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 to 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 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, \( E_i \) is the electron energy in the ionisation source of the mass spectrometer, \( E_e \) 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, Ei 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.

Results

Figure 2 shows the data for m/e=2. The fitted line (dotted) is given by \( S = 1200 (E_e - 15.0)^{1.127} \). The ionisation energy of 15.0 eV may be compared with the accepted value of 15.42 eV. Figure 3 shows the experimental work reported here was carried out using a Hiden 3F 1000 Series high sensitivity QMS in a UHV vacuum system.

\[ \text{Electron energy scan for mixture of 1000ppm of carbon monoxide in nitrogen, with the electron energy scans carried out at m/e=28, i.e. for formation of CO}^{++} \text{ and N}_2^{+} \text{ ions.} \]

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 12.65 eV for formation of CO\(^{++} \) and 14.35 eV 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 14 eV 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 15.76 eV for the two processes. While these values are both higher than those deduced from the present work, the difference between them of 1.70 eV 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 simplifies 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