

Identification of different gasoline samples and determination of MTBE and BTX using Ion Mobile Spectrometry

by Jörg Ingo Baumbach and Li Fang

The distinction between different gasolines to realise fast identification and rapid on-site and on-line quality control requires fast, inexpensive and rather small special handheld analytical equipment. Beside fast identification, a rapid quantification is often required. The realisation of a reliable and sensitive determination of gasoline components both in gaseous as well as in aqueous matrices should be considerable with one single instrument. Besides the aromatic gasoline main components of benzene, toluene and the xylenes (BTX) the oxygenate methyl tert-butyl ether (MTBE) are detectable simultaneously using ion mobility spectrometry. The method and first results are presented and discussed in detail.

Ion Mobility Spectrometry

The successful detection of the substances selected could be realized by using an ion mobility spectrometer (IMS). Ion mobility spectrometry refers to the term mobility, describing in the first order the measurement of the drift time of ions at ambient pressure for a fixed distance. The main advantages is, that an IMS can operate at ambient temperature and pressure using air as the carrier gas and without requiring a vacuum. During the last 10

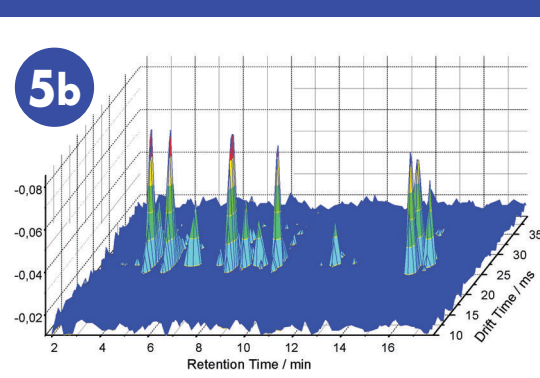
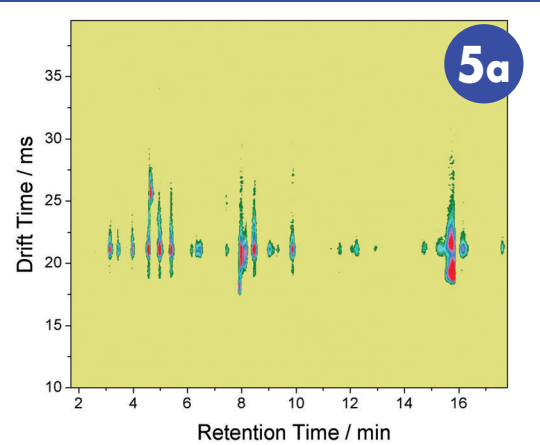


Fig. 5a & 5b: Typical peak heights as 3-D plots

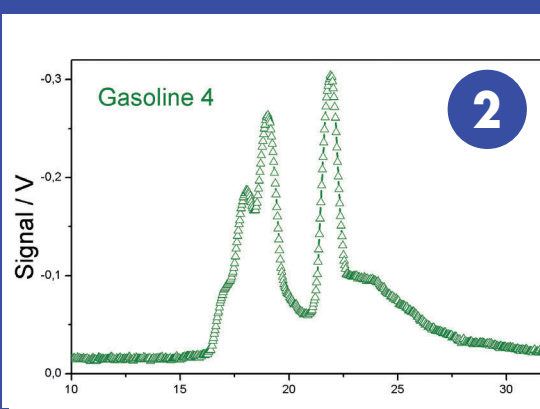


Fig. 2: Typical spectra of a selected gasoline

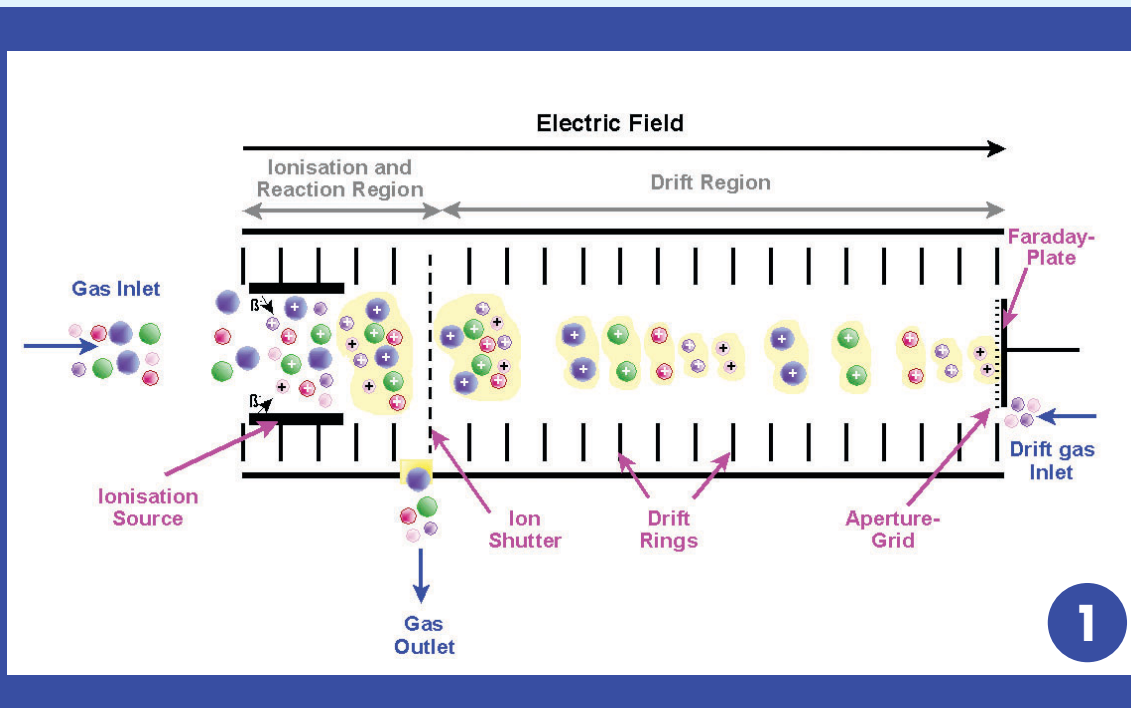


Fig. 1: IMS Drift tube

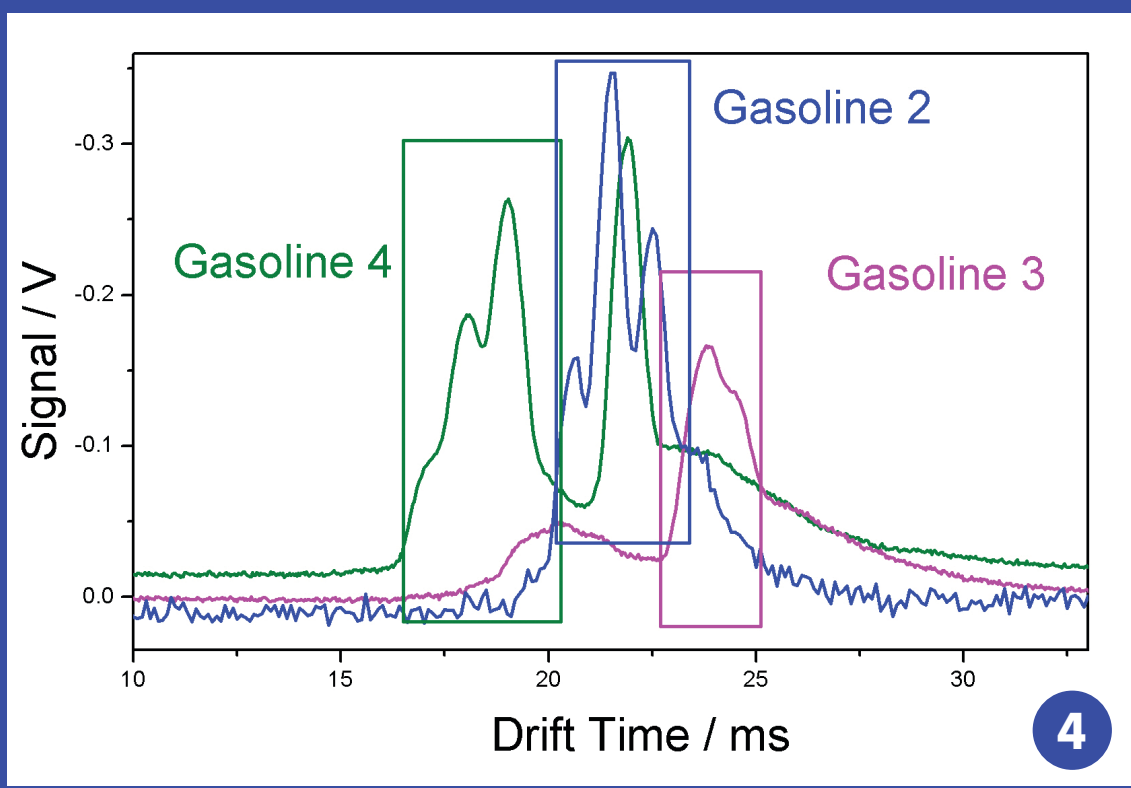


Fig. 4: Comparison of ion mobility spectra of 3 gasoline samples

years dramatic changes have occurred in the practical aspects of ion mobility spectrometry and in the understanding of underlying principles of response. In the early 1970s IMS was mostly used for the detection of chemical warfare agents. More recently the number of applications in industry and the environment has increased, not only because of the simplicity of the instrumentation but also due to the excellent detection limits in the ranges of $\mu\text{g/L}$ and sometimes even down to ng/L .

Instrumentation

Ion mobility spectrometers are operated typically at ambient pressure. IMS drift tubes consist mainly of an ionization source, a reaction region, a drift region and a Faraday-plate as detector (see Fig 1) and includes the ion shutter which is used to sample ions from the source region and inject these ions for characterization in the drift region.

In most drift tubes, a gas is passed through the drift region and this drift gas has been used traditionally to keep the drift region free of unwanted neutral impurities. Other gas flows can be used to introduce samples into the source region. Gases that are used for mobility spectrometers are normally air or nitrogen, though other gases including undiluted process gases could be used as drift gas. As shown in Fig. 1, sample vapours or supporting atmospheres can be ionized using a variety of sources including ^{63}Ni , corona discharges, electrospray ionization, laser ablation, or gaseous photo-ionization. Ions are extracted from the source and introduced into the drift region via an externally imposed electric field, usually 200-400 V/cm. The injection event creates discrete packets of ions which move from the ion shutter, through the drift region, and towards the Faraday-plate. The ion packet acquires a drift velocity that is governed by the electric field and the mobility coefficients

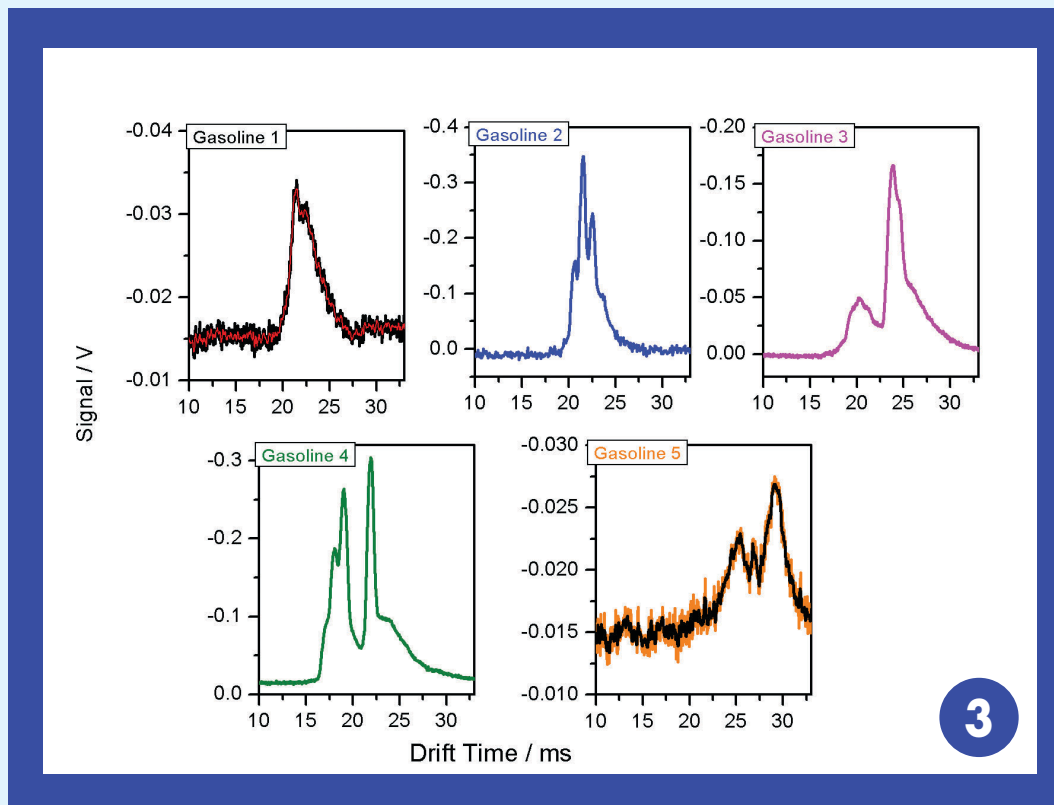


Fig. 3: Typical spectra of different gasoline samples using UV-IMS

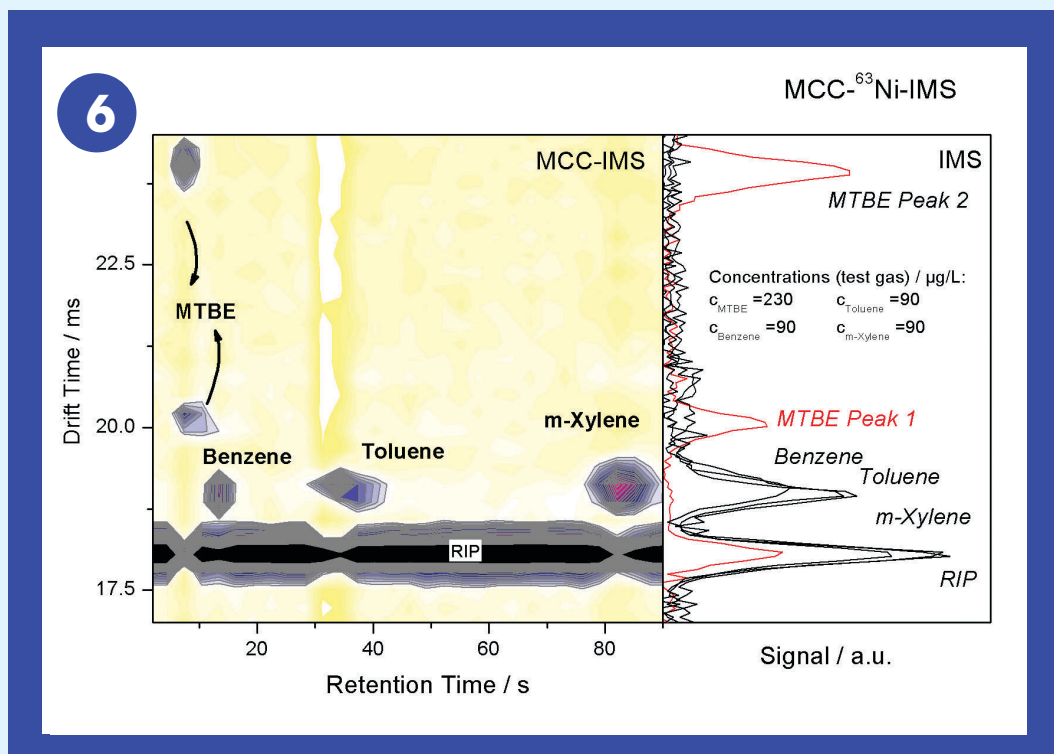


Fig. 6: Separation of MTBE and BTEX using IMS and MCC

Conclusion

IMS can be used for the rapid identification of gasoline samples according to their specific ion mobility spectra. By coupling a ^{63}Ni -IMS, as well as a UV-IMS, to an MCC an easy and sensitive method for the detection for the gasoline additive MTBE next to the mono aromatic compounds benzene, toluene and m-xylene has been demonstrated, showing detection limits for MTBE of about $2\ \mu\text{g/L}$ (UV) and $30\ \text{pg/L}$ (^{63}Ni) in nitrogen. The total analysis time at ambient temperature is only a few seconds using the arrangement reported and, by using an membrane inlet system, the system is capable of on-line and on-site monitoring. Applying the MCC-UV-IMS for the detection of the volatile substances in pure gasoline, the system enables the identification of MTBE, benzene, toluene and m-xylene according to their retention times and specific drift times and allow the quantification of the single compounds of interest.

Authors:

Jörg Ingo Baumbach
Li Fang

Institute of Spectrochemistry and Applied Spectroscopy (ISAS),
Bunsen-Kirchhoff-Str. 11, 44139 Dortmund, Germany

Stefanie Sielemann
G.A.S. Gesellschaft für Analytische Sensorsysteme mbH,
Emil-Figge-Str. 76-80, 44227 Dortmund, Germany

of the ions and these are characteristic of an ion structure. Separations of ions can occur through differences in mobilities and the time dependent current recorded at the Faraday-plate is termed a mobility spectrum. Functional comparisons exist between drift tubes for analytical IMS and time-of-flight mass spectrometry (TOF-MS) though their principles of operation differ dramatically. In TOF-MS, ion formation and characterization occurs in high vacuum and the mean free path exceeds the analyser dimensions. In contrast, the free path length is much smaller than in drift tube dimensions, at atmospheric pressure with a mobility spectrometer. Thus, collisions in IMS are essential to ion mobilities and provide a basis for ion characterization on mobilities.

Determinations of mobility are governed largely by ion size and shape, rather than by mass. In the case that a chemical system which has been well characterized, mobilities are suitable for the assignment of identity.

Typical spectra (see Figure 2 for a gasoline selected) show different peaks for different analytes within the sample. A full spectrum will be acquired within less than 50 ms. Depending on the ionization way, beside the most common β -radiation sources also non-radioactive ionization sources up to now are UV-lamps (UV-IMS) with a rated photo-ionization energy of 10.6 eV. Such UV lamps can exceptionally be used for MTBE and the aromatics BTX as the ionization energy of these substances is between 8.4 and 9.2 eV.

Typical spectra of different gasoline samples (all measured in head space) determined using an IMS with UV-source are shown in Figure 3. Similar UV-IMS systems were also used for the quantitative detection of different alcohols.

Investigations of Gasolines and MTBE and BTX

A comparison of the ion mobility spectra of 3 gasoline sample are presented in Figure 4. Using simple "window-techniques" will allow to distinguish between the different kind of gasolines because of their characteristic "finger-print" in the spectra. Thus, the use of an IMS makes the rapid identification of a gasoline sort within a couple of seconds possible.

As shown in Figure 4, the peaks in the spectra are overlapping, which makes a defined determination of single compounds in a more complex mixture difficult. Thus, for the quantitative determination of MTBE in the presence of the mono-aromatic compounds benzene, toluene and m-xylene the IMS (^{63}Ni and UV-ionization source) need to be coupled to a multi-capillary column (MCC) in order to obtain fast pre-separation of the analytes in the mixture. The effective analysis of MTBE, in a matrix of BTX, cannot be accomplished by either MCC or IMS. MCCs were introduced in the early 70's and were used for the first time in combination with IMS for the detection of explosives. In the past the combination of MCC/IMS and UV-ionization sources was successfully used for the fast separation and sensitive detection of mixtures of different volatile organic substances (VOC) within minutes. Typical Peak-height-diagrams for gasoline as 3D plots are shown in Figures 5a and 5b.

The clear separation of MTBE and BTX could be realized as shown in Figure 6 using an UV-IMS coupled to a MCC. In the right part the full ion mobility spectra of the single compounds are shown. MTBE creates two peaks at drift times of 16.7 and 23.1 ms ($K_{01}=2.03\ \text{cm}^2/\text{Vs}$, $K_{02}=1.47\ \text{cm}^2/\text{Vs}$), whereas the aromatics show single peaks with a decrease in reduced mobility according to their increase of mass. The single spectra allow the identification of the single substances in the 2-D-IMS-chromatogram shown in the left part of figure 5. The clear separation on the MCC within less than 2 minutes of all components of interest also enables the identification of the peaks according to their specific retention times of 7 s for MTBE, 13 s for benzene, 30 s for toluene, and 80 s for m-xylene. The volume integration of the peaks finally enable the quantification.



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TechnologieZentrumDortmund, Joseph-von-Fraunhofer-Str. 13
D-44227 Dortmund, Germany
Tel: +49 231 9 74 22 88 Fax: +49 231 9 74 22 89
WWW.GAS-DORTMUND.DE INFO@GAS-DORTMUND.DE