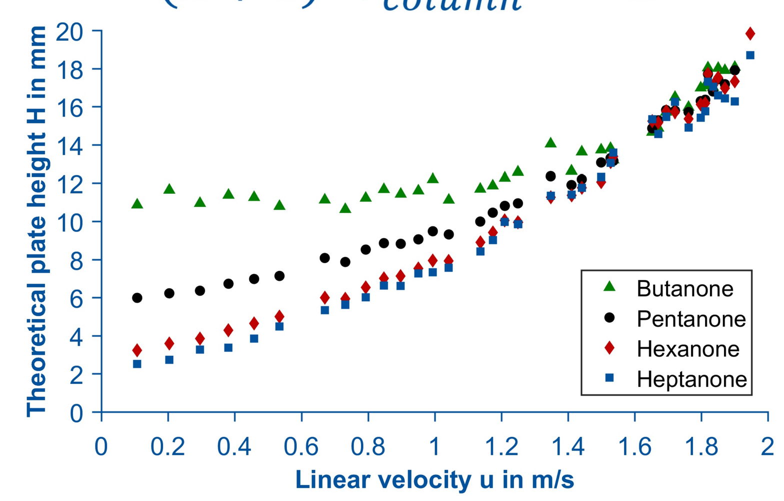
Achieving ppq_v level sensitivity in a second



- Spectrum of ≈10 ppt_v DMMP in "clean" air, one second averaged
- Limits of detection (3 sigma): Monomer 10 ppq_v & Dimer 350 ppq_v
- One to three orders of magnitude improvement compared to old setup depending on substance

Modified van Deemter equation for GC-IMS

$$H = a \frac{L}{(k+1)^2} \frac{V_{IMS}{}^2}{V_{column}{}^2} + \frac{B}{\bar{u}} + C\bar{u}$$



- New A-term, depending on the ratio of IMS to column volume
- Effective column volume increased by analyte retention
- Flat section of the van Deemter curve promotes use of higher flows to improve sensitivity
- Also explains MCC utility, as many channels increase volume

Acknowledgements & References

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[1] A.T. Kirk et al.; Analyst 2013 (138) 5200-5207; DOI: 10.1039/c3an00231d
[2] A.T. Kirk, S. Zimmermann; IJIMS 2015 (18) 129-135; DOI: 10.1007/s12127-015-0176-x
[3] P. Cochems, A. T. Kirk, S. Zimmermann; Rev. Sci. Instrum. 2014 (85) 124703; DOI: 10.1063/1.4902854
[4] S. Zimmermann, A.T. Kirk, M. Lippmann, A. Bohnhorst; Patent Application