



Application Note 120419
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APCI-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. In addition we were interested to evaluate the capabilities of this system for the direct analysis of volatile organic compounds in ambient air by the application of Atmospheric Pressure Corona Discharge Ionization (APCDI). The ambient air acts as reagent gas in this case, therefore the term APCI may be used. No GC separation and purge and trap techniques have been applied.

B) Summary

Analyses have been performed with the experimental version of a new bench-top double focusing mass spectrometer. 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 or APCI-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 which would improve sensitivity and extend the LOD to the low ppb range have not been applied because specificity was considered to be more important in this case. 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 Chemical Ionization. The influence of scan methodologies including raw data accumulation techniques on the quality of the results and analysis time are also described.

The achieved results of APCI-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 or process analysis in a wide range of concentrations. Dependent 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 an API Interface in APCI mode (APCI-MS system). System details are not reported here since an evaluation model was used for the experiments.

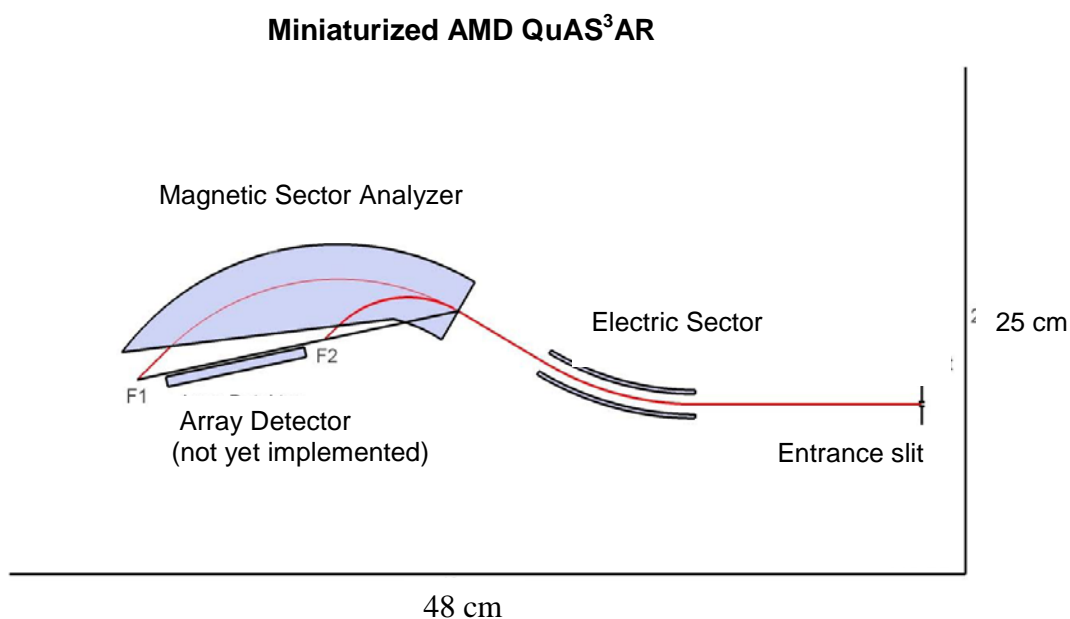
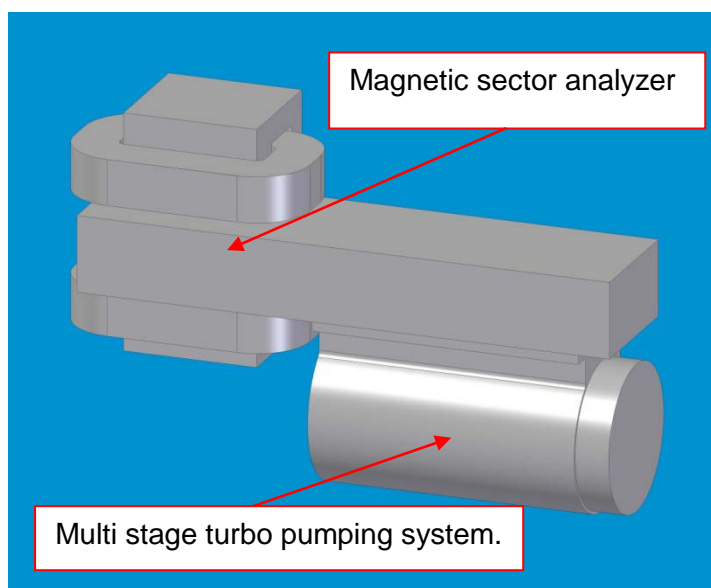


Fig. 1 Scheme of the ion optics and physical size of the bench-top double focusing MS analyzer



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 only.

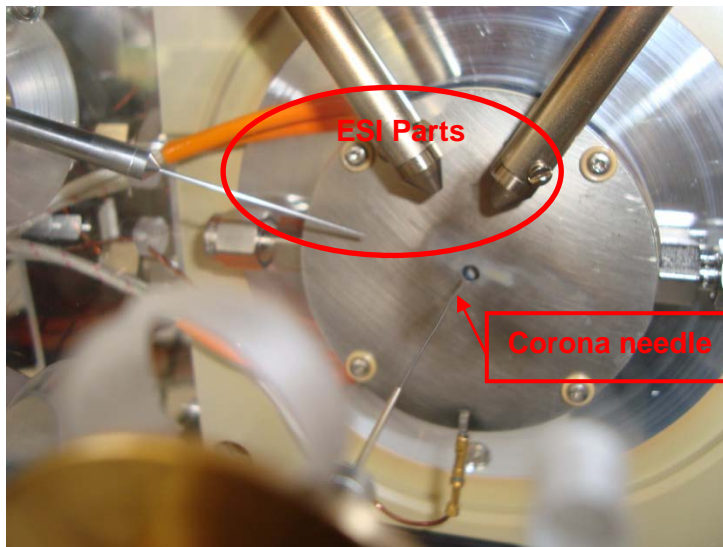
However, it incorporates the significant advantages of magnetic sector mass spectrometers for low mass ions regarding resolution and abundance sensitivity

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, specifically **dedicated to trace analysis of VOCs in ambient air**.



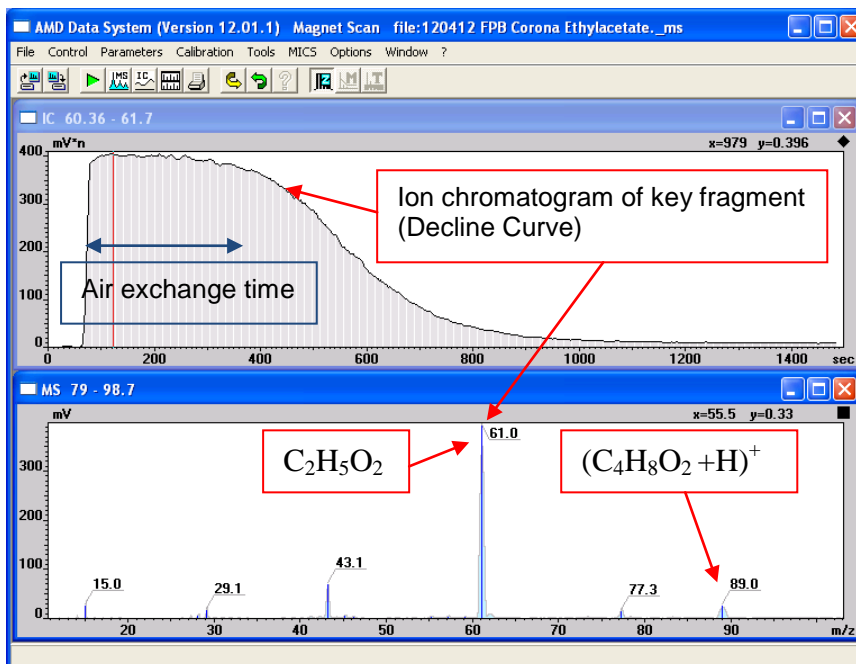
The **API ion source** of the miniaturized AMD QuAS³AR dedicated for APCI (ESI)-MS applications consists of an API room including nebulizer assisted sprayer and hot air pipes for desolvation assistance in ESI mode, which are **not** used for the APCI experiments described here.

A corona discharge needle is mounted in front of the counter electrode orifice.

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

Fig. 3 APCI (ESI)-MS interface front view of the miniaturized API-MS Evaluation Model

C.3 Measurement procedure for VOC analysis (example: Ethyl acetate) in ambient air



Analysis Details C.3

Matrix: ambient air

Sample: Ethyl acetate

Sample amount: 1 μ l

Sample introduction:

Syringe injection in API room (2 l ambient air volume) at 40 °C air temperature

Ionization: Corona discharge

$U_c \approx +3000$ V

$U_c \approx +3000$ V

Sample concentration after injection and evaporation

(approximate calculation):

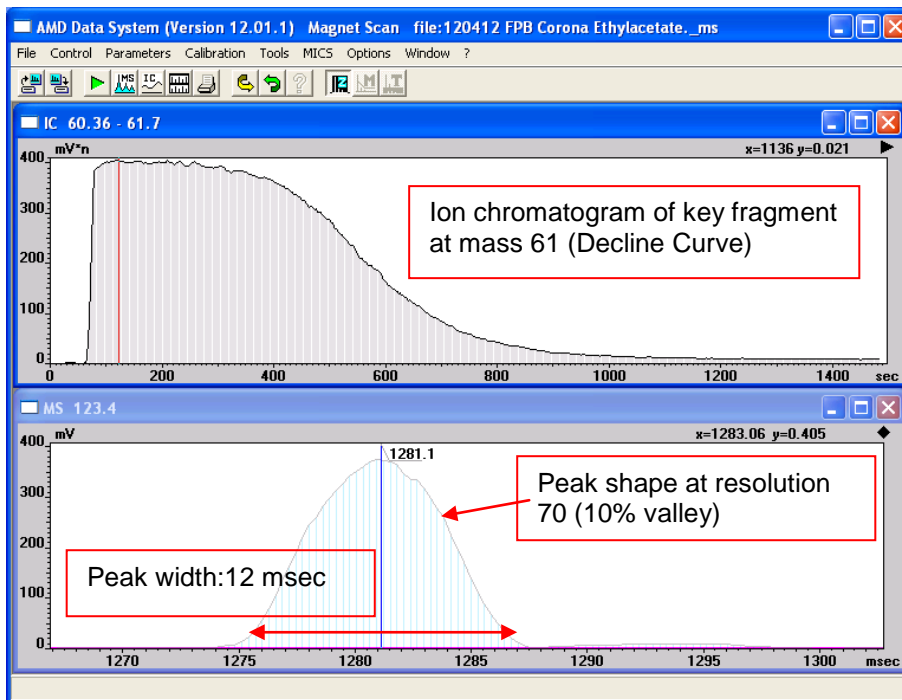
$c = 9 \times 10^{-4} \text{ g} / 2.5 \text{ g} = 3.6 \times 10^{-4}$

$c = 360 \text{ ppm}$

API Interface air intake:

0.4 l/min from API room

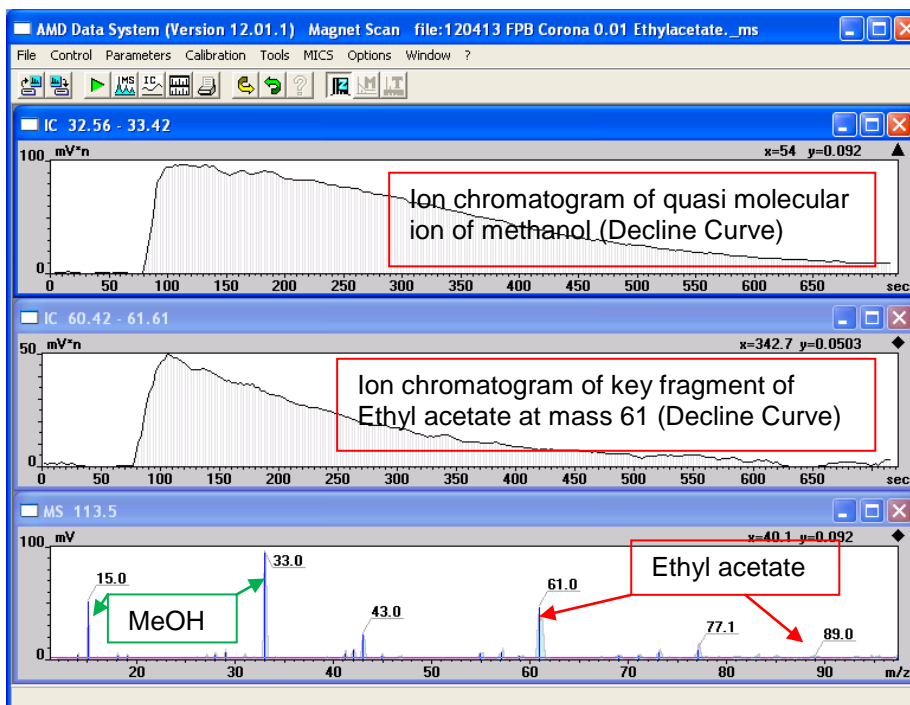
Fig. 4 APCI-MS corona discharge mass spectrum of Ethyl acetate in ambient air



Analysis Details C.3 cont'd

Scan method: magnet scan,
Mass resolution: 70 at 10% valley with fixed slits
Scan Speed: 1 sec/dec
Measuring time per peak: 12 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 1400 sec until the sample concentration in the API room was below detection limit (see below)

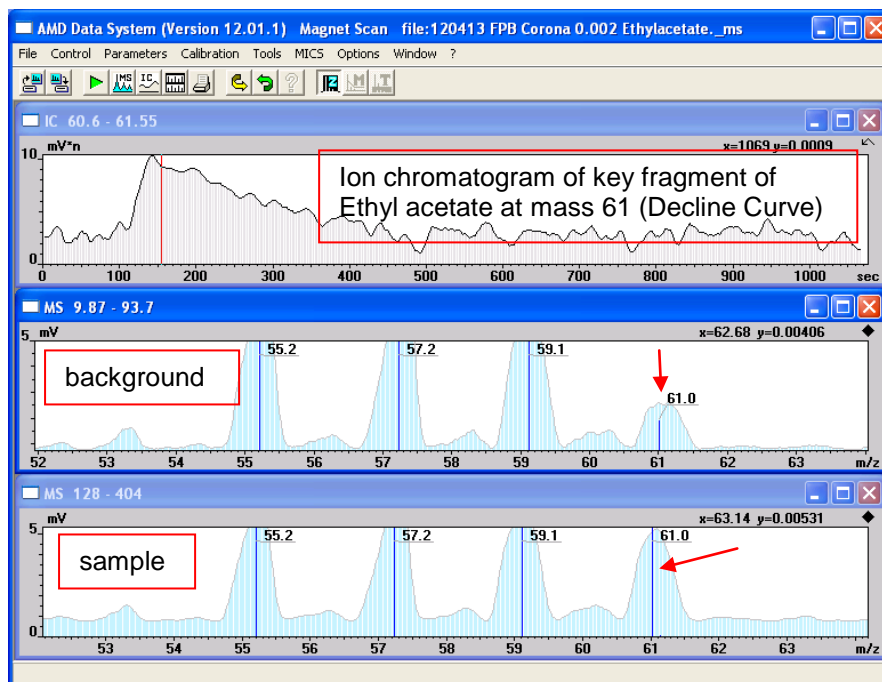
Fig.5 APCI-MS peak display of corona discharge mass spectrum of **Ethyl acetate** in ambient air



Analysis Details C.3 cont'd Limit of Detection (LOD)

Matrix: ambient air
Sample: **Ethyl acetate** diluted in Methanol (1:100)
Sample amount: 10 nl in 1 μ l Methanol
Sample introduction: Injection in API room as before
Ionization: Corona discharge as before
Sample concentration after injection and evaporation (approximate calculation):
 $c = 9 \times 10^{-6} \text{ g} / 2.5 \text{ g} = 3.6 \times 10^{-6}$
 $c = 3.6 \text{ ppm}$
API Interface air intake: as before

Fig. 6 APCI-MS corona discharge mass spectrum (single scan) of **Ethyl acetate** (diluted in Methanol) in ambient air. Methanol yield is about 4 times less than for Ethyl acetate



Analysis Details C.3 cont'd

Limit of Detection (LOD)

Matrix: ambient air
Sample: Ethyl acetate diluted in Methanol 1:500
Sample amount: 2 nl in 1 µl Methanol
Sample introduction: as before
Ionization: as before
Sample concentration after injection and evaporation (approximate calculation):
 $c = 1.8 \times 10^{-6} \text{ g} / 2.5 \text{ g} = 0.72 \times 10^{-6}$
 $c = 720 \text{ ppb}$
API Interface air intake as before

Fig. 7 APCI-MS display of key fragment ion of corona discharge mass spectrum of Ethyl acetate in ambient air at limit of detection

C.3.1 Short-form summary of the applied methodology and the result for APCI-MS analysis of Ethyl acetate (Fig. 4 -7) in ambient air

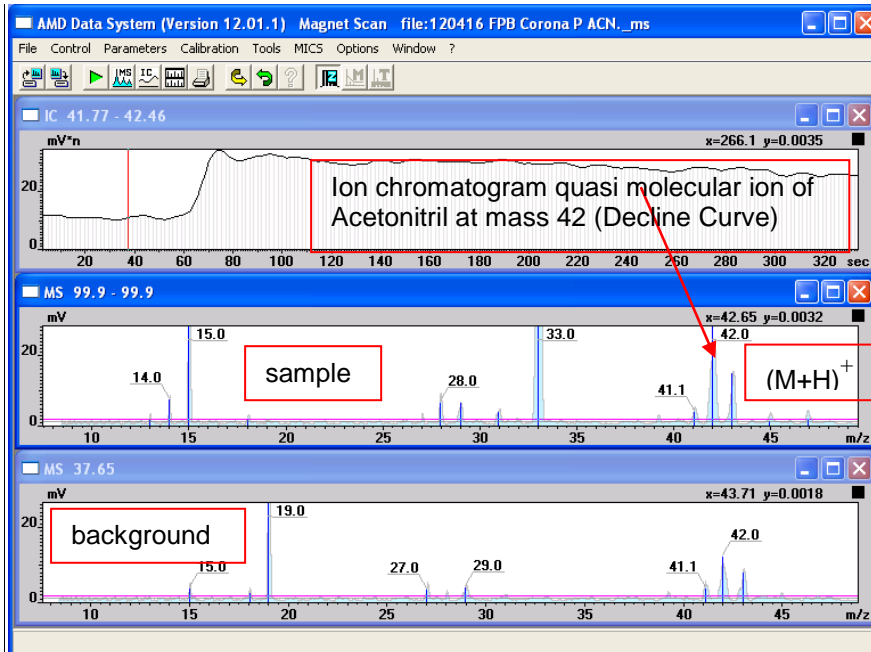
The compound has been used as an example to demonstrate the measurement procedures for **APCI-MS trace analysis of a volatile organic compound in ambient air**. The rudimentary method used here should give some orientating results for the application of a possible analytical procedure under more sophisticated sample preparation and sample introduction methodology. The counter electrode/nozzle part of the API interface was kept at a temperature of 150 °C resulting in an ambient air temperature within the API room of about 40 °C. The volatile compound was injected by a syringe directly into the air of the API room. As described in figures 4 and 5 above an amount of 1 µl Ethyl acetate 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 air continuous 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 (temperature corrected). According to the decline function about 40% of the sample at higher concentrations may be adsorbed on the inner walls and is desorbing, slowly.

In the low ppm or even ppb range a single scan may be sufficient for identification of the compound (see fig 6) in the air. The sensitivity of the method allows detection limits in the low ppb range, if SIM techniques (longer measuring times per ion, higher number of ions but short total analysis time) will be used. However, the individual background signals are the limiting factors.

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



D. APCI-MS trace analysis of Acetonitril (ACN) in ambient air



Analysis Details 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

(definition as before)

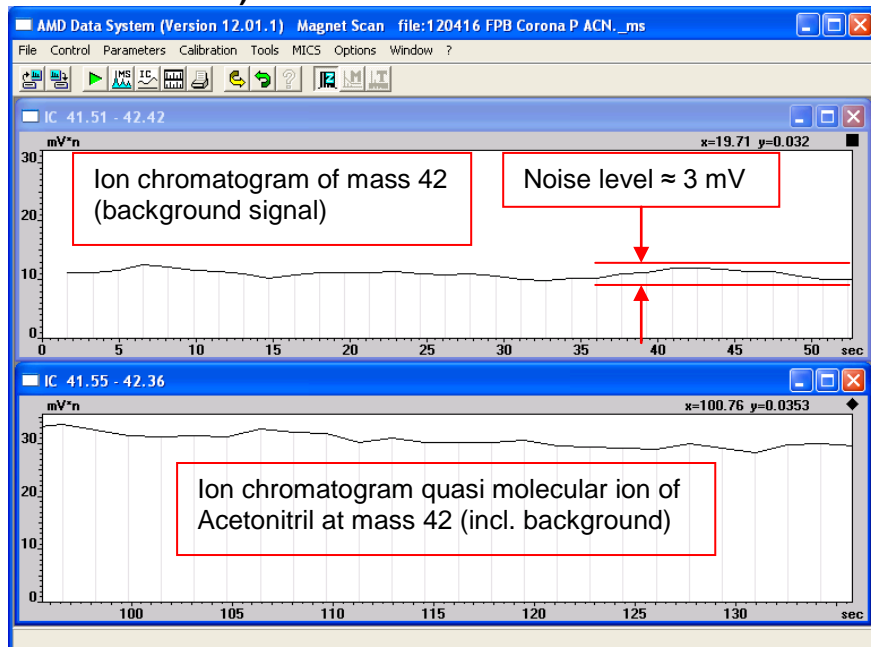
$$c = 9 \times 10^{-7} \text{ g} / 2.5 \text{ g} = 3.6 \times 10^{-7}$$

$$c = 360 \text{ ppb}$$

API Interface air intake

as before

Fig. 8 APCI-MS corona discharge mass spectrum (single scan) of Acetonitril (diluted in Methanol) in ambient air.



Analysis Details D. 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

(definition as before)

$$c = 9 \times 10^{-7} \text{ g} / 2.5 \text{ g} = 3.6 \times 10^{-7}$$

$$c = 360 \text{ ppb}$$

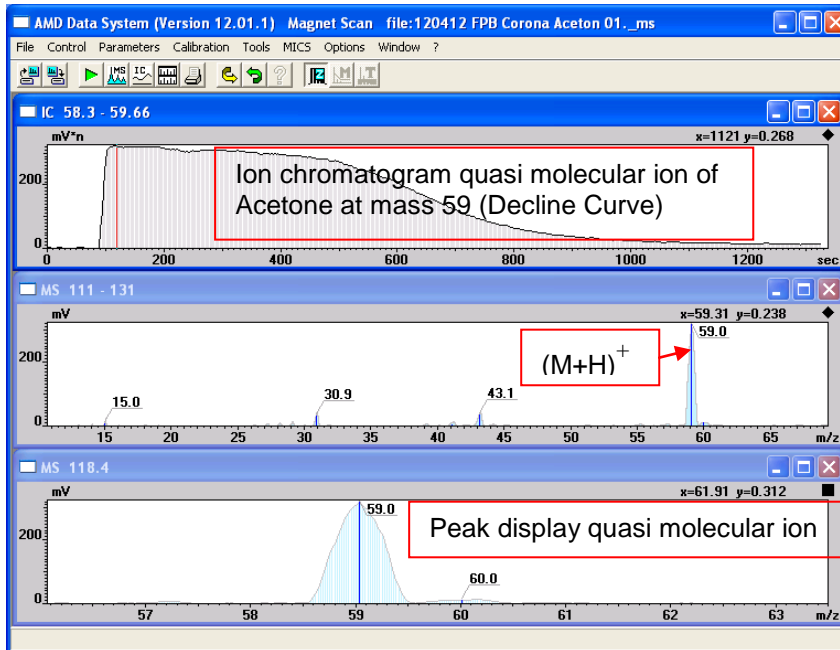
API Interface air intake

as before

Fig. 9 Ion chromatograms of Quasi-molecular ion and background signal (S/N ratio = 3:1) of Acetonitril in ambient air at limit of detection (LOD \approx 180 ppb).



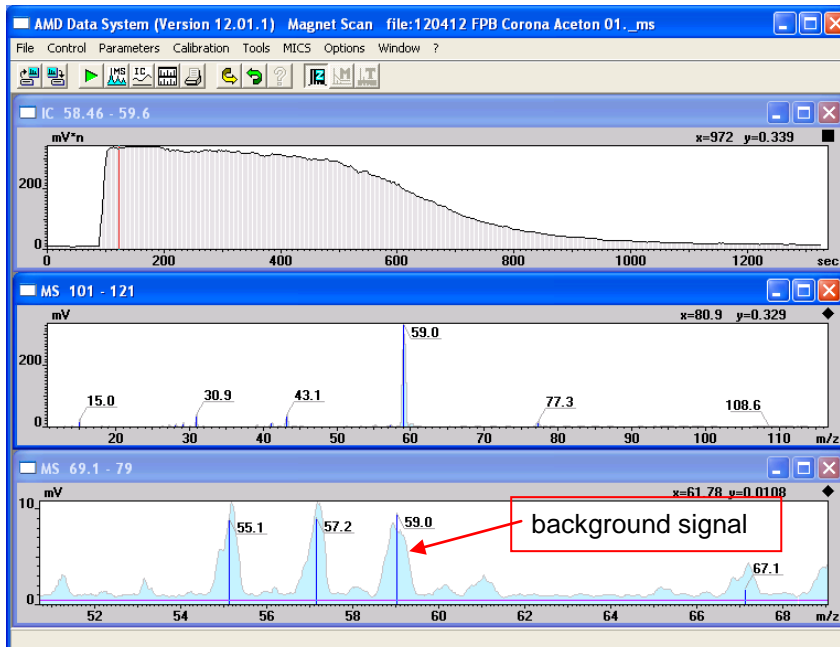
E. APCI-MS trace analysis of Acetone in ambient air



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)
 $c = 8 \times 10^{-4} \text{ g}/2.5\text{g} = 3.2 \times 10^{-4}$
 $c = 320 \text{ ppm}$
Dynamic range: see below

Fig. 10 APCI-MS corona discharge mass spectrum (single scan) of Acetone in ambient air.



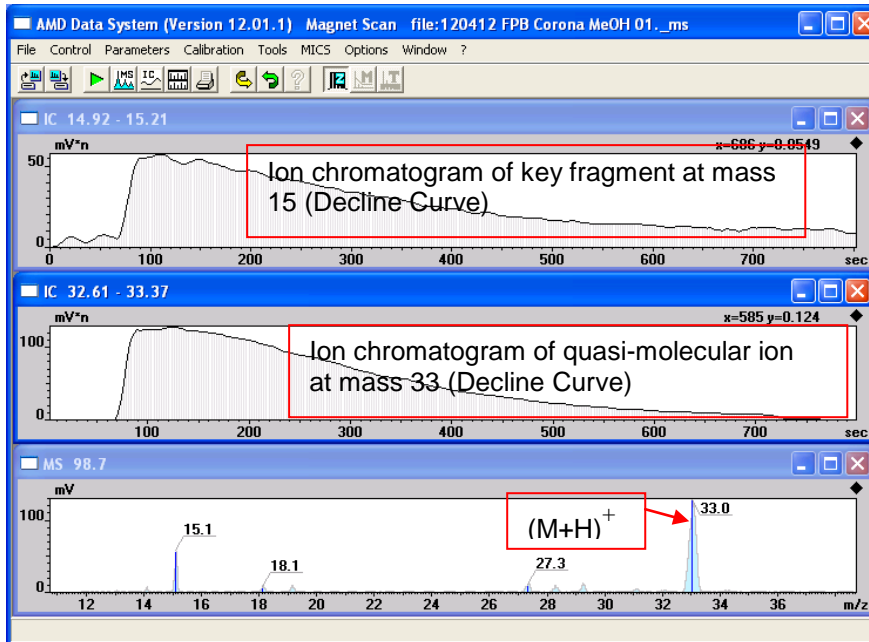
Analysis Details E. cont'd

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)
 $c = 8 \times 10^{-4} \text{ g}/2.5\text{g} = 3.2 \times 10^{-4}$
 $c = 320 \text{ ppm}$
Dynamic range: 1:200 (2 mV peak detectable)
LOD: about 3 ppm (high background signal)

Fig. 11 APCI-MS corona discharge mass spectrum (single scan) of Acetone in ambient air including background signals at quasi molecular ion



F. APCI-MS trace analysis of Methanol in ambient air

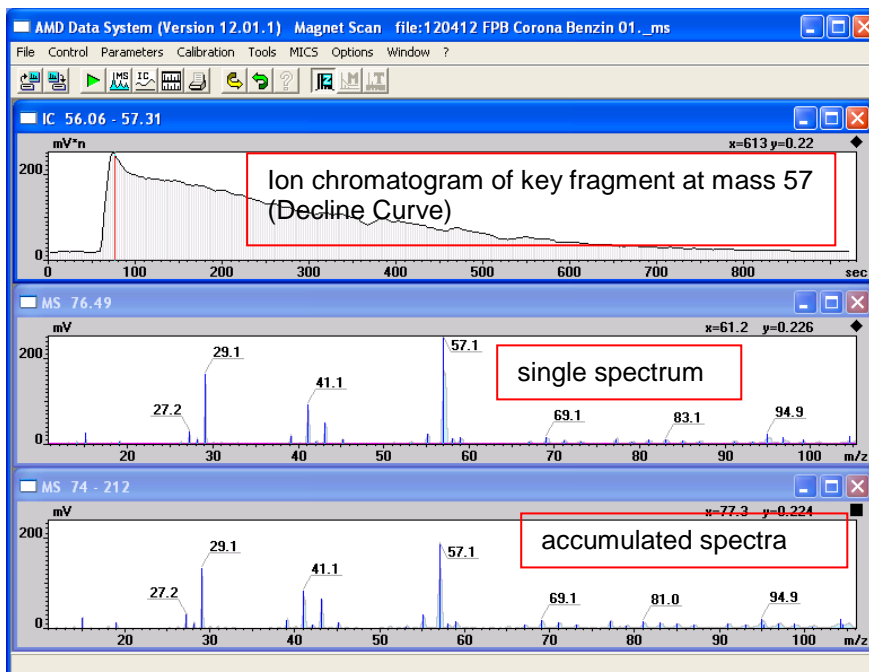


Analysis Details F.

Matrix: ambient air
Sample: **Methanol**
Sample amount: 1 μ l
Sample introduction: as before
Ionization: as before
API Interface air intake as before
Sample concentration (definition as before)
 $c = 8 \times 10^{-4} \text{ g}/2.5 \text{ g} = 3.2 \times 10^{-4}$
 $c = 320 \text{ ppm}$
Dynamic range: 1:100
LOD estimated: < 3 ppm

Fig. 12 APCI-MS corona discharge mass spectra of **Methanol** in ambient air

G. APCI-MS trace analysis of Gasoline in ambient air



Analysis Details G.

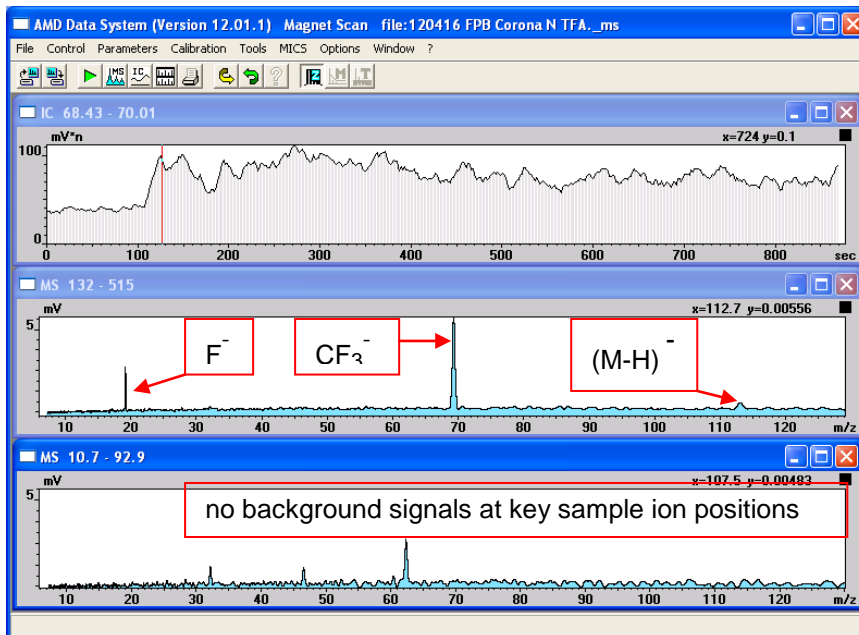
Matrix: ambient air
Sample: **Gasoline**
Sample amount: 1 μ l
Sample introduction: as before
Ionization: as before
API Interface air intake as before
Sample concentration (definition as before)
 $c = 8 \times 10^{-4} \text{ g}/2.5 \text{ g} = 3.2 \times 10^{-4}$
 $c = 320 \text{ ppm}$
Dynamic range: 1:200
LOD: Not to be defined for one component

Fig. 13 APCI-MS corona discharge mass spectra of **Gasoline** in ambient air. The spectra indicate the mixture of major acyclic hydrocarbons. The method may be useable in this or similar cases for fingerprint analyses but requires further investigations



H. APCI-MS trace analysis of volatile halogen compounds in ambient air using negative ion detection

H.1 APCI-MS trace analysis of Trifluor acetic acid in ambient air

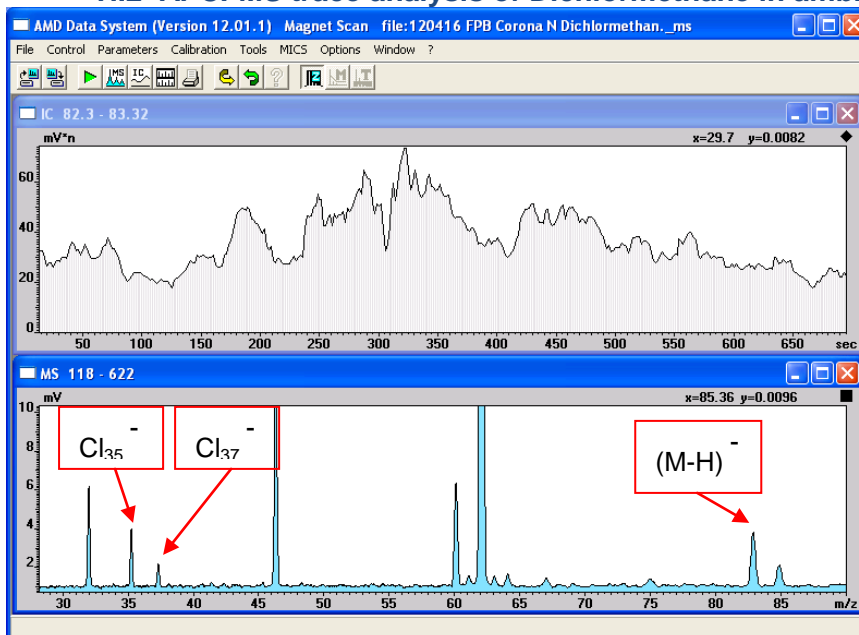


Analysis Details H.1

Matrix: ambient air
Sample: Trifluor acetic acid
Sample amount: 1 μ l
Sample introduction: as before
Ionization: Corona discharge
 $U_c \approx -3000$ V for negative ion production
API Interface air intake as before
Sample concentration (definition as before)
 $c = 1.5 \times 10^{-3} \text{ g}/2.5 \text{ g} = 6 \times 10^{-4}$
 $c = 600$ ppm
LOD: 100 ppm (estimated)

Fig. 14 APCI-MS corona discharge negative ion mass spectra of Trifluor acetic acid in ambient air

H.2 APCI-MS trace analysis of Dichlormethane in ambient air



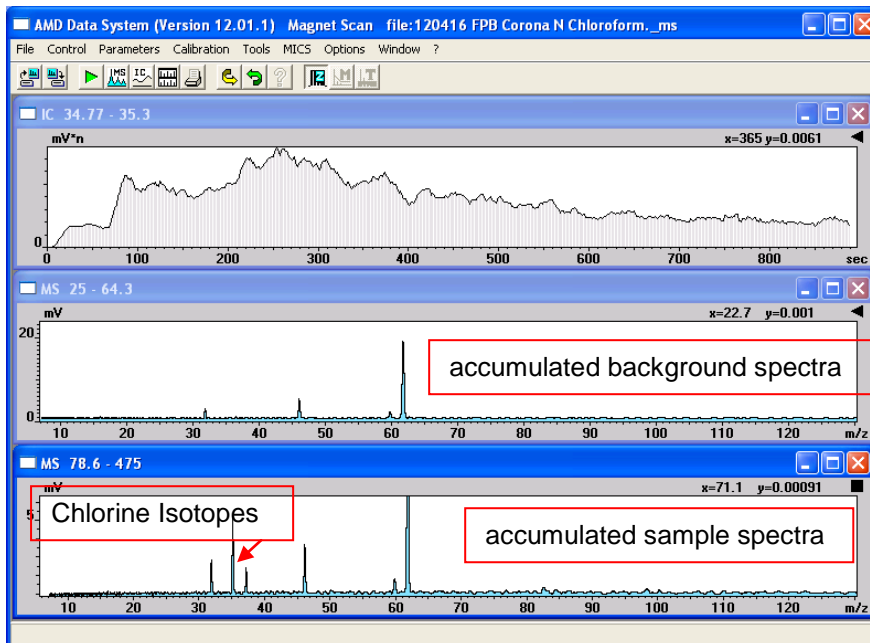
Analysis Details H.2

Matrix: ambient air
Sample: Dichlormethane
Sample amount: 1 μ l
Sample introduction: as before
Ionization: Corona discharge
 $U_c \approx -3000$ V for negative ion production
API Interface air intake as before
Sample concentration (definition as before)
 $c = 1.3 \times 10^{-3} \text{ g}/2.5 \text{ g} = 5 \times 10^{-4}$
 $c = 500$ ppm
LOD: 150 ppm (estimated)

Fig. 15 APCI-MS corona discharge negative ion mass spectra of Dichlormethane in ambient air.



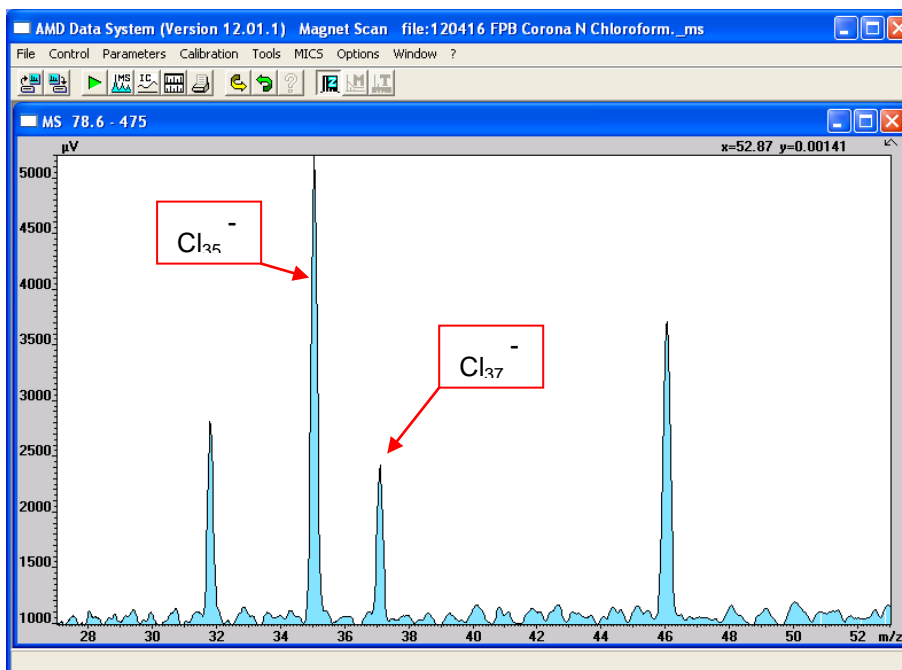
H.3 APCI-MS trace analysis of Chloroform in ambient air



Analysis Details H.3

Matrix: ambient air
Sample: Chloroform
Sample amount: 1 µl
Sample introduction: as before
Ionization: Corona discharge
 $U_c \approx -3000$ V for negative ion production
API Interface air intake as before
Sample concentration (definition as before)
 $c = 1.5 \times 10^{-3} \text{ g}/2.5 \text{ g} = 6 \times 10^{-4}$
 $c = 600$ ppm

Fig. 16 APCI-MS corona discharge negative ion mass spectra of Chloroform in ambient air.



Analysis Details H.3 cont'd

Matrix: ambient air
Sample: Chloroform
Sample amount: 1 µl
Sample introduction: as before
Ionization: Corona discharge
 $U_c \approx -3000$ V for negative ion production
API Interface air intake as before
Sample concentration (definition as before)
 $c = 1.5 \times 10^{-3} \text{ g}/2.5 \text{ g} = 6 \times 10^{-4}$
 $c = 600$ ppm
LOD: 100 ppm (estimated)

Fig. 17 APCI-MS detailed view on Chlorine Isotopes of corona discharge negative ion mass spectrum of Chloroform in ambient air.



H. 4 Short-form summary of APCI-MS trace analysis of volatile halogen compounds in ambient air using negative ion detection

The results for demonstration of the applicability of negative ion recording to volatile halogen compounds were achieved under the same rudimentary method as mentioned before for the VOC analyses in positive ion recording mode. Further investigations for clarification of improved limits of detection were beyond the scope of this application note. While for negative ion detection the background is not the limiting factor, the absolute sensitivity achieved here for the method requires further investigations regarding possible improvements. Otherwise the remarks for routine applications mentioned under C.3.1 above are applicable, too.