Measurement of Appearance Potentials

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The objective of this Application Note is to demonstrate a method for determining the appearance potential for gaseous molecules using Extrel C-50 quadrupole electronics.

I. INTRODUCTION

Appearance potentials are determined using an Extrel EXM-200 quadrupole mass spectrometer by measuring the intensity of two or more ions (one reference ion as well as one or more unknown ions) as a function of electron energy. These data are plotted, with the linear portion of the resulting curve of intensity as a function of electron energy extrapolated to zero intensity. The extrapolated filament potential for the unknown ion is then subtracted from the extrapolated filament potential of the reference ion to identify the appearance potential offset. The literature value for the reference ion is added to this offset to yield the appearance potential for the unknown ion.

II. EXPERIMENTAL

The Extrel EXM-200 quadrupole mass spectrometer used in this experiment was configured with the following features: 3/4" quadrupole, C-50 electronics, 1.2 MHz 100 Watt 150-QC, 041-11 ionizer, analog multiplier, 6-7-8 preamplifier. The mass range of this system is slightly greater than 200 amu.

In order to maximize filament lifetime, and minimize the voltage drop across the filament, emission current was maintained at 0.1 mA, although the filament supply has enough power to safely drive the emission current over one milliamp, even with electron energies lower than IO eV, at somewhat diminished filament lifetime.

The system was tuned for optimum sensitivity and peak shape for M/z 28 (nitrogen), resulting in the following tune values: ion region = +6.0 V, extraction lens = -5.2 Volts, lens 1 = lens 3 = -1 32.3 Volts, lens 2 = +45.3 Volts, and entrance lens -2.3 = Volts. Note that the extraction lens voltage was maintained at a potential close to that of the ion region in order to minimize the potential gradient within the ionizing region, and hence to minimize the actual range of electron energies at a given filament potential setting.

Data was collected using a VTI 1600 data acquisition system (Vacuum Technology Incorporated, Oak Ridge, TN) operated in analog spectrum mode. The VTI data system was mass calibrated on masses 28 and 32. The VTI data acquisition parameters were as follows: scan 15 to 45 in analog mode, 20 points per amu, 10 samples averaged per point, 8 ms between scans, 1 ms electrometer delay, and 5 us mass settling delay. Intensities were manually extracted from the resulting data files, with baseline subtraction performed using Microsoft Excel (the lowest value in the data set for each mass was chosen to represent zero intensity and was subtracted from all other values in that data set).

The filament potential (eV) was manually varied from -10 Volts to -16 Volts relative to the ion region potential in increments of 0.1 Volts. Emission current (em) was monitored with each change in filament potential to verify constant emission. Note that the indicated filament potential represents the potential of the center of the filament. The actual filament potential is a range of voltages centered around the indicated voltage with width equal to the filament voltage, typically 3 Volts.

III. RESULTS AND DISCUSSION

Figure 1 contains plots of intensity as a function of filament potential for oxygen (m/z 32) and water (m/z 18). The linear portion of each curve was manually determined (eye-ball-imetrically) with a linear least squares fit (Grapher for Windows, Golden Software) applied to the selected range of data. The resulting equation was extrapolated to y=O (solved for the x intercept) which is labeled on the graph for each compound. Note that one major source of error is the subjectivity of the selection of the range of data to fit for the extrapolation. In this experiment, a number of data ranges were evaluated, with the r^2 correlation coefficient monitored to determine goodness of fit, Note that measuring a wider range of filament potentials than demonstrated here should allow for better precision in results, as well as remove some of the subjectivity in selecting the linear portion of the curve.

This method yields a relative ionization potential which must be calibrated against some reference standard (in this ex-

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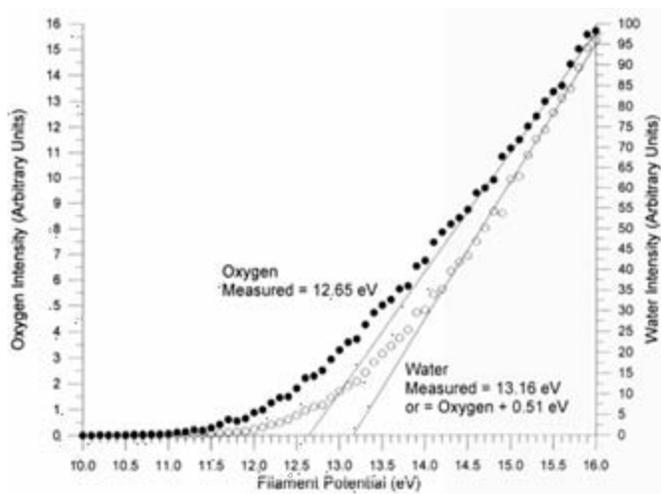
Figure 1: Measurement of Appearance for Oxygen and Water

1. Gather data over a wide range of electron energies to remove subjectivity in extrapolating to the zero intensity intercept (appearance potential).
2. Use good experimental practice to minimize the effects of hysteresis on precision.
3. Set emission current to the lowest value \with reasonable signal-to-noise to maximize filament lifetime.
4. Set the extraction lens to a potential near that of the ion region to minimize the range of actual electron energies.
5. For increased accuracy, use multiple reference compounds whose appearance potentials straddle the appearance potential of the target species.

ample, oxygen is used as the reference, with appearance potential reported as 12.063 +/-0.001 according to the 58th edition of the CRC Handbook of Chemistry and Physics, CRC Press, Cleveland, Ohio). Using this reference value, water was measured to have an appearance potential 0.51 Volts more positive than oxygen, or 12.57 Volts. The same edition of the CRC handbook identifies the appearance potential of water as 12.6 eV, in good agreement with the value determined in this experiment.

As with any analog instrumentation, hysteresis artifacts can appear in the data, such as the discontinuities in the oxygen data. One must be careful to be consistent in approaching the setpoint; in this experiment the filament potential setpoint was selected by slowly turning the 'eV' potentiometer from lower to higher voltage, discontinuities in the data appeared when the desired potential was overshot, resulting in the potentiometer being turned from high to low, and are attributed to hysteresis. The net effect of this hysteresis is loss in precision.

An alternative method for determining appearance potentials involves the measurement of appearance potentials for two reference compounds with widely differing appearance potentials (helium is typically used as one of the reference compounds). Such an approach should result in more accurate appearance potentials because it removes some uncertainties about the accuracy of the voltmeter.

IV. CONCLUSIONS AND RECOMMENDATIONS

The method demonstrated in this report resulted in good accuracy in the measurement of the appearance potential for water. Experimental error can be minimized in this method by focusing on the following:

1 The EXM-200 is an obsolete model. The current model number is MAX-200

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