

IMS SOFTWARE DEVELOPMENTS FOR THE DETECTION OF CHEMICAL WARFARE AGENT

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Interference compounds like gasoline, diesel, burning wood or fuel etc. are present in common battlefield situations. These compounds can cause detectors to respond as a false positive or interfere with the detector's ability to respond to target compounds such as chemical warfare agents. To ensure proper response of the ion mobility spectrometer to chemical warfare agents, two special software packages were developed and incorporated into the Bruker RAID-1. The programs suppress interfering signals caused by car exhaust or smoke gases resulting from burning materials and correct the influence of variable sample gas humidity which is important for detection and quantification of blister agents like mustard gas or lewisite.

1. SUPPRESSION OF INTERFERENCE GASES

Many interference gases can be found in battle field scenarios. Typical compounds are nitrogen oxides, sulfur dioxide, chlorine, ammonia, formaldehyde or carbonmonoxide and carbondioxide. Others like gasoline, diesel or smoke gases from burning materials consist of many organic compounds. The latter cause "broad band" ion mobility spectra without any structure in most cases. Fig 1 shows a typical series of ion mobility spectra of burning fuel and wood.

In case of the above described spectra it is likely that standard ion mobility spectra analysis will come up with typical CWA peaks hidden somewhere under the broadband smoke ion mobility spectrum. Fig. 2 shows an evaluated spectrum of wood and fuel smoke gases recorded in the positive ion mode. After deconvolution, all nerve agents stored in the library are identified. This means a false positive alarm is given by the device if it is used in the stand alone mode.

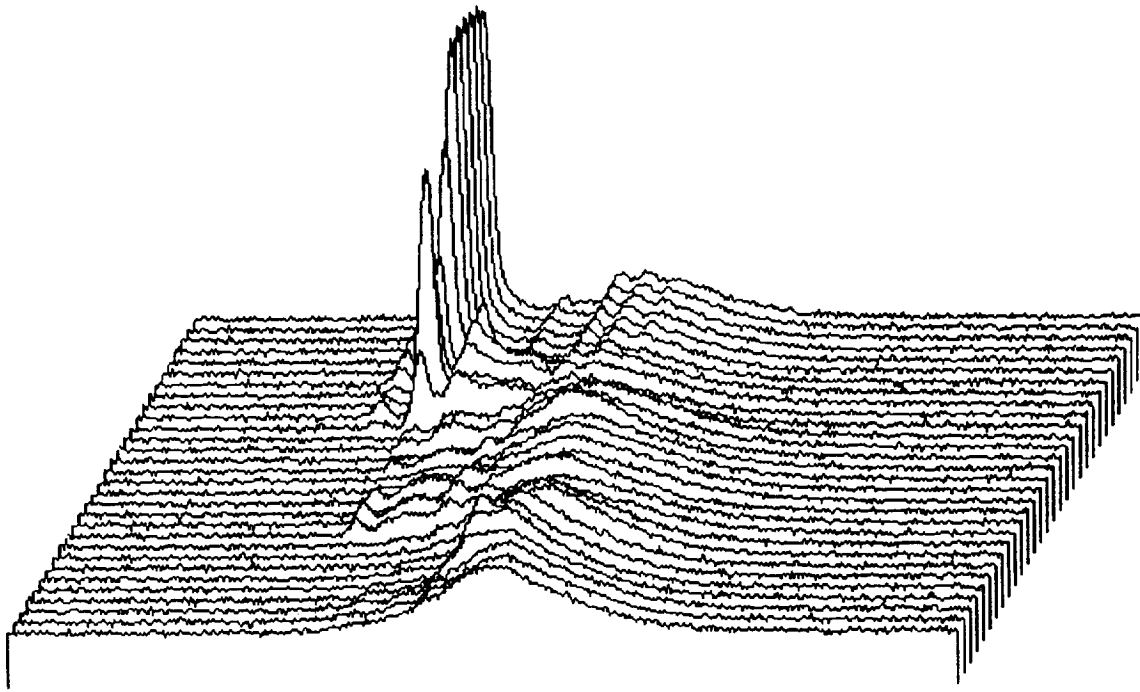


Fig. 1: Series of ion mobility spectra of positive ions obtained from smoke gases from burning wood and fuel

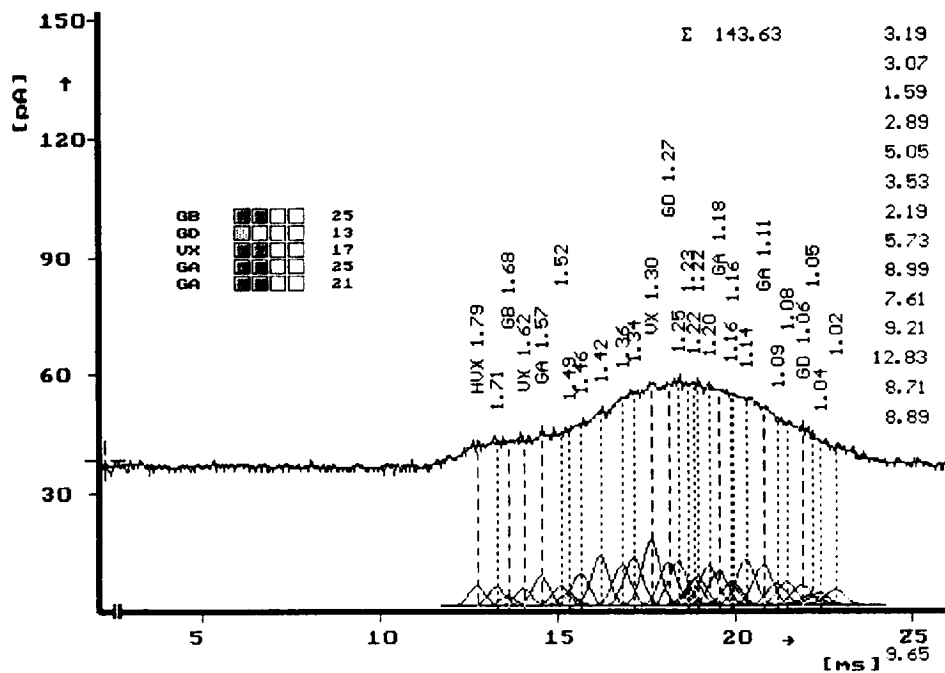


Fig. 2: Evaluated spectrum of smoke from burning wood and fuel: The nerve agents GA, GB, GD and VX were identified.

If vapours of nerve agents are added to smoke gases, the resulting ion mobility spectra show beside a broad peak discrete signals due to the formation of monomer and dimer ions of the phosphor organic compound. This means that substances with a high proton affinity are ionized by means of APCI processes also in presence of high amounts of smoke gases. A corresponding spectrum is shown in Fig. 3.

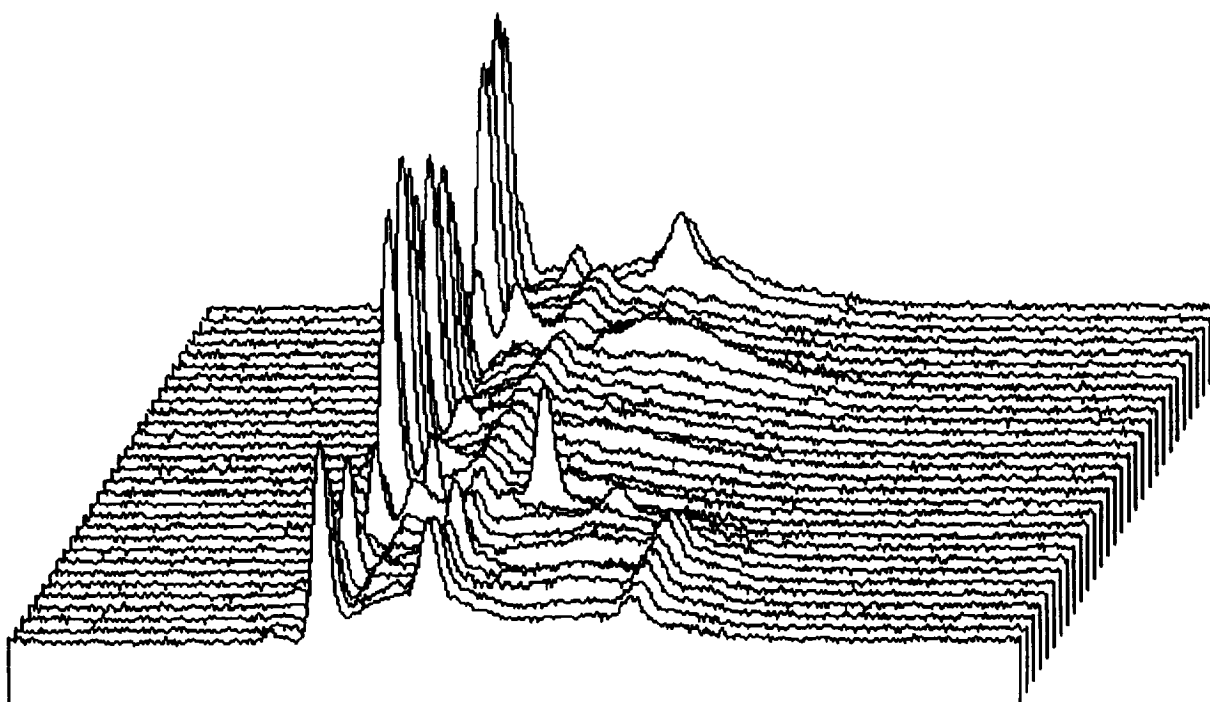


Fig. 3: Series of ion mobility spectra (positive ions) of smoke gases from burning fuel and isopropyldimethylphosphonate (IDMP)

These findings give the possibility to suppress broad signals caused by interfering substances. A special software package called "Partial Spectra Analysis" (PSA) uses base line correction and peak identification algorithms for the evaluation of ion mobility spectra. As shown in Fig. 4, the broad peak of the smoke gases is completely suppressed and the signals of the IDMP are identified by comparison with the data stored in the library.

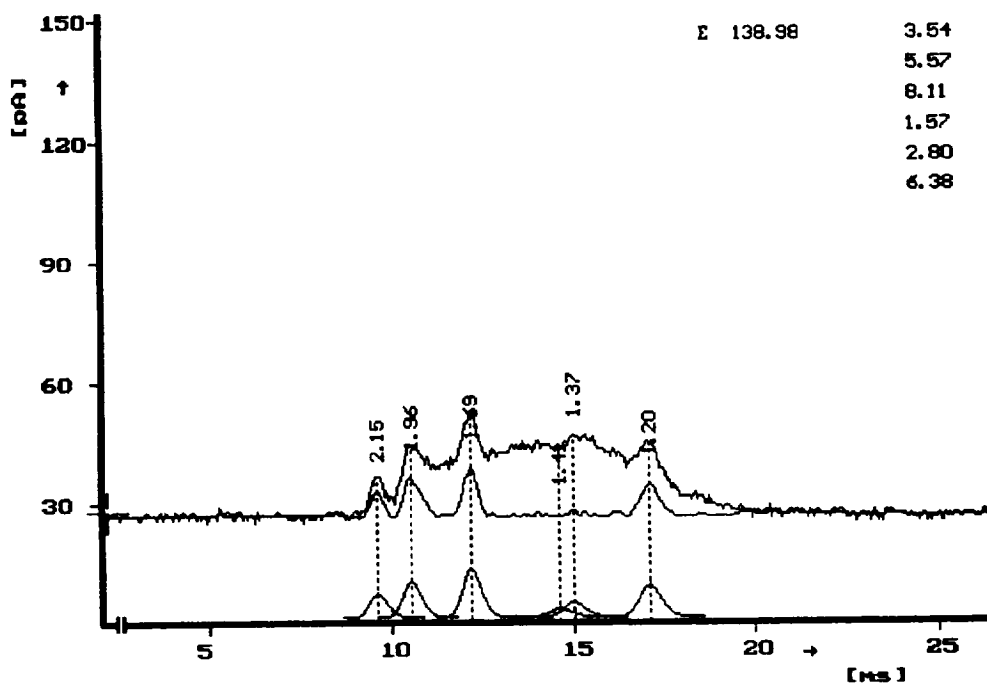


Fig. 4: Evaluation of an ion mobility spectrum (positive Ions) of a sample of smoke gases and IDMP

2. INFLUENCE OF HUMIDITY ON ION MOBILITY SPECTRA OF CHEMICAL WARFARE AGENTS

The ion mobility spectra of chemical warfare agents especially blister agents like sulfur mustard (HD) depend strongly on the relative humidity of the ambient air. Fig. 5 shows a series of ion mobility spectra of sulfur mustard recorded with different humidity of the sample gas. Beside the mustard gas signal, $(\text{HD})\text{O}_2^-$, peaks caused by Cl^- , $(\text{H}_2\text{O})_2\text{Cl}^-$ and reactant ions are shown in Fig. 5. Another weak signal can be assigned to thiodiclycol a hydrolysis product of sulfur mustard. The identification of sulfur mustard in the RAID-1 is based on the $(\text{HD})\text{O}_2^-$ and the Cl^- peak [2]. The formation of chloride ions or chloride water clusters is well known for chlorinated organic compounds [1]. In the case of mustard gas, this dissociative charge transfer reaction depends on the humidity of the sample gas. With increasing relative humidity the intensity of the $(\text{HD})\text{O}_2^-$ signal decreases and the intensity of the chloride signal increases. Fig. 6 shows a three-dimensional plot the signal intensities with varying concentration and humidity.

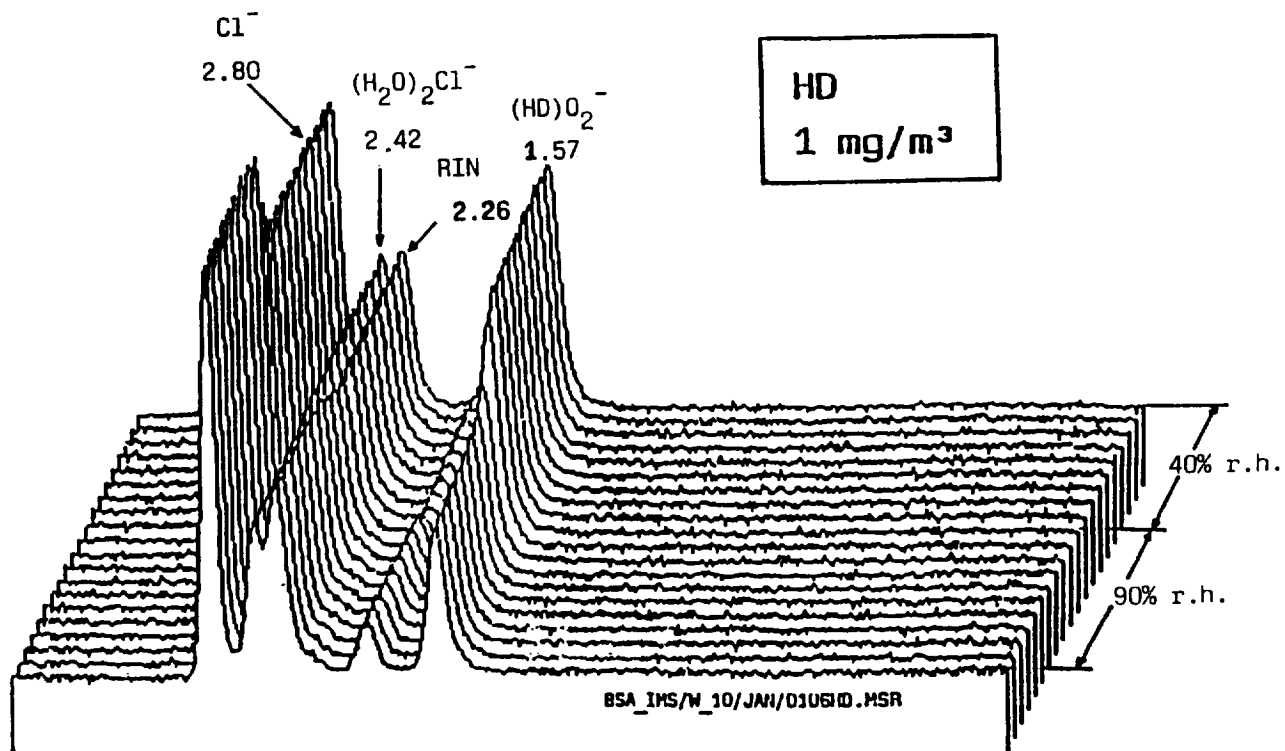


Fig. 5: Series of ion mobility spectra of sulfur mustard recorded at different humidities

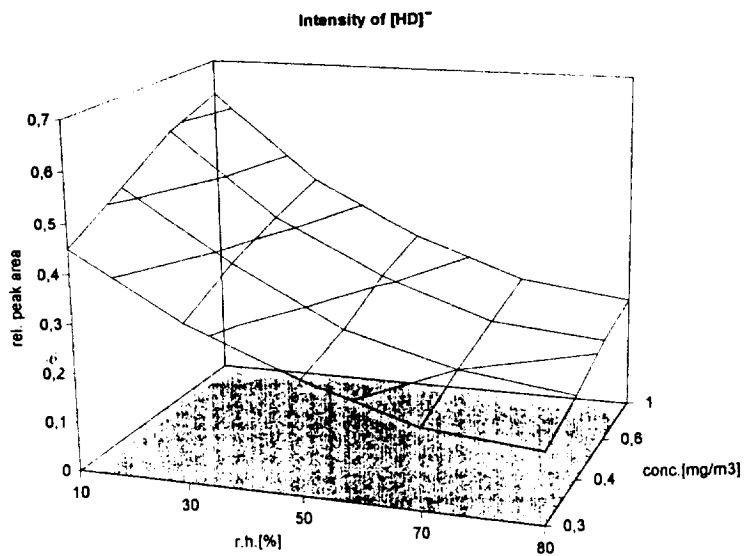


Fig 6. Dependence of the HD signal intensity on humidity and concentration.

The strong dependence of the HD signal on humidity causes strong deviations in the estimated concentrations if a calibration curve, recorded, e.g., for a medium humidity, is used for quantification. However, the reaction kinetics of the observed hydrolyses reactions of suflur mustard can be described regarding the reaction region of the ion mobility spectrometer as a "tube" reactor. On the basis of this model concentrations of HD can be calculated using the HD and the Cl⁻ peak areas. The result is shown by means of calibration curves for HD calculated without and with hydrolysis correction (see Fig. 7). Interferences of other chlorinated compounds which also form Cl⁻ ions in the ion mobility spectrometer are considered by this model.

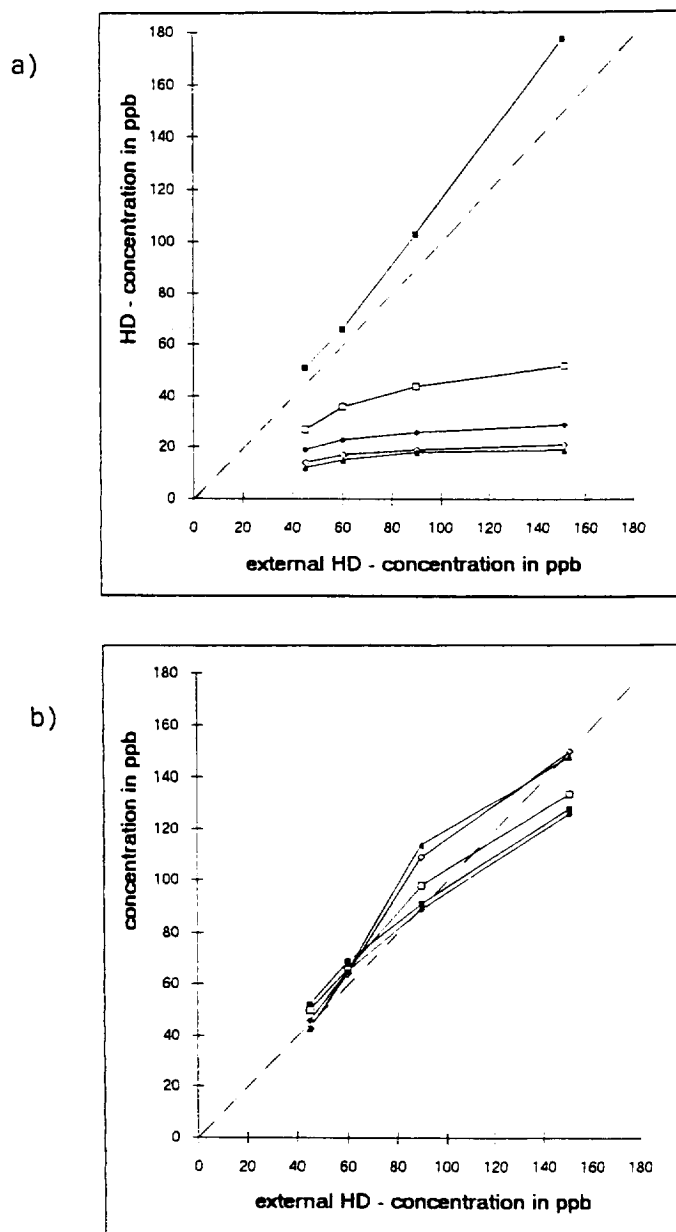


Fig. 7: Calibration curves for HD obtained for humidities of 10(●), 30(□), 50(◆), 70(◇) and 80% (▲). Fig 7b shows the calibration curves calculated taking into account the hydrolysis of HD

3. LITERATURE

- [1] Miller, D.A. and Grimsrud, E.P., *Anal. Chem.* 51 (1979) 851.
- [2] Starrock, V., Krippendorf, A. and Döring, H.-R. Second International Workshop on Ion Mobility Spectrometry, Quebec City, Canada, 15.-18.8.1993.