

Hiden HPR-60 Modulated Molecular Beam Mass Spectrometer for Reaction Kinetics

Quantitative measurement of reactive or condensable species from the gas phase requires careful design of the mass spectrometer sampling system. In both low pressure applications, such as plasma processing, and high pressure applications, such as combustion studies and thermal analysis, the efficient transfer to and subsequent detection of reactive species within the mass spectrometer are critical.

Hiden Analytical manufacture compact MBMS systems for a variety of applications. Here we review the design criteria, and describe the application of the Hiden HPR-60 MBMS to Combustion Research.

Mass spectrometry provides fast, unequivocal identification of the various components of a gaseous mixture. Since most combustion processes are at atmospheric pressure however, and mass spectrometers operate at around 10^{-5} mbar, a suitable pressure reduction scheme must be employed.

If the species to be measured are stable molecules then this pressure reduction may take the form of e.g. a long, narrow capillary (for processes around atmospheric pressure), or a single orifice separating the process from the mass spectrometer (for lower pressures). Other schemes exist for intermediate pressures.

If the species to be measured are reactive or condensable however, then they would make many collisions during transit through the capillary and be lost before they reached the mass spectrometer. For low pressure cases, where a single orifice inlet is used, quantification of reactive species is possible but difficult because the small number of reactive species are superimposed on a very large background signal. Several stages of differential pumping help to reduce the background to a much lower level. Modulation of the sampled beam then allows this small background to be separated accurately from the overall spectrum, which in turn allows accurate quantification of the reactive or condensable species.

A schematic of the Hiden HPR-60 MBMS system is shown in Figure 1. The mass spectrometer is housed in its own vacuum chamber with a further two intermediate expansion chambers between it and the process. Both the mass spectrometer chamber and expansion chambers are continuously pumped by separate turbomolecular pump sets. Small aperture plates separate these different, low pressure chambers from the process chamber. Process gases undergo free jet expansion from the higher pressure combustion chamber to the lower pressure expansion chambers and then to the mass spectrometer. In doing so a molecular beam is formed in which the gas molecules no longer collide with each other or the walls. This molecular beam then contains a mixture of stable and reactive gas molecules which pass to the mass spectrometer ioniser without further reaction, maintaining the same state with which they left the combustion chamber.

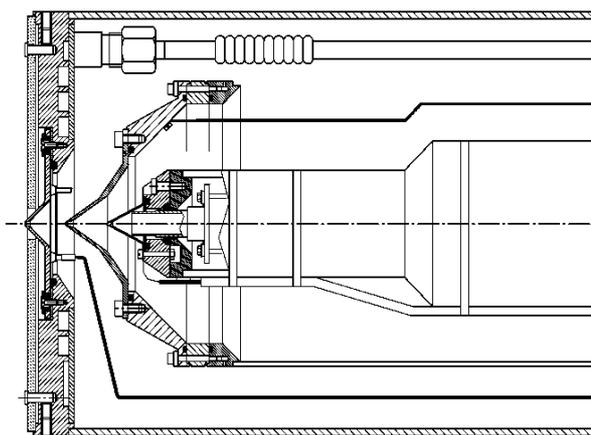


Figure 1. MBMS Detail Schematic

If the molecular beam is then periodically interrupted (with a rotating disk chopper for example), the result is a modulated molecular beam. The spectrum of this modulated molecular beam can then be separated from the combined beam-plus-background spectrum, greatly enhancing the beam-to-background signal ratio. Figure 2 shows the corresponding timing diagram. The gate and delay functions are provided in the HPR-60 control electronics and controlled via the MASsoft software program.

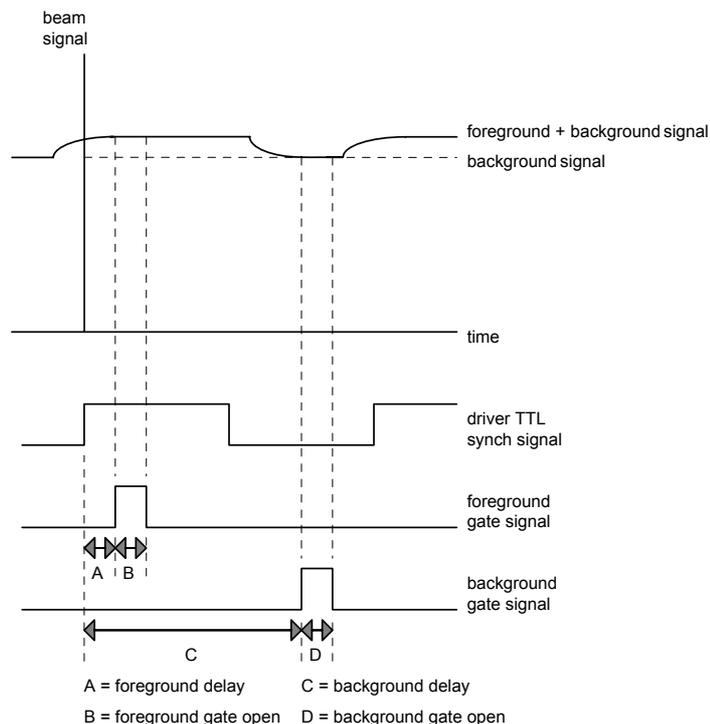


Figure 2. Modulation Timing Diagram

The addition of several stages of differential pumping, together with a modulation scheme greatly enhances the beam-to-background signal ratio. These additional stages increase the distance between the process aperture and mass spectrometer ioniser however, which in turn reduces the beam component density in the ioniser. Adding further stages also increases the effect of any misalignment between the ioniser and molecular beam path. Conversely, positioning the apertures close together reduces the overall effectiveness of the differential pumping which in turn increases the background component density in the ioniser. A careful design should therefore incorporate optimal positioning of the apertures together with the facility to align the ioniser with the molecular beam whilst maximising the effective pumping of background gases. If the reactive species to be measured include an ionic component then it is also desirable to have the facility to set the electrical conditions (DC or RF biased, grounded, floating) of the sampling aperture plate. All of these design features can be incorporated into the Hiden HPR-60 MBMS system for maximum flexibility.

MBMS techniques are ideally suited for the measurement of pyrolysis products from combustion processes and the Hiden HPR-60 MBMS system has been employed to measure reactive and condensable alkali trace metals from gasification environments as part of the wider research into forms of sustainable energy.

The main components of the apparatus are the sample preparation system, the electrical furnace, and the Hiden HPR-60 MBMS analyser, Figure 3. In this example, the sample preparation system consists of a gas flow (carrier gas) system which is normally argon or helium, together with a nebuliser system for the introduction into the carrier gas of samples of gases such as Hydrogen Chloride, Chlorine, or liquid Potassium Chloride, Sodium Chloride, etc. The furnace, which is about 1.5 metres tall, can be set to run at temperatures up to at least 1500 degrees. The gas samples are introduced at the top of the furnace and the HPR-60 MBMS is mounted on a mobile cart that can be wheeled up to the bottom end of the furnace. It can be readily retracted when necessary, to clean away condensed material that may otherwise block the inlet orifice to the analyser when working with samples such as KCl. The HPR-60 MBMS system in this example is capable of sampling either ions or neutral species from atmospheric pressure.

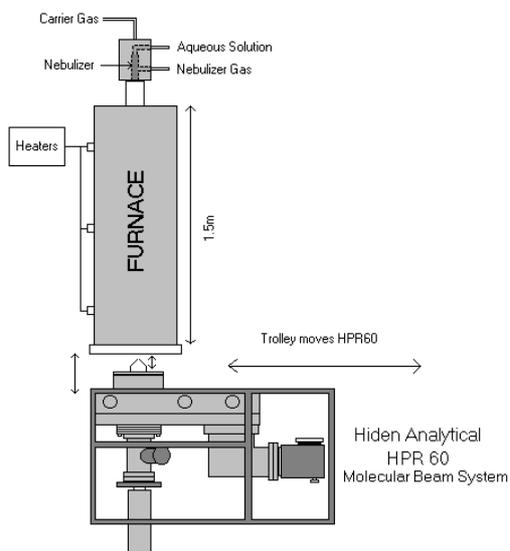


Figure 3. Furnace/MBMS System

Threshold Ionisation techniques are a valuable method of identifying the origin of a particular reactive species. Gas samples of Ar/HCl and Ar/Cl₂ were used to compare measured threshold ionisation energies with published data for the production of HCl⁺ and Cl⁺ ions from HCl or Cl₂. Figure 4 shows a typical scan for Cl⁺ from HCl at a furnace temperature of 1000C; Figure 5 shows the corresponding scan for Cl₂. Clearly identifiable are Cl⁺ derived from the undissociated parent molecules (HCl in Fig 4; Cl₂ in Fig 5) and from the dissociation products in the reactor (Cl and Cl₂ in Fig 4; Cl in Fig 5).

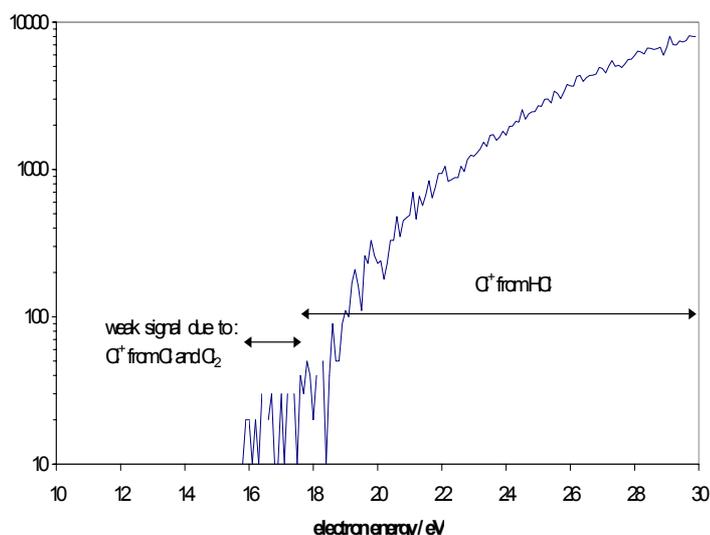


Figure 4. Appearance Potential: Cl⁺ from HCl at 1000C

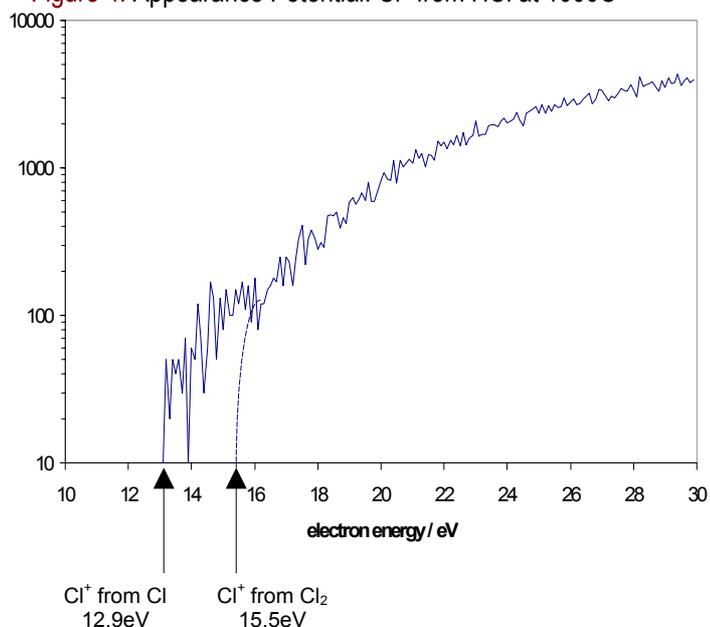
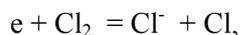


Figure 5. Appearance Potential: Cl⁺ from Cl₂ at 1000C

In addition to these threshold ionisation measurements the HPR-60 MBMS may be operated in the complementary negative ion mode (Figure 6) to look for negative ions formed by either (i) electron attachment through a reaction in the HPR60's ionisation source such as;



or through (ii) pair production, such as,

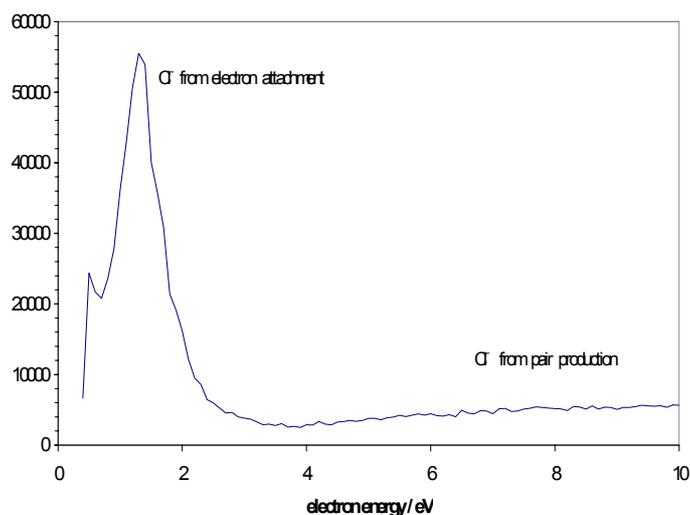


Figure 6. Cl⁻ from electron attachment/pair production from Cl₂/Ar

Similar results are obtained for the formation of Cl⁻ from KCl/Ar mixtures as seen in Figure 7.

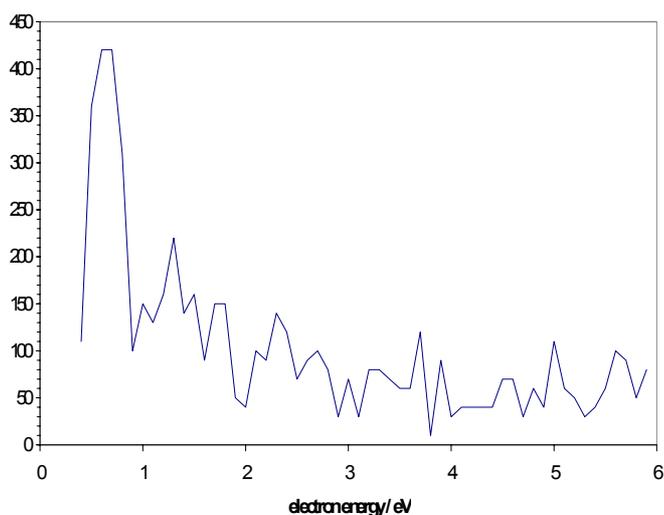
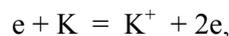


Figure 7. Cl⁻ from electron attachment from KCl/Ar

Figure 8 shows the appearance potential scan for the formation of K⁺ ions at a furnace temperature of 1500C. There is an ionisation threshold at around 5.5 eV together with a significant increase in the rate of ionisation at around 15 eV. After calibration against an argon standard, the threshold energy of about 5.5eV can be attributed to the process;



the K being formed by dissociation of KCl in the furnace. The increase in signal at 15eV is attributed to formation of potassium ions from the undissociated parent KCl.

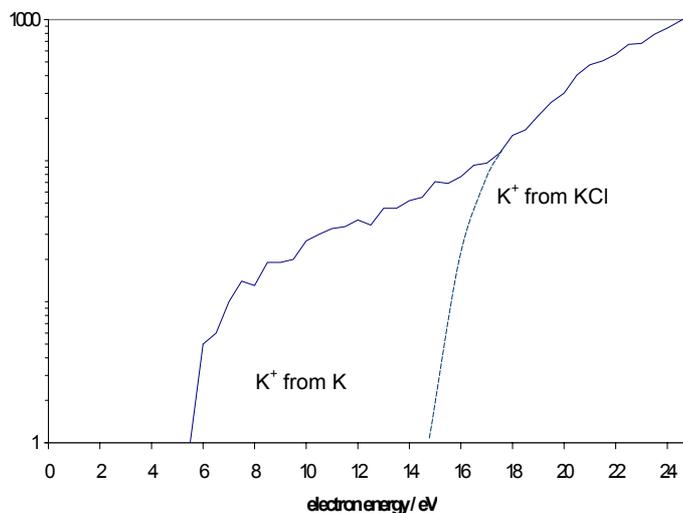


Figure 8. K⁺ ions from KCl/Ar at 1500C

The **Hidden HPR-60 MBMS** is available with mass range options upto 1000amu and with configurations suited to applications in **atmospheric physics & chemistry** and in **low & high pressure plasma research**.

For further information, specifications or a formal quotation please contact your local representative or;

Hidden Analytical Ltd.
420 Europa Blvd.
Warrington, WA5 7UN
England

Tel. +44 (0) 1925 445225
Fax. +44 (0) 1925 416518
Email info@hidden.co.uk
Web <http://www.HiddenAnalytical.com>