SRS Tech Note

Residual Gas Analysis Basics

The SRS RGA can perform both qualitative and quantitative analysis of the gases in a vacuum system. Obtaining spectra with the SRS RGA is very simple. Interpreting the spectra, that is understanding what the spectra is trying to tell you about your vacuum system, requires some work.

The following sections will introduce some basic concepts of spectral analysis emphasizing the main aspects of residual gas analysis.

How Mass Spectra are Interpreted

A mass spectrum, taken in a real system, will almost always contain signals from a mixture of various gases. Careful and complete interpretation of the spectrum (i.e. a complete spectral analysis) should reveal the identity, as well as the concentrations, of the various components which have produced the spectrum.

The first step in the spectral analysis process is to correctly identify the mass-to-charge ratio of all the peaks in the mass spectrum.

Once all the peaks have been labeled, the next step is to identify the residual gases that have produced the spectrum. Knowledge of the recent history of your system may provide very valuable clues as to the possible gases that may be residuals in the vacuum chamber. A familiarity with the standard spectra of commonly expected gases will generally help to determine the major and minor components in the system. Any peak in the spectrum may consist of contributions from molecular ions and/or fragment ions, or multiple ionized species. The qualitative spectral analysis is complete when all the peaks in the spectrum have been "uniquely assigned" to the components of a gas mixture, in complete agreement with the known fragmentation patterns of the components.

In cases where only the major components are of interest, some of the minor peaks of the spectrum will remain unassigned. If only a few species are being monitored, only the peaks corresponding to the substances of interest need to be assigned and monitored.

Notes on Fragmentation Patterns:

> The electron impact type of ionizer used in modern RGA's almost always causes more than one kind of ion to be produced from a single type of gas molecule. Multiple ionization, molecular fragmentation and changes in the isotopic composition of the molecule are responsible for the effect. All ions formed contribute to the mass spectrum of the molecule and define its fragmentation pattern. The identification and interpretation of mass spectra must begin with a knowledge and understanding of the standard fragment patterns of atoms and molecules that may exist in the system. The standard fragment patterns of most molecules commonly encountered in residual gas analysis are well established and listed in the general RGA Literature. A very complete library can also be accessed through the Library Search Utility of the RGA Windows software.

Virtually every vacuum system will have detectable amounts of hydrogen (2 amu), water (18 amu), carbon monoxide (28 amu) and carbon dioxide (44 amu). Become familiar with these species and their fragmentation patterns, and use their peaks to verify the correct performance of the instrument while operating the RGA.

Partial Pressure Measurement

Once the different components of a mixture have been identified, it is possible to use the SRS RGA to obtain quantitative values for the various partial pressures. This section describes the basic steps needed to perform quantitative measurements with the instrument. The formalism presented assumes multiple gas analysis, but is equally valid for single gas measurements. The entire mathematical formalism used to derive the partial pressures of a mixture based on a single mass spectrum is based on one assumption:

The total spectrum is a linear combination of the spectra of the different species that are present in the mixture. In other words, the total spectrum is equal to the sum of the individual peaks that would be observed if each constituent were alone in the system.

In mathematical terms, the assumption stated above can be written as the following linear equation:

$$H_M = \Sigma_g \, h_{Mg} \qquad\qquad (1)$$

where:

g is an integer variable that represents the gases present (i.e. assign an integer to each gas starting with one)

M is an integer variable that represents the mass numbers for the entire mass range of the spectrum.

H_M = total peak height (amps) of the spectrum at mass number M.

h_{Mg} = peak height contribution (amps) from gas g at mass M.

h_{Mg} is related to the fragmentation pattern, the RGA's sensitivity, and the partial pressure of gas g by the equation:

$$h_{Mg} = \alpha_{Mg} \, S_g \, P_g \qquad\qquad (2)$$

where:

α_{Mg} = Fragmentation factor of gas g at mass M: Ratio of ion signal at mass M to the ion signal at the principal mass peak for gas g.

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S_g = RGA's partial pressure sensitivity factor for gas g, in amp/Torr (see Partial Pressure Sensitivity Factor below)

P_g = Partial pressure of gas g in the system.

Equations (1) and (2) are combined to obtain the system of equations:

$$H_M = \Sigma_g \,(S_g\, \alpha_{Mg})\, P_g \qquad\qquad (3)$$

Since all gases have more than one peak in their fragmentation pattern, the number of peaks (M) in a real spectrum is generally larger than the number of gases (g). As a result, the system of equations (3) usually has more equations than unknowns. This situation is sometimes simplified eliminating some of the extra equations; however, the best results are obtained using all the equations and a multiple linear regression procedure to calculate the best possible fit to the data.

Obviously, accurate results can only be obtained if the constants α_{Mg} and S_g are well known for the RGA being used.

Note:

> The Analyze Utility of RGA Windows uses a multiple linear regression algorithm, as mentioned above, to automatically calculate the composition of a "typical residual gas environment" at the end of any 1-50 amu spectral scan.

Standard fragmentation patterns (for example, the fragmentation patterns included in the RGA Library of RGA Windows) can be used as a source of α_{Mg} values in moderately quantitative determinations. However, when very precise numbers are desired, one should obtain the appropriate fragment patterns by introducing pure gas into the RGA being used. The fragment patterns must be obtained under the same conditions that will be used during regular spectral analysis since they depend on many instrumental parameters, including: electron energy, emission current, ionizer design, mass filter settings, detector type, multiplier gain, etc. The principal mass peak of a fragmentation pattern is simply the most intense peak of the spectrum, and the intensity of all the other peaks in the pattern are normalized to its height for the calculation of fragmentation factors. Note that by our definition the α_{Mg} value for the principal mass peak of any gas is equal to one. Principal mass peaks are used in the calculation of the sensitivity of the SRS RGA to different gases as shown below.

Partial Pressure Sensitivity Factors

The partial pressure sensitivity of the RGA to a gas g, S_g, is defined as the ratio of the change $(H - H_0)$ in principal mass peak height to the corresponding change $(P - P_0)$ in total pressure due to a change in partial pressure of the particular gas species. H_0 and P_0 are background values.

$$S_g = (H - H_0) \,/\, (P - P_0)$$

The units of S_g are of ion current per unit pressure (amp/Torr, for example).

The sensitivity of the RGA varies with different gases, changes with time due to aging of the head, and is a strong function of the operating conditions of the instrument. Careful quantitative analysis requires that the sensitivity factor, S_g, be determined for every gas which may be a component gas in the system being analyzed. The sensitivity factors must be obtained under the same operating conditions that will be used during general partial pressure analysis since they depend on many instrumental parameters, including: ionization energy, emission current, mass filter setting, type of detector, etc.

In order to separate the gain of the electron multiplier from the intrinsic sensitivity of the RGA head, the sensitivity factors of the SRS RGA are defined for Faraday Cup detection. A separate electron multiplier *Gain Factor* is used to correct the ion signals when the electron multiplier is turned on.

The basic procedure for determining the sensitivity of a particular gas in the RGA is the following:

· Introduce the pure gas into the vacuum system, at a known or calculable pressure (typically around 10^{-6} Torr).

· Measure the output signal from the RGA for the principal mass peak of that gas using the Faraday cup detector.

· The ratio of this output signal to the pressure of the gas is the sensitivity factor, S_g.

During these measurements it is very important to insure that the partial pressures of all other gases in the system are small enough so that they may be neglected. The sensitivity factors calculated can only be applied to situations where the RGA is used with the same operating parameters.