Measuring Toxic Gases in Low Concentrations with Ion Mobility Spectrometry- Overview of the Technology, its Advantages and Disadvantages

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Abstract:

Different ion mobility spectrometers (IMS) are reviewed and the limitations regarding the detection of toxic industrial chemicals and chemical warfare agents are discussed. Actual and future solutions based on gas detector arrays containing IMS systems are presented.

Key words: Time of Flight Ion Mobility Spectrometer, Field Asymmetric Ion Mobility Spectrometer, Toxic Industrial Chemicals, Gas Detector Array, First Responder.

Introduction

First responders need instrumentation that is capable to detect hazardous gases instantly. Besides the detection also identification or at least a first hint of the nature of the released chemical is required. The most common and toxic chemicals transported in Germany are listed in the ETW list (Einsatz-Toleranz-Werte) with values similar or identical to the AEGL-2 (Acute Exposure Guideline Levels) for 4 hours exposure [1]. The instrumentation should detect the 44 compounds of the list and should also be capable to detect the most common chemical warfare agents (CWA). Portable, easy to use and fast responding (in a few seconds) instruments are required.

Ion mobility spectrometry (IMS) is already widely used in military applications for detection of chemical warfare agents and also for trace detection of explosives at airports. It is the most promising technology which could fulfill the requirements. This article will show the advantages and disadvantages of IMS for the detection of the toxic chemicals and will also present solutions for improvement.

IMS – Overview of Main Components

The main components of an IMS are an inlet, an ion source, a device for separation of the ions at atmospheric pressure and an ion detector. Portable instruments usually have a small pump for guiding the toxic gases to the inlet, which usually consists of a membrane or a switching valve. The toxic gases entering the ionization chamber are then ionized, usually by a radioactive ion source. Depending on the toxic gas positive and negative ions, in form of ion clusters containing molecular ions or fragments ions, are produced. The separation of the ions is performed by applying electric fields in a drift gas consisting of filtered air. Detection of the ions is done by a Faraday plate.

The main advantage of IMS when comparing it to sophisticated laboratory instruments, such as mass spectrometry, is that no vacuum system is required, permitting the development of really portable and hand-held instruments. This advantage is also its disadvantage, because the ionization is always accompanied by complex chemical reactions at atmospheric pressure.

Ion Sources for IMS and Ion Chemistry

The most common ion sources are radioactive sources using ^{63}Ni, ^{241}Am or ^{3}H (Tritium). The sources are stable and do not require external power, but often need special permits and licensing procedures. Non-radioactive sources are also available in some instruments, but they require additional power and are less stable. Examples are electron gun sources, corona discharge and photoionization. With radioactive sources the high energy electrons emitted by the ß-source (e.g. ^{63}Ni) will first hit and ionize the nitrogen in the air. The electrons will continue to ionize the main molecules in air until they lose their kinetic energy. Due to collisions at ambient pressure the charge is transferred to

a water cluster $H^+(H_2O)_n$ which is called the reactant ion. Usually the humidity of the drift gas in the IMS is kept at very dry conditions (a few ppm) such that the reactant ion consists of 2 or 3 water molecules (n=2..3). Negative ions are formed by thermalized or low energy electrons which attach to oxygen. Through collisions a negative reactant ion containing oxygen and water clusters is formed: $O_2^-(H_2O)_n$.

After a while the reactant ions will hit the unknown molecules (toxic gases) in order to produce a product ion. Positive reactant ions will produce a product ion through association or transfer of a proton to the analyte molecule. The proton affinity of the analyte molecule plays an important factor. The higher the proton affinity of the analyte molecule compared to the reactant ion the higher the probability that the charge is transferred. Aromatic amines, amines and phosphorous compounds (such as nerve gases) have the highest proton affinities. Negative reactant ions will produce a hydrated adduct ion between the negative oxygen and the analyte molecule. Reactions by charge transfer and proton abstraction may also occur. Similar to the proton affinity for positive ions the electro negativity of the analyte will provide an indication if the analyte will keep the charge and can be detected by the IMS. It is important to keep in mind that in complex mixtures only the molecules with the highest proton affinities or the highest electro-negativities will be seen.

Electron gun sources are new non-radioactive sources which behave exactly like radioactive sources. Electrons are produced in vacuum by a heated filament. The electrons are accelerated by a high voltage in order to hit a thin membrane, which separates the vacuum from the atmospheric pressure. The electrons have enough energy in order to trespass the membrane and to undergo the ionization processes explained above. Another version of the electron gun uses membranes which are coated with a metallic layer in order to generate soft X-rays, which can also be used as ion sources.

All other ion sources do not produce the same spectra as the radioactive ion sources. Corona discharge produces also nitrogen oxides which have a high electro negativity leading to problems for the detection of some negative product ions because of the high electro negativity of nitrogen oxides. With photoionization ultraviolet light is used in order to ionize molecules directly. Glow discharge lamps with energies of 10.6 eV (VUV-light) can be used for example in order to directly ionize molecules with lower ionization potentials (IP), such as aromatic hydrocarbons. With this ion

source no reactant ions are produced and different spectra, with only positive ions, is generated. In complex mixtures only molecules with the lowest IP can be seen, because also here charge will be transferred from molecules with higher IP to molecules with lower IP during collisions.

Very low detection limits in the low ppb region can be achieved with IMS due to the ionization at ambient pressures. The drawback is that also complex ion reactions occur in the ion source making it impossible to detect some toxic gases with IMS. The following table Tab.1 shows some of the compounds from the ETW list and some ionization mechanisms which could be used to detect them. It shows that not all compounds can be detected with an IMS.

Tab. 1: Selection of compounds from the ETW list and ionization capabilities of ß-radiation and VUV radiation

Name	ß-radiation / electron impact	VUV radiation (10.6eV)
Acetic acid	✓(+/-)	no
Acetone	✓(+)	✓(9.7eV) (+)
Acrolein	✓(+)	✓(10.1eV) (+)
Ammonia	✓(+)	✓(10.2eV) (+)
Benzene	✓(+)	✓(9.25eV) (+)
Phosgene	✓(-)	no
Chlorine	✓(-)	no
Cyanogen chloride	✓(-)	no
Hydrogen cyanide	✓(-)	no
Carbon monoxide	no	no
Ethylenoxide	✓(+)	✓(10.57eV) (+)
Methanol	✓(+)	no
Phosphine	no	✓(9.87eV) (+)
Sulfur dioxide	✓(-)	no
Toluene diisocyanate	✓(-)	✓(?eV) (+)

(+)= positive ions, (-) =negative ions, (+/-) =positive and negative ions

Separation of Ions by DC voltages (Time of Flight IMS)

First time of flight IMS (ToF-IMS) appeared in the 70s and used drift tubes for separation of ions in weak electric fields. Ions from the ion source are injected into a drift tube by an ion gate. The ion gate often consists of wires with alternating polarity (Bradbury-Nielsen design). By switching off the voltage from the shutter gate during micro seconds the ions are attracted by the electric field from the drift chamber and are injected into the drift tube. The drift tube consists of a series of electrodes building up a homogeneous field with field strength of about 200 to 300V/cm. Fig. 1 shows a sketch of a ToF-IMS.
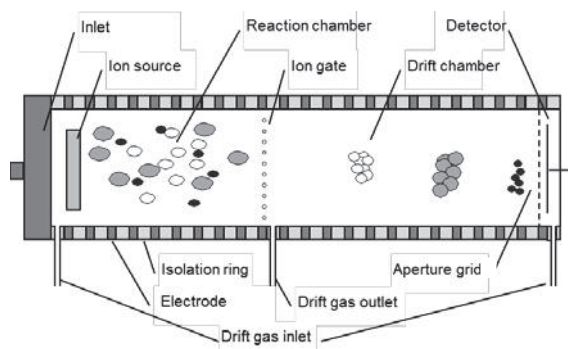
Fig. 1.   Main components in a ToF-IMS.

The ions collide constantly with the molecules of the drift gas and reach the faraday cup in milliseconds. Different ions arrive at different times at the detector. The polarity of the drift tube has to be changed in order to measure positive and negative ions.

The drift velocity v is directly proportional to the electric field E (eq.1). The different shape and mass of the ions is reflected in the mobility factor K.

$$v = K \cdot E \qquad (1)$$

The mobility factor also depends on the temperature and the pressure. For comparison purposes the temperature and pressure compensated mobility value K_0 is used ($K_0 = K \cdot (273°K/T) \cdot (p/1013hPa)$). The IMS spectrum consists of a graph showing the ion current (in pA) as a function of the time of flight (in ms). Fig. 2 shows a spectrum of a toxic gas (toluene diisocyanate).

Typically portable ToF-IMS have resolutions of 15 to 40. A resolution of 30 to 40 is enough for most of the toxic gases of the ETW list, but not for all. Benzene for example cannot be detected by a low or medium resolution IMS because the product ion co-elutes with the positive reactant ion.
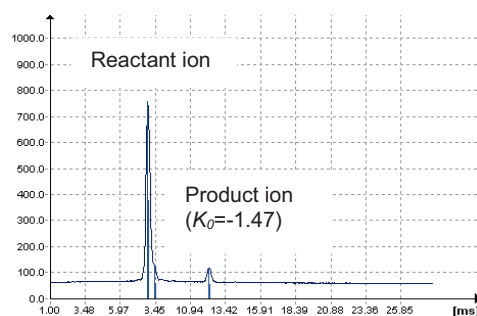

Fig. 2.   Time of flight IMS spectrum of 0.2ppm toluene diisocyanate (negative ions)

Separation of Ions by AC voltages (Field Asymmetric IMS)

When increasing the electric field by some orders of magnitude the linear equation (1) is not valid anymore because nonlinear effects start to dominate the equation, which can be expressed by equation (2).

$$v = K(E) \cdot E \qquad (2)$$

with

$$K(E) = K + k_1 \cdot E^2 + k_2 \cdot E^4 + ... \qquad (3)$$

When an asymmetric alternating electric field, having high field strength during a short time and low field strength during a long time, is applied a separation of different ions can be achieved because of the non-linearity of equation (3). Fig. 3 shows the main components of a Field Asymmetric IMS (FAIMS) also known as Differential Mobility Spectrometer (DMS) including the path ways of three different ions in the alternating electric field.
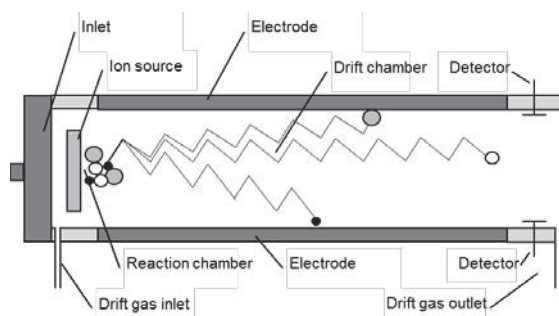

Fig. 3.   Main components in a FAIMS.

Positive and negative ions from the ion source are transported by a constant gas flow through two parallel electrodes from the drift gas inlet to the drift gas outlet. By applying an asymmetric voltage between the electrodes the ions can be separated depending on the substance specific mobility coefficients. The mean velocity of the

ions is directed to one electrode if the mobility value at high electric fields is higher than the mobility value at low electric fields. The mean velocity is directed to the other electrode if the mobility value at high electric fields is lower than the mobility value at low electric fields. In order to avoid the loss of ions at the electrodes a DC compensation voltage is applied. By changing the amplitude of the compensation voltage with time a spectrum can be achieved. Fig. 4 shows a spectrum of a FAIMS at fixed amplitude of the AC voltage. It can be seen that with the dimensions of the actual spectrometer a compensation voltage of ca. -10V is needed in order to guide the product ions to the detector. It is important to emphasize that the separation of ions is based on the differences of the mobilities at low and high electric fields. Therefore the separation is different to the time of flight based IMS systems and can be considered as an orthogonal detection system.
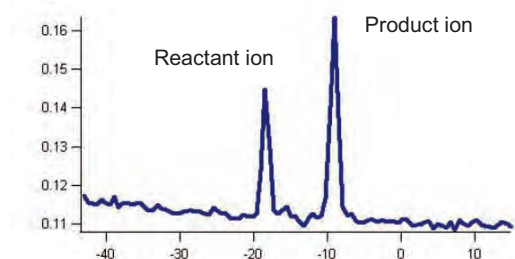

Fig. 4. *Field asymmetric IMS spectrum of 1ppm sulfur dioxide (negative ion, ACV=1000V)*

If after each scan, where the compensation voltage is changed, the amplitude of the AC voltage is also changed a so called dispersion plot can be generated. The next Fig. 5 shows a dispersion plot of sulfur dioxide (negative ions). With this dispersion plots more information can be gathered with the drawback that some minutes are needed for the acquirement of the data.
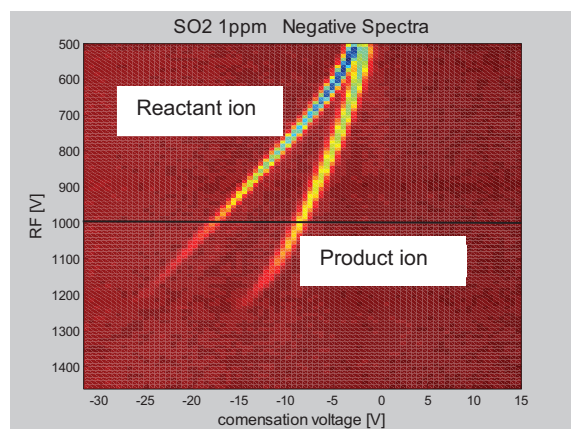

Fig. 5. *Dispersion plot of 1ppm sulfur dioxide generated by a series of FAIMS spectra (negative ions, ACV=500 to 1500V). The black line shows the position of the spectrum of Fig. 4.*

Detection of Toxic Gases with IMS and Comparison of the Separation Techniques

The list of toxic compounds was analyzed with two IMS systems, a FAIMS (DMS) system from Sionex (SVAC with a 370MBq [63]Ni source) and a ToF-IMS from Airsense (GDA2 with a 100MBq [63]Ni source), both IMS systems had the same gas inlet (membrane inlet). Additionally also simulants for warfare agents were measured. The next examples show some of the main differences in the detection of the toxic gases.

The detection of benzene is not possible with a ToF-IMS with low or medium resolution, because the product ion has nearly the same time of flight than the reactant ion. The FAIMS system can clearly separate the benzene ion as shown in the dispersion plot in Fig.6.
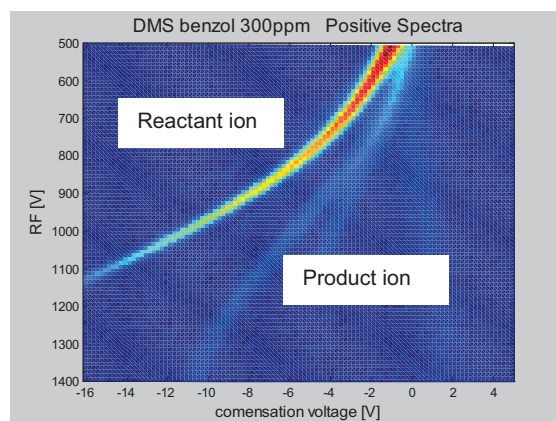

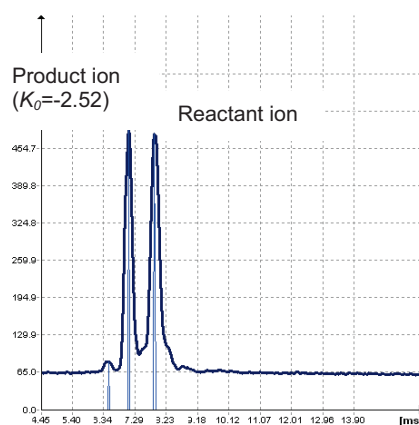Fig. 6. *Dispersion plot of 300ppm benzene (positive ions).*

Fig. 7. *ToF-IMS spectra of 1ppm cyanogen chloride (negative ions)*

Fig.7 shows the ToF-IMS spectrum of cyanogen chloride. The cyanide fragment ion can be seen at the left side of the negative reactant ion.

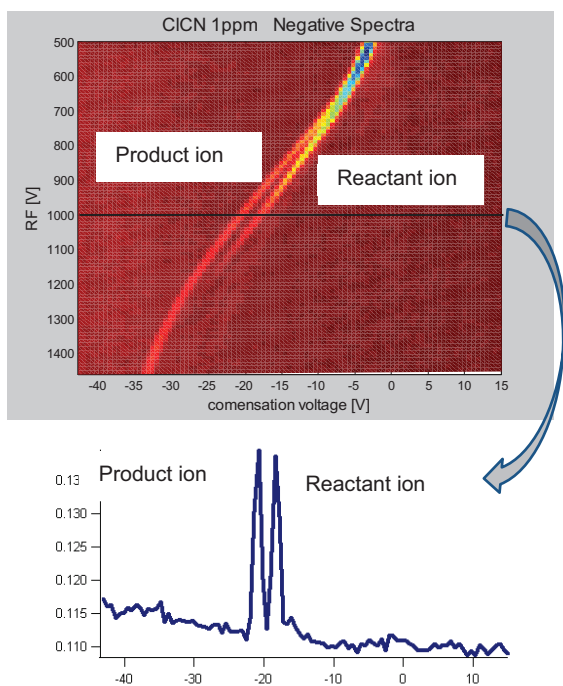Fig. 8 shows the dispersion plot and the spectrum at a fixed AC voltage. The response of both systems is similar.

Fig. 8.   Dispersion plot and FAIMS spectrum (at 1000V) of 1ppm cyanogen chloride

The last example shows in Fig.9 ToF-IMS spectra of two nerve gas simulants, one is diisopropyl methyl phosphonate (DIMP, a phosphor organic compound) and the other is dipropylene glycol monomethyl ether (DPM).
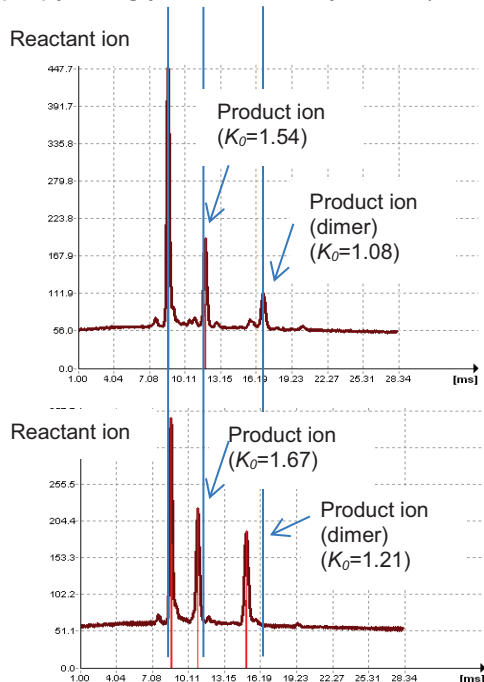

Fig. 9.   ToF-IMS spectra of 0.1ppm of DIMP (upper spectrum) and 0.1ppm DPM (positive ions).

When comparing the ToF-IMS spectra both compounds can be clearly distinguished. Fig.10 shows the FAIMS spectra at the same concentration. It can be seen that the resolution

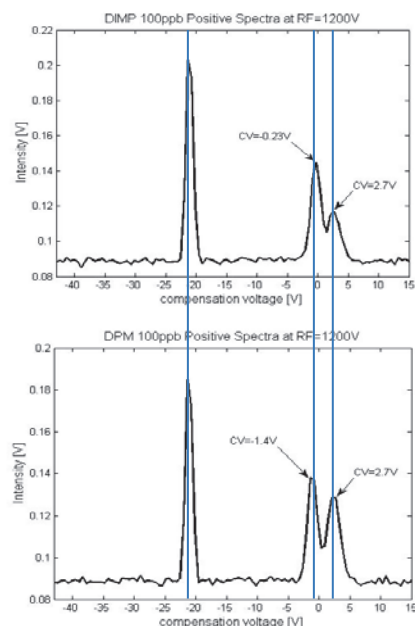of the FAIMS system is not high enough in order to distinguish both compounds.

Fig. 10. FAIMS spectra of 0.1ppm of DIMP (upper spectrum) and 0.1ppm DPM (positive ions, ACV=1200V)

When comparing the systems with similar gas inlets it can be concluded that for small molecules (ions with high mobility) FAIMS seems to be better. The drawback is that for a clear discrimination often a time consuming dispersion plot is needed. For bigger molecules, such as the warfare simulants a better resolution is possible with the ToF-IMS.

Although there are differences in the two independent ion separation technologies, they have also same advantages and disadvantages. Both technologies use the same ion sources and therefore have similar detection limits but also the same problems. Molecules with lower proton affinities or electro negativities than the water clusters cannot be measured. In complex mixtures only the toxic gases with the highest proton affinities or highest electro negativities can be detected. This means that for example high concentrations of acetone will prevent the detection of aromatics such as benzene. Some toxic compounds cannot be measured with both systems, examples are carbon monoxide, phosphine and arsine.

Improving the Detection Capabilities of IMS

As shown in the chapter before, ToF-IMS and FAIMS are orthogonal detection techniques. A combination of both technologies could increase the selectivity considerably. A solution was presented 2005 at the ISISM conference in Paris by Eiceman et.al. and published in 2007

[2]. The construction was basically a planar FAIMS system as shown in Fig. 3, with the difference that two ToF-IMS (one for positive, the other for negative ions) were positioned instead of the detection electrodes. The next Fig. 11 shows the results obtainable with such a system. At a fixed AC voltage a two dimensional graph is displayed showing the compensation voltage of the FAIMS system against the time of flight of the ToF-IMS system. Measuring acetone shows that a monomer and a dimer peak are present, even at relatively low concentrations. The monomer peak is normally not seen with portable ToF-IMS systems, but is now separated due to the FAIMS.
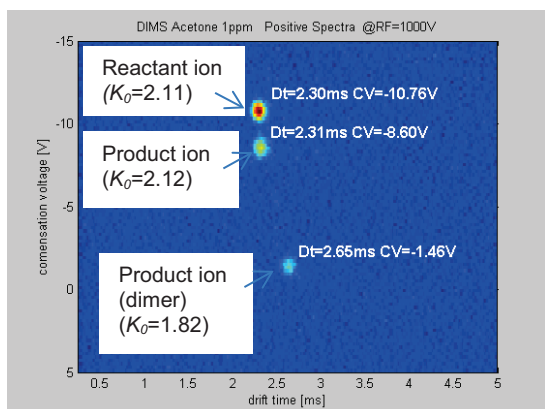

Fig. 11   2D-Plot of Acetone (1ppm) measured with a FAIMS-ToF-IMS² system.

FAIMS and especially the tandem FAIMS-ToF-IMS systems are very suitable for detecting toxic compounds which are known a priori. In case of emergencies the first responder normally does not know what he has to look for. Due to the time required for obtaining dispersion plots with actual FAIMS systems, which can take minutes, the technology is not ideal for first responders. ToF-IMS systems are much faster, providing results in seconds.

As mentioned before IMS technology cannot detect all toxic gases, therefore the Gas Detector Array GDA system was developed by Airsense. It consists of a combination of ToF-IMS with a photo ionization detector (PID), an electrochemical cell (EC) and two metal oxide sensors (MOS). The next Fig. 12 shows the newest version, the GDA-X system, which is also suitable for detection of explosives through a wipe desorption unit which has to be connected to the front of the system.

By combining different gas detectors also compounds which cannot be detected with IMS can be detected now. Phosphine at very low concentrations for example will react with the electrochemical cell and the metal oxide sensors. Carbon monoxide will only react with the MOS sensors. Benzene will give a sensitive response on the PID.

Fig. 12   The new GDA-X based on a combination of ToF-IMS and other detectors suitable for the trace detection of TICs, CWA and with the new desorption tool also for explosives.

Fig. 13 shows some pattern obtained with a GDA when measuring some toxic gases. The first two spectra just show the spectra of air (no IMS response on benzene and arsine). It can be seen that in case of benzene the PID and the MOS sensors are reacting. During the exposure to arsine the electrochemical cell and the MOS sensors react. If the concentration is increased, also the PID will start to react. At sub ppm concentrations also the electrochemical cell reacts, besides the IMS, to phosgene. During exposure to high concentrations of ethylene oxide the PID, the MOS and the IMS reacts.
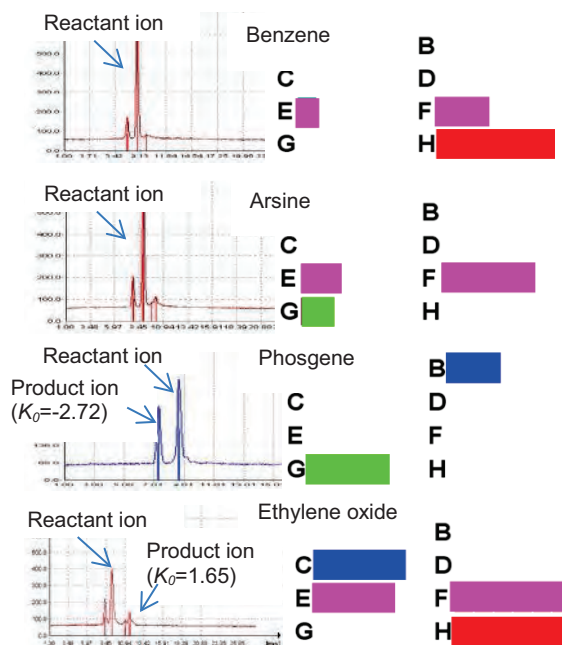

Fig. 13 Response of the GDA to different toxic gases: benzene, arsine, phosgene and ethylene oxide. The colored bars represent the response of the detectors: E&F are the metal oxide sensors, G is the electrochemical cell and H the PID.

Besides the improvement in detection capabilities the additional detectors can be also used to improve selectivity. The next Fig.14 shows ToF-IMS spectra of two very toxic compounds: hydrogen cyanide and cyanogen chloride. Both gases cannot be distinguished by portable ToF-IMS. Interesting is, that only one of the two gases also reacts with the electrochemical cell.
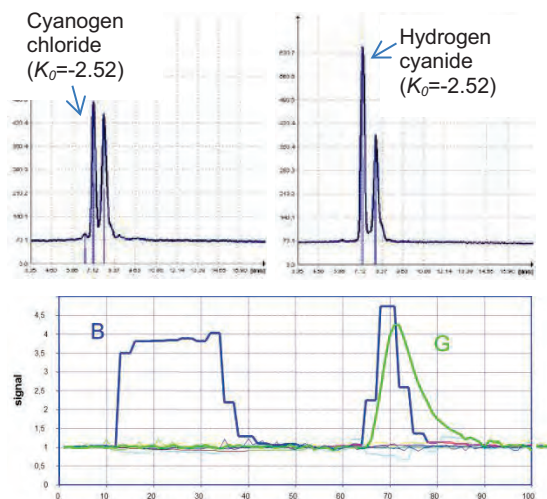

Fig. 14 The upper picture shows the ToF-IMS spectra of ClCN und HCN. The negative ions have the same mobility. The lower picture shows the response of the IMS (B=blue line) and the response of the electrochemical cell (G=green line) after exposure to the gases.

This example shows that the response of the other sensors can be used to improve identification.

A detection of the toxic compounds is performed in only a few seconds. The polarity of the IMS tube is switched very fast so that positive or negative spectra are available every 1.5 seconds.

In complex mixtures the identification of toxic gases is often very difficult. In this situation a gas chromatographic (GC) separation is often helpful. A combination of GC with a ToF-IMS and further detectors was developed during the research project DACHS [3] funded by the German Federal Ministry of Education and Research.

The prototype instrument has an array of 2 electrochemical cells, a PID, 3 metal oxide sensors and a new ToF-IMS. The IMS consists of two tubes with an unique ion injection system in order to measure positive and negative ions simultaneously, which is important when placing an IMS behind a GC-column. With this system complex mixtures can be separated by a short GC-column and the eluted gases can be analyzed by the detector array. A special inlet system allows the utilization of the detector

similar to a GDA system for instant detection. In case of detecting something a further GC separation and analysis can be started in order to validate the results.

The following Fig. 15 shows an analysis of a mixture of toluene (no IMS signal) m-xylene (no IMS signal) and tetrachloroethene (signal in the negative spectrum). It can be seen that toluene and tetrachloroethene are nearly coeluting on the short column and the PID is showing two peaks (light blue color). The IMS is reacting only on the second peak at 117s, showing that the second peak is tetrachloroethene. The spectra of the IMS show that there is no response with positive ions, but a small response with the negative ions with K_0 values matching tetrachloroethene. The 3rd clearly separated peak eluting after 130s is xylene. Fig.16 shows a picture of the prototype system.
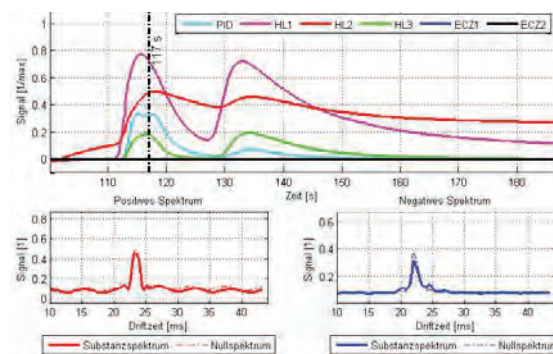

Fig. 15 The upper picture shows the GC separation of a mixture of three compounds: toluene, tetrachloroethene and m-xylene. 3 peaks can be seen with the PID detector. The second peak also generated a small response on the negative IMS spectrum (lower picture at the right side).

Fig. 16 Picture of the first prototype GC-gas detector array systems (DACHS).

Conclusions

First responders need portable instrumentation that detects and alarms in case of release of toxic gases such as industrial gases or warfare agents. IMS is a promising technology suitable

to fulfill many of the requirements. Some gases cannot be measured with IMS, therefore further detectors are required. ToF-IMS and FAIMS are IMS technologies suitable for the task, but they have some advantages and disadvantages. In case of a release of unknown compounds fast detection is a necessity which is one of the reasons why ToF-IMS is preferred by the authors. Resolution for bigger molecules is also better with ToF-IMS. In the near future gas detector array systems using ToF-IMS with an optional GC seem to be the optimal solution. Further work is necessary to increase resolution of IMS. In terms of IMS resolution FAIMS-Tof-IMS tandem systems seem to be the optimal IMS-solution, but the speed of analysis has to be increased considerably.

References

[1] Vfdb 10-01en, Evaluation of Harmful Concentrations in Fire Service Operations (Guidelines of Vereinigung zur Förderung des Deutschen Brandschutzes –vfdb), summer 2013

[2] G. Eiceman, et.al., Miniature DMS-IMS detector for enhanced revolving power, *IJIMS* 10, 1-5 (2007)

[3] B. Ungethüm, A. Walte, Joint project: Detector array with a gas chromatograph for identification of toxic substances (DACHS) – Project: Development of a detection system for fast identification of toxic compounds, Ref. No. 13N9530, Final Report (BMBF), March 2012