



# COLUMNA ANALYTICA

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Chimia 54 (2000) 367–370  
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ISSN 0009–4293

## Pittcon 2000 – Recent Advances in Ion Mobility Spectrometry and Air Sampling Techniques

Personal impressions from Henrik Ørnsnes, Laboratorium für Organische Chemie, ETH-Zürich, CH-8092 Zürich

**Keywords:** Air sampling · Ion mobility spectroscopy · Pittcon 2000 · Solid phase microextraction · Surface acoustic wave technology

This year's Pittsburgh Conference attracted about 30 000 participants from all over the world to New Orleans, Louisiana, USA. The conference is known as the largest annual meeting in analytical chemistry. In contrast to other meetings in analytical chemistry, the conference featured an exhibition floor with the largest annual display in the world of analytical instrumentation and services at one time and under one roof. More than 1250 companies occupying 365 000 square feet (33 910 m<sup>2</sup>) of exhibit space presented their products in the newly expanded Morial Convention Center in New Orleans. The conference additionally boasted around 40 parallel oral sessions each day. The aim of my visit was biased towards the fields of ion mobility spectrometry and novel air sampling techniques. Presented below are my personal favorites among the contributions.

### Microfabrication of a New Radio Frequency Ion Mobility Spectrometer (RF-IMS)

Environmental, medical and security requirements for on-site chemical screening have motivated researchers at the Charles Stark Draper Laboratories, USA ([www.draper.com](http://www.draper.com)) to develop a low cost, miniature IMS instrument with a performance comparable to that of larger devices. The leading technology for on-site monitoring is low electric field ion mobility spectrometry (IMS) which has been used extensively for detecting chemical weapons and explosives. The researchers from Draper Laboratories claim that the conventional low-field drift tube designs suffer from reduced resolution or sensitivity when miniaturized. Instead radio frequency ion mobility spectrometry (RF-IMS) allows miniaturization of IMS through microfabrication, while preserv-

ing sensitivity and resolution. At the conference the production of the first microfabricated radio frequency ion mobility spectrometer (RF-IMS) with drift-tube dimensions of 3 x 1 x 0.2 cm<sup>3</sup> was presented by Raanan Miller. The device exhibits excellent performance characteristics and offers low cost and reproducibility. The device consists of a micromachined drift-tube containing an ionization source (radioactive americium, 100 µCi), a tunable ion filter, and a detector. A carrier gas (flow rate of 1–4 l/min) transports the ions through the drift region where they are filtered by applying a dc bias-voltage and a radio frequency waveform to ion filter electrodes. Adjusting the ratio of dc bias voltage to RF voltage selects the ions that can pass through the filter and reach a detector. Characterizations using benzene and substituted benzenes demonstrate the ppb detection limits and a new mechanism for separating ions in a man-

ner not seen in low-field traditional ion mobility spectrometers. The application of this device as an inlet for a mass spectrometer was also illustrated.

Basically the instrument consists of two squared surfaces positioned 0.2 cm apart from each other. A periodical electric waveform is applied to the surfaces wherein there is a significant difference between a peak positive voltage and a peak negative voltage during the applied waveform. If a mixture of ions of different sizes and types is introduced between the plates, the application of the appropriate voltage to the plates will create a condition where some types of ions drift and hit the plates while other types of ions remain between the plates. The latter ones are, so to speak, balanced and will be detected. The separation of the ions between the plates will require the application of a specialized waveform called an 'asymmetric' waveform. If the electric field during the high-voltage part of the waveform is above about 5000 volts/cm, then the application of the waveform may cause the ion to drift in one or the other direction towards one of the plates. The reason the ion will drift towards a plate is that the ion mobility during the application of the high electric field is different than the ion mobility during the low electric field. Since the mobility of the ion defines how fast the ion moves in the field, the ion will move 'proportionately' farther in one field than the other. Since this waveform is applied at high frequency (over 200 kHz), the small extra distance traveled during each high-voltage period translates into a net drift of the ion towards one of the plates. The drift of an ion towards one of the metal plates can be stopped by the application of a small dc voltage to either of the plates. If the voltage is applied with the appropriate magnitude and polarity, the ion will feel the force of this field and the drift of the ion will be stopped. The voltage which is applied to reverse or compensate for the ion drift is called the 'compensation voltage' or 'CV' for short. The CV is therefore the 'handle' used to control the separation of ions. The 'spectrum' of peaks observed in this manner is called a CV spectrum.

#### **Side-by-Side Comparison of Small, Hand-held Ion Mobility Spectrometers and Surface Acoustic Wave Devices**

Within the US Armed Services there has been a long-term debate with respect to the relative attributes of ion mobility

spectrometry (IMS) and Surface Acoustic Wave (SAW) technology for the detection and identification of chemical warfare agents. Almost all of the claims in favor of one technology or the other have been made on the basis of experimental data gathered in unrelated tests. Because the US Department of Defense has entered into a development program aimed at the production of small gas detectors, side-by-side evaluations of prototype IMS and SAW field instruments have been performed at the US Army Edgewood Chemical Biological Center (<http://www.sbccom.army.mil/products/nbc.htm>). Dennis Davis from the US Army presented some of the most recent observations.

The purpose of the evaluation was to describe relative performance characteristics of devices based on the two technologies in experiments consisting of exposures to the same sample conditions at the same time – ambiguities resulting from exposures to different analyte concentrations, water vapor concentrations and sample gas temperatures would thus be eliminated. Analytes used in these evaluations included toxic and non-toxic organophosphorous compounds, organosulfur compounds, hydrogen cyanide and cyanogen chloride. Analyte concentrations ranged from 10 ppb to 10 ppm in air, air temperatures of 25 °C to 40 °C and relative humidity conditions up to 90% were used – these conditions, especially those of high temperature and humidity, are generally problematic for hand-held detection systems.

The SAW systems contain: 1) an acoustic wave sensor, 2) a gas sampling system, and 3) electronics to operate and monitor the sensor. Changes in the speed and power of the wave are monitored as it travels across the sensor. These changes occur because a film coating the sensor softens and becomes heavier when it absorbs the contaminant/analyte. Basically an amorphous polymer is utilized as an absorption reservoir for the analytes. When an acoustic wave is applied it will induce oscillations in the polymer, which are characteristic for the amount of absorbed analyte. In order to distinguish between different sets of analytes, an array of different polymers is used. Some analytes will dissolve in favor of one polymer whereas other analytes tend to partition into another polymer. Using an array of differently coated sensors, therefore, can provide a set of responses whose pattern can be decoded statistically to identify (and quantify) an individual vapor. In this way selectivity is obtained within the

SAW device. The technique does not seem to have as high specificity as IMS devices.

SAWs can perform continuous monitoring with rapid and reversible response and can perform real-time monitoring of many volatile organic compounds. SAWs have a wide dynamic range and can handle high concentrations, e.g. parts-per-thousand. Detection limits are compound dependent, but generally the minimum detected analyte concentration will be in the range of parts-per-million.

The IMS instrument used in the present evaluation was a lightweight chemical detector manufactured by Graseby-Dynamics. This prototype version is under development by the US Army Edgewood Research Center. The instrument is probably the smallest linear IMS that can be provided commercially. With dimensions 20x8x3 cm<sup>3</sup> and a weight of around 0.9 kg, the instrument is easily carried in a pocket of a soldier's uniform. It should be noted that the system has no pumps for circulating the humidified carrier gas through a water absorbing unit (molecular sieves), but instead the inner walls of the instrument are coated with a material that traps excess water. Furthermore the inlet is semi-continuous with a valve that opens shortly for sample introduction. This approach only lets a minute stream of sample into the instrument (15 µl air sample per opening), and an automatic contamination control has been implemented, which ensures that the inlet-valve immediately locks if the IMS chamber is exposed to high concentrations of interferents. Due to the direct introduction of the sample very rapid response times can be achieved, generally on the order of 1 s. IMS instruments equipped with membrane inlets are sometimes subject to a long relaxation time of the diffusion through the membrane material, this may extend the response times up to the order of minutes.

The direct comparison between the above-mentioned SAW and IMS instruments was based on sensitivity, linearity, ability to measure complex air mixtures, tolerance to humidity, and long-term reproduction of the measurements.

The IMS instrument used in this study should be able to detect most volatile compounds in the low ppb level. The speaker, however, did not mention if this sensitivity range could be obtained for compounds measured in the presence of high levels of interfering substances, such as cigarette smoke and fuel vapor. Personally, I consider that such environ-

ments could give rise to problematic measurements due to the fact that compounds present in high concentration might easily 'steal' the charges from analytes present in trace amounts. The speaker emphasized the need for a pre-concentration module to reach lower detection limits. The SAW device was not sensitive to all compounds, but for those that could be measured, detection limits in the ppm range were obtained. The SAW technique however suffers from very poor detection limits (if any) when exposed to complex mixtures – the system simply drifts. Other important parameters are humidity and temperature conditions in the environment. The speaker briefly stated that SAW is more temperature sensitive than the IMS. The SAW device was shown to be extremely sensitive to humidity changes, whereas the IMS instrument coped quite well with changes in relative humidity. Regarding quantitation, the IMS instrument has demonstrated a linear range between 12 and 1000 pbb. This should be considered as a very general statement, as the experimental evidence was gathered in the laboratory and not in the field. Hence the measurements have not been carried out in the presence of interfering compounds. Obviously the IMS has major advantages in most of the tests. I consulted the speaker after his presentation in order to know if other IMS instruments had been considered by the US army. He responded that Barringer, Bruker and Environics instruments had been tested, but Graseby's miniaturized IMS was selected for further development. This decision was mainly based on size and weight considerations.

Extraction provides a method for pre-concentrating the analytes and removing interferences. Coupling solid phase extraction (SPE) with IMS is a potential tool for the identification of small amounts of, for example, explosives and other less volatile compounds. A new emerging technique, solid-phase microextraction seems to offer even better results, along with simplicity and low cost. I therefore visited some presentations regarding this novel approach.

#### **Fast Sampling and Analysis of Volatile Organic Compounds in Air by Solid-Phase Microextraction/Field-Portable Gas Chromatography (GC)**

Solid-phase microextraction (SPME) is a sample preparation and sample intro-

duction method in which analytes partition from a sample into a polymer, coated on a fused silica rod of typically 1 cm length and 100 µm in diameter. The fiber is fastened onto the end of a fine stainless steel tube contained in a syringe-like device. The SPME fiber is protected by an outer stainless steel needle and may be moved forth and back within the needle.

The absorbed analytes are thermally desorbed in the injector of a GC for separation and detection. The fiber is mounted in the syringe-like holder as described above, which facilitates the protection of the SPME fiber during penetration through a septum into the analysis device. The syringe mimics an ordinary GC syringe for sample injection. The technology has been patented and the intellectual property is owned by the University of Waterloo (<http://spme.uwaterloo.ca>).

This method can be applied to liquid, gaseous or headspace samples. The fiber can be used to extract target analytes directly in the field. The speaker mentioned that the SPME technique has shown applicability for the analysis of semi-volatile and volatile organic compounds in both air, aqueous matrices and in headspace above dirty aqueous samples, slurries and soils.

The oral presentation was given by Dr. Jacek Koziel (University of Waterloo). SPME was used in the study to sample five target volatile organic compounds (VOCs), including benzene, toluene, ethylbenzene, xylenes, and hexane in indoor air. Concentrations of target VOCs were determined using SPME with a poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) porous coating and only 1 min exposure time. A portable SRI 8610C GC was modified and used for on-site field analysis. The method detection limits for the target VOCs in air ranged from 10 to 20 parts-per-trillion (ppt).

Solid-phase microextraction has several advantages for sample preparation including reduced time per sample, less sample manipulation, elimination of organic solvents, and reduced analyte loss. While originally introduced for the analysis of volatile organic compounds in environmental samples, the technique has now gained acceptance for a wide variety of additional applications. The speaker invited the audience to SRI's (the Canadian company manufacturing the portable GC used in the present study) booth on the company exhibition floor in order to demonstrate the performance of this novel approach to air sampling. Dr.

Koziel had modified a hairdryer for purging air onto the SPME fiber, and after 1 min 'air sampling' with a flow velocity of 0.8 cm<sup>3</sup>/min the fiber was inserted into a portable GC. The fiber introduction was performed by protecting the SPME fiber inside the stainless steel needle (as described above) during penetration through the GC septum. A subsequent thermal desorption (200 °C) evaporated the analytes onto the GC column for rapid GC separation (5 min). GC peaks arising from formaldehyde, acetone and other non-identified contaminants were seen in the spectrum. The SPME was hereafter capable of another extraction/analysis cycle, and *vice versa* – the SPME fiber has a life-time corresponding to at least 100 trapping/desorption events. The technique looks very promising and more information may be provided by Supelco Inc., who has commercialized the SPME technique.

#### **Choice of SPME Fiber for the Qualitative and Quantitative Analysis of VOCs in Air**

Solid-phase microextraction is a fast, cheap and solventless technique which does not need any specific equipment. Ludovic Tuduri *et al.* from Ecole des Mines d'Alès (France) showed the ability of SPME to screen various VOCs in air samples. With this aim in view, the sampling performances of different fibers were compared on a VOC gaseous mixture. They showed reproducible results for each fiber type with equilibrium times varying between 5 min (PDMS fiber) and 90 min (PDMS/caboxen fiber). Many compounds could be detected at very low levels (µg/m<sup>3</sup>), but experimental evidence brought them to the conclusion that high molecular weight compounds displaced low molecular weight compounds, such as methanol and water. Such competitive sorption seems to be a major advantage when analyzing semi-volatiles with low vapor pressures.

#### **Construction and Evaluation of a Field Portable Electrospray Ion Mobility Spectrometer for Detection of Chemical Warfare Agents and Pesticides from Aqueous Samples**

Due to the operation of electrospray ionization (ESI) under atmospheric pressure it is highly compatible with the IMS technique. Pete Tornatore from Dr. Hill's group (Washington State University) pre-

sented a poster about the applicability of ESI-IMS to analyze aqueous samples containing chemical weapon agents and their degradation products. The ESI-IMS system is supposed to be portable and may be utilized not only for detection of warfare agents, but also for monitoring of water supplies for safe use such as drinking water.

### Rapid Separation of Illicit Drugs by Electrospray Ion Mobility Spectrometry/Mass Spectrometry IMS/MS

Laura Markowski from Hill's group presented recent results from the group's

new home-built high-resolution IMS/MS instrument which now enables IMS to be utilized as a rapid separation device for complex mixtures. She mentioned that although ion mobility spectrometry (IMS) has been widely employed as a field-monitoring device for illicit drug detection, it has been limited to field applications due to the low resolution of commercial instruments. The group has demonstrated the rapid separation of illicit and therapeutic drugs (benzodiazepines, opiates, barbiturates, and amphetamines) by IMS/MS. The effects of complex mixtures did not affect sensitivity and selectivity significantly, possibly due to the nature of the ESI method that has an excess of charges to ionize the an-

alytes efficiently. The ESI-IMS/MS instrument can be seen on <http://www.wsu.edu/~hillh/esiimsms.html>.

The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy is an annual event and the next meeting is scheduled for March 4–9, 2001, New Orleans. A specific meeting on IMS has been organized by the International Society for Ion Mobility Spectrometry in August 13–17, 2000, Halifax, Canada. The latter one may be of interest for those who want to get some first hands-on experience in this field.

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Received: March 6, 2000

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# FH – HES

Fachhochschulen – Hautes Ecoles Spécialisées

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Chimia 54 (2000) 370–372  
© Neue Schweizerische Chemische Gesellschaft  
ISSN 0009–4293

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## Computational Chemistry for Kids

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**Abstract:** This article aims to show that computational chemistry is not exclusively restricted to molecular energy and structure calculations but also includes chemical process control and reaction simulation. By having fun with LEGO and a fundamental knowledge of LabVIEW, it is shown how a novice can be introduced to this exciting and challenging field of chemistry.

**Keywords:** Automation · Computational chemistry · Kids · LEGO

### 1. Introduction

Computational chemistry is exotic for many people. Chemists often think that computational chemistry is restricted to

the calculation of molecular energies and geometries.

However, computational chemistry is not limited to this definition. Every chemical process that is associated with the computer, such as the control and the optimization of industrial chemical reactions, is included in computational chemistry. We can say chemical automation, but to do an online optimization of a chemical process, we need to understand not only the automation part but also the kinetics of the reaction as well as the mass and energy balance. Fig. 1 explains

the set-up of the computational chemistry study course at the University of Applied Sciences for Architecture and Technology of Fribourg (EIA-FR).

To help students or children to understand computational chemistry, the best way is to use LEGO. With LEGO, you can build a true reactor to make a simple chemical process like the dilution of a syrup. This process is interesting, because you can use ice cubes of syrup and you can automatically cool the drink. Fig. 2 gives the R&I scheme (resource and instrumentation) of this reactor.

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