ABSTRACT

Fast, on-site identification of hazardous compounds for correct assessment of possible risks to the population and the environment is essential in case of fire and chemical disasters. The aim of this project, funded by the German Ministry of research, has been to design a semi-automatic GC/MS system and procedures that make it possible to perform sampling and analysis in less than 10 minutes.

Objects of research:
- helicopter based emergency response
- standard procedures for air, water and soil analysis
- advanced software for skilled fire fighters
- wireless data transfer
- field study experience

INSTRUMENTAL APPROACH

The Bruker-Franzen EM 640 GC/MS system is used because it is a compact, mobile and rugged instrument suitable for field applications. The system consists of modules for sample injection or desorption, two different GC modules, carrier gas supply and peripheral electronic modules, the MS module and a personal computer. The modules are connected to the central MS unit with quick plug-in connectors (fig. 2a,b).

The two gas chromatographs, GC 1 for the analysis of volatiles and GC 2 for semivolatiles, are equipped with different fused silica capillary columns: GC 1 with a 7.5 m capillary (0.32 mm i.d., stationary phase 5 µm DB 1) and GC 2 with a 3.5 m capillary (0.32 mm i.d., stationary phase 0.25 µm DB 5). These GC modules can be exchanged without venting the vacuum system.

The entire system, including batteries for two-hour operation and a data transmission system, is mounted on a stretcher (fig. 3) and weighs 120 kg. Thus, it can be transported by van or helicopter (fig.4).

FIELD APPLICATION RESULTS

Sampling procedures and analyses have been performed by fire fighters. Experience has been gained by the treatment of 500 samples since 1992 taken by 20 professional fire departments. In this way more than 300 different organic compounds have been identified. All the results are listed in a database (tab. 1) and combined with substance information and case study for further evaluation. The mass spectra are gathered in different MS databases. They operate hierarchically together with the NIST database for fast and automatic identification with high reliability. By arrangement of the field sampling results 3 analytical categories have been found.
Category I: chemical accident - single substance

Category II: chemical accident with reaction - several substances

Category III: fire - complex mixtures

In the case shown in fig. 5, an unknown fluid was spilled. Generally, in chemical accidents, the absolute amount of the emitted substances ranges from kilograms to tons. As sample concentrations are high, identification tend to be straightforward and the automatic evaluation procedure works properly.

In a chemical accident with reactions or explosions (category II), some known but also unknown compounds are emitted. As an example, fig. 6 shows the analysis of a soil sample, taken at a site where a chemical reactor for nitroanisole exploded. 10 tons of chemicals were emitted into the environment. Generally, the main compounds can be identified and the analysis of category II samples can be carried out with quite good reliability.

In case of fires (category III) many organic compounds are emitted in complex mixtures. Fig. 7 shows a GC/MS run of combustion gases after an explosion and fire in a chemical store. Twentyfour organic compounds were separated and identified automatically (black line), some in overlapping peaks.

Experts are needed for correct evaluation because the identification and assessment of these complex mixtures are difficult. New strategies in toxicological evaluation are needed and will be the subject of further studies to be performed by toxicologists.

FAST EMERGENCY RESPONSE

Fig. 8 demonstrates the operation of an envisaged future emergency response team. As soon as the GC/MS system arrives at the site by helicopter, samples already taken by firemen can be injected and analyzed. First information about the hazardous compounds is provided within approximately 5 min. A team of experts on stand-by will receive the complete GC/MS data on their PC and may help to interpret the results to give advice. Therefore, it is essential that the on-site analytical team is strictly operating according to the standard procedures.

CONCLUSION

This field analytical project has proven that analyses - including sampling, operation of the mobile GC/MS and assessment - can be carried out by fire fighters. The instrument is controlled and automatic evaluation is achieved using a special operating software. The results necessary for risk assessment are obtained directly in the field. Moreover experts off site may judge the results. Their PCs are linked to the GC/MS on demand by wireless data transfer. The optimized data bases and the simple standard procedures improve the reliability of the results [1].

Meanwhile about 10 European fire departments, emergency groups and two chemical spill vessels are equipped with this mobile GC/MS system. Our project has been influenced by their experience. Special training courses have been run in Hamburg with 60 participants so far. Further cooperation between the users will help to establish this kind of emergency response analysis.

LITERATURE

Field study:

- sampling equipment for air, water and soil
- co-operation with 20 German fire departments (fig.1)
- analyzed: 500 samples at 150 real actions (fire, chemical spill, chemical accident)

Fig. 1: Field study all over Germany

Fig. 2: Mobile GC/MS, EM 640; view of the unit (a) and principle diagram of the gas chromatographic system (b)
Fig. 3: GC/MS system mounted on a stretcher

Fig. 4: Transportation by helicopter
Tab. 1: Part of the matrix of GC/MS analysis; substances vs. samples

<table>
<thead>
<tr>
<th>Substance</th>
<th>CAS</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahydrothiophene</td>
<td>110-01-0</td>
<td>60</td>
</tr>
<tr>
<td>Pyridine</td>
<td>110-86-1</td>
<td>79</td>
</tr>
<tr>
<td>Xylene</td>
<td>95-47-6</td>
<td>1,90E+05 5,10E+04 1,00E+07</td>
</tr>
<tr>
<td>Furaldehyde</td>
<td>98-01-1</td>
<td>1,40E+06 4,20E+06</td>
</tr>
<tr>
<td>Xylene</td>
<td>95-47-6</td>
<td>2,40E+04</td>
</tr>
<tr>
<td>Di-n-butylether</td>
<td>142-96-1</td>
<td>57</td>
</tr>
<tr>
<td>Dichloro-diethylether</td>
<td>111-44-4</td>
<td>93</td>
</tr>
<tr>
<td>Isopropylbenzene</td>
<td>135-98-8</td>
<td>105</td>
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<tr>
<td>Ethynylbenzene</td>
<td>536-74-3</td>
<td>1,70E+07</td>
</tr>
<tr>
<td>Styrene</td>
<td>100-42-5</td>
<td>1,60E+07 1,00E+07</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>108-86-1</td>
<td>77</td>
</tr>
<tr>
<td>Nitroanisole</td>
<td>91-23-6</td>
<td>77</td>
</tr>
</tbody>
</table>

Fig. 5: GC with MS of the main peak; case: spill of unknown fluid
**Category II**

Fig. 6: Gas chromatogram with 5 mass spectra of the main compounds; case: explosion and emergency breakdown in the production of nitroanisole (emission of 10 tons reaction products)

**Category III**

Fig. 7: Gas chromatogram with 24 organic substances identified on the basis of their mass spectral patterns. Case: explosion and fire in a chemical store
mobile GC/MS system
wireless data transfer
transportation by helicopter
less than 30min
results in 5 min
fire-brigade rescue
sample
data transfer
fire GC/MS system
on-site
mobile

Fig. 8: Fast emergency response by mobile GC/MS