

Mass Spectrometry

Mass Spectrometry in Real Time

Peter Hatton & Dr David Lundie, Hiden Analytical Ltd

Mass spectrometry as a technique has grown significantly in recent decades, and this is an understatement. Many analytical requirements are addressed by mass spectrometry in some form or other.

The techniques of ionisation, mass separation and detection are varied, and the process is now used in analytical sectors ranging from relatively simple vacuum and vacuum process monitoring to the more complex life sciences and biomedical applications.

In this article we address the little known but powerful technique of real time mass spectrometry by quadrupole mass spectrometry applied to gas analysis and dissolved gas analysis in environmental studies, catalysis, electrochemistry and thermo-gravimetric mass spectrometry, TG-MS.

The benefits of real time analysis are clear; you get instant results! Real time data is available for following reactions, and can be used for diagnostics, and monitoring. Less well known is the incredibly high dynamic range, and user selectivity for the species to be analysed. Up to 10 orders of magnitude can be achieved, and routinely the technique provides for analysis of species from sub PPM concentration and up to 100% concentration within a few seconds.

The versatile nature of the quadrupole mass spectrometer provides for fast scanning and selectivity of any species that has spectral lines within the mass range of the instrument.

Software with a typical modern sophisticated graphical user interface allows users to automatically acquire quantitative data from multiple species where the concentration may be dynamically changing from PPB to 100%.

Real time mass spectrometry applies to applications that operate over a wide range of sample pressure from $<1e-6$ mbar UHV to high pressure > 30 bar.

This article will describe how the technology works, and how it is applied to several key applications at near atmospheric pressure with both portable and laboratory devices.

How does real time mass spectrometry work?

The term real time mass spectrometry applies to mass spectrometry where there is no sample preparation, no preconditioning and no separation of analytes before analysis. The time from sampling to receiving data points is of the order of a few seconds.

The techniques described here use electron impact ionisation (EI), quadrupole mass filter separation and ion detection by Faraday cup and electron multiplier detector.

EI- electron impact ionisation

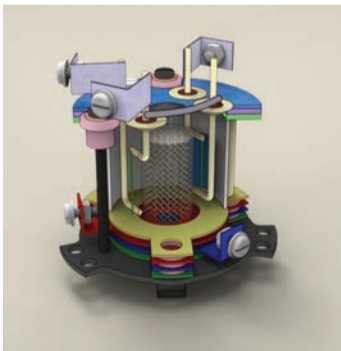


Figure 1: Electron Impact ioniser cut away.

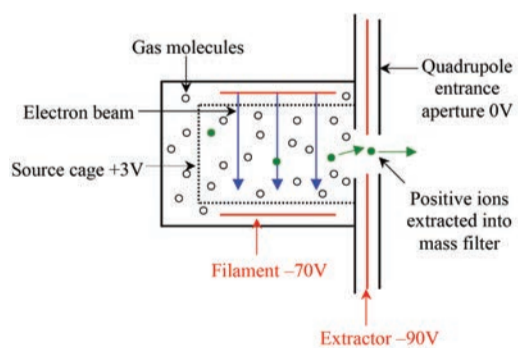


Figure 2: Diagram illustrating electron impact ion source operation.

In electron impact ionisation the gas molecules are ionised by electrons emitted from a hot filament. Here a filament creating electrons at 70 eV is illustrated.

Together with ionisation the ion source is equipped with extraction optics that extract the ions into the mass filter.

The mass filter:

The mass filter differentiates the ions produced and selects species for detection. A common form of mass filter is the quadrupole. Other types include time of flight, TOF and the classic magnetic sector.

The quadrupole is often recognised as the best choice of mass filter for real time mass

spectrometry due to its speed for scanning, and the high dynamic range.

A quadrupole is 2 pairs of parallel, equidistant metal rods (poles) biased at equal, but opposite potentials. These twin potentials contain fixed direct current, DC and alternating radio frequency, RF components. By varying the RF component, the resultant field produced by the rods may be varied.

Any ions entering the quadrupole field experience potential differences deflecting them from their original trajectory. The extent of deflection of any ion entering the field is related to its mass: charge (m/e or m/z) ratio.

At each interval on the RF scan only one m/e ratio resonates with the field allowing the ion to pass along the z-axis. All other species are deflected and neutralised by impact upon the rods of the quadrupole and play no further role.

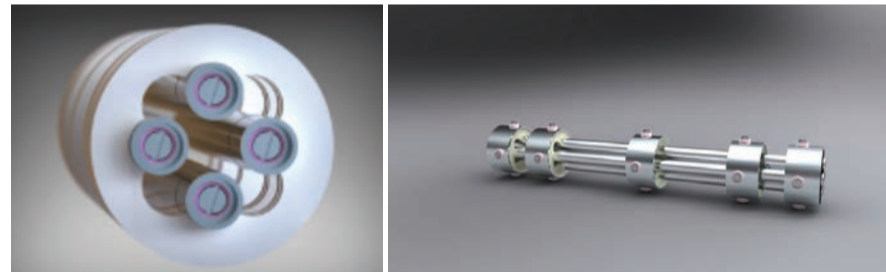


Figure 3: Quadrupole mass filters shown, from 20mm pole diameter to 6mm pole diameter offer mass range options up to 5000u. 200u mass range is typically used for most real time gas analysis applications.

The detector(s)

Filtered ions that strike the detector result in an ion current which is measured by a sensitive amplifier or counted as pulses.

Two types of detector are commonly used:

1) The Faraday Cup - an earthed passive conducting surface with a suppressor electrode to avoid false measurement.

Fast moving ions strike the cup cause a 'shower' of 'secondary' electrons. The use of the 'cup' rather than a plate, allows all electrons to be collected.

Any electrons that do escape the geometric shape of the cup are reflected by the negative potential of the suppressor plate back into the cup. Thus the only current measured is that of the arriving ion.

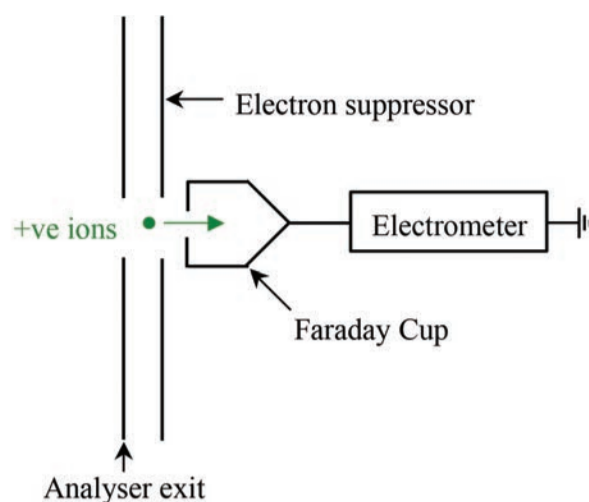


Figure 4: Diagram of Faraday cup detector.

The Faraday Cup: Detection limit can be evaluated for looking at an example for detecting nitrogen:

Ion current for N_2 produced in the EI source and mass selected is of the order of 10^{-4} amps / hPa

At 10^{-8} hPa of N_2 ,

$$10^{-8} * 10^{-4} = 10^{-12} \text{ amps}$$

At 10^{-11} hPa of $N_2 = 10^{-15}$ amps

10^{-15} amps is the typical detection limit for a high sensitivity electrometer, giving the detection limit for Faraday cup detection of the order of 10^{-11} hPa.

2) The Secondary Electron Multiplier / Single Channel Electron Multiplier (SEM / SCEM):

The SEM/SCEM is a device operated at high voltage (typically 1 kV) with a surface engineered to have a strong secondary electron yield. When an ion impacts it, a shower of electrons is released. Each of these electrons undergoes further collisions with the surface, again releasing more electrons, until the cascade reaches the anode, providing a measurable current. The voltage applied gives a gain of typically 103 and it is this gain that increases the analyser performance by lowering the detection limit from 10^{-11} hPa achieved with a Faraday detector to 10^{-14} hPa for the SEM/SCEM.

When used with advanced ion counting electronics, each ion event arriving at the SEM/SCEM detector is detected as a pulse of electrons, coupled with the low noise of pulse ion counting detection leads to fast and sensitive detection, typically a factor of 10 greater sensitivity is achieved compared to a conventional analogue SEM/SCEM.

The combination of EI ion source, mass filter and combination of Faraday cup /SEM/SCEM detectors that gives the real time QMS the high dynamic range, of ~ 10 decades.

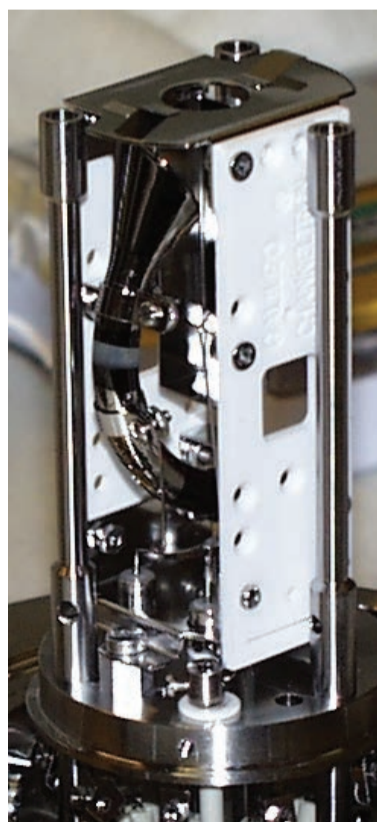


Figure 5: Close up of a Faraday cup and SEM/SCEM dual detector assembly.



Figure 6: Flange mounted analyser gauge head with ioniser (EI) mass filter, detectors Faraday and SEM/SCEM.

Real Time mass spectrometry - the whole package.

The ioniser, mass filter and detector are packaged as a flange mounted assembly, often referred to as the 'analyser gauge head'.

To make the analyser gauge head useful for gas analysis it is supplied as a complete gas analyser with the following:

A sample inlet, an ultra-high vacuum system, a safe sample exhaust connection and a PC running software with advanced graphical user interface for control, data acquisition and data display.

The design and configuration of the sample inlet are critical to the performance of the real time mass spectrometer for real world applications.

The sample inlet provides the interface from the application to the quadrupole mass spectrometer and is probably the most important part of the system.



Figure 7: A complete bench top real time mass spectrometer with heated capillary sample inlet.

Sample inlets for real time mass spectrometry near atmospheric pressure include:

For gas and vapour analysis:

A capillary inlet made from silica or stainless steel. The capillary internal diameter, length and gas flow are specified to provide viscous flow. The assembly is heated and pumped to provide fast gas and vapour transport to the mass spectrometer. The length of the capillary is typically one or two metres. Response times to changes in gas/vapour composition of < 150 milliseconds are achievable with a capillary inlet.

For dissolved gas analysis in soils, sludges and liquids

A membrane inlet using permeable silicone or polymer membrane for dissolved gas analysis. The membrane provides the interface from sample to the mass spectrometer. The membrane inlet can be configured to have sample flow past the membrane close coupled to the mass spectrometer or designed as a probe to immerse in sample with typical length ~ 500 mm. The response time of the membrane inlet to changes in dissolved gas composition is typically less than one minute.

Many applications for dissolved gas analysis are away from the laboratory in the field, near rivers, lakes or at sea. For these applications portability and low power consumption are vital to enable researchers' access to real time data directly from the environment. The system shown below is powered from 12 V DC



Figure 8: Dissolved species probe inlet shown in flow through housing with integral thermocouple.



Figure 9: Portable Real Time Mass Spectrometer.

Mass Spectrometry

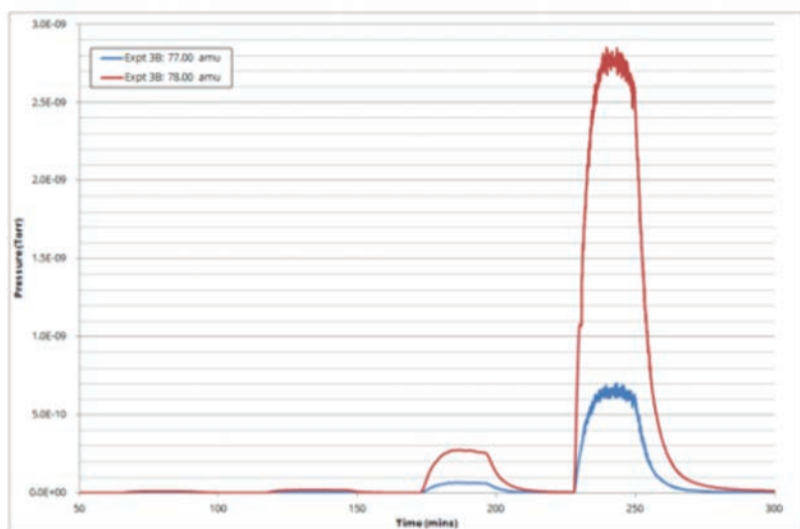


Figure 10: Benzene in water analysed by MIMS at low concentration.

and can operate from solar powered rechargeable battery packs.

An example of the advantages of real time gas analysis is in water contamination studies. The example below shows the analysis of dissolved benzene in water. Without real time analysis water samples would need to be taken to a laboratory for analysis.

For electrochemistry studies

Real time mass spectrometry in electrochemistry uses a special interface designed that includes a Nano-porous membrane interface for fast response *in-situ* determination of gaseous and volatile electrochemical reactants, reaction

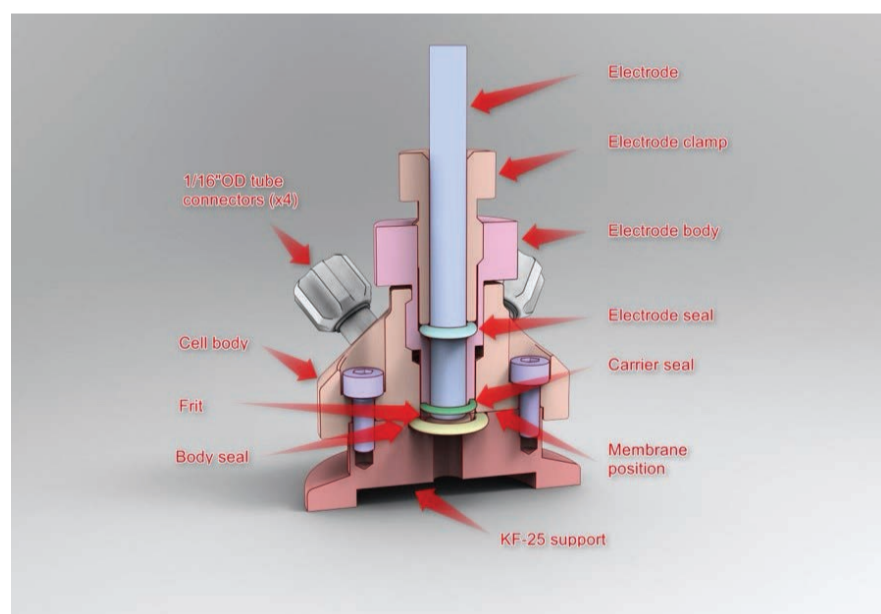


Figure 11: A typical DEMS cell that couples to real time mass spectrometer via the KF-25 support flange shown.

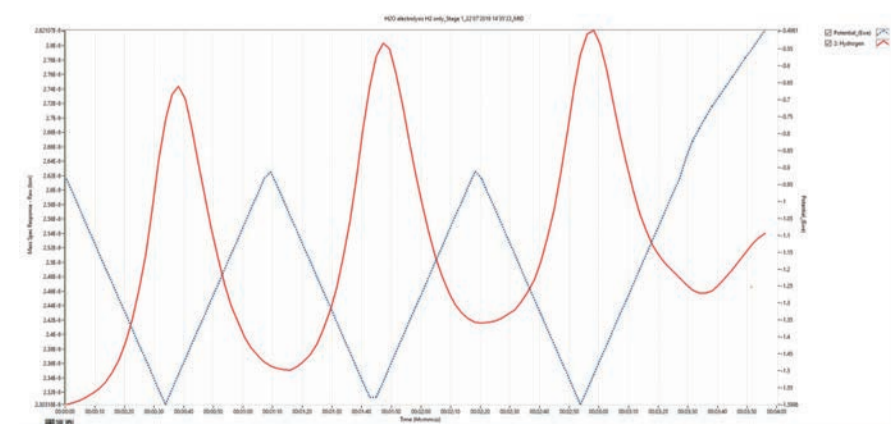


Figure 12: Data from a DEMS experiment.

intermediates and products in *real time*. In some applications the off-gas is measured with special microflow capillaries to minimise depletion. The response to gas composition changes measured through the nano-porous membrane is typically less than 0.5 second.

Fast response of the mass spectrometer is crucial when following dynamic experiments such as DEMS (differential electrochemistry mass spectrometry). Here an electrochemical cell is coupled to a *real-time* mass spectrometer via a porous membrane. The experiment is performed by scanning the electrode potential while analysing the gas evolution using the mass spectrometer. The data below shows the H₂ evolution during a DEMS experiment.

For thermo-gravimetric mass spectrometry, TG-MS

Using special adaptors, Real time mass spectrometry can be configured for continuous analysis of evolved gases and vapours from thermogravimetric analysers, TGA.

This coupling is known as TGA-MS. Each TGA model requires its own connection type interface. The TGA interface includes re-entrant furnace sampling, providing close coupling to the TGA furnace region for optimised evolved gas/vapour analysis.

The coupling interface includes bespoke cables connecting the TGA and MS for TGA-MS synchronised data acquisition including automatic start / stop with TGA operation. Without *real-time* mass spectrometry the data available from a TGA does not provide any information about the identity of the evolving gas.



Figure 13: TGA interface with mounting clamp and re-entrant alumina furnace probe.

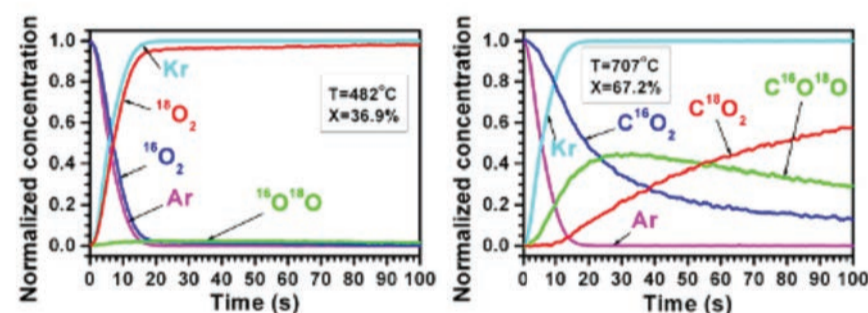


Figure 14: Real-time gas analysis study of the kinetics of the methane oxidation reaction.

For Catalysis Studies

Real time mass spectrometry offers solutions for experimental catalysis research, from initial catalyst characterisation and reaction testing to downstream optimisation of catalytic activity. The ability to follow multiple species in real time over a high dynamic range makes the real time mass spectrometer ideal for catalysis studies including temperature programmed reaction, oxidation and reduction studies.

The use of real time mass spectrometry can be crucial for studying the kinetics of catalytic reactions where delays in analysis would affect the results considerably. The data below shows the fast kinetically useful data available with real time mass spectrometry.

Conclusion

We have illustrated how the components of a quadrupole mass spectrometer; the ioniser, mass filter, and detector assembled as a flange mounted analyser gauge head, configured with UHV system and special sample inlet become a powerful real time analyser with fast response, and high dynamic range for detecting multiple species.