

Gas analysis by IMR-MS: a comparison to conventional mass spectrometry

U. Tegtmeier, H. P. Weiss and R. Schlögl

Institut für Anorganische Chemie der Johann Wolfgang Goethe-Universität, Niederurseler Hang, D-60439 Frankfurt, Germany

Received November 5, 1992; revised January 13, 1993

Summary. Ionisation of small molecules via ion-molecule reactions (IMR) offers the possibility to reduce fragmentation caused by high energy electron impact ionisation. Widely varying rate constants for the IMR processes allow to introduce additional species selectivity together with the mass selection in a quadrupole system. A comparison between low energy electron impact ionisation and IMR illustrates the potential of this new ionisation method in gas analysis applications.

Introduction

Multicomponent, time resolved gas analysis with electron impact (EI) quadrupole mass spectrometers is a commercial analytical technique. The large number of instruments offered and the high degree of automatisations in these instruments indicate the significance of this technique in a large number of industrial and research applications.

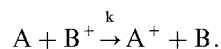
A major draw-back with these instruments is the fragmentation of molecules leading to complex mass spectra and multiple overlapping intensities in complex gas mixtures; quantification and even qualitative gas analysis may become impossible. Commercial instruments quantify their results with calibration gases using mass peaks with no overlap. This procedure finds quickly its limits with complex gas mixtures. But even in simple cases considerable problems can occur. In carbon oxidation kinetics the product ratio CO/CO₂ is of great significance but difficult to quantify due to the pressure-dependent fragmentation of CO₂ into CO and oxygen. The partial oxidation of methanol to formaldehyde over catalysts with air produces a gas mixture of steam/CO/CO₂/methanol/formaldehyde/oxygen/hydrogen which is not to be analysed with a conventional electron impact MS. Similar problems arise in the determination of NO₂/NO/water/air.

Recent publications [1, 2] advocated the IMR mass spectrometry (IMR-MS) technique as solution to such problems; it offers the selectivity of gas chromatography (one species – one peak) with the time resolution and analytical convenience of mass spectrometry. The – in comparison to a

commercial quadrupole mass spectrometer for gas analysis – significantly more complex (and costly) IMR mass spectrometer was tested in its performance in some practical applications against conventional electron impact ionisation at low energies. A home-modified pre-commercial version of the laboratory IMR-MS instrument of Ionentechnik-Atomika was used for the experiments.

The ion-molecule reaction

The IMR process is well-known in ion physics. It is an important path of primary ion loss in a plasma and can be symbolised as follows:



At thermal interaction energies (IE) the energy balance of the reaction can be written as

$$IE_B = IE_A + DE.$$

with DE standing for the sum of excitation energy stored in the secondary ion and the translational energy stored in all reaction products. No fragmentation will occur only if the internal energy is smaller than the first dissociation level in the secondary molecule. For polyatomic molecules the amount of internal energy stored in electronic and vibrational excitations can be large and the first level of dissociation may be low above the ground state. In such cases the primary ion must be selected such that the difference in ionisation potentials between primary and secondary ions is as small as possible. These considerations lead to the conclusion that the noble gas primaries used here are only good for small two and three atomic molecules but organic molecules with their low ionisation potentials (below ca. 9 eV) will store in many cases more excitation energy as needed to break one chemical bond. The ionisation energies for the primary ions used here are 14.00 eV for Kr⁺ and 12.13 eV for Xe⁺ [3]. These rather large values for the chemically non-reactive noble gas primaries require a very narrow distribution in energy as crucial design parameter for the IMR-MS instrument in order to really exploit the advantages of IMR ionisation over EI.

IMR-MS is in principle a well-known technique in mass spectrometry of medium-sized organic molecules known there as chemical ionisation. The potential of the method

was described some 25 years ago [4] and the state of the art is described in a recent book on the subject [5]. The present work has, however, no reference in this compilation of known applications.

A large number of reaction systems for IMR-MS applications have been developed over the years. The types of reaction involved can be classified in proton transfer reactions, condensation reactions between the operation ion and the molecule for analysis and charge transfer reactions. The present study is limited to the last type of chemically non-reactive charge transfer reactions with noble gases as they are conceptually most simple in relation to EI.

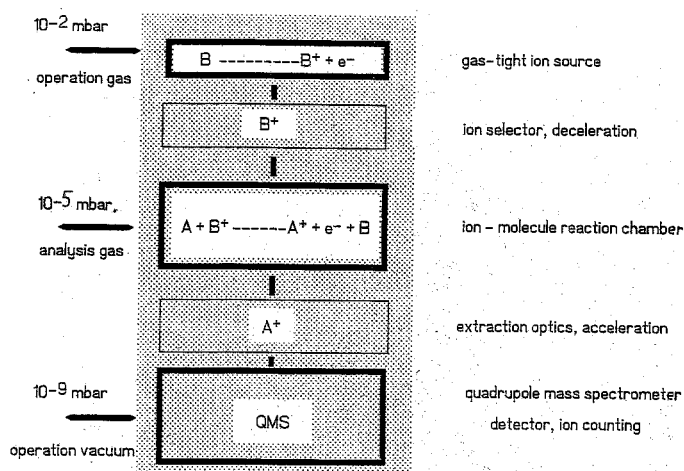
Comparisons of the fragmentation yields between EI and IMR in organic chemistry have been published earlier for e.g. cyclohexane [6] and the analytical advantages of IMR being low fragmentation combined with high sensitivity have been stated [7] without extending the analysis to small gas molecules.

The instrumentation

The determination of rate constants [8] which significantly affect the relative intensities in IMR mass spectrometry was the driving force to develop instrumentation [9] of which the analytical instrument used here is a simplified off-spring. Scheme 1 illustrates the principal components of the system. In the present realisation the linear arrangement of all components is used as shown in the scheme. The commercial Ionentechnik-Atomika instrument is more complex. It uses a sector field primary ion mass spectrometer combined with a Wien filter for immediate selection of several primary ion species with narrow and well-defined energy distributions. The presence of unwanted other ions or stray electrons in the main collision chamber is also excluded. An improved ion optics ensures high definition of all energetic parameters and efficient transfer of the A^+ ions into the quadrupole analyser and so greatly enhances the sensitivity compared to the present instrument.

The operation gas (here Kr, Xe) is ionised in a conventional gas-tight electron impact ion source. Electrostatic lenses allow only the ions to travel with a controlled kinetic energy into the main reaction chamber which is a high frequency octopole field enclosing the ions. Here the primary ions react with the injected analysis gas introduced via an electrically from the octopole insulated capillary from a pressure reduction system (differentially pumped gas-jet separator). An electrostatic extraction optic and a post-acceleration system transfer the analysis gas ions (and a fair fraction of the primary ions which have not reacted) into the conventional quadrupole mass analyser equipped with a 90° off-axis photomultiplier detector, multiple peak trend analysis system and counting electronics (all computer-controlled).

The whole instrument is placed in a spherical stainless steel vessel. A heated stainless-steel capillary (0.1 mm i.d.) provides the interface to the analysis gas. Heating of the whole vacuum system during operation to 395 K and sufficient pump speed (500 Is^{-1}) ensure a dynamic response of below 1 s (90% to 10% abs. intensity) for polar molecules such as water, ammonia or methanol. The distinction between polar and non-polar analysis gases made earlier [1] with respect to the dynamic response is not required in the present system.

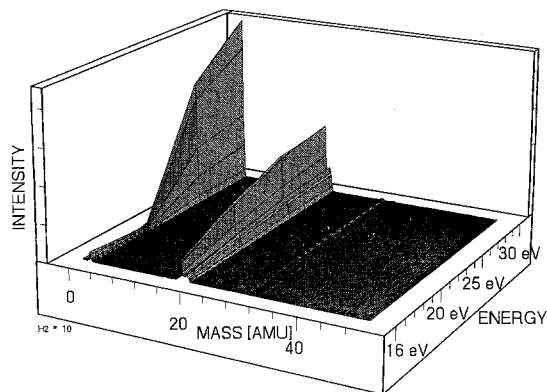


Scheme 1. Principal components of the IMR-MS instrument used in this study. The operation pressures are typical values maintained through a twofold differential pumping system with two 240 l turbomolecular pumps. The analysis gas jet separator has its own differential rotary pumping system

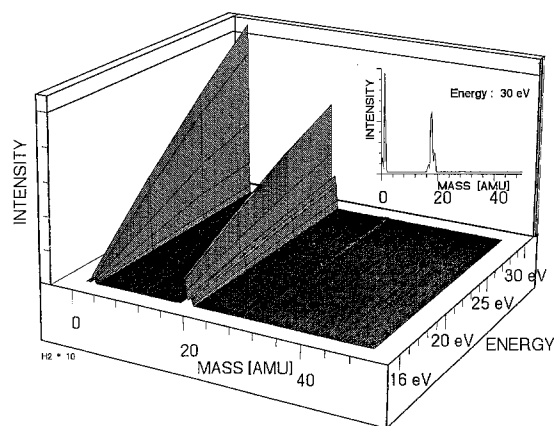
This arrangement allows mild ionisation of analysis gases. Selecting the proper primary gas adds additional selectivity to the system. The rate constants of IMR processes vary over several orders of magnitude and are well-known for many reactions. Exploiting this information allows to enhance or suppress the IMR of individual components of the gas mix. In the present example (see Fig. 2) the detection of nitrogen is fully suppressed. Minimisation of the count rate at m/e 28 with respect to the reference intensity of the primary ion current allows a convenient alignment of the lens and filter system in order to suppress direct electron impact ionisation. Detuning of these systems permits recording of the electron impact mass spectrum at any chosen energy between 10 and 30 eV. This detuned mode was used for the electron impact spectra shown in the present study. Reference experiments with a conventional quadrupole mass spectrometer at the same low energies gave no indications of specific intensity losses in the spectra due to the presence of the IMR elements.

Characteristic data were collected over a period of 7 months of permanent operation to illustrate the performance of the instrument in the analysis of real gases. These were used as research-grade qualities without any purification from a gas manifold connected to an integral reactor for heterogeneous catalytic conversion tests. All tubing was of baked stainless steel equipped with Swagelock fittings and taps. Gas flow rates of typically 60 lmin^{-1} were used. The sample fraction for the IMR-MS was pumped through the capillary which was aligned parallel to the main gas stream in downstream direction.

The example spectra were recorded in total times of 100 ms illustrating the time resolution for dynamic changes in the gas composition possible with the present instrument. A faster measuring rate is not helpful as the pumping characteristics of the analysis gas limits the total dynamic response and not the data acquisition. A trend analysis of a complex gas mixture with up to 10 components is possible with one data point per second allowing to use the instrument in temperature-programmed desorption analysis applications



a



b

Fig. 1. Intensity vs. ionisation energy curves for wet hydrogen in **a** the EI mode and **b** the IMR mode. The intensity scales are the same in both Figures. The inset in **b** shows the 30 eV IMR spectrum indicating the extent of protonation and fragmentation. The primary ion was Kr^+

or to obtain accurate profiles of rapidly changing chemical reactions e. g. of combustion processes.

The total pressure in the IMR chamber was about 10^{-5} mbar during operation in a sensitive mode without fragmentation. The dominant partial pressure was that of the operation gas. This pressure is high with respect to possible ion scattering processes complicating fragmentation and quantification. It turned out, however, that at substantially lower pressures the IMR mode did not come into operation.

Results and discussion

Wet hydrogen is used to illustrate the different evolution of ion intensities in the IMR mode and after conventional (EI) at low energies. In Fig. 1 the pronounced threshold in the m/e 1 EI signal can be seen together with the different behaviour for the easier to ionise water signal at m/e 18. Extensive protonation (m/e 19) (see inset in Fig. 1b) occurs in both modes and is a consequence of the presence of low-energy H^+ ions. At impact energies of conventionally used 70 eV the protonation of water is negligible with ion sources used in commercial instruments for gas analysis.

With IMR ionisation the threshold is not observed and rather similar intensity vs. primary energy curves for water and hydrogen are obtained. Ionisation occurs in IMR via transfer of charges which is not constrained by molecular binding energies causing the appearance potential barrier.

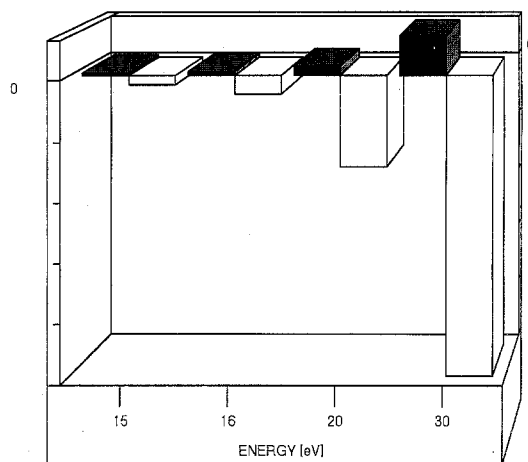


Fig. 2. Evolution of the m/e 28 nitrogen signal from ambient air generated by Kr^+ IMR (*top*) and EI (*bottom*) ionisation as function of increasing primary energy. The intensity scale is enlarged by a factor of 10 for the IMR series. □ MS; ■ IMR-MS

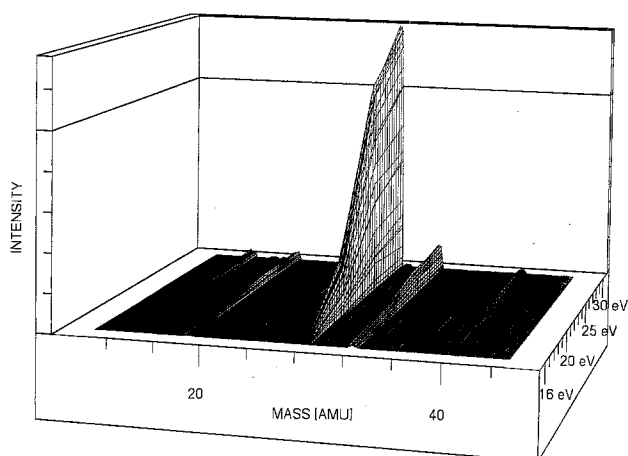


Fig. 3. EI spectra of ambient air as function of electron energy

Fragmentation of hydrogen is observed with both primary ion species as the corresponding ion molecule reactions involving molecular hydrogen are strongly endothermic (Kr^+ : 1.43 eV, Xe^+ : 3.3 eV [10]).

Figure 2 illustrates the suppression of an intense signal by selective IMR. The nitrogen m/e 28 signal from ambient air is used. It can be seen that at conventional primary ion energies the nitrogen signal can be widely suppressed (the intensity is expanded by a factor of 10 for the IMR series). It may be concluded that this is only due to the low kinetic energy of the ionising particle and not a benefit from the small rate constant of the particular charge transfer reaction. This is clearly not the case as can be seen from the complete air spectrum measured with EI shown in Fig. 3. In the electron energy range 16 to 20 eV all ion intensities are very weak. The N_2^+ ion is formed with significant preference over all other ions as can be seen from the intensity ratio between m/e 28 and m/e 32 which should be for air approximately 4:1 but is found to be 12:1 at 30 eV ionisation energy.

The advantage of IMR over EI is illustrated by the analysis of 80 mbar methanol in nitrogen at ambient pressure

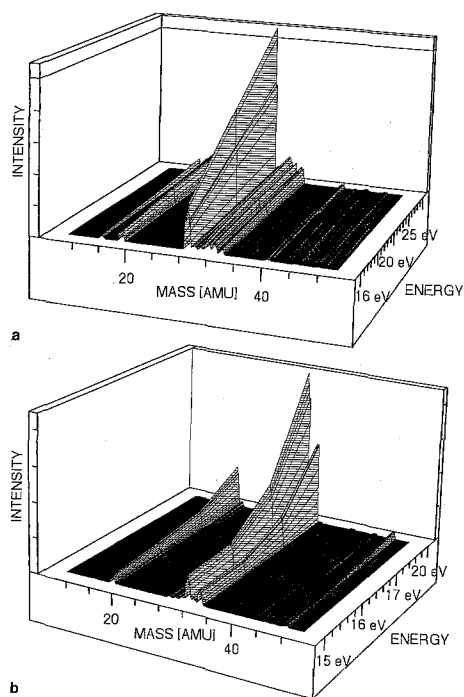


Fig. 4a, b. Intensity vs. ionisation energy curves for 80 mbar methanol in nitrogen. Plot **a** shows the EI mode data, plot **b** the IMR data. The primary ion was Kr^+

illustrated in Fig. 4. In the EI spectrum the carrier gas nitrogen results in the dominant intensity followed by water as impurity in the methanol. The methanol spectrum is least in intensity and is split into 4 signals in the range m/e 31– m/e 34. An additional contamination of formic acid at m/e 48 is barely visible due to almost complete fragmentation of the molecule. In the IMR mode the carrier gas signal is fully absent and the dominant signal is the molecular ion peak of methanol at m/e 32. The second most intense signal is a twofold protonated molecular ion. Impurities of water and formic acid are detected as clear signals. No fragmentation occurs as can be seen from the absence of peaks at m/e 12 and m/e 16.

The IMR rate constants can be significantly different for different primary ions. In Fig. 5 the spectra of ambient air are displayed which were recorded with different primary ions. The Xe^+ ion enhances the oxygen signal by a factor of 5. The IMR rate constants from the literature [2] are for Xe^+ $1.1 \times 10^8 \text{ cm}^3 \text{ s}^{-1}$ and for Kr^+ $0.3 \times 10^8 \text{ cm}^3 \text{ s}^{-1}$ suggesting an intensity ratio of 3.6. Again no fragmentation of molecular oxygen is observed. Xe^+ ionisation leads further to a significantly reduced water signal with no fragmentation in both cases.

Fragmentation in the IMR mode depends strongly on the abundance of primary ions in the reaction chamber. This effect is believed to arise not only from the ionised species but also from the presence of a large abundance of neutral noble gas atoms. They can act as diluent for the analysis gas ions preventing them from collisions with neutral analysis gas molecules. The influence of the operation gas pressure on the fragmentation is illustrated in Fig. 6 showing that CO_2 at ambient pressure can be analysed without any fragmentation (into CO and O_2 , see traces at m/e 28 and 32) after adjusting suitably the primary ion abundance. CO_2

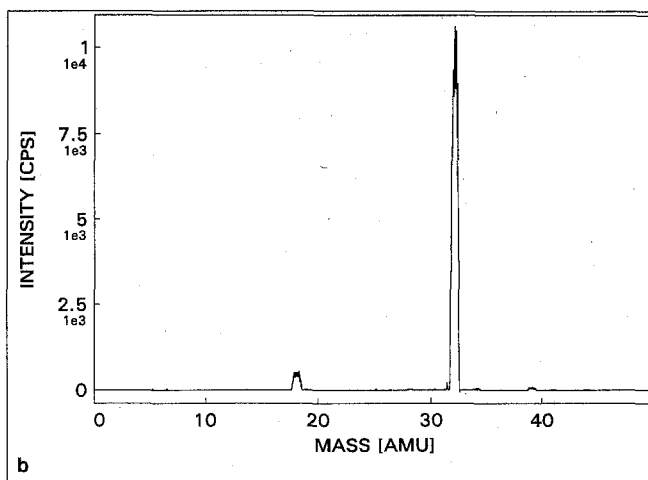
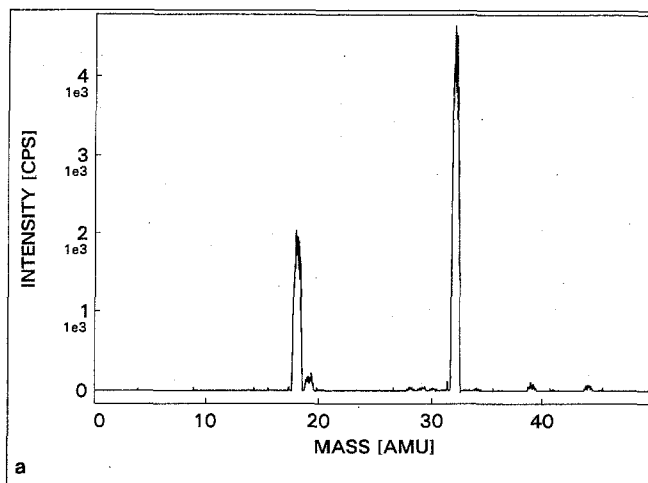


Fig. 5. IMR spectra of ambient air recorded with **a** Kr^+ and **b** Xe^+ at 16 eV energy

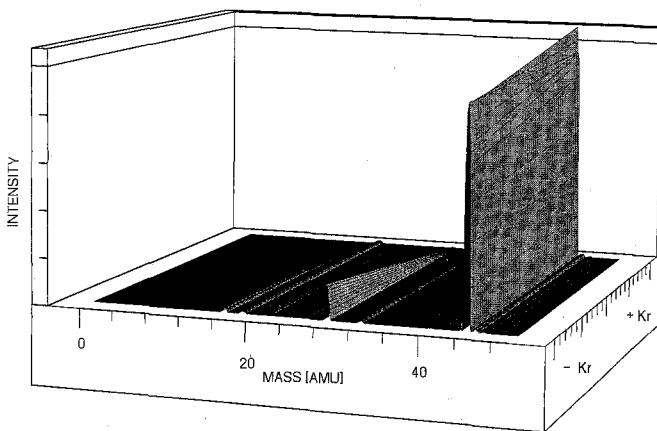


Fig. 6. IMR data of CO_2 at ambient pressure as function of the primary Kr^+ ion abundance present in the reaction chamber

was found to react sensitively to the adjustment, with many other gases the primary ion abundance is much less critical.

Analysis of mixtures of methanol and formaldehyde in air is not possible with EI due to extensive fragmentation. A quantitative determination was possible with IMR-MS

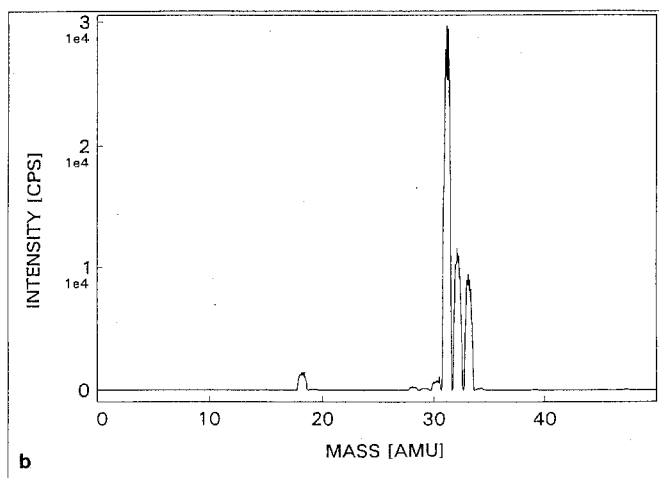
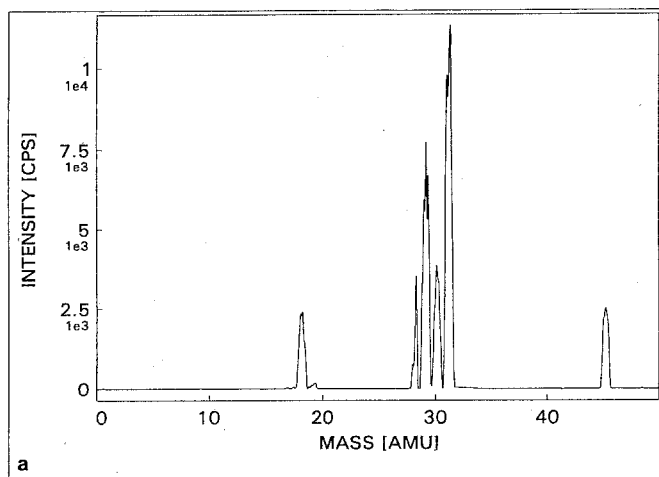


Fig. 7. Analysis of **a** formaldehyde and **b** methanol with IMR. Maximum sensitivity is achieved with Kr^+ for formaldehyde (base peak $\text{M} + \text{H}$, at 16 eV) and with Xe^+ for methanol (base peak $\text{M} - \text{H}$, at 16 eV). The aqueous solution of formaldehyde used for evaporation was heavily contaminated with CO_2 (m/e 44 in plot a)

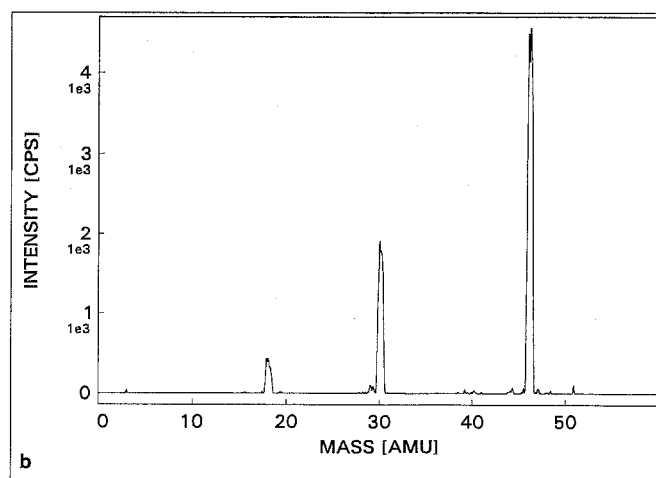
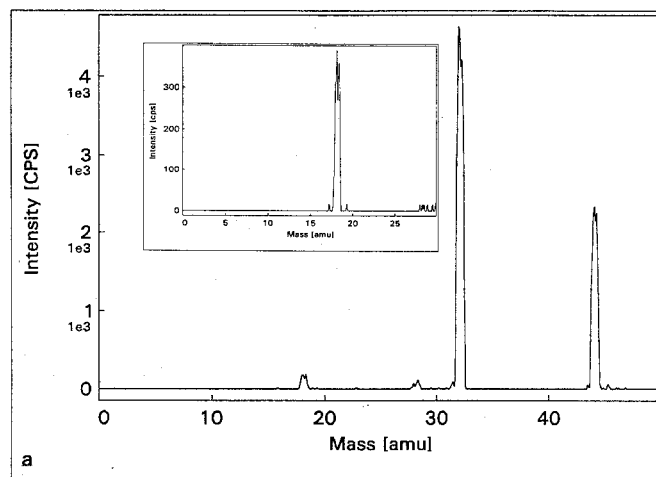


Fig. 8a, b. IMR data of major combustion products. **a** A mixture of CO_2 and O_2 (10:1) in nitrogen analysed with Kr^+ at 16 eV. The inset illustrates the complete absence of any fragmentation. Plot **b** shows a mixture of NO and NO_2 in moist nitrogen analysed with Xe^+ at 16 eV. The absence of peaks at m/e 14 and m/e 16 documents the absence of fragmentation

using two different primary ion species. Figure 7 illustrates that formaldehyde can be analysed with high sensitivity using Kr^+ at m/e 29 and methanol with Xe^+ at m/e 33. The data show clearly that in IMR no fragmentation does occur involving breaking of the C-O bonds. The signals acquired in 100 ms represent concentrations of about 10000 ppm in nitrogen. The detection limit at fast acquisition times is about 10 ppm for each component but can be improved by a factor of 10 with a slow acquisition time of 30 s. A precise quantitative analysis of this gas mixture is conveniently made by switching the operation gas from Kr to Xe in subsequent scans. Facilities for such an automated mode of operation are provided by the commercial instrument.

The absence of fragmentation in small molecules using the IMR ionisation technique is finally demonstrated in Fig. 8. Mixtures of CO_2 and O_2 show no fragments at m/e 12 and m/e 16 as can be seen from the inset in Fig. 8a. As there is also no signal at m/e 28 from nitrogen the products from combustion or fermentation can be easily analysed quantitatively with high time resolution using IMR. Mixtures of NO and NO_2 in moist nitrogen (22 mbar water

vapour) can be analysed quantitatively without fragmentation and cross sensitivity between NO and NO_2 as shown in Fig. 8b. The two plots illustrate that the instrument can be used to analyse the major high temperature combustion product mixtures (water, CO , CO_2 , NO_x oxygen) without any pre-separation or gas drying procedure with a time resolution of ca. 1 s. Quantification is facile as no overlapping peaks occur. Rapid switching between primary ion species [2] allows to maximise the sensitivity of the instrument for each of the combustion components. Literature data [11] suggest that the difficult to detect species N_2O may be analysed with Ne^+ with a cross section enhancement over CO_2 by a factor of 7.

Conclusions

Ionising small molecules with noble gas primary ions using ion-molecule reactions is of significant advantage over conventional electron impact ion generation used in present commercial instruments for gas analysis. The suppression of

fragmentation was demonstrated in a number of critical cases. Additional selectivity in the IMR process for complex gas mixtures can be achieved with selected primary ion species. A large data set is available of kinetic rate constants for many possible IMR processes [2, 5, 7, 8, 12] allowing a systematic choice of appropriate primary ions. The future commercial version of the present instrument will have facilities for using multiple primary ions. Then the whole range of different types of ion molecule ionisation reactions developed for organic molecules can be applied to gas analysis. With such an instrument true quantification of selected components in complex gas matrices will be possible without corrections for overlapping peak. The total quantitative analysis of real multicomponent gas mixtures requires, however, significant additional efforts in developing new modes of operation of this versatile new analytical tool.

Acknowledgements. Many discussions with W. Lindinger, K. Leiter and J. Hirber are gratefully acknowledged. Ionentechnik (Innsbruck, Austria) provided the test instrument. Ionentechnik-Atomika (Munich, Germany) supported the hardware modifications. Calibrated gas mixtures were donated by A. Schäfer-

Sindlinger from Degussa. Additional support came from the Fonds the Chemischen Industrie.

References

1. Lindinger W (1990) Chem Tech 19:93
2. Lindinger W, Leiter K, Anriollo M (1991) Chem Tech, p 20
3. Marx R, Mauclaire G, Derai R (1983) Int J Mass Spectr Ion Phys 47:155
4. Field FH, Munson MSB, Becker DA (1966) Adv Chem Ser 58:167
5. Harrison AG (1992) Chemical ionisation mass spectrometry. 2nd edn. CRC Press
6. Harrison AG, Lin MS (1984) Org Mass Spectrom 19:67
7. Macoll A (1986) Org Mass Spectrom 21:601
8. Pahl M (1957) Z Naturforsch 12:632
9. Lindinger W (1975) Phys Rev (A) 7:328
10. Smith RD, Smith DL, Futrell JH (1976) Int J Mass Spectr Ion Phys 19:395
11. Laudenslager JB, Huntress WT, Bowers MT (1974) J Chem Phys 61:4600
12. Jones TTC, Birkinshaw K, Jones JDC, Twiddy ND (1982) J Phys B 15:2439