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Application Note Number 8: What do Those RGA Peaks Really Represent?

Abstract: Basically an RGA peak represents the ion current collected when the mass spectrometer is tuned across one amu per electron charge. What this can be made to represent is discussed in the current application note.

All mass spectrometers, and therefore all residual gas analyzers (RGAs), measure a current which is either directly due to or, in the case of an electron multiplier unit, derived from the ions produced in a source and selected by some mass to charge selection device. With careful handling of these currents and an understanding of how they are produced, an amazing amount of information about the residual gas contents of a vacuum system can be derived. Conversely, an understanding of these currents will point out the limitations of such a device.

The residual gases within a vacuum chamber may come from a number of sources but they may be classified as coming from the original gaseous content of the chamber, gas emission from the walls of the chamber, or leaks from the outside of the chamber. Each of these classifications may have sub classes such as virtual leaks which are due to the original gas in the system before pump-down. Some Classifications may be interrelated such as water in the original gas sticking to the inside walls of the chamber and sub sequentially emitting water from surfaces seemingly forever.

However these residual molecules get into the system, they can not be measured until the pressure in which the RGA is operated is such that the mean free path between the residual molecules is much longer than the dimensions of the path they take through the RGA. Since the rule of thumb is that the mean free path of nitrogen is 5 cm when the pressure is at a millitorr, the application of "much" may be considered a factor of 100 and we would expect good RGA operation at a pressure of 10^{-5} torr. This is indeed the case.

As these molecules travel through the volume of the vacuum chamber, some will pass through a conductive grid set a fixed potential. Outside this grid is a heated filament at a potential usually 70 volts below the grid potential. Some of these electrons, perhaps one in a thousand will hit and ionize a molecule. The resulting ion will be directed by electrostatic fields within the grid toward a mass to charge selection device. For an RGA, this is usually a quadrupole tuned to an RF and DC voltage at a precise frequency. If these voltages and frequency is exactly right for the mass to charge ratio of the ion, it will pass through the length of the rods and be detected as a current to a sensitive electrometer.

The amount of current at particular masses (unit charge is usually assumed) depends on a number of different factors. These are:

The probability that an electron will cause ionization which is derived from the cross section for ionization.

The probability that a particular molecular fragment will produce an ion.

The probability that an ion so produced will make it into the quadrupole.

The probability that the ion will pass through the quadrupole and be detected.

Example: What will be the relative peak height of peaks due to nitrogen and H₂S?

The first thing to do is to look up their cross sections for ionization. NIST has a site at http://physics.nist.gov/PhysRefData/Ionization/EII_table.html which give some ionization cross sections.

At 70 eV H₂S has a cross section of 3.96 square angstroms and N₂ has a cross section of 2.5 square angstroms. So H₂S gives twice as much ion current as does N₂. This is not the end of the story since we need to know the cracking pattern of N₂ and H₂S. Again, the NST site give this information. H₂S produces peaks at 32, 33, and 34 with 32 and 33 each about 40% of the 34 peak. Nitrogen produces peaks at 28 and 14 (about 7% of 28). Putting both of these bits of information together gives the 34 peak at about the same size as the 28 peak if both gasses are present in equal amounts.

This sort of calculation can only give a first approximation to relative peak heights. Some commonly available spectra are taken on magnetic not quadrupole machines and even spectra due to quadrupole machines are often quite variable from one machine to the next. If precision is required, calibration by observing the peak heights due to the application of carefully mixed gases into the chamber is required.

Typically, RGAs do not just report peak heights in terms of current. Partial pressures are measured in terms of torr, mbar or pascal. Since cross sections for ionization can not be predicted for any arbitrary mass, RGAs are calibrated for all peaks being produced with the arbitrary nitrogen cross section. This is usually good to within a few tens of percent but may occasionally be off by a factor of two or more.