



Application Note 120427
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GD-MS Trace Analysis of volatile organic compounds in ambient air

A) Introduction

Trace analysis of volatile organic compounds (VOCs) by mass spectrometry (MS) is usually performed by Electron impact (EI) or classical Chemical Ionization techniques (CI). In these cases the matrix gas is introduced by a heated capillary interface and the matrix gas amount used for MS analysis is in the order of 0.3 -1 ml/min. Special technologies as proton transfer reaction mass spectrometry (PTR-MS) and related selected ion-flow-tube mass spectrometry (SIFT-MS) play a role, too. For mass spectrometric analysis of polar and non volatile molecules in liquid matrices the established method of choice are API-MS techniques with dedicated interfaces. We have recently reported (Application Note 120329) about a specific ESI-MS system, suitable for the direct analysis of low atomic number elements. We also reported (Application Note 120419) about this API-MS system used for the direct analysis of volatile organic compounds in ambient air by the application of Atmospheric Pressure Corona Discharge Ionization (APCI). In addition we were interested to evaluate the same system for the **direct analysis of volatile organic compounds in ambient air by the application Glow Discharge Ionization (GD-MS)**. No GC separation and purge and trap or selective membrane enrichment techniques have been applied.

B) Summary

As previously reported analyses have been performed with the experimental version of a **new bench-top double focusing mass spectrometer of Mattauch-Herzog type**. The dedicated and miniaturized system is based on the original AMD QuAS³AR Technology. Emphasis has been placed to the analysis of volatile organic compounds in the gas phase, logically producing mass spectra of low molecular weight compounds. Within the scope of the reported semi-quantification methods no official certified procedures were applied, since the aim here was to achieve orientating results for possible future applications.

The existing API Interface useable for ESI-MS, APCI-MS, GD-MS and the mass analyzer are integrated with a multi-stage turbo pumping system. It has been demonstrated again that the special features of a small double focusing mass spectrometer regarding peak shape, mass resolution and abundance sensitivity are of significant advantage for the qualitative and quantitative analysis of ions in the low mass range.

Semi-Quantitative Trace Analyses of a number of VOCs (typically used as solvents) in ambient air were performed, exemplarily. Limits of detection (LOD) in the **upper ppb range** were achieved for a number of these compounds **in full scan mode**. **SIM techniques** extended the LOD to the **low ppb range**. The results depend on the ionization efficiency and the production of quasi-molecular ions, respectively on the low number of key fragments which is typical for a Chemical Ionization process.

The achieved results here using GD-MS applications on VOCs in ambient air indicate the usefulness of the method for trace analysis in gaseous matrices. This may be of interest for **environmental and process analysis** as well as for medical research applications in a wide range of concentrations. Depending on the complexity of the gaseous matrix the method may be applied without chromatographic separation (GC). In this context it is of specificity advantage that either mainly quasi-molecular ions or only a few intense key fragment ions are formed.



C) Methodology

C.1 Mass spectrometer

The mass analyzer was a miniaturized dedicated version of the AMD QuAS³AR (Quasar070206.pdf) double focusing system, equipped with a universal API Interface in GD mode (GD-MS system). System details are not reported here since an evaluation model was used for the experiments.

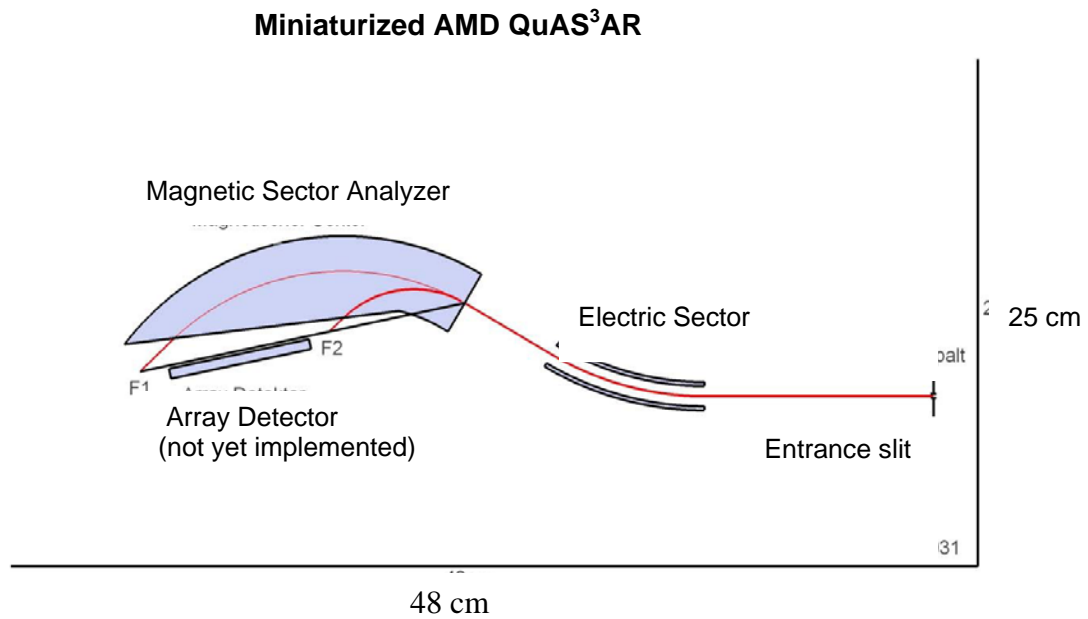
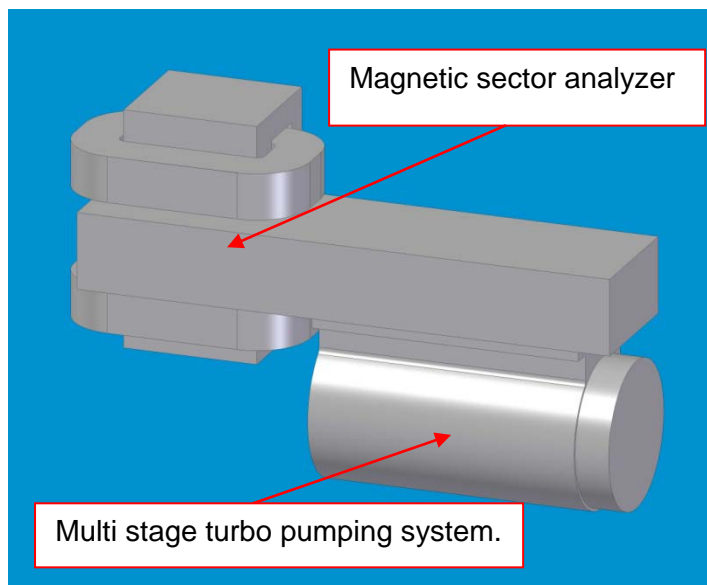


Fig. 1 Scheme of the ion optics and physical size of the bench-top double focusing MS analyzer



The **miniaturized AMD QuAS³AR** is based on the original AMD QuAS³AR Technology as a multifunctional high performance system and previously described in a system description: SD040617_ AMD Quasar.pdf.

The new current miniaturized version is downsized significantly, dedicated to low mass resolution and API-Interfacing, currently

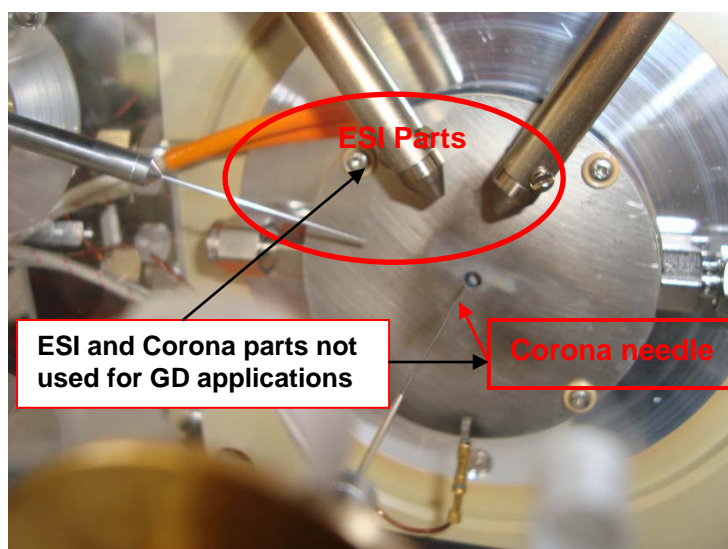
However, it incorporates the significant advantages of magnetic sector mass spectrometers for low mass ions regarding resolution and abundance sensitivity

Fig. 2 CAD Design of the **Miniaturized AMD QuAS³AR** API-MS system



C.2 API-MS Interface

As a dedicated API-MS (APCI or ESI) bench-top system the interface and the mass analyzer are mounted on a multistage turbo pumping system. The system is fully optimized for highest transmission of low mass ions through the interface to the MS detector and in so far relevant for the applications reported here in GD-MS mode for **trace analysis of VOCs in ambient air**.



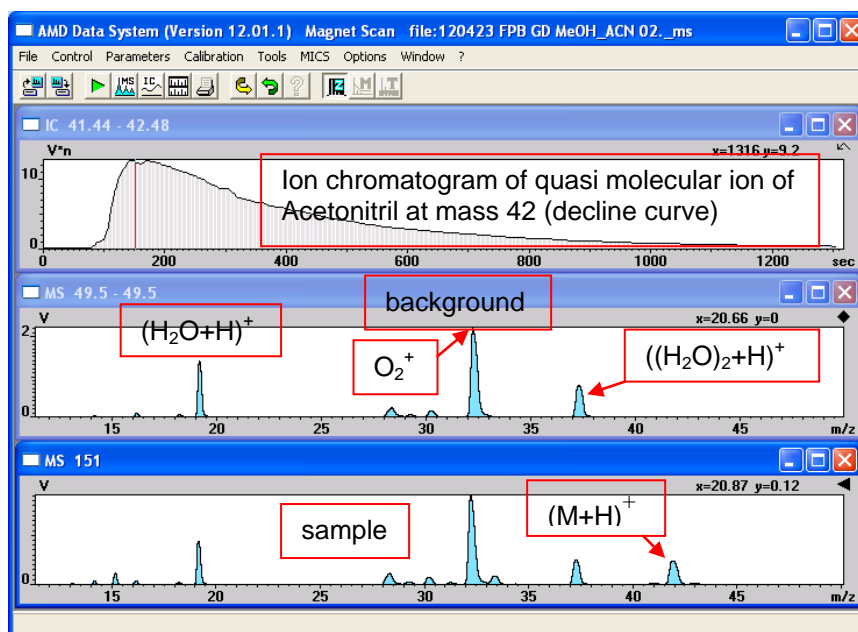
The **API ion source** of the miniaturized AMD QuAS³AR dedicated for APCI (ESI)-MS applications consists of an API room including nebulizer assisted sprayer and hot air pipes for desolvation assistance in ESI mode, which are **not** used for the GD-MS experiments described here. Also the corona discharge needle mounted in front of the counter electrode orifice was **not** used.

The multi-stage vacuum interface is integrated with the analyzer multi-stage turbo pumping system.

Glow discharge was initiated in the first stage at a pressure of 1 mbar

Fig. 3 API-MS interface in GD-MS mode for multiple applications; front view of the miniaturized API-MS Evaluation Model

C.3 GD-MS measurement procedure for VOC analysis in ambient air



Analysis Details C.3

Matrix: ambient air

Sample: Acetonitril

Sample amount: 1 μ l

Sample introduction:

Syringe injection in API room (2 l ambient air volume) at 20 °C air temperature

Ionization: **Glow Discharge** at 1 mbar in stage 1 of the API interface

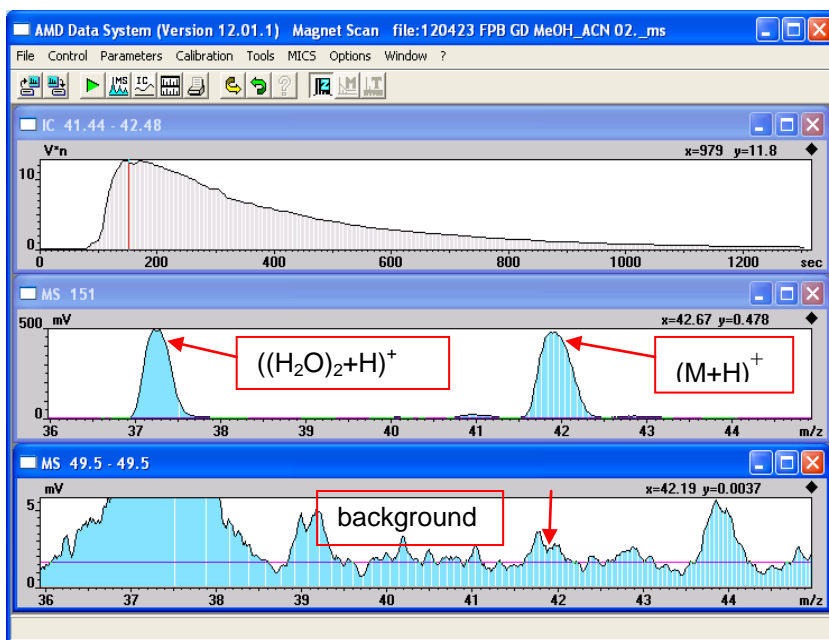
Sample concentration: after injection and evaporation

$c = 9 \times 10^{-4} \text{ g} / 2.6 \text{ g} = 3.46 \times 10^{-4}$
 $c = 346 \text{ ppm}$

API Interface air intake:

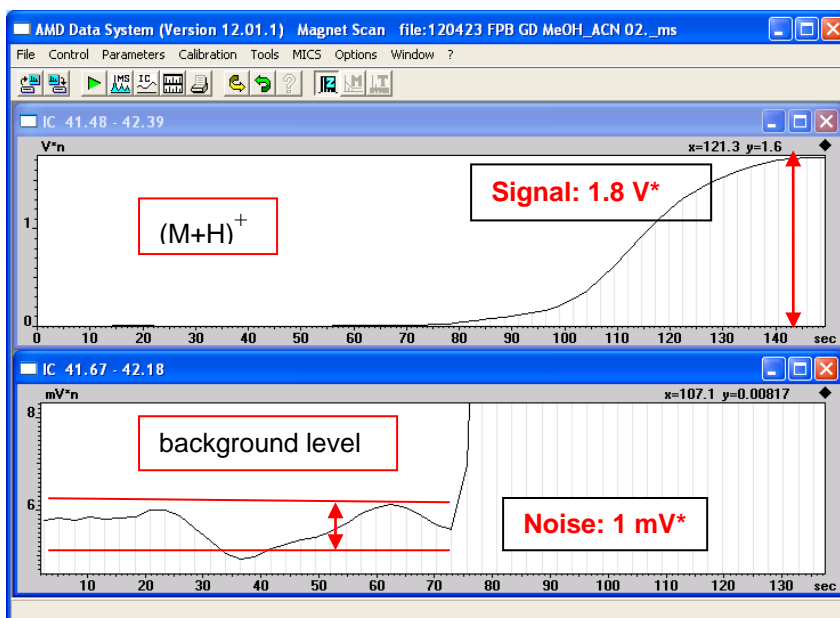
0.4 l/min from API room

Fig. 4 GD-MS mass spectra of **Acetonitril** and background in ambient air. Water cluster and oxygen matrix ions form the background in all spectra (see also below)



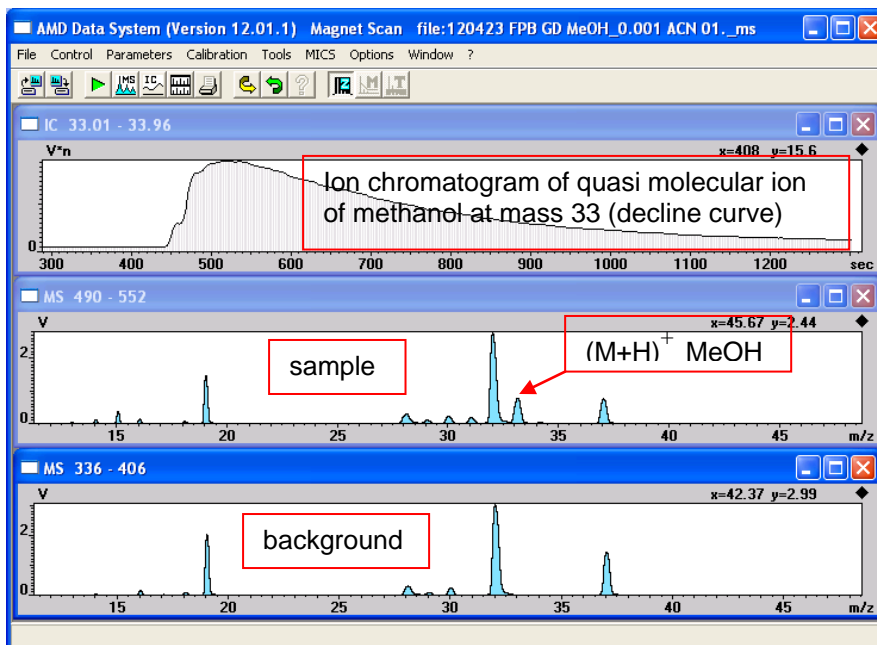
Analysis Details C.3 cont'd
Scan method: magnet scan,
Mass resolution: 60 at 10% valley with fixed slits
Scan Speed: 2 sec/dec
Measuring time per peak: 18 msec
Data acquisition: single scan or raw data accumulation
Detector: post acceleration and Channeltron type SEM
Data System: AMD Version 12.01.1
Analysis time:
 Data were recorded over the a time of about 1300 sec until the sample concentration in the API room was at detection limit

Fig. 5 GD-MS partial mass spectrum of **Acetonitril** in ambient air



Analysis Details C.3 cont'd
Limit of Detection (LOD)
Matrix: ambient air
Sample: **Acetonitril**
Sample amount: 1 μ l
Sample introduction: Injection in API room as before
Ionization: **Glow discharge** as before
Sample concentration after injection and evaporation
 $c = 9 \times 10^{-4} \text{ g} / 2.6 \text{ g} = 3.5 \times 10^{-4}$
 $c = 350 \text{ ppm}$
API Interface air intake: as before
S/N: 1800:1
LOD: $\approx 600 \text{ ppb}$ (single scan)

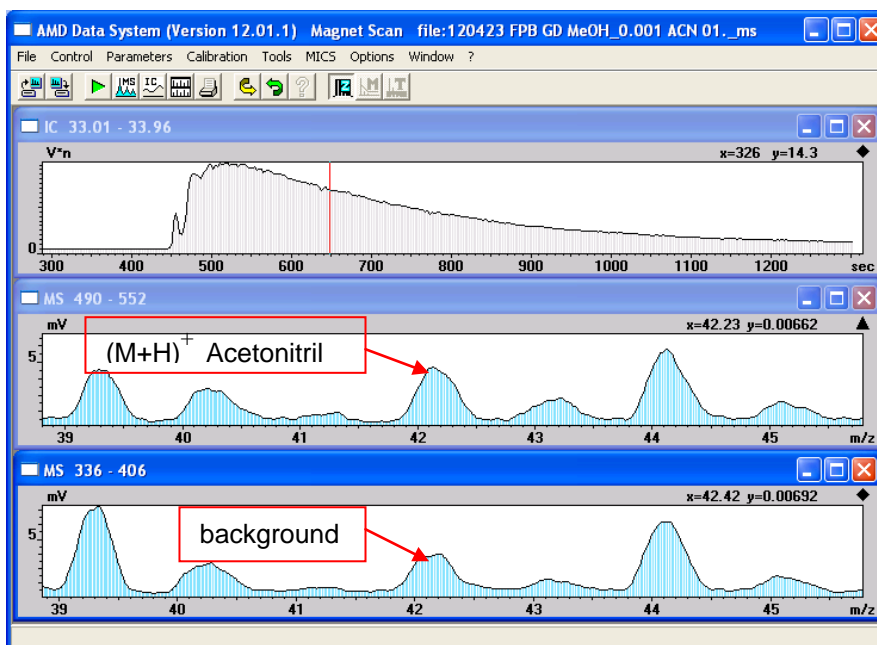
Fig. 6 GD-MS ion chromatogram of quasi-molecular ion of **Acetonitril** in ambient air



Analysis Details C.3 cont'd

Matrix: ambient air
Sample: Acetonitril diluted in Methanol 1:1000
Sample amount: 1 nl in 1 μ l Methanol
Sample introduction: as before
Ionization: as before
Sample concentration after injection and evaporation
 $c = 9 \times 10^{-7} \text{ g} / 2.6 \text{ g} = 3.5 \times 10^{-7}$
 $c = 350 \text{ ppb}$
API Interface air intake: as before

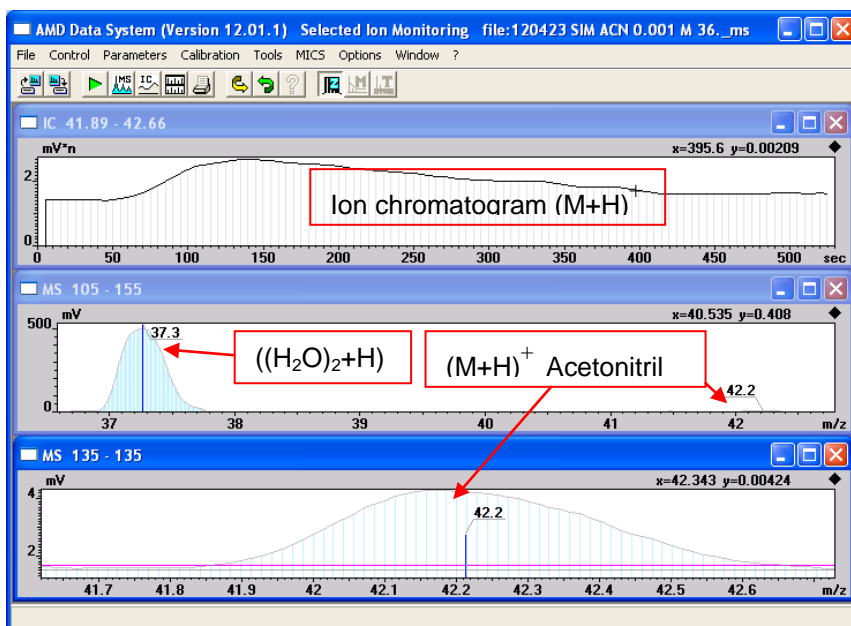
Fig. 7 GD-MS accumulated mass spectra of Acetonitril (diluted 1:1000 in MeOH) in ambient air (sample peak at mass 42 not visible here but see fig. 8 below)



Analysis Details C.3 cont'd

Limit of Detection (LOD)
Matrix: ambient air
Sample: Acetonitril diluted in Methanol 1:1000
Sample amount: 1 nl in 1 μ l Methanol
Sample introduction: as before
Ionization: as before
Sample concentration after injection and evaporation
 $c = 9 \times 10^{-7} \text{ g} / 2.6 \text{ g} = 3.5 \times 10^{-7}$
 $c = 350 \text{ ppb}$
API Interface air intake: as before
LOD: $\approx 100 \text{ ppb}$ (accumulated scans)

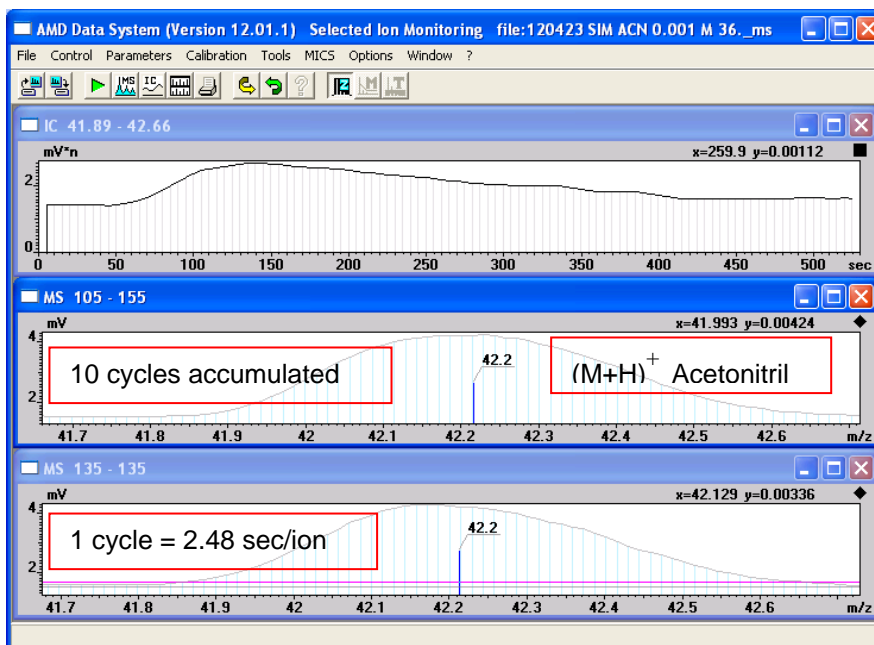
Fig. 8 GD-MS accumulated mass spectra of Acetonitril (diluted 1:1000 in MeOH) in ambient air at limit of detection



**Analysis Details C.3 cont'd
Selected Ion Monitoring (SIM)**

Matrix: ambient air
Sample: Acetonitril diluted in Methanol 1:1000
Sample amount: 1 nl in 1 µl Methanol
Sample introduction: as before
Ionization: as before
Sample concentration after injection and evaporation
 $c = 9 \times 10^{-7} \text{ g} / 2.6 \text{ g} = 3.5 \times 10^{-7}$
 $c = 350 \text{ ppb}$
API Interface air intake: as before

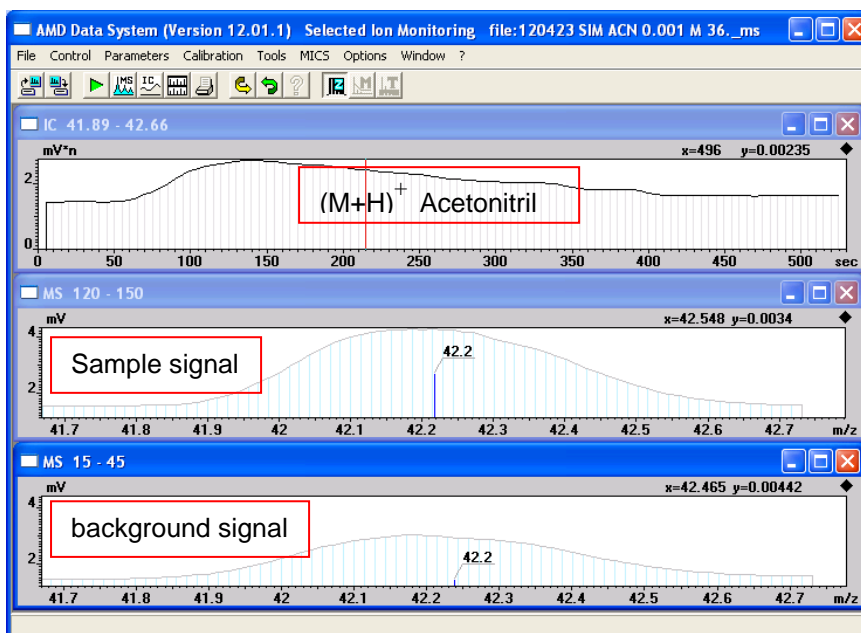
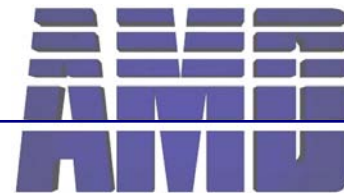
Fig. 9 GD-MS Quasi-molecular ion signal of Acetonitril (diluted 1:1000 in MeOH) in ambient air (SIM mode)



**Analysis Details C.3 cont'd
Selected Ion Monitoring (SIM)**

Matrix: ambient air
Sample: Acetonitril diluted in Methanol 1:1000
Sample amount: 1 nl in 1 µl Methanol
Sample introduction: as before
Ionization: as before
Sample concentration after injection and evaporation
 $c = 9 \times 10^{-7} \text{ g} / 2.6 \text{ g} = 3.5 \times 10^{-7}$
 $c = 350 \text{ ppb}$
API Interface air intake: as before

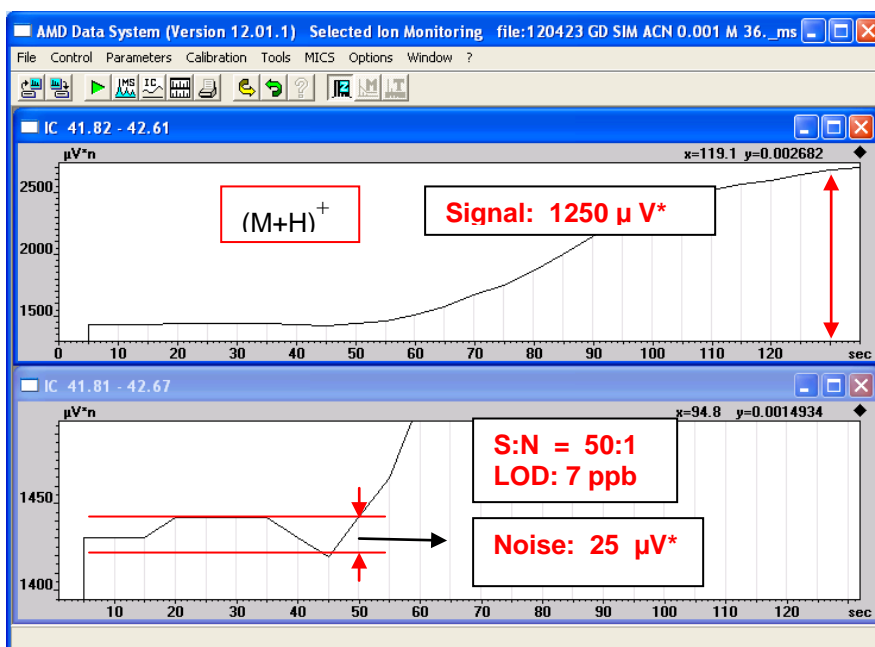
Fig. 10 GD-MS Quasi-molecular ion signal of Acetonitril (diluted 1:1000 in MeOH) in ambient air (SIM mode, cycle time for 2 ions = 5 sec)



Analysis Details C.3 cont'd Selected Ion Monitoring (SIM)

Matrix: ambient air
Sample: Acetonitril diluted in Methanol 1:1000
Sample amount: 1 nl in 1 μ l Methanol
Sample introduction: as before
Ionization: as before
Sample concentration after injection and evaporation
 $c = 9 \times 10^{-7} \text{ g} / 2.6 \text{ g} = 3.5 \times 10^{-7}$
 $c = 350 \text{ ppb}$
API Interface air intake: as before

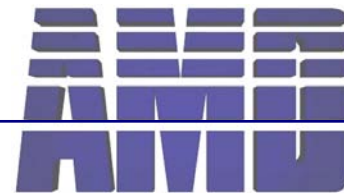
Fig. 11 GD-MS Quasi-molecular ion signal of Acetonitril (diluted 1:1000 in MeOH) in ambient air (SIM mode) at limit of detection



Analysis Details C.3 cont'd Selected Ion Monitoring (SIM) Limit of Detection (LOD)

Matrix: ambient air
Sample: Acetonitril diluted in Methanol 1:1000
Sample amount: 1 nl in 1 μ l Methanol
Sample introduction: as before
Ionization: as before
Sample concentration after injection and evaporation
 $c = 9 \times 10^{-7} \text{ g} / 2.6 \text{ g} = 3.5 \times 10^{-7}$
 $c = 350 \text{ ppb}$
API Interface air intake: as before
LOD: 7 ppb (SIM mode)

Fig. 11 GD-MS Quasi-molecular ion chromatogram of Acetonitril (diluted 1:1000 in MeOH) in ambient air (SIM mode) at limit of detection



C.3.1 Short-form summary of the applied methodology and the result for GD-MS analysis of Acetonitril (Fig. 4 -12) in ambient air

The compound has been used as an example to demonstrate the measurement procedures for **GD-MS trace analysis of a volatile organic compound in ambient air**. The rudimentary method used here should give some orientating results for the application of a possible analytical procedure under more sophisticated sample preparation and sample introduction methodology. The counter electrode/nozzle part of the API interface and the API room with ambient air were kept at room temperature.

At higher concentrations the volatile compound was injected by a syringe directly into the air of the API room. As described in figures 4 - 6 above an amount of 1 μl Acetonitril was injected and evaporated immediately. The API interface air intake of 0.4 l/min diluted the evaporated sample in the ambient air of the API room (2 l volume) by continuous air exchange from outside. The immediate sample concentration was calculated (see fig. 4) by the ratio of evaporated sample quantity to the air quantity in the API room. According to the decline function about 40% of the sample at higher concentrations may be adsorbed on the inner walls and is desorbing, slowly. A **single scan** resulted in a Limit of Detection (LOD) of **600 ppb** (scan cycle 2.5 sec).

At lower concentrations the volatile target compound was diluted 1:1000 in Methanol and 1 μl Methanol (containing 1 nl Acetonitril) was injected by a syringe directly into the air of the 2l API room. In this case a Limit of Detection of **100 ppb** (see fig. 7-8) was reached for **24 accumulated spectra** (analysis time: 60 sec).

In **selected ion monitoring** (SIM) mode the detection limit (see fig 9-12) was **7 ppb** (analysis time: 35 sec). As reported for APCI-MS analyses, previously, it turns out that the individual background signals are the limiting factors (chemical noise) while the sensitivity of the method (number of ions created) would allow even lower limits of detection.

Routine applications will require a controlled introduction (gas pumping) of the air matrix containing the analyte gas sample into the counter electrode/nozzle zone of the API interface. The use of external volumes for the sample and the clean flushing gas as well as corresponding switch valves will be mandatory for efficient and precise analyses.

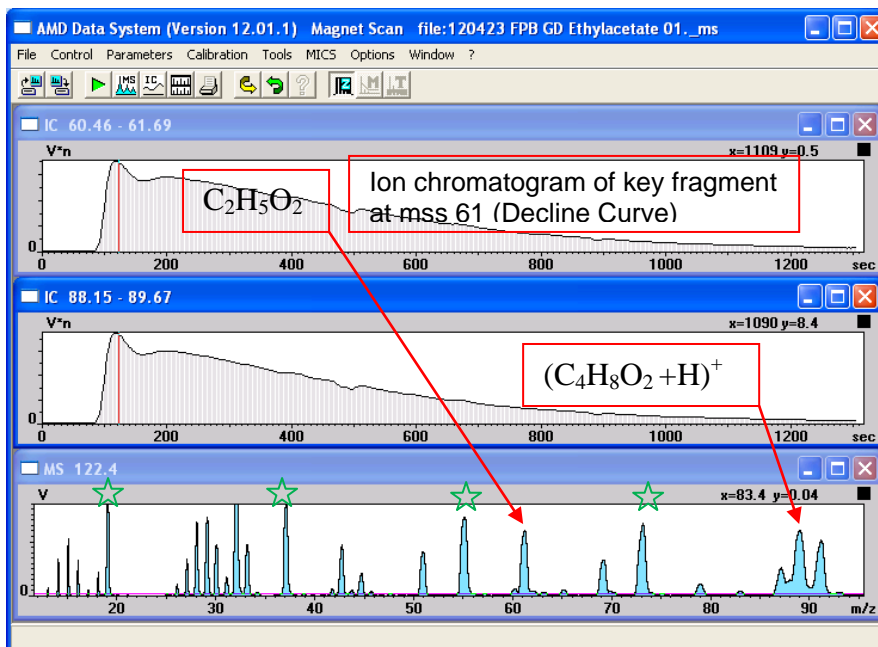
All measurements were performed on laboratory ambient air with an approx. water content of 50 %. The results indicate that water acts as a reagent gas which is the basis for the method. The spectra obtained are very similar to those of APCI or classical CI methodologies. The formation of cluster ions of water accompanies the GD-MS method used here.

The possibility of using dry air or any other dry matrix gas and exchanging the water by another reagent gas (Methane for instance) for VOC analysis was not investigated within the scope of this application note.

Results of some more VOC GD-MS measurements are described in the following figures below yielding similar LOD numbers as for Acetonitril. It will be demonstrated (Isopropanol example) that short analysis times can be reached for one sample by more rapid exchange of the ambient air sample as used in our experiments, usually. This may be of importance for automated routine analysis, if applicable.



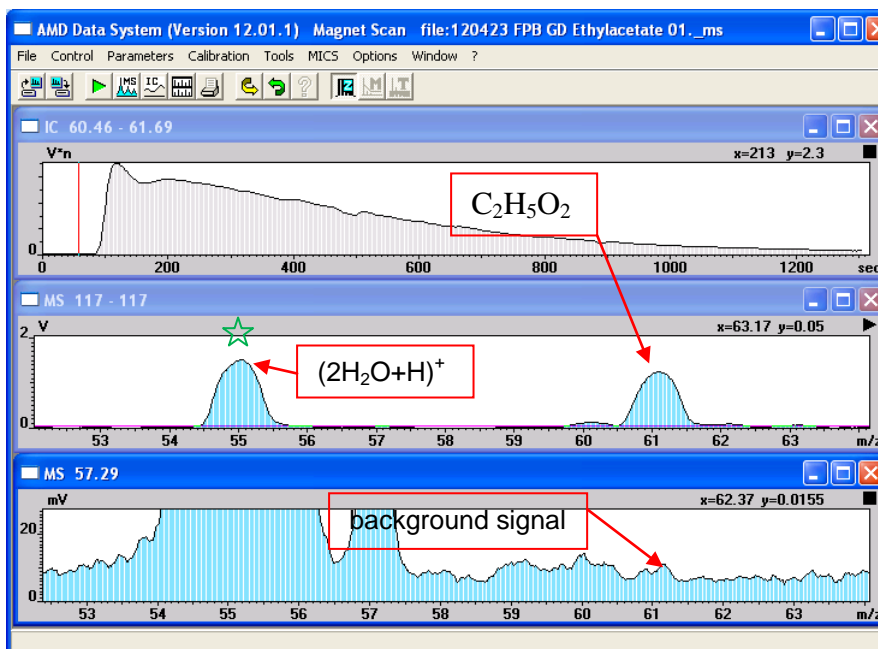
D. GD-MS trace analysis of Ethylacetate in ambient air



Analysis Details D.

Matrix: ambient air
Sample: Ethylacetate
Sample amount: 1 µl
Sample introduction: as before
Ionization: as before
Sample concentration after injection and evaporation
 $c = 9 \times 10^{-4} \text{ g} / 2.6 \text{ g} = 3.5 \times 10^{-4}$
 $c = 350 \text{ ppm}$
API Interface air intake: as before

Fig. 12 GD-MS mass spectrum of Ethylacetate in ambient air (full scan including water cluster ☆ formation)



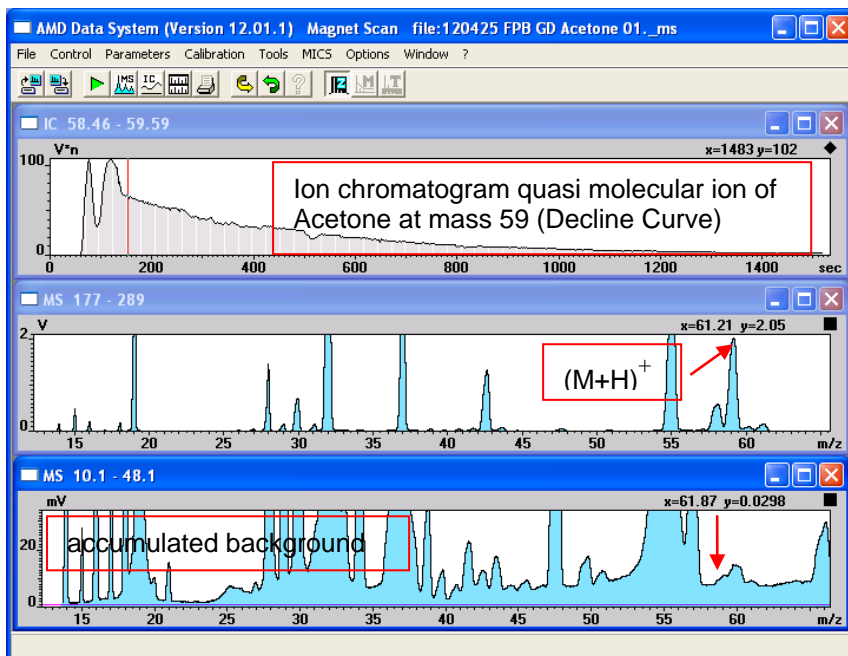
Analysis Details D. cont'd

Limit of Detection (LOD)
Matrix: ambient air
Sample: Ethylacetate
Sample amount: 1 µl
Sample introduction: as before
Ionization: as before
Sample concentration after injection and evaporation
 $c = 9 \times 10^{-4} \text{ g} / 2.6 \text{ g} = 3.5 \times 10^{-4}$
 $c = 350 \text{ ppm}$
API Interface air intake: as before
Dynamic range : 500:1
LOD estimated: 1 ppm (full scan)

Fig. 12 GD-MS partial mass spectrum with key fragment of Ethylacetate in ambient air



E. GD-MS trace analysis of Acetone in ambient air

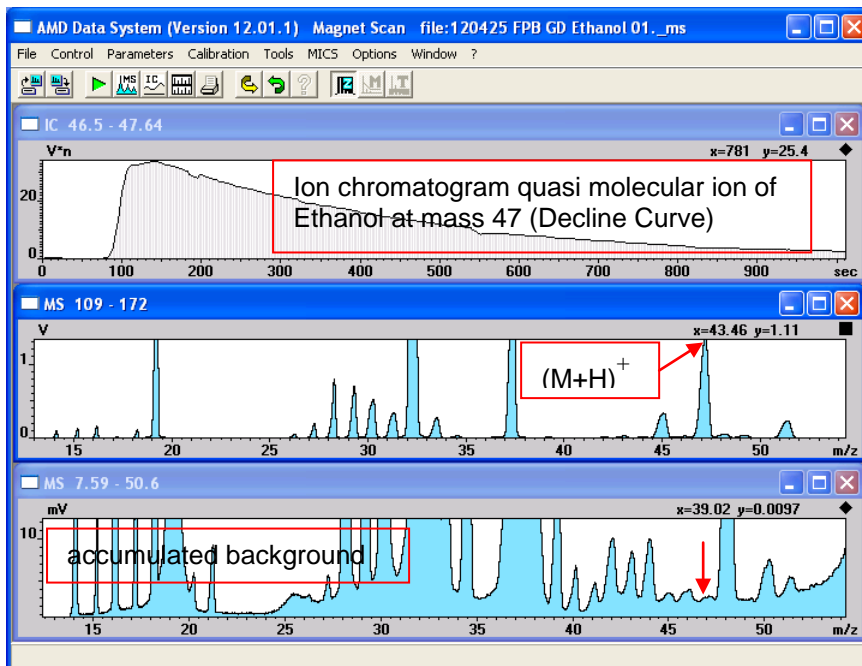


Analysis Details E.

Matrix: ambient air
Sample: Acetone
Sample amount: 1 μ l
Sample introduction: as before
Ionization: as before
API Interface air intake as before
Sample concentration (definition as before)
 $c = 8 \times 10^{-4} \text{ g} / 2.6 \text{ g} = 3 \times 10^{-4}$
 $c = 300 \text{ ppm}$
Dynamic range: 1:500 (4 mV peak detectable)
LOD: \approx 600 ppb (accumulated scans)

Fig. 13 GD-MS accumulated mass spectra of Acetone in ambient air.

F. GD-MS trace analysis of Ethanol in ambient air



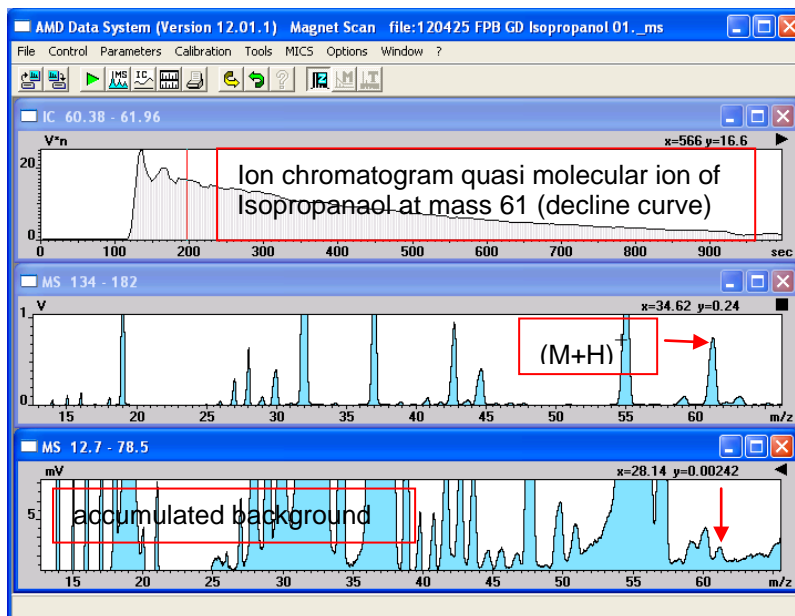
Analysis Details E.

Matrix: ambient air
Sample: Ethanol
Sample amount: 1 μ l
Sample introduction: as before
Ionization: as before
API Interface air intake as before
Sample concentration (definition as before)
 $c = 8 \times 10^{-4} \text{ g} / 2.6 \text{ g} = 3 \times 10^{-4}$
 $c = 300 \text{ ppm}$
Dynamic range: 1:500 (2 mV peak detectable)
LOD: \approx 600 ppb (accumulated scans)

Fig. 14 GD-MS accumulated mass spectra of Ethanol in ambient air.



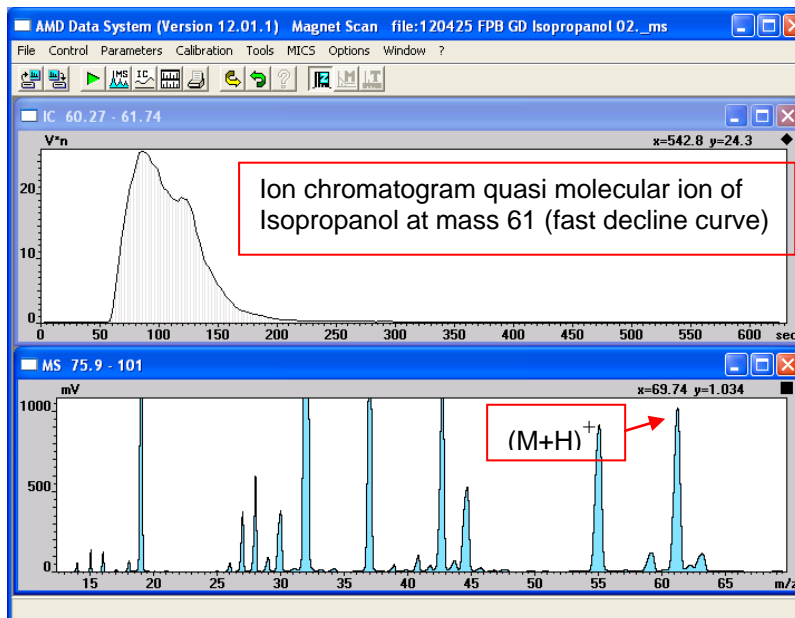
G. GD-MS trace analysis of Isopropanol in ambient air



Analysis Details E.

Matrix: ambient air
Sample: Isopropanol
Sample amount: 1 μ l
Sample introduction: as before
Ionization: as before
API Interface air intake as before
Sample concentration (definition as before)
 $c = 8 \times 10^{-4} \text{ g}/2.6 \text{ g} = 3 \times 10^{-4}$
 $c = 300 \text{ ppm}$
Dynamic range: 1:300 (3 mV peak detectable)
LOD: $\approx 1 \text{ ppm}$ (accumulated scans)

Fig. 15 GD-MS accumulated mass spectra of Isopropanol in ambient air.



Analysis Details E.

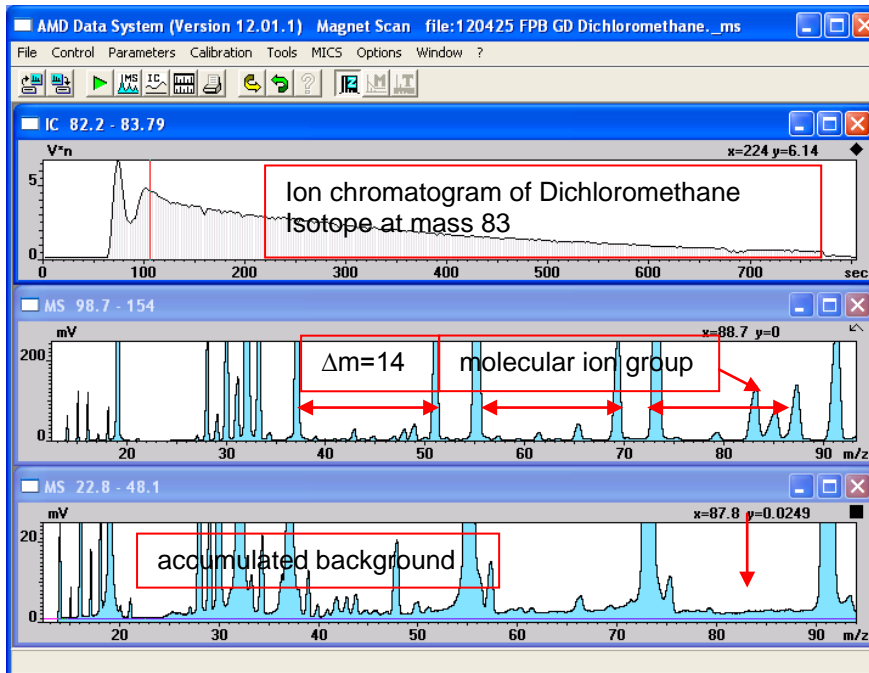
Matrix: ambient air
Sample: Isopropanol
Sample amount: 1 μ l
Sample introduction: as before
Ionization: as before
API Interface air intake as before
Sample concentration (definition as before)
 $c = 8 \times 10^{-4} \text{ g}/2.6 \text{ g} = 3 \times 10^{-4}$
 $c = 300 \text{ ppm}$
LOD: $\approx 1 \text{ ppm}$ (same as above)

Fig. 16 GD-MS accumulated mass spectra of Isopropanol in ambient air at shortened analysis time



H. GD-MS trace analysis of volatile halogen compounds in ambient air

H.1 GD-MS trace analysis of Dichloromethane in ambient air



Analysis Details H.2

Matrix: ambient air

Sample: Dichloromethane

Sample amount: 1 μ l

Sample introduction:
as before

Ionization: as before

API Interface air intake
as before

Sample concentration

(definition as before)

$$c = 1.3 \times 10^{-3} \text{ g}/2.6 \text{ g} = 5 \times 10^{-4}$$

$$c = 500 \text{ ppm}$$

Dynamic range:

1:200 (1 mV peak detectable)

LOD: \approx 2.5 ppm

(accumulated scans)

Fig. 17 GD-MS accumulated mass spectra of Dichloromethane in ambient air. CH_2 is attached to the water clusters