

# A high resolution IMS for environmental studies

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## ABSTRACT

IUT Ltd. develops various IMS devices for environmental purposes. The analysis of mixtures of aromatics has shown that there are problems to separate benzene and toluene ions properly by means of a low resolution cell ( $R=25$ ). Similar problems exist in the negative mode for various halocarbons, for example trichloroethylene and dibromomethane. Therefore a new basic equipment was developed in order to improve resolution and transmission. New detector cells have a 50 or 100 mm long drift tube with diameters of 20 or 30 mm respectively. Ionisation is produced by tritium  $\beta$ -sources or by UV-lamps. The trigger pulse can be varied in the range of 10 - 350 microseconds, the drift field is 400 - 700 V/cm. A resolution better than 100 was achieved. This value could be improved up to 200 by use of a deconvolution program. The simultaneous detection of chlorine and bromine ions produced in a sample of bromochloromethane is demonstrated. Further applications are discussed for benzene, toluene, xylene, halothan, isofluorene, formaldehyde etc.

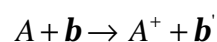
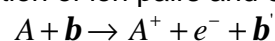
## INTRODUCTION

Small concentrations of toxic compounds in atmospheric air, in exhaust gases, in air at workplaces have to be measured selectively by a portable equipment. Ion mobility spectrometers were used to solve problems like the monitoring of phosphor organic agents, explosives and drugs [1-3].

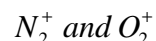
The IUT Ltd. has developed some types of such spectrometers with high resolution and sensitivity. Monitors for benzene, toluene, xylene, formaldehyde, ethylenoxide, phosgene and halocarbons are available now [4].

In the developed systems tritium sources as well as UV-lamps are used as ionisation sources. Due to the high ionisation efficiency of tritium - all  $\beta$ -energy is transferred to gas molecules within a thin layer (thickness of about 1,5 mm) along the electrode - the sensitivity could be improved by one order of magnitude.

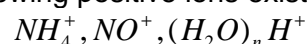
The basic interaction of  $\beta$ -particles in a gas mixture - ambient air, dried air or carrier gases - is the production of ion pairs and excited states:



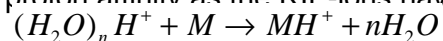
At normal air pressure ions like



are not stable and get changed into cluster ions due to the water content. It can be assumed that the following positive ions exist in air [8]:



These three cluster ions are called reaction ions. They produce the reaction ion peak RIP, which is a visible triplet. Charge transfer is realised in the presence of a molecule M with a higher proton affinity as the RIP-ions have:



In the negative mode the negative cluster ions - the reaction ions - are



associated with some water. Their charge transfer goes to the molecule with a higher electron affinity.

## METHODS

### 1. The Ion Mobility Cell

The ion mobility detector is designed with cylindrical geometry. As shown in fig. 1 a tritium loaded disc electrode with 10 mm diameter in a

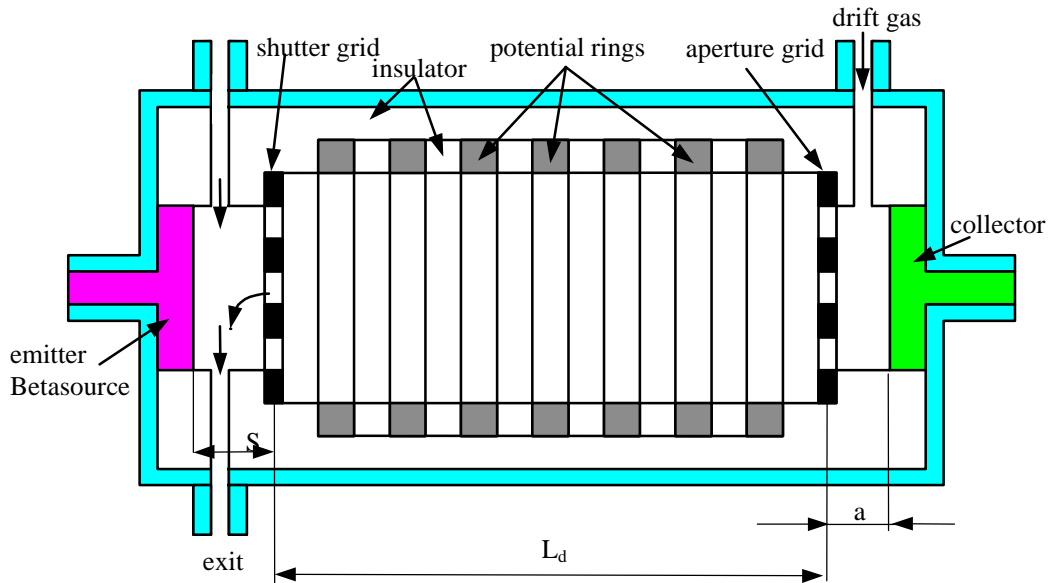


Figure 1: Scheme of an IUT - IM cell

distance of 1..10 mm to a shutter grid electrode is used as ionisation source. Between these electrodes are the gas inlet and outlet. The ionisation volume may vary from 50  $\mu$ l to 1,5 ml. The drift tube is behind the shutter grid with ring electrodes. The collector electrode is also a disc protected by an aperture grid at the last ring electrode. The b-source can be substituted by an UV-lamp.

where  $w$  is the mean energy necessary to produce one ion pair.  $De(z)$  can be evaluated by Bethe's formula for b-absorption in the non relativistic case as follows:

$$(2) \quad -\frac{\Delta e}{\Delta z} = 0.3j \frac{N}{A} \cdot \frac{e_o}{e(z)} \ln \frac{1,16e(z)}{I}$$

$$e_o = 0.511 MeV ;$$

## 2. Ionisation Sources

### Beta <sup>3</sup>H-sources.

Beta-tritium-ionisation sources were developed in a joint venture with the Radium Institut in St. Petersburg. This special type of a ionisation source is used as emitter electrode, its energy spectrum is given in fig. 2.

The spectrum demonstrates that tritium is gettered in a thin titanium layer only. The mean energy of emitted Beta particles is equal to  $\langle \epsilon \rangle = 3.6$  keV. The absolute activity may vary from  $a_c = 0.42$  MBq (free limit) up to 10 GBq. The ion production rate  $q(z)$  at a given distance from the emitter  $z$  can be evaluated by the formula (1).

$$(1) \quad q(z) = \frac{a_c}{w} \cdot \Delta e(z)$$

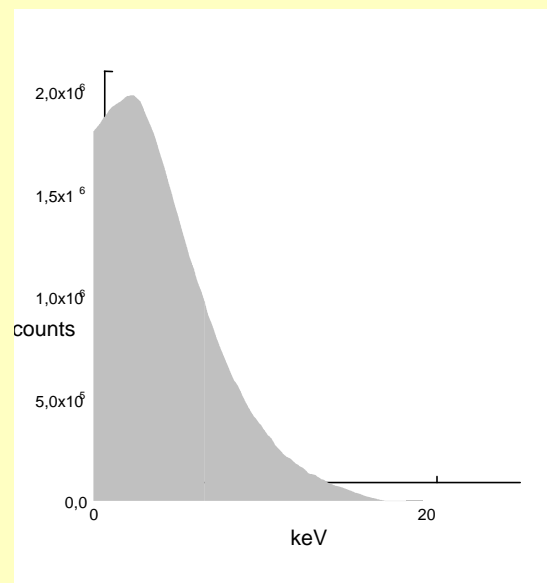


Figure 2:  
Beta spectrum of a tritium source with low activity

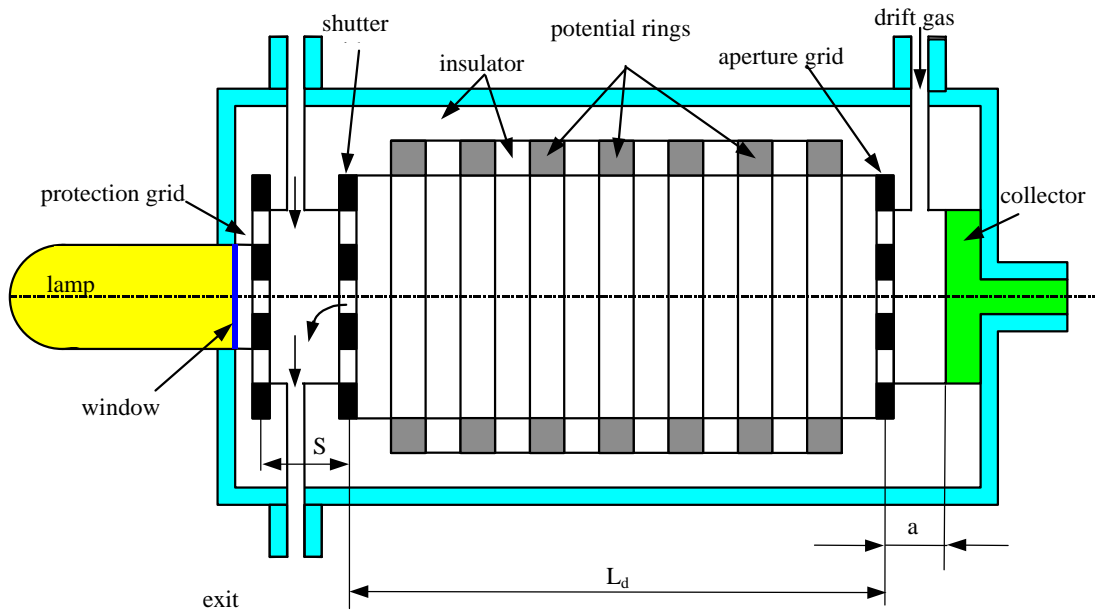


Figure 3: Scheme of the IUT - IMS with a photoionisation discharge tube

N, A: atomic and mass numbers;  $I=94.5\text{eV}$ ,  $j$  = density. The mean number of ion pairs produced by one b-tritium particle is  $\langle w \rangle = 102.8$ . About 30 % of the tritium in the emitter will contribute to the ionisation of the gas. That kind of ionisation source is available at IUT and Radium Institute in the range of 0.5 MBq up to 0.5 GBq.

**UV-photoionisation lamps.**

Hydrogen plasma discharge lamps were successfully checked for IMS-application too. The scheme of an ionisation source using photoionisation is given in fig. 3 - the exit window of the lamp is placed at the same position as the b-source. A special grid acts as an „emitting“ electrode, which avoids windows charging. There is the problem that photons should not enter the drift space. The geometry of the ionisation source has to be optimised with respect to the „shining“ into the drift space and to the carrier production rate. Unfortunately the ion distribution along z is much smoother as in the case of a b-source. This reduces the efficiency of such an arrangement. Photons flux of the lamp is typically  $10^{12} \text{ cm}^{-2}\text{s}^{-1}$ .

**3. IMS-Resolution**

As discussed by R. St. Louis and H. H. Hill jr. [5] the defined resolution R is dominated by 1) the pulse width,  $t_{\text{Pulse}}$ , 2) the diffusion

broadening,  $t_{\text{diff}}$ , 3) the capacitive coupling between aperture and collector,  $t_{\text{ap}}$ , 4) the gate depletion,  $t_g$ , 5) temperature changes, 6) pressure changes, 7) coulombic repulsion and 8) the amplifiers' rise time,  $t_R$ . The modified formula is equal to

$$R = \frac{1}{\sqrt{16 \ln 2 \frac{U_T}{U_d} + \frac{K^2 U_d^2}{L_d^4} \left( t_{\text{Pulse}} - \frac{S^2}{K U_{\text{Pulse}}} \right)^2 + \left( \frac{a^2 U_d}{L_d^2 U_{\text{ap}}} \right)^2 + \frac{t_{\text{Pulse}}^2 K^2 U_d^2}{L_d^4}}} \quad (3)$$

where K = mobility,  $U_T$  = temperature voltage,  $U_{\text{ap}}$  = voltage at aperture grid,  $U_d$  = drift voltage, a - distance between aperture grid and collector, S = distance between space charge and gate,  $L_d$  = drift length. The discussion of (3) shows that R can reach 150 and even more at  $L_d = 10 \text{ cm}$ ,  $t_R < 10 \mu\text{s}$  and  $E = 1.5 \text{ kV/cm}$ . These high field strengths may produce some problems in routine devices. The cells designed have the following specific parameters:

System	Drift length [cm]	$U_d$ [kV]	$t_{\text{Pulse}}$ [ $\mu\text{s}$ ]	$U_{\text{pulse}}$ [kV]	$t_R$ [ $\mu\text{s}$ ]	R	T
IUT-25 $\beta/\text{UV}$	2,5	0,8	350	0,2-2	30	25	0,03
IUT-50 $\beta/\text{UV}$	5,0	2,0	30	0,2-2	30	50	0,3
IUT-100 $\beta/\text{UV}$	10,0	5 - 7	10	0,2-2	30	120	0,3

In fig. 4 the resolutions of the reaction ion peaks for these three cell types are shown.

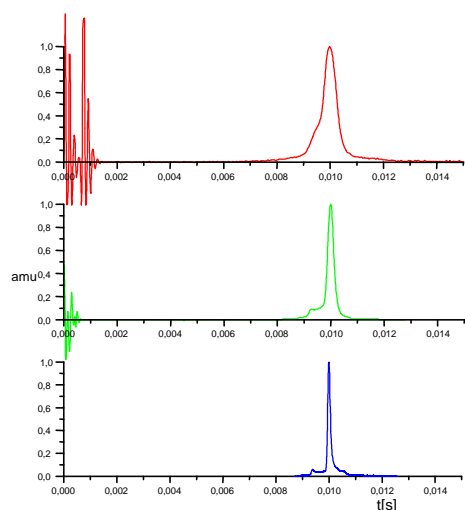


Figure 4:  
Reaction ion peaks of 3 IM - detectors demonstrating the progress in the resolution

#### 4. Transmission

The total charge picked off by the collector electrode with reference to the DC-ionisation current at saturation,  $I_o$ , multiplied by  $t_{FWHM}$  may characterise the transmission, that means the quality of the system:

$$(4) \quad T = \frac{\int_0^{\infty} i(t) dt}{I_o \cdot t_{FWHM}}$$

The transmission of a photoionisation IMS can be determined by a given compound at a suitable concentration. The determination of  $I_o$  may demand a special calibration arrangement. The used amplifier has a sensitivity of  $5 \times 10^9$  V/A and a rise time of 30  $\mu$ s. Pulses with voltages between 0,2 - 2 kV were applied to the b-source. The IUT-50 system can be used as portable, hand held device or as a stationary unit. The data processing is carried out by means of a 32-bit processor. There is an alpha-numerical display for certain compounds in the mixture. The spectrum can be transferred to a PC. A special output is prepared for data transfer. The printed circuit board is designed in SMD-technology.

#### RESULTS

The photoionisation IUT-50 is designed for the sensitive detection of benzene down to the 10 ppb level and in presence of other aromatics like toluene, xylene, cumene - often in much higher concentrations. The first version of a hand held system was checked in a chemical

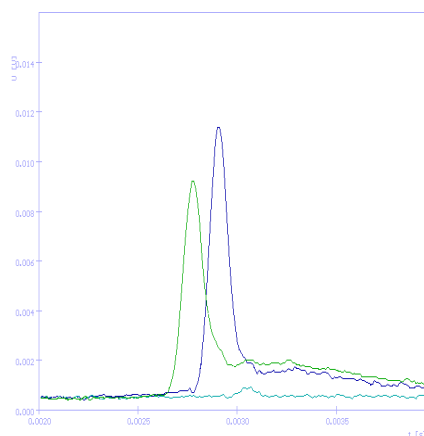


Figure 5:  
Peaks of benzene, toluene and xylene measured by means of an IUT - IMS - 25, photoionisation

factory. It works with a membrane inlet system (fig. 5). Benzene could be measured down to 30 ppb in ambient air. Benzene ions get quenched in presence of toluene, xylene and also cumene. As long as the device is used in

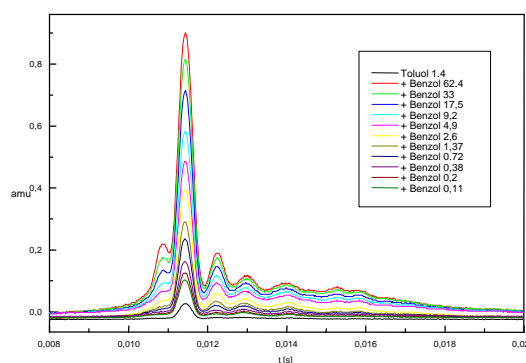
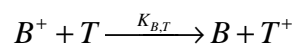


Figure 6:  
Mixture of toluene (1.4 ppm ) plus different concentration of benzene

the trace level  $c < 1$  ppm the benzene content still can be evaluated from the remaining benzene peak in the spectrum as shown in fig. 6.

The probability of the quenching reaction, like between benzene and toluene,  $j$ , is rather high:



At benzene concentration of 1 ppm 1,4 ppm toluene cause a charge transfer of 80 % of the benzene ions.

The region of response is up to 100 ppm. The situation could remarkably improved by the pre-separation of the aromatic compounds after sampling using an integrated column inside the

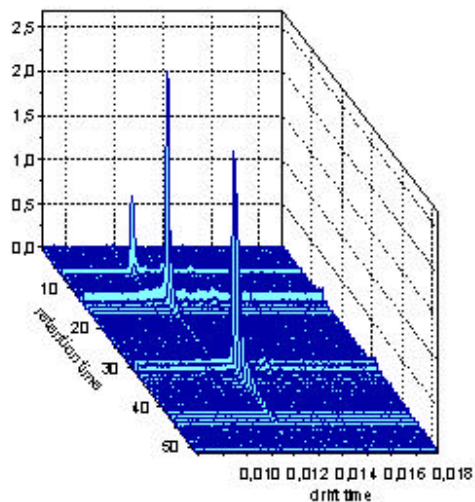


Figure 7:  
3D spectrum of 1 ppm benzene in toluene, xylene

inner loop of the system. No additional carrier gas is needed.

A 3-dimensional spectrum of about 1 ppm benzene in toluene, xylene is shown in fig. 7. Similar applications are thinkable for all compounds with a suitable photoionisation cross section at 10,2 or 10,6 eV. A typical

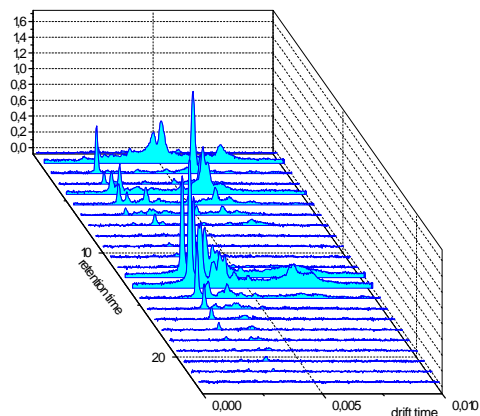


Figure 8:  
IM - Spectrum of a gasoline sample (Super Plus, BP)

application is the 3D-spectrum of gasoline (British Petrol, Super plus) shown in fig. 8, in which aromatics and alkanes produce a fingerprint picture. The identification of gasoline is possible.

The determination of phosgene in ambient air is a classical industrial application. The typical spectra are given in fig. 9 (a) and (b). While (a) mainly resolves the Cl<sup>-</sup> ion, the high resolution

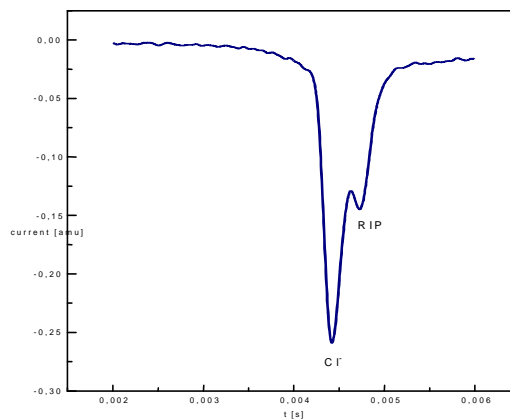


Figure 9a:  
5 ppm phosgene in air, resolution 25

cell ( $R \gg 100$ ) gives 2 peaks in the spectrum: Cl<sup>-</sup> and P(-Cl)<sup>-</sup>. This situation can be used to identify the mentioned compound.

The detection of anaesthetic gases is described by Eiceman [7] and has been carried out by means of the 25/50 devices. Spectra are given in fig. 10 for halothane, isoflurane and enflurane.

This system can be applied excellently for the halocarbon determination in the GC-IMS mode.

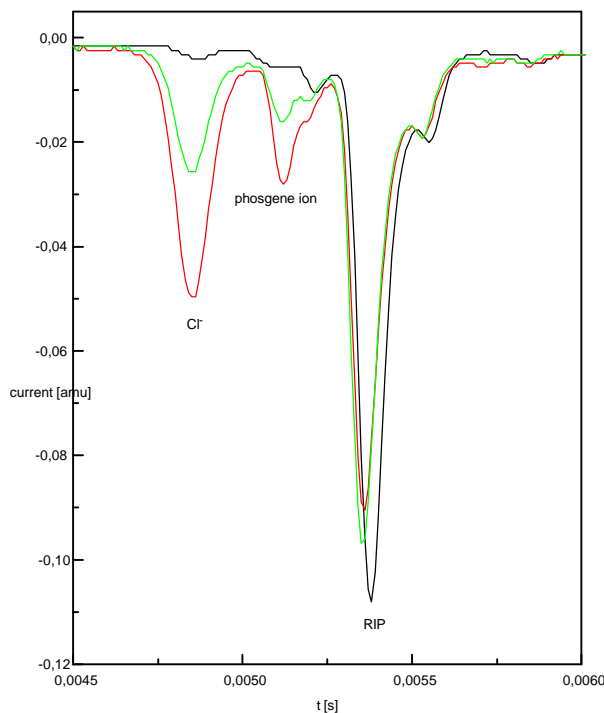


Figure 9b:  
Phosgene ion peaks and reaction ion peak, resolution 100

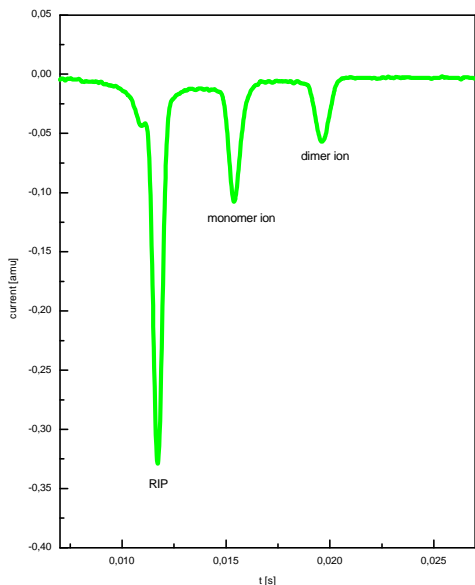


Figure 10:  
Ion mobility spectrum of isofluran (narcotic) in the negative mode with membrane - inletsystem, 2.4 ppm)

The resolution power of 100 is demonstrated in fig. 11. (1) shows the Cl<sup>-</sup> and Br<sup>-</sup> peaks being produced from bromochloromethane. Using the mathematical deconvolution [6] the spectrum could be improved again by a factor 2.

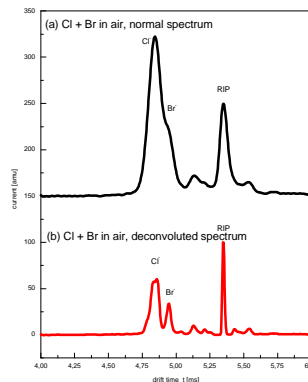


Figure 11:  
Simultaneous detection of chloride and bromide ions in a sample of bromochloromethane a: normal spectrum b: deconvoluted spectrum

In fig. 12 the spectrum of malonacidester as somane simulance is shown. At a concentration of 100 ppb the monomer and dimer peaks can be seen clearly. Other examples for the positive mode are acrolein in fig. 13 and formaldehyde in fig. 14. In case of formaldehyde the gas inlet system is rather sophisticated.

### DISCUSSION

The application of IMS-equipment is limited obviously by the still incomplete basic knowledge about reactions and mechanisms and furthermore by missing data bases. Therefore the suggestion of Karpas et al [3] to use calibration standards of the mobility scale is a very useful method to make comparable various systems. The GC-IMS is an interesting feature to improve the acceptance of this method [11]. An interesting contribution to the IMS application activities may be the system with an integrated column in the gas loop. This

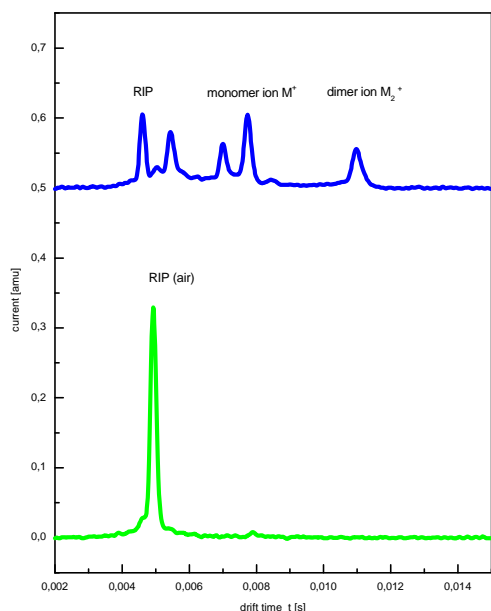


Figure 12:  
0.1 mg/m<sup>3</sup> soman-simulance (malonacidester) and reaction ion peak (RIP) - positive mode

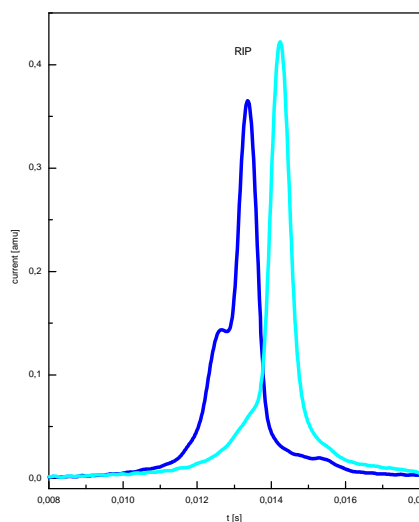


Figure 13: Acrolein in air - positive mode

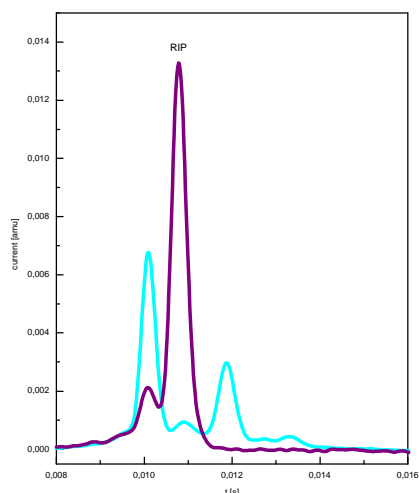


Figure 14:  
Formaldehyde spectrum - positive mode

system equipped with a photoionisation source is able to avoid and toluene. Fingerprints of flammable and other organic mixtures can be evaluated by a portable system. The PI-GC-IMS has good prospects to reach the sub-ppb range for many compounds. So far we are convinced that this method will have a good future also in emission determination. New application fields of IMS-devices are coming up in electrotechnical engineering [9] and microelectronics. The control of gas purity but also the characterisation of outgassings of polymers are topics of high interest [10].

### Acknowledgments

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