

Tests regarding the Suitability and Use of Ion Mobility Spectrometers for Early Detection of Chemical Degradation Products

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Abstract

Extensive research has been devoted in the past few years to early discovery of fire via detection of gasses emitted in the phase of origin of a fire using suitable gas sensor technology. In the present research, the suitability and use of ion mobility spectrometers (IMS) for the early detection of thermal degradation products are investigated. It provides a review of the measurement method, their possible fields of application and performance ability.

The specific thermolysis products are identified on the basis of the signal patterns measured. Comparative measurements with other sensors for early fire detection concerning the response behaviour under different fire development scenarios demonstrate the possible implementation conditions for early detection of fires and hazard situations with the aid of the ion mobility spectrometer.

1 Introduction

The sources of a fire are often local, narrowly delimited overheating. Smouldering fires, which remain undetected or are detected too late in their initial phase, often cause major damage as a result. Under thermal stress, degradation products specific to the material involved are released in variable concentrations.

Since the overwhelming majority of potential inflammable materials involve organic substances, knowledge of the thermal behaviour of organic materials is of decisive importance.

Depending on the anticipated danger, a variety of early detection devices are in use. For the early detection of thermal degradation products in the phase of origin of a fire gas detection systems based on different gas sensor technologies can be used [1-3]. In the present research, the suitability and use of ion mobility spectrometers (IMS) are investigated. In particular, this study focused on three main questions:

1. Which specific compounds develop from different materials under thermal stress?
2. Is it possible to detect these specific compounds with an ion mobility spectrometer?
3. Is an ion mobility spectrometer a suitable detection unit in comparison to common fire detectors?

To answer the first question it is necessary to use powerful and expensive analytical methods to analyse the compounds. In this study infrared spectroscopy and gas chromatography/mass spectroscopy were used to analyse and to identify the compounds.

In order to study the thermal behaviour (i.e. to determine whether there are any characteristic exothermal or endothermal drifts during a defined heating rate) differential thermal analysis by simultaneous thermogravimetry (TG/DTA) was used. The TG/DTA-system was then coupled to an ion mobility spectrometer to correlate the loss in weight and the exothermal or endothermal signals with the signal patterns of the ion mobility spectrometer.

2 Basic principles of an Ion Mobility Spectrometer

Ion mobility spectrometry (IMS) is a technique used to identify traces of chemical vapours by measuring their mobility in the gas phase in an electric field [4, 5]. In modern analytical IMS methods, ion mobilities are determined on the basis of ion velocities that are measured in a drift cell with supporting electronics.

The heart of the IMS technique is the IMS-cell. In figure 1, a schematic overview of the IMS-cell and its functional principle with the resulting signals are shown.

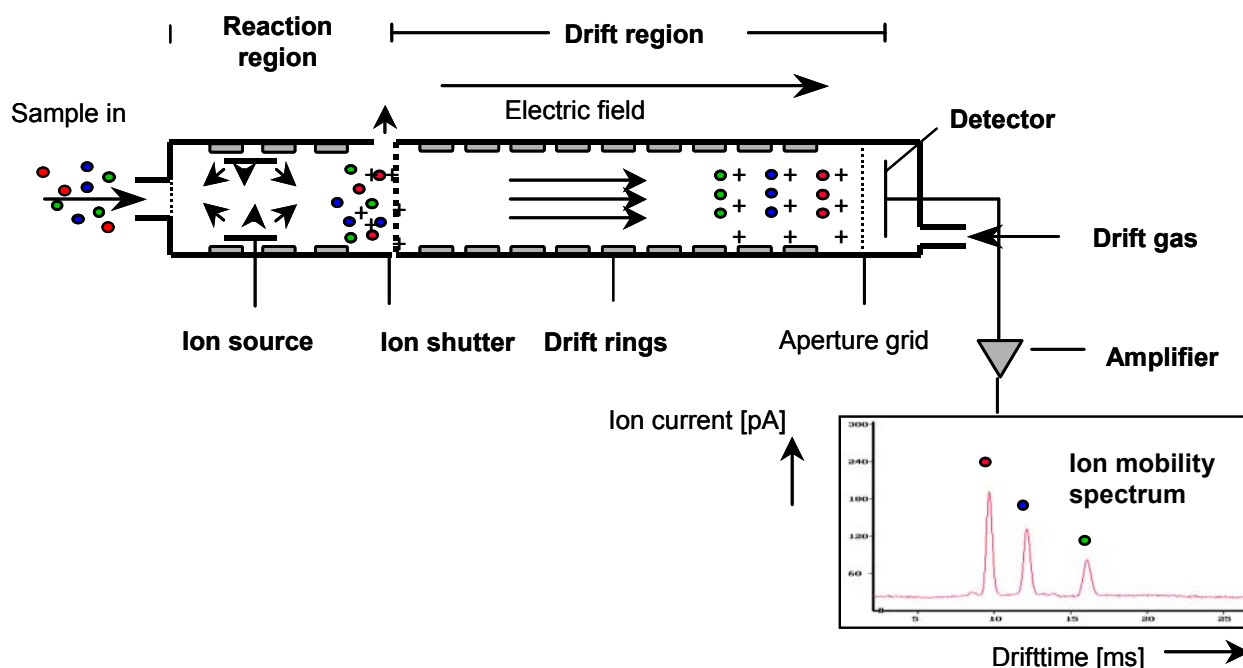


Fig. 1 Schematic of IMS-cell with resulting ion mobility spectrum

The cell is composed of a reaction region and a drift region, both under an electric field gradient.

The first measurement stage involves the ionisation of the neutral molecules of a sample. These ion processes occur in the gas phase via chemical reactions between sample molecules (A, B) and a reservoir of reactive ions (C⁺).

The reservoir of reactive ions is formed by ionisation of the nitrogen in air using a radioactive source (e.g. Ni⁶³) and by a further series of ion-molecule reactions with trace amounts of H₂O, NH₃ and NO in the absence of a sample.

By means of air aspirated from the area to be monitored the neutral sample (A, B) is introduced into the reaction region and reactant ions undergo further ion-molecule reactions to produce analyte “product-ions“ (A⁺ and B⁺).

A pulsed electric shutter grid “opens“ for a very short period of time (about 300μs) and among collisions with drift gas molecules a proportion of all ions is accelerated in the direction of the field.

The combination of acceleration by the electric field and collision with neutral gas molecules leads to an average ion velocity v_D that is directly related to the strength of the electric field (E).

$$\vec{v}_D = K \times \vec{E}$$

$$K = \vec{v}_D / \vec{E} = L^2 / Vt_D$$

The constant of proportionality K is called the ion mobility, usually in units of cm²/Vs. where L is the ion drift distance in centimetres, V the voltage drop across L , and t_D is the drift time.

Ion mobilities are characteristics of substances and can be used for detecting and identifying vapours. Ion mobility spectrometry can measure specific ion currents below 10⁻¹² A and it is therefore also highly sensitive as a detection technique.

3 Experimental

3.1 Preparation for detecting specific degradation products with IMS

In order to develop a monitoring application for the IMS, some preparatory work has to be done. First of all, the thermal degradation of some plastic materials was studied. A simultaneous thermogravimetry-differential thermal analysis (TG/DTA) yielded information about the thermal stability and monitored the degradation with different programmed heating rates. To detect the specific volatiles released from the materials an IMS was connected to the TG/DTA-system as shown in figure 2.

The results i.e. the detection and identification of the gaseous products were compared by using infrared spectroscopy and gas chromatography/mass spectrometry (GC/MS).

Figure 3 gives an example of monitoring of a flame-retarded polyurethane with the described combination. The flame retardant used was trichloro-ethyl-phosphat. The heating rate was 10°C/min. The IMS-scanning rate was about 5 seconds and the sample weight was 12 mg.

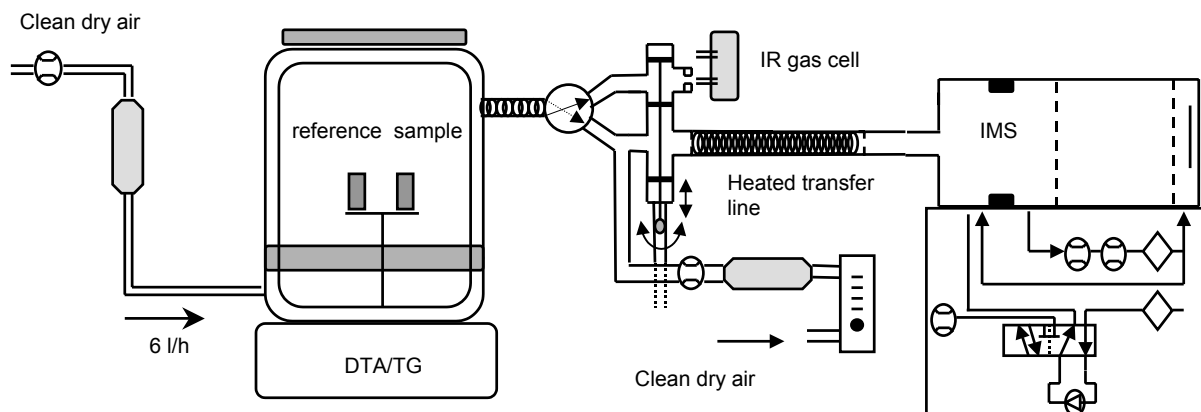


Fig.2 Combination of TG/DTA with IMS

The TG-signal shows the percentage weight loss of the sample. At nearly 200°C the decomposition stage occurs with a drastic loss in weight.

At this moment the DTA-signal shows a strong exothermal drift reaching a maximum at 270°C. Before this stage, at a temperature of about 160°C the selected mobility monitoring of the IMS detected some gases containing chlorine.

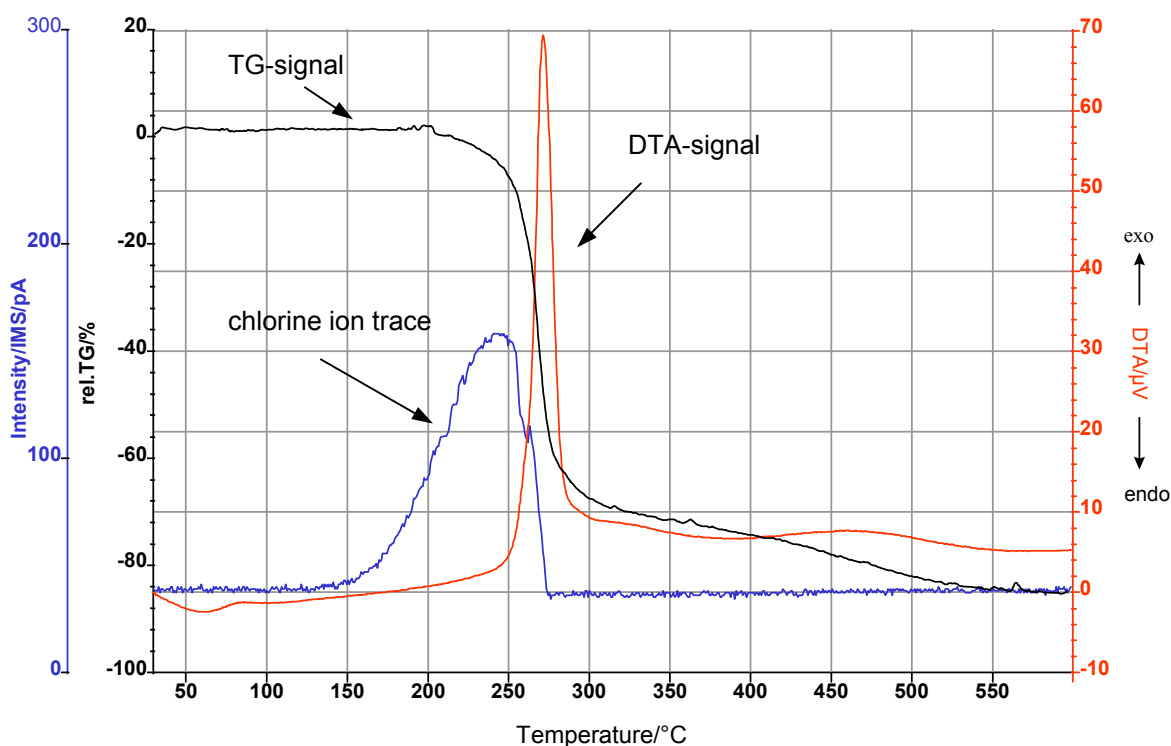


Fig.3 TG/DTA-signal and selected ion mobility trace of a flame retarded polyurethane

The ion mobility constant is $2.58 \text{ cm}^2/\text{Vs}$. This trace has been shown by GC/MS to be due to the liberation of ethyl- and methylchlorine. The corresponding ion mobility spectrum is given in figure 4c. Figure 4b shows the typical spectrum of clean air at room temperature.

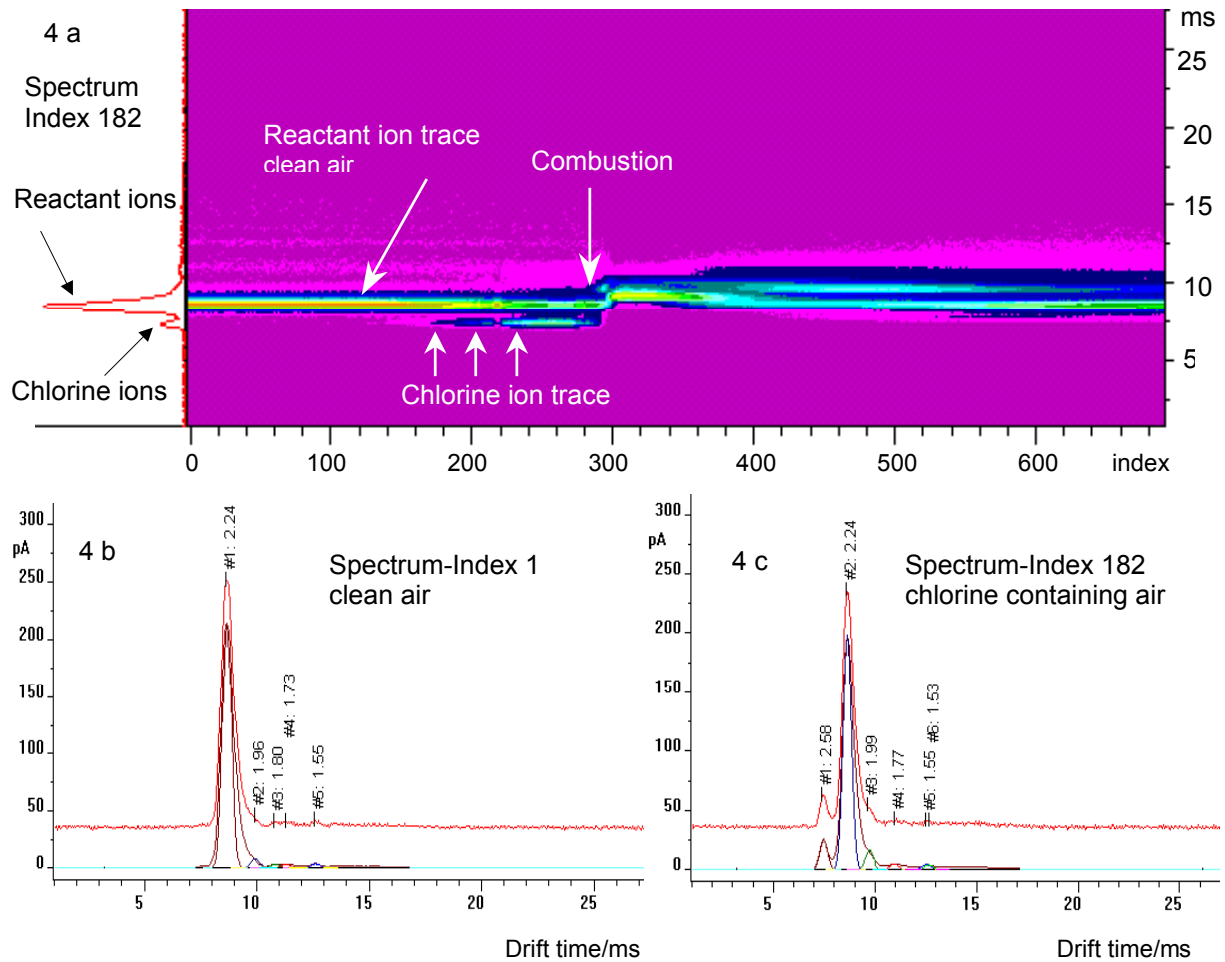


Fig.4 Contour-plot and ion mobility spectra (negative mode) of clean air and chlorine containing gases

Another example is given in figure 5. The thermogram shows the thermal degradation of a flame-retarded printed circuit board.

The flame retardant was tetrabrombisphenol A (TBBA). Before the first combustion step began at 285°C the IMS detected some gases containing bromine at 170°C . The ion mobility constant is $2.44 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The corresponding ion mobility spectrum recorded at 172°C is given in figure 6.

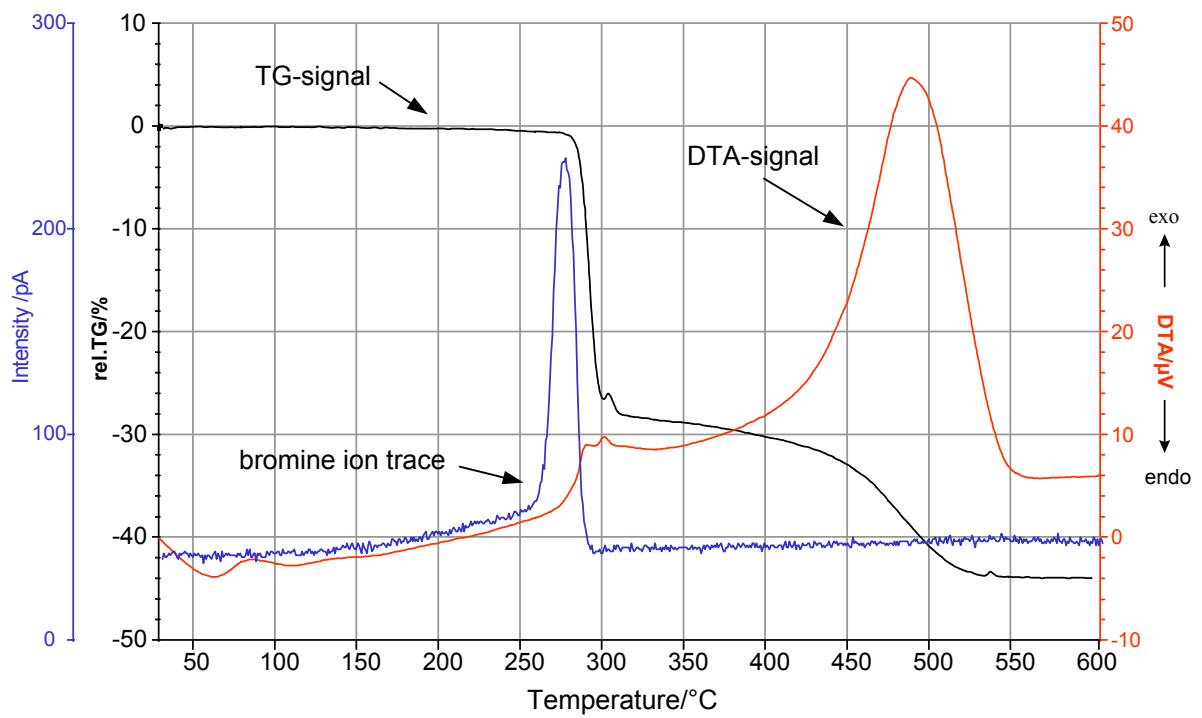


Fig.5 TG/DTA-signal and selected ion mobility trace of a flame retarded printed circuit board

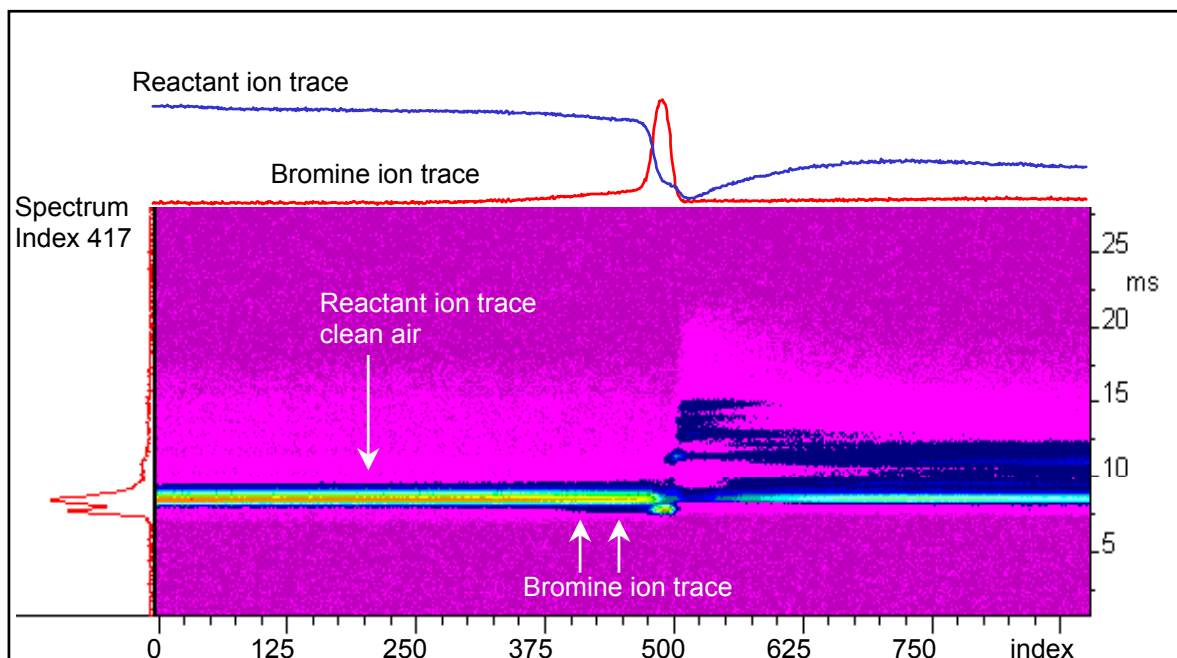


Fig.6 Monitoring of a flame retarded printed circuit board

3.2 Comparative measurements on the response behaviour of IMS and conventional smoke detectors

We carried out a series of tests in a MINIMAX fire room that complies with EN-54-9. The test involved the thermolysis of a variety of materials, such as milk powder, beechwood, cotton and various plastics in a number of different ways. During the test the resulting thermolysis products were to be detected by an ion mobility spectrometer and by smoke detectors.

The aspirating hole of the IMS and the smoke detectors were situated on the three-metre circle under the ceiling of the fire room. During thermolysis several complete IMS spectrums were recorded at five-second intervals.

To display the typical response pattern of the IMS and the smoke detectors, we have displayed results from the simulation of a smouldering fire of beechwood chips in figure 7. In this experiment we exposed 600 mg of beechwood chips to a 200°C temperature increase in a pre-heated tube furnace. The temperature at the beginning of the signal measurements was 200°C, which was increased to 400°C within 10 minutes.

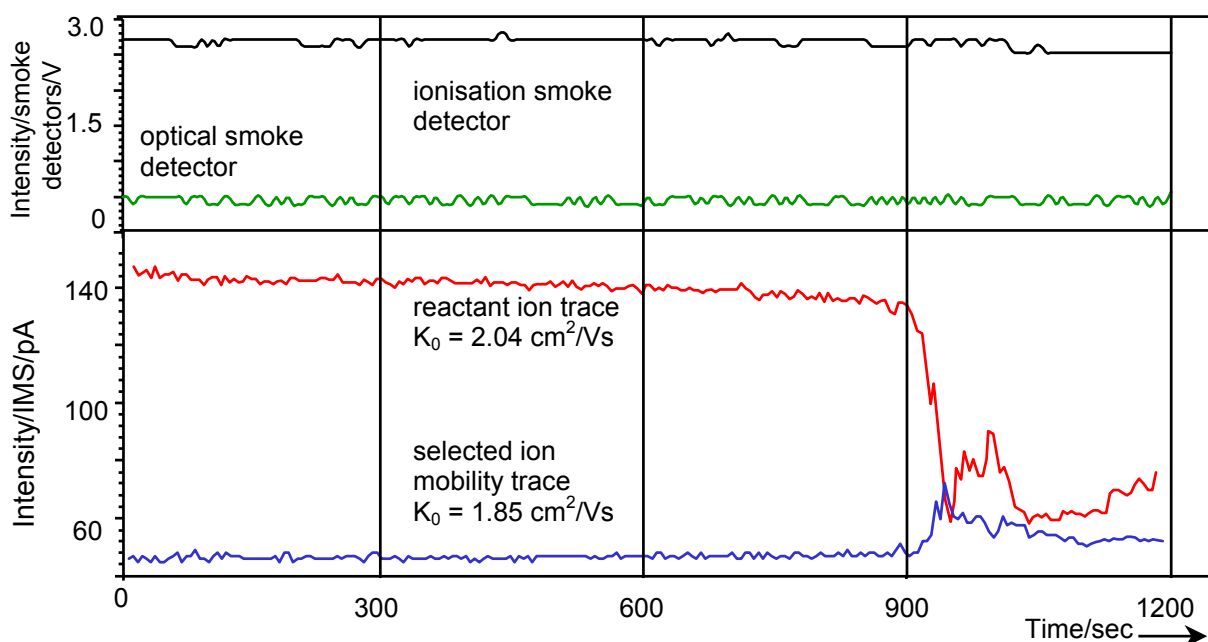


Fig.7 Response behaviour of conventional smoke detectors and IMS

The results demonstrate the time dependence of the output signals of the ionisation and optical detectors, the intensity of the reactant-ion signals and the selected ion mobility trace with a constant of $K_0 = 1.85 \text{ cm}^2/\text{Vs}$.

Here, you can see a clear correlation between the decrease in the intensity of the reactant-ion signal and the increase in characteristic peaks after 933 seconds whereas the other smoke detectors gave no response.

The thermolyses of the milk powder samples, the beechwood and the cotton showed another important feature. As well as extremely specific degradation products, such as maltol and a number of fatty acids, the thermolysis of all these natural, organic substances produced furane derivatives, such as furfuryl alcohol and furfural. The reason for the production of these substances was that the substances studied here often contain large quantities of oligo- and polysaccharids.

Because of their increase in proton affinity, owing to alkaline side chains, these furane derivatives led us to expect excellent detectability with the ion mobility spectrometer. This was confirmed, among other things, by the test readings in the MINIMAX fire room.

4 Conclusions

Test readings for the detection of thermal degradation products were also conducted under real conditions in a fire test room. Smouldering pyrolysis wood fire, glowing smouldering cotton fire and thermal degradation products of PVC, polyurethane and other organic materials were analysed using IMS, ionisation smoke detectors, gas detectors and highly sensitive smoke detectors.

The comparison of the response values of the different detector types shows that the significantly reduced intensity of the reactant ions (observed in the IMS spectrum) and the identification of specific degradation products can be used for a very early detection of fire for fire development scenarios in which the other systems do not respond or, if they do, not until after a long delay.

In order to use ion mobility spectrometers for the early detection of fires, particularly smouldering fires, it is important to be aware of any degradation or degasification products of the burnt materials.

This can be realised by comparative preliminary studies, using different analysis methods (such as GC/MS or IR-spectroscopy).

The main advantages of the IMS are its high sensitivity, excellent detection limits, instrumental simplicity, robust configuration and real-time capability.

5 References

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