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

**Abstract:** An RGA peak represents the ion current collected when the mass spectrometer is tuned across a one amu mass range. What this can be made to represent is discussed in this application note.

All mass spectrometers, and therefore all residual gas analyzers (RGAs), measure a current which is generated by ions created in a source and filtered by some mass to charge selection device. With careful handling of the ion current and an understanding of how it is produced, an amazing amount of useful information about the residual gases can be obtained. This insight will also point out the limitations of the device.

The residual gases in a vacuum chamber may come from a number of sources. They may come from the original gaseous content of the chamber, gas desorbing off of the walls of the chamber, or leaks from the outside of the chamber. However these residual gas molecules get into the system, they cannot be measured until the pressure is low enough for the RGA quadrupole to operate. This requires a mean free path between the residual molecules that is longer than the path that the ions take through the RGA. The distance between the ionizer and the detector on the Extorr XT Series probe is about 15 cm so the mean free path must be at least 10 times longer (about 150 cm) for proper quadrupole operation. The rule of thumb is that the mean free path equals 5 cm at a pressure of  $1 \times 10^{-3}$  Torr so the chamber pressure must be about  $3 \times 10^{-5}$  Torr or lower for the RGA quadrupole to operate.

As the gas molecules travel inside the vacuum chamber, some pass through the RGA ionizer. Electrons from a hot filament strike some of the molecules producing ions. These ions are directed into the quadrupole where they are filtered by their mass (actually by their mass to charge ratio). The ions that make it through the quadrupole produce a current at the Faraday cup that is measured by a sensitive electrometer.

The amount of ion current that is measured at a particular mass depends on a number of different factors. These are:

The probability that an electron striking the molecule will cause ionization. This is derived from the ionization cross section and varies from one molecule to another.

The probability that a particular molecular fragment will produce an ion. Many molecules break apart when hit by an electron. This can produce ions from the original molecule and ions from each of the fragments.

The probability that any ion produced will make it into the quadrupole. Some of the ions collide with the surfaces of the ionizer and do not enter the quadrupole.

The probability that the ion will pass through the quadrupole and be detected. Some ions may have trajectories that cause them to be rejected even though they are of the correct mass.

As an example, what will the relative intensities be of the peaks from N<sub>2</sub> (molecular nitrogen) and H<sub>2</sub>S (hydrogen sulfide)?

The first thing to do is to look up the ionization cross sections for both molecules. The Chemistry WebBook on the NIST website at <http://webbook.nist.gov/chemistry/> contains a great deal of information and has an ionization cross section calculator. Use the Formula search option and enter N<sub>2</sub> or H<sub>2</sub>S in the formula box and then click on the Search button. Next click on the Electron Impact Ionization Cross Sections link on the species page. Enter 70 into the Incident Electron Energy box and click on the Calculate Cross Section button. For electron impact ionization, 70 eV of electron energy produces the largest number of singly charged ions and is the factory setting for the Extorr XT Series RGAs.

Using 70 eV electrons, H<sub>2</sub>S has a cross section of 4.15 square angstroms and N<sub>2</sub> has a cross section of 2.5 square angstroms. This means that H<sub>2</sub>S will generate about twice as much ion current as N<sub>2</sub> if both gasses are present in equal amounts.

This is not the end of the story since we need to know the fragmentation (cracking) patterns of the N<sub>2</sub> and H<sub>2</sub>S molecules to determine the relative intensities of the mass peaks produced.

Again, the NIST Chemistry WebBook provides this information for each molecule at the Mass Spectrum link on the species page.

H<sub>2</sub>S produces peaks at 34 amu, 33 amu, and 32 amu with the 34 amu peak being the largest. The peaks at 33 amu and 32 amu are each about 40% of the 34 amu peak. So for any amount of H<sub>2</sub>S in the chamber, the ion current measured for the 34 amu fragment is about 50% of the total ion current from H<sub>2</sub>S. The ion currents measured for the 33 amu and 32 amu fragments are each about 25% of the total ion current from H<sub>2</sub>S. Adding the ion currents (partial pressures) of the three fragments together approximately equals the total ion current (total pressure) from H<sub>2</sub>S.

N<sub>2</sub> produces peaks at 28 amu and 14 amu with the 28 amu peak being the largest. The 14 amu peak is about 15% of the 28 amu peak. So for any amount of N<sub>2</sub> in the chamber, the ion current measured for the 28 amu fragment is about 85% of the total ion current from N<sub>2</sub>. The ion current measured for the 14 amu fragment is about 15% of the total ion current from N<sub>2</sub>. Adding the ion currents (partial pressures) of the two fragments together approximately equals the total ion current (total pressure) from N<sub>2</sub>.

Putting all of this information together we find that H<sub>2</sub>S produces about twice as many ions as N<sub>2</sub> because it has a larger ionization cross section. However, H<sub>2</sub>S fragments into three peaks with the largest at 34 amu containing only about 50% of the ions. N<sub>2</sub> fragments into only 2 peaks with the largest at 28 amu containing about 85% of the ions.

So the 34 amu peak from H<sub>2</sub>S and the 28 amu peak from N<sub>2</sub> will be about the same size if both gasses are present in equal amounts.

This sort of calculation can only give a first approximation of the relative peak heights. Some commonly available spectra are taken on magnetic mass spectrometers not quadrupole machines. Even spectra from other quadrupole mass spectrometers are often quite variable from one instrument to the next. If high precision is required, the RGA may be calibrated by observing the peak heights produced when carefully mixed gases are introduced into the chamber.

The Extorr XT Series RGAs do not just display the peak heights in terms of ion current. The intensities may be shown as partial pressures in units of torr or pascal.

Since ionization cross sections cannot be predicted for any arbitrary molecule, the Extorr XT Series RGAs are calibrated for nitrogen. This produces good results to within a few tens of percent, but may be off by a factor of two or more for certain gasses.