

# REAL TIME MONITORING OF VOCs AND INORGANIC POLLUTANTS IN AMBIENT AIR BY ION MOLECULE REACTION - MASS SPECTROMETRY: A POTENTIAL ALTERNATIVE TOOL TO REFERENCE METHODS

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## Abstract

The analysis of VOCs and inorganic gaseous pollutants is a major demand in understanding air quality and the climate change. Current reference methods are mainly offline methods, i.e. passive sampling, preconcentration steps prior to the analysis. They allow the interpretation of environmental conditions as averages over hours, days or even longer periods. The authors present a technology that is based on IMR-MS (ion molecule reaction - mass spectrometry) that allows the simultaneous real time monitoring of hazardous components, like benzene, toluene, butadiene, styrene, chlorinated components, nitrogen dioxide, hydrogen sulfide etc.. Typical time of analysis at ppt up to ppm – concentrations is one second for each molecule avoiding any kind of passive sample collection and -pretreatment.

Example 1 shows results of online monitoring by IMR-MS of the VOCs benzene and vinylchloride in ambient air in comparison with offline US-EPA TO-15 (GC-MS) method at Environmental Research and Training Center (ERTC) in Pathumthani, Thailand.

Example 2 describes environmental monitoring using IMR-MS of various organic and inorganic volatile pollutants from heavy industries (refineries) in Sicily, Italy in comparison with classical single component monitors.

In summary not only in Asia but all over the world it is a today's major demand to better understand the quality of air and IMR-MS has a contribution to offer.

**Keywords:** ambient air quality, real time analysis, VOCs.

## Introduction

There exist numerous reference methods for the analysis of VOCs and inorganic gaseous pollutants (1-8). Most of them are offline methods, i.e. passive sampling, preconcentration steps prior to the analysis. They show values of pollutants as averages over hours, days or even longer periods. Other types of methods contain single-component analyzers that give results within seconds, minutes or hours.

In contrast to reference methods *Airsense*, a multi-component gas analyzer, based on the principle of Ion Molecule Reaction - Mass Spectrometry (IMR-MS) is a valuable tool for the real time analysis of volatile organic and inorganic compounds in environmental monitoring. This monitoring technique, avoiding any kind of passive sample collection and pretreatment, has been used for more than 20 years in environmental monitoring, in the analysis of gases from internal combustion engines (exhaust gases), gases from fuel cells and in catalytic converter research, as well as in the food industry and in breath analysis (9).

## Methods

A schematic diagram and a picture of the IMR-MS is shown in figure 1. In the IMR-MS analyzers, the principle of ion–molecule reactions is applied as the interaction of positively charged atomic ions with neutral sample gas molecules resulting in the formation of product ions whenever the ionization potential of the sample molecule is less than the potential energy of the incoming primary ion (10-13). The IMR-MS uses krypton, xenon, or mercury atomic gas to form the primary ion beam via electron impact ionization (section 1, Fig. 1). The patented IMR ionization method can use the atomic mass scale to detect different molecules with the same molecular weight. As an example, acetaldehyde and carbon dioxide have the same mass (44). The mercury beam with an ionization potential of 10.4 eV does not ionize carbon dioxide (13.8 eV), but it ionizes acetaldehyde (10.2 eV). Switching different ion beams and hence energy levels is fast and takes 400 ms. Krypton ions (14.0 eV) do well separate nitrogen (15.6 eV—not ionized) against carbon monoxide (13.7 eV) on mass 28. The instrument uses two octopole systems (section 2 and 3, fig. 1) operated at high frequencies to store primary as well as product ions in a confined volume against their coulomb repulsion and transmit ions to the quadrupole mass analyzing section. The quadrupole mass separator (section 4, fig. 1), driven by direct current and alternating current, operates as an electromagnetic filter according to a parametric resonance to a specific mass over charge ratio. At a given alternating to direct current ratio, only one specific mass of ions experiences a stable trajectory through the quadrupole. A secondary electron multiplier (section 5, fig. 1) may generate as much as  $10^8$  electrons for each incoming ion. This allows the generation of an electrical pulse strong enough to be accepted by a computer counting system. The pulse rate represents the concentration of the molecular species in the gas sample brought to the instrument. The sample gas (section 7, fig. 1) is transferred in a 2.5-m-long heated capillary system (Silcosteel®; Restek, Bellefonte, PA) at a typical flow rate of 50 ml/min to the instrument.

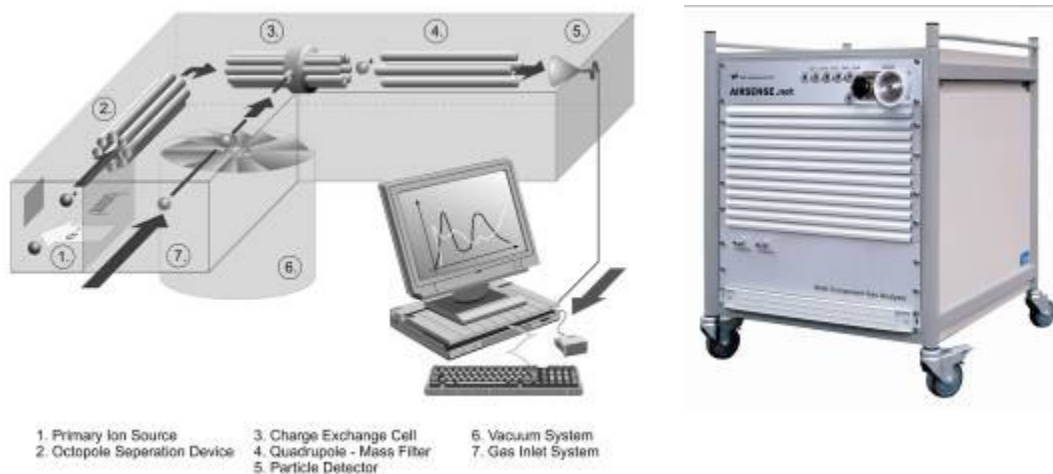


Fig. 1 Schematic diagram and picture of the IMR-MS

With this technical principle it is possible to detect simultaneously organic and inorganic compounds, e.g. benzene, toluene, butadiene, styrene, vinylchloride, nitrogen dioxide, hydrogen sulfide, methane, acetaldehyde, acetone, ammonia, methylmercaptane, etc., in online or offline mode. Thus aliphatics, aromatics, alcohols, amines, aldehydes, ketones, carboxylic acids, inorganic acids and bases, halogenated HCs can be detected at the same time. The range of concentrations starts at pptv reaching Vol% levels with one setting of the instrument. The time of analysis is  $\geq 1$  msec per mass and typically 1 – 5 seconds in environmental monitoring to detect concentrations in the pptv and ppbv mode and may be reduced down to 1 msec at concentrations in the Vol% range. The software is based on Microsoft.net for full remote operation.

## Results - Example 1:

VOCs in ambient air: Online IMR-MS in comparison with offline US-EPA TO-15 (GC-MS) method at Environmental Research and Training Center (ERTC) in Pathumthani, Thailand

The multi component IMR-MS was installed in a mobile laboratory at the Environmental Research and Training Center (ERTC) in Pathumthani, Thailand in May 2008. ERTC is a division operating under the Department of Environmental Quality Promotion (DEQP) and under the overall jurisdiction of the Ministry of Natural Resources and Environmental (MONRE). The fundamental purports of ERTC are to carry out research and to provide technical support in the implementation of natural resources and environmental policies and natural resources and environmental initiatives (14).

From May 9-12 2008 benzene and vinylchloride were measured on line by IMR-MS. At the same time samples were taken according to the US-EPA Compendium Method TO-15 (2). In short, with this method the atmosphere is sampled by introduction of air into a specially prepared evacuated stainless steel canister. A pump ventilated sampling line is used during sample collection. To analyze the sample in the laboratory, a known volume of sample is directed from the canister through a solid multisorbent concentrator. After the concentration and drying steps, the VOCs are thermally desorbed and carried onto a gas chromatographic column for separation and are usually detected by QMS (quadrupole mass spectrometry).

During this study the sampling time was 24 hours.

Figure 2 shows one hour averages of benzene and vinylchloride measured by IMR-MS at ERTC. Within this period of four days 15192 values per molecule were measured at a measurement time of 2 sec.

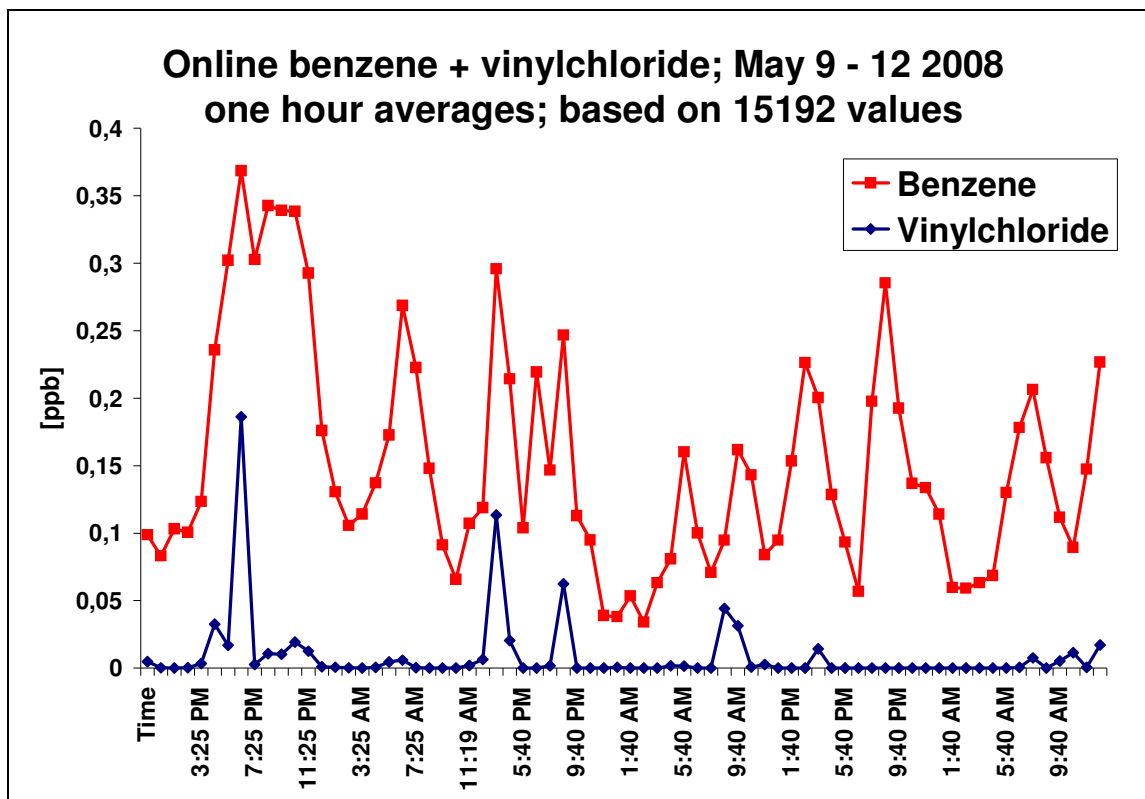


Fig. 2 Online benzene and vinylchloride concentrations at ERTC

Figure 2 shows that the variations of the signals reflect the effective concentrations of the pollutants during this period.

For a comparison of the IMR-MS results of figure 2 with those of the US-EPA TO-15 method, table 1

shows the results as 24 hours averages.

Tab. 1 Comparison of benzene and vinylchloride by online IMR-MS with offline US-EPA TO-15

24 Hour Average	Benzene [ppb]		Vinylchloride [ppb]	
	Online IMR-MS	Offline US-EPA TO-15 (GC-MS)	Online IMR-MS	Offline US-EPA TO-15 (GC-MS)
May 9 2008	0.194	0.220	0.013	0.009
May 10 2008	0.120	0.083	0.012	0.008
May 11 2008	0.142	0.270	0.002	0.012
May 12 2008	0.184	0.150	0.008	0.010
Total Average	0.160	0.181	0.009	0.010

Summarizing the content of table 1 the total average difference of the results between IMR-MS and US-EPA TO-15 is 11.6% for benzene and 9.0% for vinylchloride.

## Results - Example 2:

Environmental monitoring of pollutants from heavy industries in Sicily, Italy: IMR-MS in comparison with classical monitors

In the east of the island of Sicily in Italy there are a lot of heavy industries, e.g. refineries and waste processing plants in close neighborhood to villages and cities. Supposed to be emitted by these plants in this study in 2007 the IMR-MS was used to measure the following hazardous components:

Acetylene, propene, 1,3-butadiene, sum of dimethylsulfide and ethylmercaptane, vinylchloride, benzene, sum of vinylacetate and hexane, toluene, heptane, styrene, sum of xylenes and ethylbenzene, thiophene and nitrogen dioxide.

From these 16 components the results of benzene, toluene and nitrogen dioxide were compared with single-component analyzers and with a NMHC- (non methane hydrocarbons) analyzer.

Figures 3 and 4 show the results of benzene- and toluene measured by IMR-MS in comparison with a BTX-analyzer. The measurement time for benzene and toluene was 2 sec per molecule for the IMR-MS and 15 min for the BTX-analyzer, the total period was eight days. The values are displayed as one hour averages.

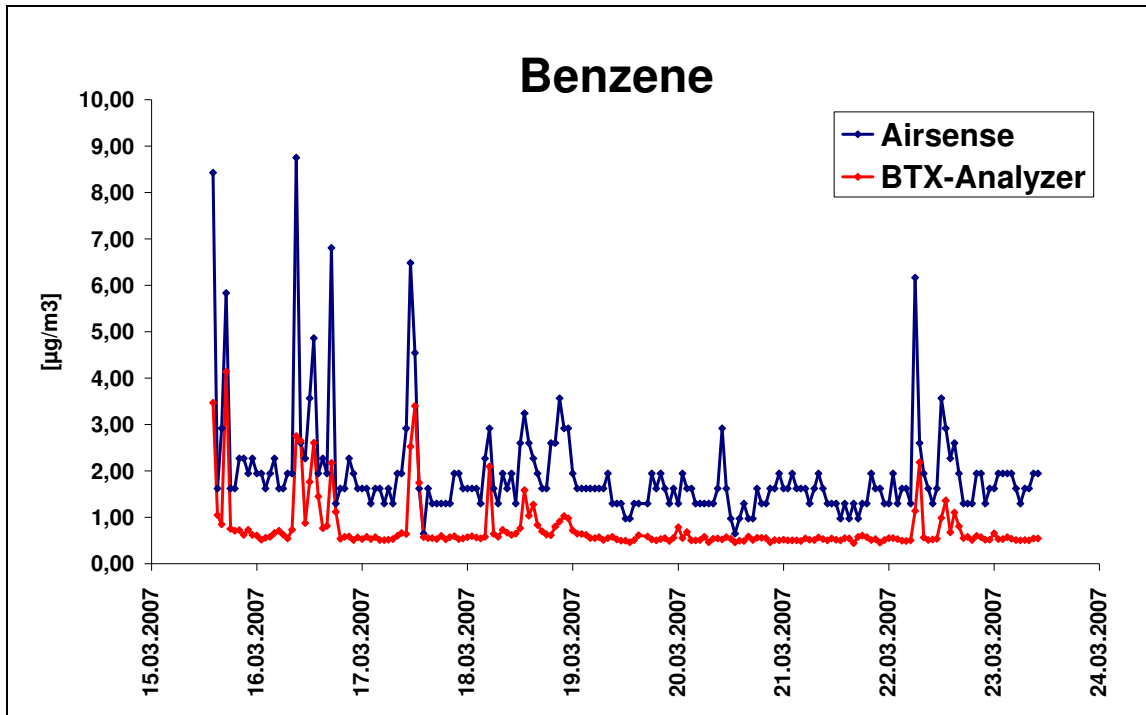


Fig. 3 Online benzene concentrations in comparison with BTX-analyzer

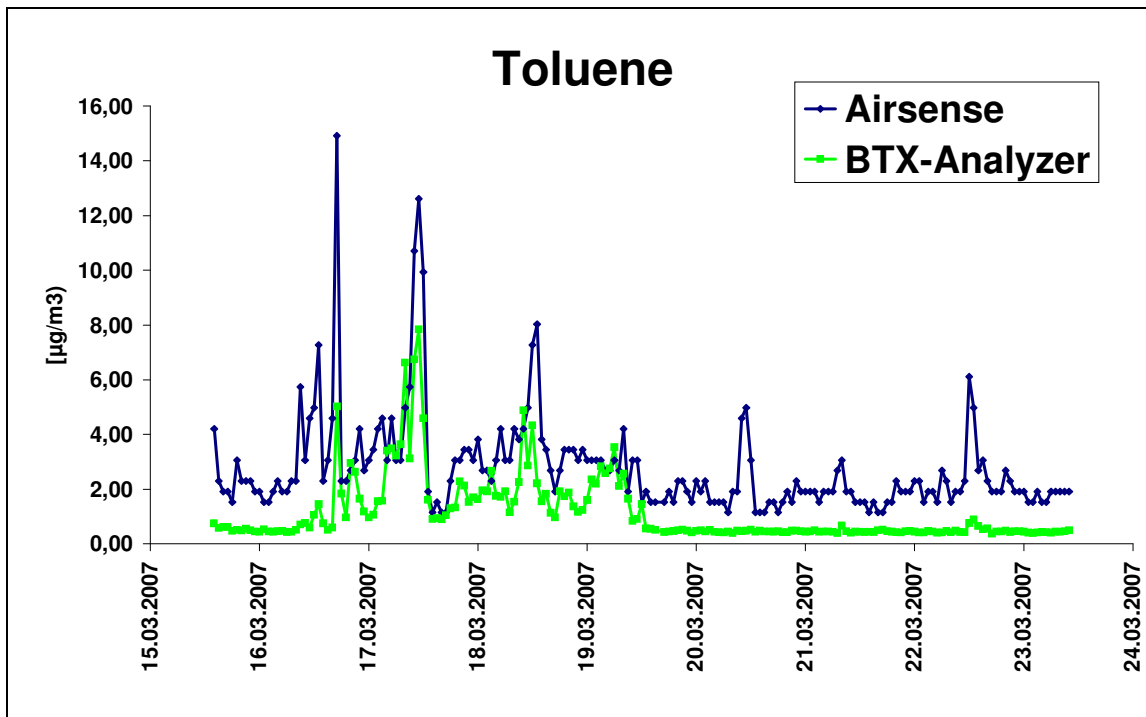


Fig. 4 Online toluene concentrations in comparison with BTX-analyzer

The coefficients of correlation ( $r$ ) of both technologies for the whole period of eight days was 0.80 for the results of benzene and 0.73 for toluene.

Figure 5 shows the result of nitrogen dioxide ( $\text{NO}_2$ ) measured by IMR-MS in comparison with a  $\text{NO}_x$ -analyzer. The measurement time of nitrogen dioxide by IMR-MS was 2 sec and 10 sec by the  $\text{NO}_x$ -

analyzer, the total period was one month. The values are displayed as one hour averages.

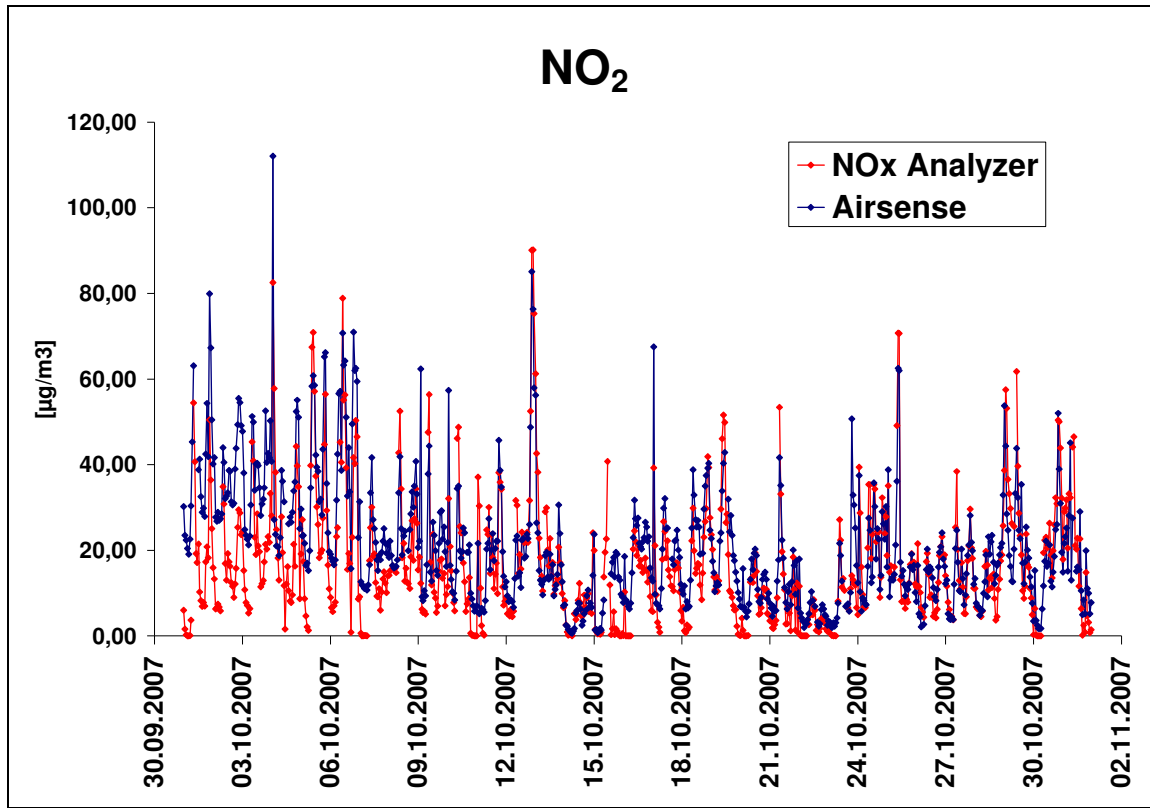


Fig. 5 IMR-MS concentrations of nitrogen dioxide in comparison with NOx-analyzer

The coefficient of correlation ( $r$ ) for the results of  $\text{NO}_2$  for both technologies for the whole period of one month was 0.80.

Figure 6 shows the result of acetylene, propene, 1,3-butadiene, sum of dimethylsulfide and ethylmercaptane, vinylchloride, benzene, sum of vinylacetate and hexane, toluene, heptane, styrene, sum of xylenes and ethylbenzene and thiophene measured by IMR-MS in comparison with a NOx-analyzer. The measurement time of the IMR-MS analytes was 2 sec for each molecule and 4 min for the NMHC-analyzer, the total period was one month. The values are displayed as one hour averages.

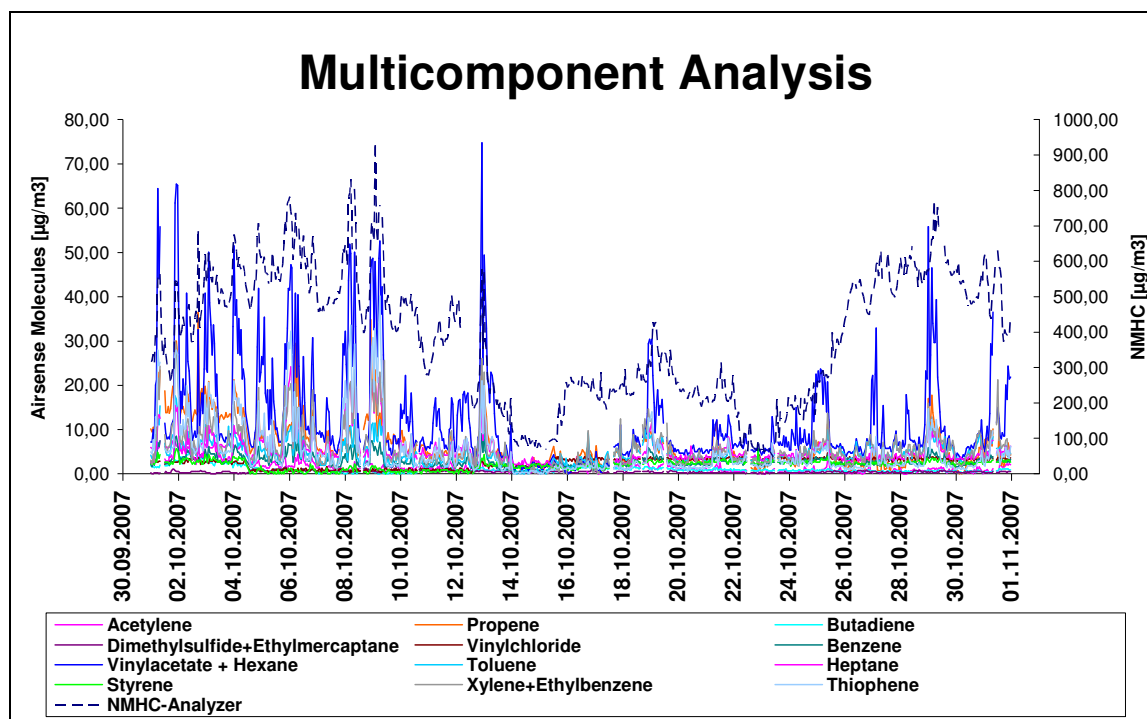


Fig. 6 IMR-MS concentrations of acetylene, propene, butadiene, sum of dimethylsulfide and ethylmercaptane, vinylchloride, benzene, sum of vinylacetate and hexane, toluene, heptane, styrene, sum of xylenes and ethylbenzene and thiophene in comparison with NMHC-analyzer

For the period of one month the coefficients of correlation ( $r$ ) of the components measured by IMR-MS in comparison with the NMHC-analyzer were as follows:

Acetylene: 0.23; propene: 0.45; 1,3-butadiene: -0.02; dimethylsulfide + ethylmercaptane: 0.27; vinylchloride: -0.30; benzene: 0.54; vinylacetate + hexane: 0.55; toluene: 0.54; heptane: 0.55; styrene: -0.12; xylenes + ethylbenzene: 0.55 and thiophene: 0.54.

Figure 6 shows that the trend of the results obtained by IMR-MS and the NMHC-analyzer mainly go in parallel. However the coefficients of correlation ( $r$ ) range from -0.30 to 0.55 which shows that selective multicomponent monitoring provides a deeper insight into actual environmental situations. In contrast to the results from figure 3 – 5 where the IMR-MS results correlated well with the results obtained by single-component analyzers a total compound-class analyzer like a NMHC monitor may not reflect actual concentrations of selective pollutants in real time.

## Conclusion

Airsense, a multi-component gas analyzer, based on the principle of Ion Molecule Reaction - Mass Spectrometry (IMR-MS) is a valuable tool for the real time analysis of hazardous, i.e. volatile organic and inorganic, compounds in the environment. In comparison with reference resp. classical methods it provides in real time a deeper insight into actual environmental pollutions. Thus not only in Asia but all over the world it is a today's major demand to better understand the quality of air and IMR-MS has a contribution to offer.

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