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Improved Threshold Ionisation Mass Spectrometry

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3F 1000 Series QMS and Hiden HAL 201RC

Abstract

Threshold ionisation mass spectrometry (TIMS) is well established as a technique for improving on standard methods of residual gas analysis, particularly when the dominant peaks in the mass spectrum occur at very nearly the same mass/charge ratio. The mass peaks are then difficult to separate using standard quadrupole mass spectrometric methods. We have described elsewhere several applications in which TIMS has proved to be very effective. More recently, we have examined ways in which the interpretation of TIMS measurements can be improved by fitting to the experimental data trend lines calculated from theoretical expressions.

Experimental

The experimental work reported here was carried out using a Hiden 3F 1000 Series high sensitivity QMS in a simple UHV vacuum system as shown in Figure 1.

Ion signal (S) in c/s may be expressed as:

$$S = A\,(E_e - E_i)^m$$

where A is a numerical scaling factor, E_e is the electron energy in the ionisation source of the mass spectrometer, E_i is the ionisation energy for formation of the detected ions, and m is a constant which depends on the particular ionisation process involved. For simple cases, such as formation of Ar^+ ions from atomic argon, the factor m is known to be 1.127. The scaling factor A depends on the electron current used in the ionisation source and other experimental conditions. In our analysis, the three parameters A, E_i and m are treated as adjustable parameters and varied until an acceptable fit to the experimental variation of the detected ion signal, with E_e is obtained.

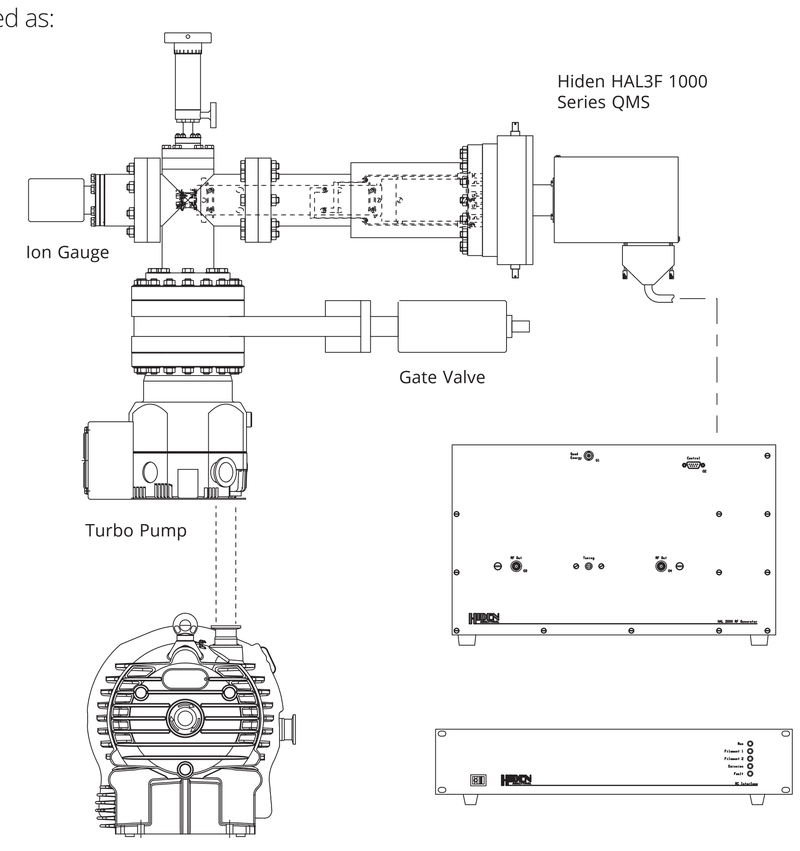

Figure 1.

Hiden 3F 1000 Series high sensitivity QMS in a UHV vacuum system.

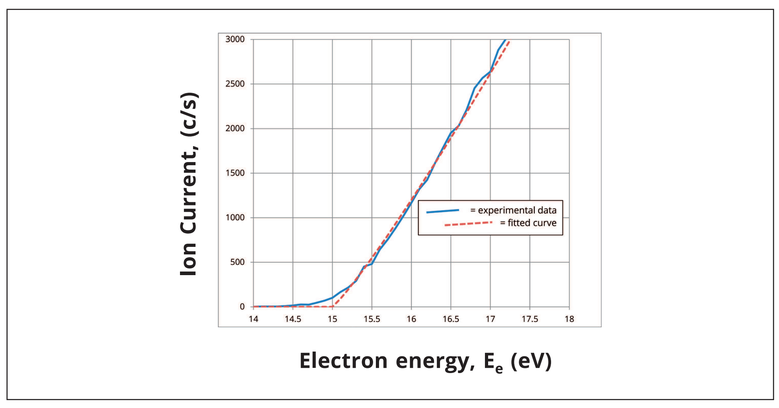

Figure 2.

Electron energy scan for m/e=2, H_2^+. Fitted curve is $S=1{,}200\,(E_e - 15.0)^{1.127}$.

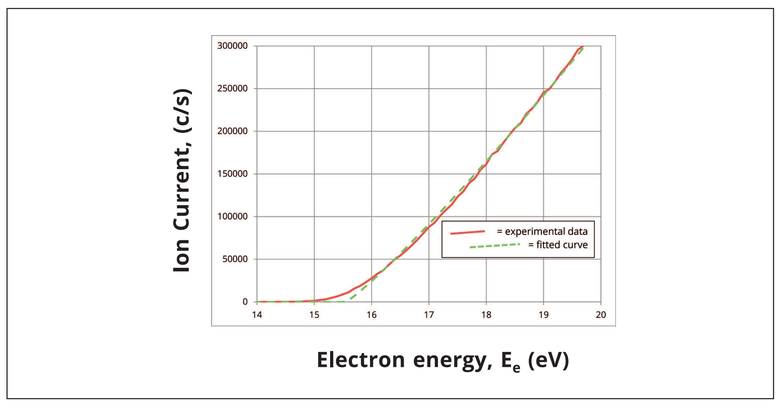

Figure 3.

Electron energy scan for m/e=40, Ar^+. Fitted curve is $S=59{,}500\,(E_e - 15.55)^{1.127}$.

Results

Figure 2 shows the data for m/e=2. The fitted line (dotted) is given by $S = 1200(E_e\text{-}15.0)^{1.127}$. The ionisation energy of 15.0eV may be compared with the accepted value of 15.42eV. Figure 3 shows the corresponding data for m/e =40. The fitted line again has m=1.127, as expected. The fitted ionisation energy is 15.55eV which may be compared with the accepted value of 15.76eV. If the electron energy scale for both figures (which is the original uncalibrated scale) is corrected by adding 0.3eV, the agreement for both H_2^+ and Ar^+ between the fitted and published values of E_i is within 0.15eV.

When the range of energies used for the scanning was increased considerably, up to a maximum of 120eV, a mass peak with m/e=13.4 was found. This could be attributed to the formation of Ar^{+++} ions. The electron energy scan was of the form shown in figure 4. It was possible to fit the curve with m=1.95 and an ionisation energy of 85.5eV. A plot of the experimental data on a logarithmic scale (see the inset plot in the figure) shows there is some uncertainty about our data at energies just below 86eV. The data are not inconsistent with published data which range from 83.7 to 85eV.

An electron energy scan for m/e=20 was expected to show the creation Ar^{++} ions with an onset energy of 43.4eV. Figure 5 shows this onset but also a much lower threshold at 12eV. This lower value is consistent with the formation of H_2O^+. H_2 ions from water vapour and hydrogen outgassed from the walls of the ionisation source.

In a separate experiment, data were obtained for a mixture of 1000ppm of carbon monoxide in nitrogen, with the electron energy scans carried out at m/e=28, (i.e for formation of CO^+ and N_2^+ ions).

Figure 6 shows a typical scan. The experimental data are shown as Series 1. Series 2 and Series 3 are the curves calculated with onset ionisation energies of 12.65eV for formation of CO^+ and 14.35eV for formation of N_2^+ and Series 4 is the sum of Series 2 and 3. The portion of the experimental curve at energies below 14eV is attributed to the formation of CO^+ ions from the carbon monoxide in the mixture while that at higher energies includes the contribution from the formation of N_2^+ from the more abundant nitrogen. The fitted onset energies may be compared to accepted published values of 14.01 and 15.7eV for the two processes. While these values are both higher than those deduced from the present work, the difference between them of 1.70eV is exactly that shown in figure 6.

Conclusion

The measurements summarised above, and their analysis using the fitting technique described, demonstrate how effective such threshold ionisation measurements can be in tackling problems in the mass spectrometry of gas mixtures in which the dominant ions produced may be difficult to assign to a particular component in the mixture purely on the basis of the ion masses. In particular, the fitting technique simpifies the identification of the onset ionisation energies for the components of a gas mixture which in turn improves the reliability of conclusions to be drawn from the measurements.

References

[1] S. Davies et al, Vacuum (2013) 101, 416-422

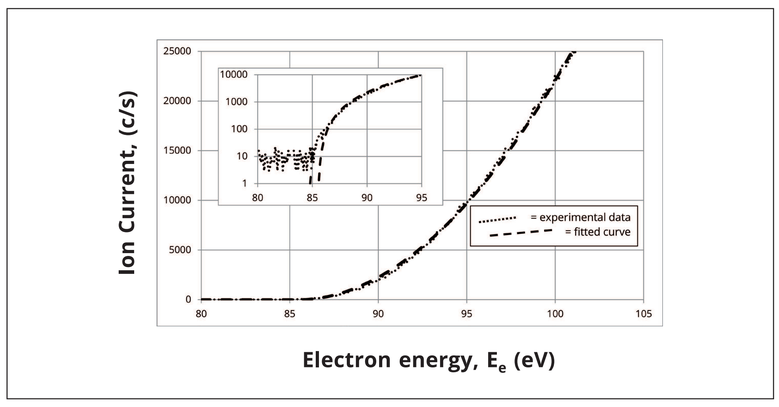

Figure 4.

Electron energy scan for m/e=13.4, Ar+++. Fitted curve is $S=120\,(E_e - 85.5)^{1.95}$.

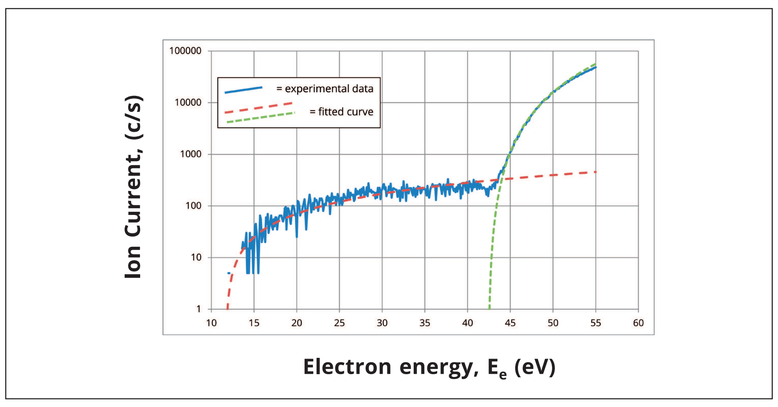

Figure 5.

Electron energy scan for m/e=20. Onset energies of 12.0 and 42.7eV attributed to H_2O^+. H_2 and Ar^{++} ions, respectively.

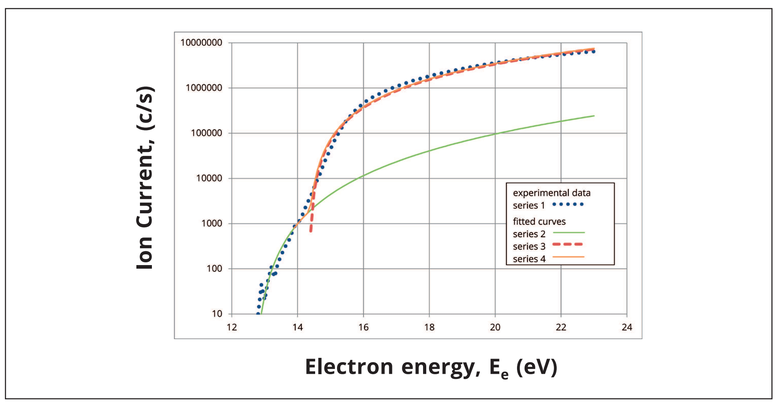

Figure 6.

Electron energy scan for mixture of 1000ppm of carbon monoxide in nitrogen, measured at m/e=28, CO^+ and N_2^+.

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