

**SIMS 500 -
RAPID LOW ENERGY SECONDARY ION MASS SPECTROMETER FOR IN-LINE
ANALYSIS OF GASEOUS COMPOUNDS - TECHNOLOGY AND APPLICATIONS**

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Abstract:

A new multichannel gas analyzer based on ion-molecule reactions is introduced. This gas phase secondary ion mass spectrometer uses four well defined energy levels for ionization and can quantitatively analyze gas mixtures without any pre-selection techniques. Beside a high sensitivity > 10 ppb for many compounds the instrument allows a fast analysis cycle of > 10 msec per compound. Applications in Dioxin precursor monitoring, VOC ambient air and BTX emission monitoring prove the versatility of the equipment.

Introduction:

The use of an ion beam in forming sample gas secondary ions differs significantly from electron impact or other high energy ionization techniques and opens a new field in analytical and process mass spectrometry. The high detection speed of a mass analyzing system can be utilized for time resolved studies of thermodynamic processes. A characteristic ionization structure of the underlying charge transfer reaction allows to work in complex Hydrocarbon matrices as automotive or incinerator emissions. Possible interferences of isobaric molecules can often be resolved by switching different ionization energy levels and allow the multiple use of the same mass number for different molecules, e.g. mass 30 for NO or HCOH, mass 44 for CO₂ or N₂O. By blocking off the ionization of the background or bulk gas components like N₂, O₂, CO₂, H₂O - as they occur in most emissions - a high sensitivity is gained for trace compounds under study.

Technology:

Electron impact ionization is somehow simplified proceeding through a momentum transfer of the electron's motion in respect to the molecule onto the molecule. This fast process covers all different energies from 0 eV to the kinetic energy of the electron resulting in the formation of various fragment ions. On the contrary, a well prepared ground state ion beam carries a sharp internal energy level (the ionization potential) and the interaction with a molecule gives defined ion products. Picture 1 shows the schematic setup of the analyzing system. A pressure controlled gas inlet system feeds a flow of 1.5 cm³/min STP of e.g. Xe to a source chamber (section A). An electron impact source generates a several microampere strong ion beam of Xe^{+3/2} ground state ions. This ion beam is imported to a high frequency 8-pole field with translational energies of less than 5 eV (lab).

In section B, sample gas is introduced to a gas cell and crossed with the ion beam. All secondary ions formed in charge transfer reactions are again stored in a high frequency field. Mass analysis is done through a 200 mm long quadrupole mass filter.

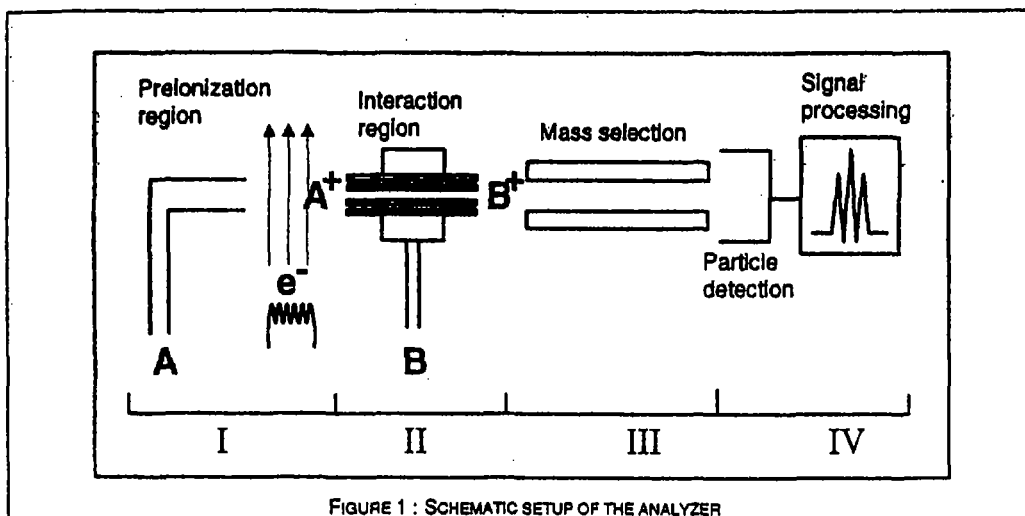
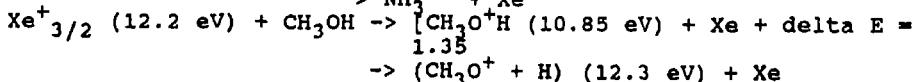
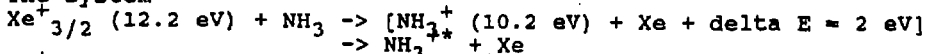


FIGURE 1 : SCHEMATIC SETUP OF THE ANALYZER

Generally, all sample gas molecules with a lower ionization potential than the incoming ion beam will be ionized. However, the excess energy of the reaction, e.g. ΔJ_p , has to be distributed to internal degrees of freedom or bond rupture of the molecular ion.

The reaction system $Kr^{+}_{3/2}$ (13.99 eV) + $N_2 \rightarrow N_2^+$ (15.5) + Kr
 $Kr^{+}_{3/2}$ (13.99 eV) + CO \rightarrow CO $^+$ (13.98) + Kr
 demonstrates the separation of mass identical (isobaric) molecules by the ionization process. As the ionization potential of the Nitrogen molecule is higher than the Krypton ions, no ionization occurs and Carbon Monoxide can be detected easily on mass 28.

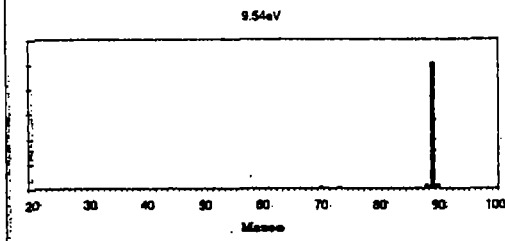
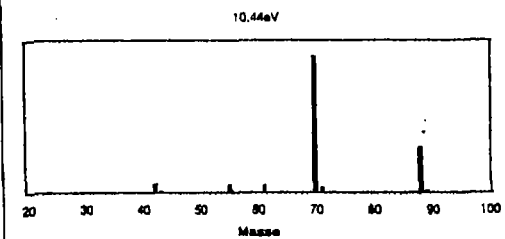
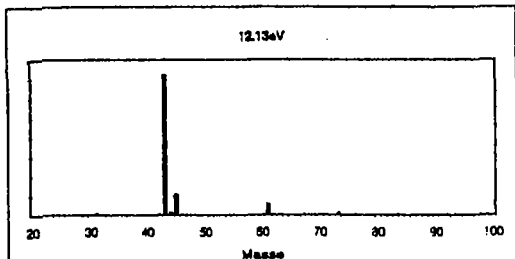
The system



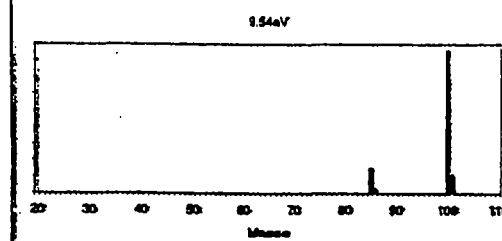
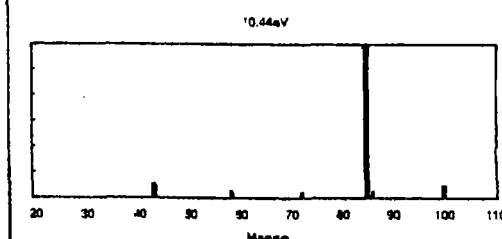
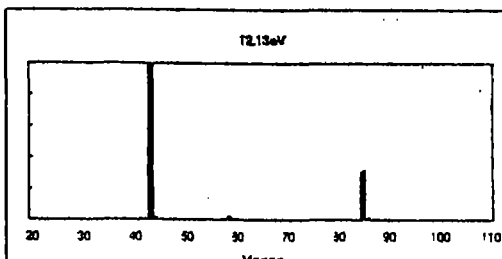
shows how excess energy of the collision (the difference of ionization potential of the reaction partners) either populates internal vibrational levels as in the Xe-Ammonia system, or leads to a bond rupture and loss of a Hydrogen atom as in case of the Xe-Methanol collision system.

Picture 2 shows the mass spectra of 2 different fragile molecules ionized with 3 different ion beams. The 9.54 eV ion beam is a prolonged ion beam - thus for Ethylacetate with ionization potential above 9.54 eV a proton transfer becomes available to form the M+1 peak.

Ethylacetat Molecular Weight: Ionisation Potential:
 C₄H₈O₂ 88 amu 10.08 eV



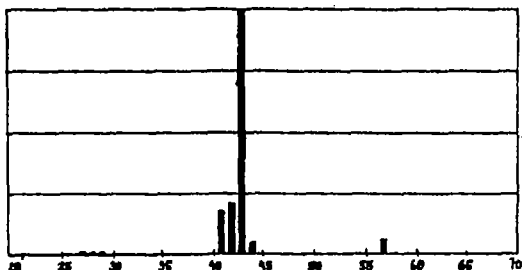
Acetylacetone Molecular Weight: Ionisation Potential:
 C₅H₈O₂ 100 amu 8.87 eV



The switching process between ionization levels is a matter of < 5 sec and so a large number of different molecules can be measured. In fact, some mass numbers represent different molecular species within different ionization energies. The advantage of a sharp energy level in the ionization process can be used to quantitatively separate isomers. When enough excess energy is applied in the ionization process, the distribution of the fragment ions represents the isomeric structure of the molecule as shown in picture 3 and treating the molecules as vectors instead of single masses

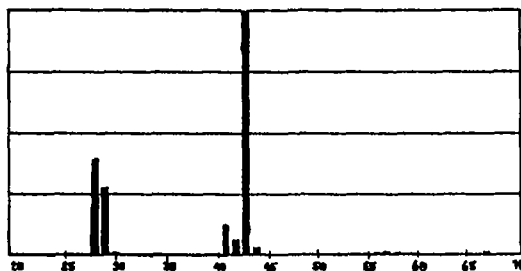
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UMF / SC7 - Bar Graph Plotter Output



I-BUTANE C4H10 N=58

UMF / SC7 - Bar Graph Plotter Output



N-BUTANE C4H10 N=58

with a fast matrix calculation will quantify isomers in Hydrocarbon mixtures.

Applications:

A) Halogenated Hydrocarbons

Over the last four years a method has been developed to study Chlorobenzenes and Chlorophenoles in the raw gas of waste incinerator systems (PMS: University of Umea, Sweden). These gas phase molecules correlate strongly to the dioxin formation potential of the plant (correlation factor is function of plant).

A fast optimization of the incinerator setup and input rate is possible by minimizing the chloro-aromatic concentrations in the incinerator raw gas. Halogenated Hydrocarbon detection of soil gases give useful information of soil contamination by landfill deposits and near industrial areas. Metro Toronto, Canada, successfully uses the instrument to monitor the sewer house and protect workers from toxic solvents introduced by sewer water. The instrument controls up to 20 individual compounds up into a carrier gas stream by headspace. As different industrial processes use specific solvents, an easy identification of the cause is possible.

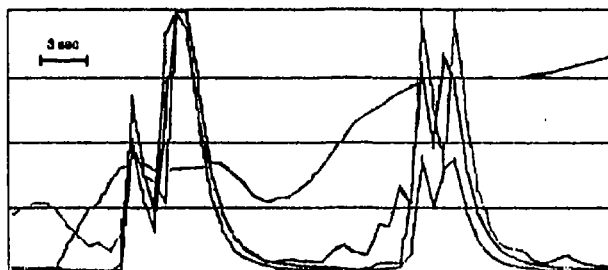
B) VOC monitoring

Industrial hygiene and ambient air monitoring of heavily industrialized areas use the SIMS 500 technology as automated control equipment, e.g. Tula - Russia, Ciba Geigy - Switzerland, Eco Logic - Canada.

C) BTX automotive emissions

Toluene, Styrene, 3-M-Benzene as anti-knock additives to fuels together with Benzene being formed in engine combustion as well as catalytic converter systems under special operating conditions are studied by many relevant auto makers and environmental protection agencies. Emissions of the above mentioned compounds are strongest in transient conditions as start up acceleration and deceleration, and only a fast and sensitive analytical system can demonstrate when and to what concentrations the emissions are generated.

Picture 4 shows the acceleration of a modern vehicle from 0 to 80 km/h and the corresponding emissions of Benzene, Toluene and Methane.



Speed / 100 km/h

Toluene / 50 ppm

Benzene / 50 ppm

Methane / 70 ppm

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