Stach, J., Arthen-Engeland, T., **Flachowsky, J.**, **Borsdorf, H.** (2002):
A simple field method for determination of MTBE in water using hand-held ion mobility (IMS)
International Journal for Ion Mobility Spectrometry **5** (3), 82 - 86

A SIMPLE FIELD METHOD FOR DETERMINATION OF MTBE IN WATER USING HAND HELD ION MOBILITY (IMS)

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ABSTRACT

The paper describes an analytical method for on-site detection of MTBE (Methyl tert-Butyl Ether, CAS 1634-04-4) using ion mobility spectrometry (IMS). The ion mobility spectra of MTBE show a typical dimer ion with a reduced ion mobility constant k_0 = 1,50 cm^2/Vs. Using this signal, it is possible to measure the contamination of MTBE in water in the range > 30 µg/l. Interference of matrix compounds like alkane's, alkene's and cycloalkane's can be neglected due to their low proton affinity.

A simple and fast one-way sample preparation technique was developed for on-site analysis. For separation of MTBE from water and other volatile organic compounds (VOC's), a water binding material (EXtrelut) in head space vials can be used. The gas phase above the EXtrelut is then injected in the hand-held IMS RAID-1 (Bruker Saxonia Analytik GmbH). The needed time for the determination of MTBE including sample preparation is about 5 minutes.

Mobile GC/MS (EM 640 from Bruker Daltonik GmbH) was used for verification of the IMS results. Detection limits below 1 µg/l MTBE were obtained with the same sample preparation procedures.

INTRODUCTION

MTBE is a chemical additive to increase the oxygen content in gasoline. The concentration of MTBE in gasoline is in the percent range. The large scale use of MTBE, in Germany approximately 0,45 million t in 1997 [1] and its high solubility [2] in water (26 g/l) has resulted in an extensive contamination of soil, ground and surface water [3, 4, 5]. In most cases careless use of gasoline and leaking underground storage tanks (LUST sites) can be considered as reasons for the contamination.

MTBE was classified precautionary as a possible human carcinogen by US EPA. However, up to now no general regulations for e. g. for drinking water standards exist. The German threshold value is 20 µg/L. The state of California has set the stringent action levels of MTBE between 13 µg/L (primary level) and 5 µg/L (secondary level).

Reliable analytical results were achieved with the EPA Method 8240B/60B (mass spectrometry) and ASTM Method D4815 (FID) whereas Method 8020A/21B (PID) suffers on the non-specific detection of the analyte [6]. In the most cases purge and trap techniques are used for sample preparation. Only GC/MS methods allow a safe identification of the MTBE. The nonspecific detectors like PID's may cause false-positive results due to coelution with other gasoline components.

Sample transport and preparation is time consuming. In addition transport and storage also contributes to the analysis errors. Therefore a simple and low cost field analysis method can provide sufficient results concerning distribution and transport of MTBE in the groundwater zone.

Hand-held ion mobility spectrometry and mobile mass spectrometry are well suited detection methods for volatile organic analytes. Especially IMS seems to be the method of choice due to the high proton affinity of MTBE [7,8].

However, for both IMS and GC/MS a simple, fast, and cheap sample preparation procedure is required. The developed method makes use of EXtrelute as water adsorbing material. Due to the water adsorption the analyte is released in the gas phase and can be injected into the ion mobility spectrometer or GC/MS system.

Experimental Section

MTBE-Standards were made from a 2600 µg/L stock solution (water or methanol). The stock solution and the different standard solutions should be fresh prepared each day. For dilutions distilled or drinking water was used.

The sample temperature during the adsorption process was held at room temperature. In some cases adsorption was carried out at 50^0C. The water was adsorbed on EXtrelut NT from Merck KgaA (CAS 68855-54-9)in a batch technique. EXtrelut is a infusorial earth with a high adsorption capacity. Main application is the use for extraction of lipophilic compounds from aqueous solutions.

The following procedures have been used for sample preparation:

a) 10 ml EXtrelut are filled into a 20 ml or 37 ml headspace vial. The vial is capsulated and evacuated using a 10 ml syringe.
b) 5ml of the water sample are injected in the evacuated vial.
c) After about 1 minute the release of MTBE in the vial can be supported using a 50 ml syringe which is loaded and unloaded at least three times.
d) 50 ml of the gas phase are than taken from the vial for evaluation.
e) The gas is injected into a special inlet of the IMS or injected in a TENAX tube for thermal desorption GC/MS determination.

For IMS determination of MTBE the dimer ion peak with $k_0 = 1.50$ cm^2 /Vs can be used. The time dependence of this peak is recorded and the signal area against measuring time is integrated.

In GC/MS complete mass spectra can be used for identification. SIM with using the MS peak at m/e 73 can be used for quantification as well.

The measurements were carried using RAID 1 of Bruker Saxonia Analytik GmbH, Germany and an EM 640 S GC/MS from Bruker Daltonik GmbH, Bremen, Germany.

Results and discussion

a) GC/MS studies

MTBE can be easily identified by MS spectra comparison and the retention time. The mass spectrum of MTBE shows a characteristic peak at m/z 73 (see Fig. 2). Calibration curve based on that peak (recalculated ion trace) is shown in Fig.1. An example for identification and quantification of MTBE in a contaminated ground water sample is shown in Fig. 2. The complete cycle time for the analysis was <5 minutes. The detection limit using the described sample preparation method is << 1µg/L MTBE in water.

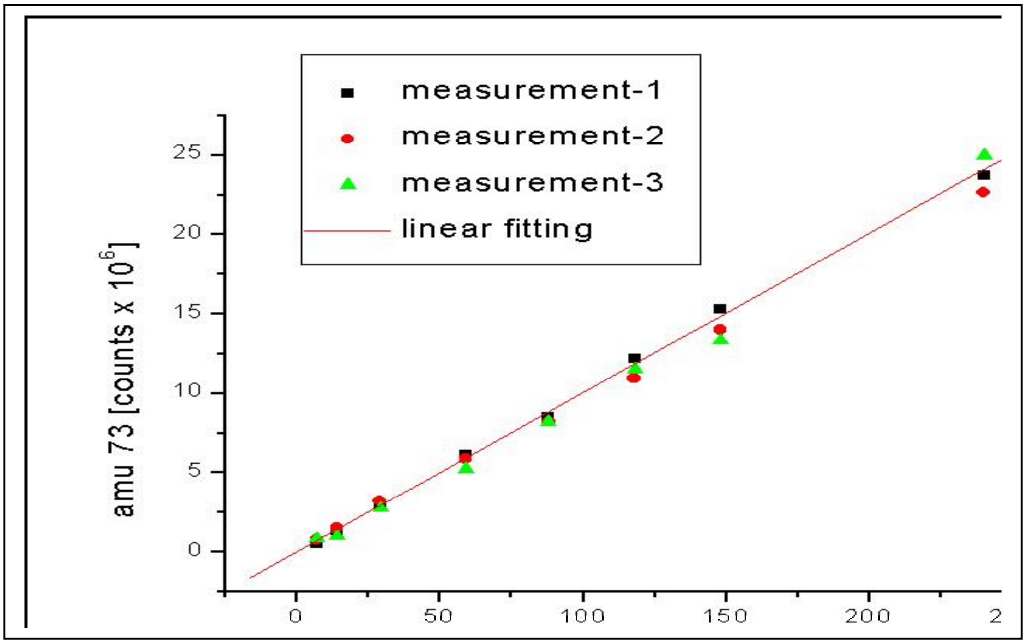

Fig. 1: Calibration curve of MTBE determination in water (GC/MS)

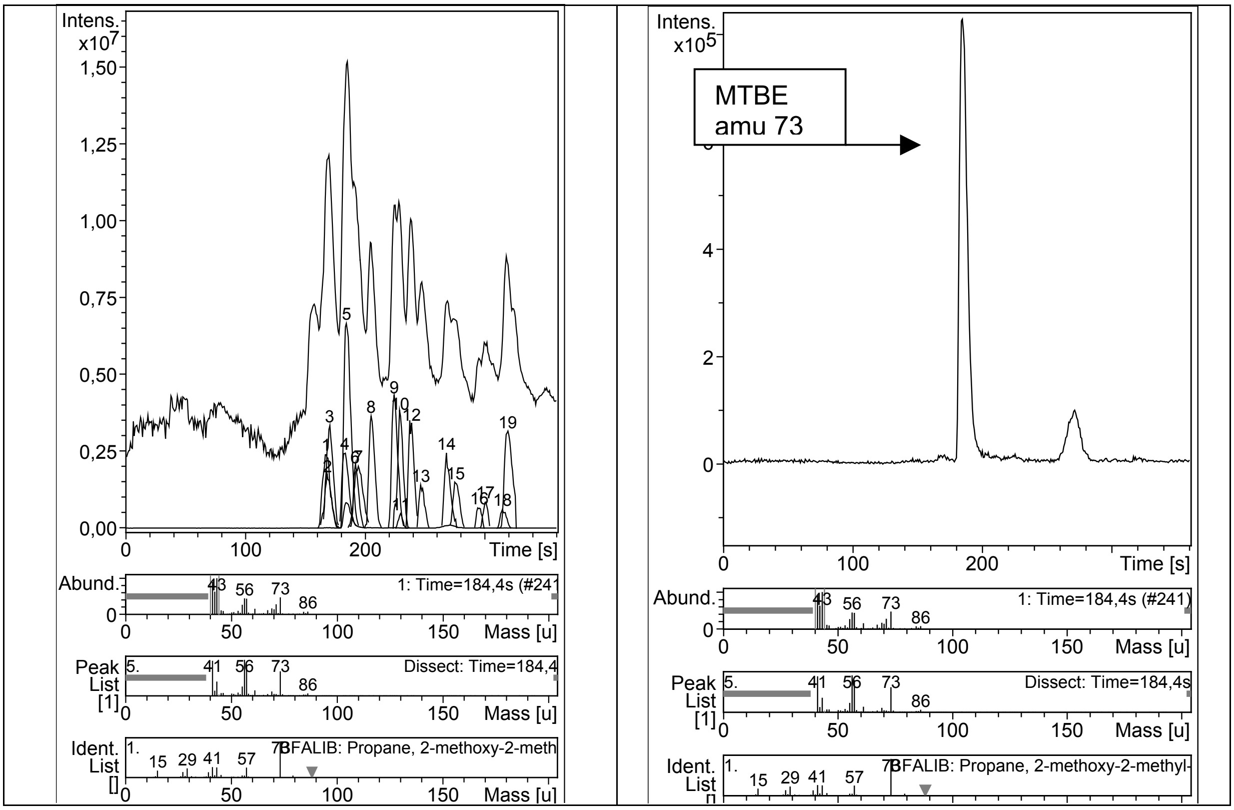

Fig. 2: Determination of MTBE in contaminated water using sample preparation with EXtrelut and GC/MS (Bruker EM 640S; left side TIC and substance identification, right side identification of MTBE via amu 73 with a concentration of 14,7 µg/l MTBE in water, sample diluted 1:10; concentration of the original sample = 147 µg/L MTBE).

b) IMS studies

For IMS detection of MTBE an additional septum inlet installed in front of the usual septum inlet was used. MTBE samples were injected in a purified air stream provided by the sample gas pump of the IMS using a syringe.

IMS spectra of MTBE show a typical dimer ion peak with $k_0 = 1.50 \pm 0.01\ \text{cm}^2 / \text{Vs}$. Due to the relatively high proton affinity of MTBE low detection limits can be reached and the number of interfering compounds especially of gasoline components is comparatively low.

A typical series of ion mobility spectra recorded after sample preparation of a contaminated ground water sample is shown in Fig. 3. The MTBE peak can be clearly identified. The calculated concentration is 179 µg/L. A single ion mobility spectrum is shown in Fig. 4. Beside minor peaks caused by unidentified compounds only the MTBE dimer ion is shown.

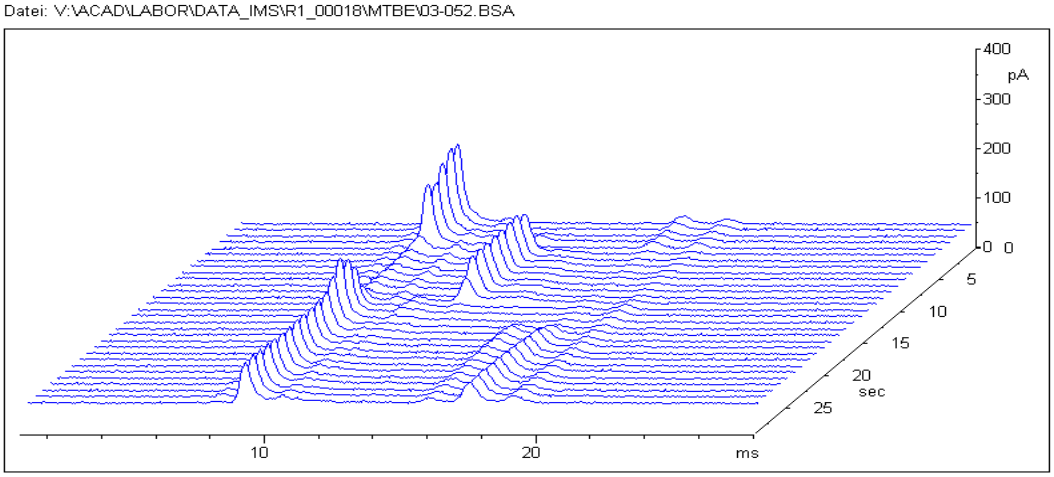

Fig. 3: Series of ion mobility spectra of gasoline contaminated water (MTBE conc.: 179 µg/L)

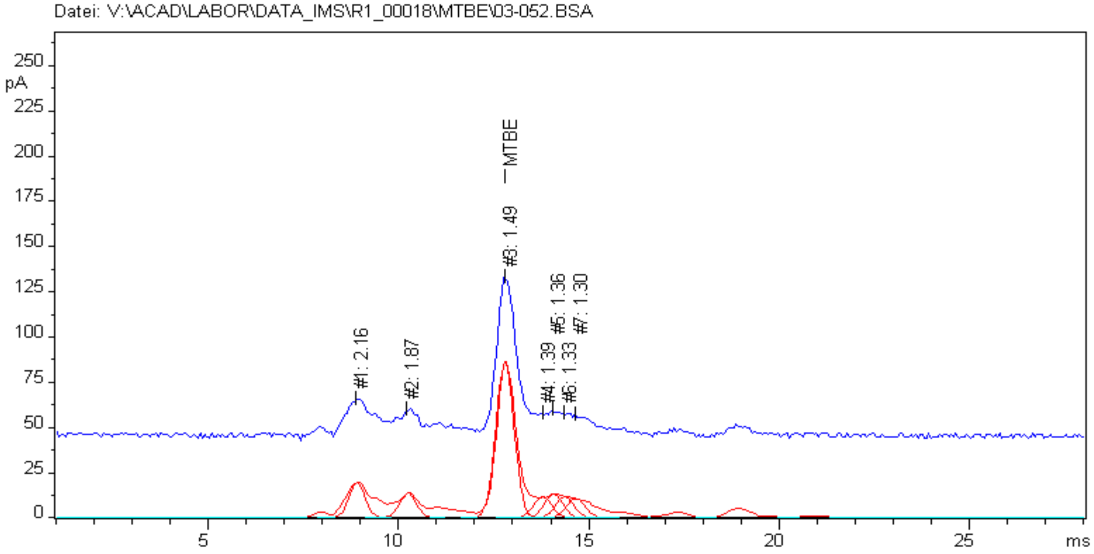

Fig. 4: Single IMS spectrum with the dominant MTBE Peak. Spectrum taken from the series of ion mobility spectra shown in Fig.3

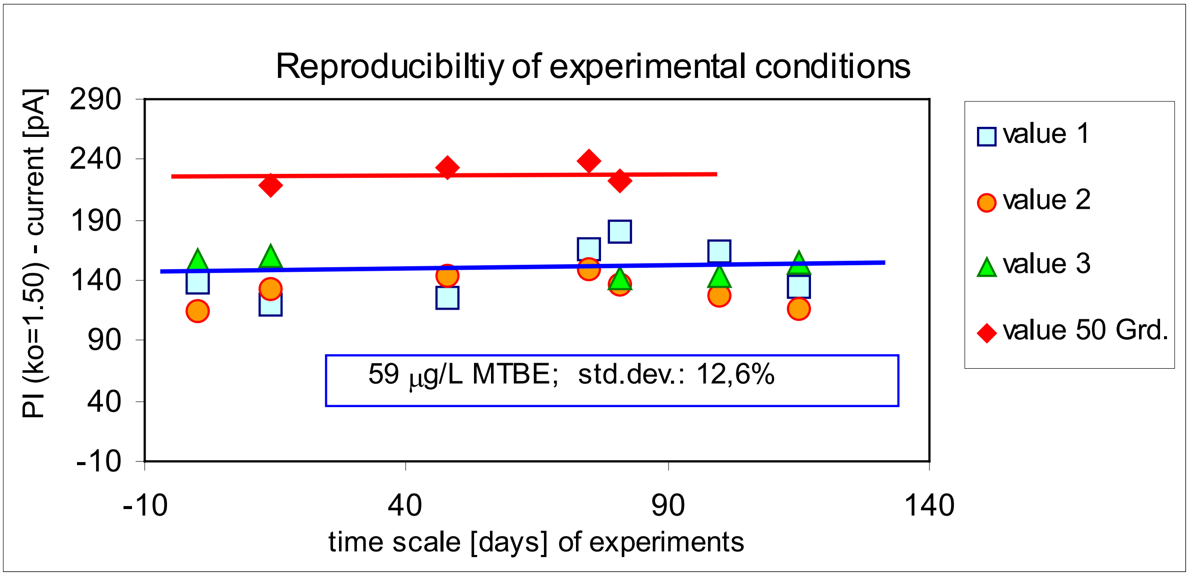

Fig. 5: Reproducibility of the signal intensities of the ko-Peak of MTBE as function of different calibration times (measuring conditions: at room temperature, upper line at 50^0C)

The long term reproducibility of IMS determination/calibration of MTBE including sample preparation is shown in Fig. 5. The chosen sample concentration is 59µg/L. The calculated standard deviation is 12,6 %.

The detection limit of MTBE is in the range of 30 µg/L MTBE in water.

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