Mass Spectrometer

A Comparison of Positive and Negative Ion RGA Methods

Summary

Hiden quadrupole mass-spectrometers provide the user with unique data through their high precision manufacture and flexible MASsoft operating system. An example of this is the ability to perform negative ion RGA to analyse ions produced via electron attachment, which facilitates the detection, discrimination and identification of species not normally detected by conventional RGA. This note describes measurements of SF_6 using the Hiden HPR-20 – QIC / EPIC mass spectrometer to compare the differing ions produced by electron impact (positive RGA) and electron attachment (negative RGA) and the effects of ioniser conditions on ion stability. The two sets of data illustrate widely different ion production profiles and show that negative ion RGA can detect the parent SF_6 (as SF_6^-) highlighting the ability of the HPR series QMS to perform analyses not available to other systems.

Manufactured in England by:

HIDEN ANALYTICAL LTD
420 Europa Boulevard, Warrington, WA5 7UN, England
t: +44 (0) 1925 445225 f: +44 (0) 1925 416518
e: info@hiden.co.uk w: www.HidenAnalytical.com

Negative Ion Analysis

In Hiden quadrupole mass spectrometers Electron Impact ionisation (E.I.) is used to generate positive ions which undergo subsequent mass filtration and detection. However, this process typically uses high-energy electrons which provides little molecular discrimination, as described in Hiden Application note 541. This lack of specificity may be further complicated by the need to analyse parent ions of reactive gases which may undergo rapid fragmentation upon ionisation. Hence it is clear the mass spectroscopist requires additional tools and techniques to aid in the identification and analysis of the residual gas profile in certain demanding applications.

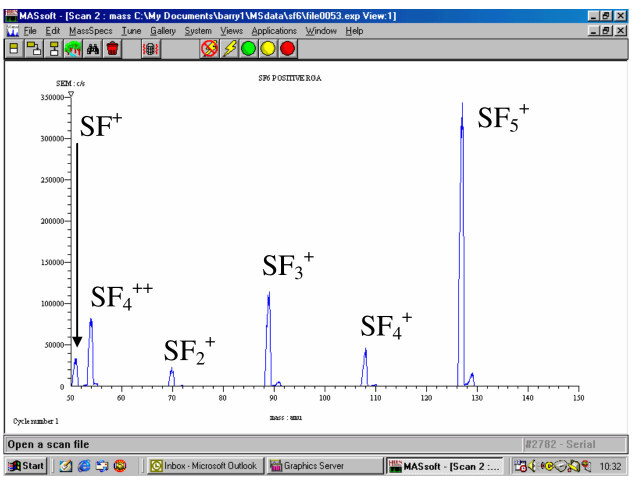


Figure 1. SF_6 Positive Ion RGA (50-150 amu).

To aid the MS user in these applications Hiden PIC mass spectrometers are available with negative ion RGA mode. This permits the analysis of negatively charged molecular species produced in the ioniser by associative or dissociative electron attachment. The mechanism of electron attachment is described in more detail in Application Note 231-a and may itself be used to identify species by their characteristic attachment profiles and low energy resonance, but also provides the MS user with a highly useful tool for the analysis of unstable species. The lower energies used in electron attachment are of particular importance in this regard as they facilitate ion formation and subsequent detection without resulting in the extensive fragmentation seen when using electron impact. These differences are clearly shown in Figures 1 and 2 which contrast the RGA profiles of SF_6 (1% in N_2) in positive and negative ion modes.

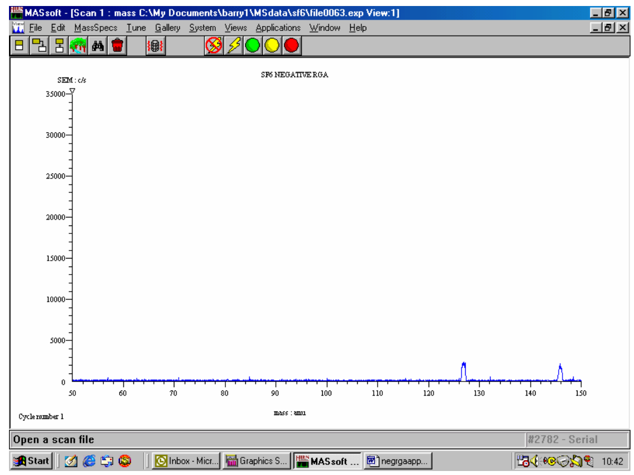


Figure 2. SF_6 Negative Ion RGA (50-150 a.m.u.)

The first major difference between the profiles is in the intensity and complexity of the peaks. In positive RGA there is a multiplicity of intense peaks for the fragment ions of SF_5^+, SF_4^+, SF_3^+ etc. with their corresponding S_{34} isotope 'satellite' peaks, consistent with extensive ionisation and fragmentation by impact from high-energy electrons. In contrast, the negative ion profile is both far less intense and complex reflecting the lower electron attachment cross-section but illustrating the large reduction in fragmentation due to attachment of lower energy electrons c.a. 0.2 eV [1]. Hence the only features observed, in addition to F^- at m/z 19 (not shown to enable direct comparison), are SF_6^- and SF_5^- at m/z 146 and 127 respectively. This direct detection of the parent SF_6^- highlights the unique potential of negative ion RGA, as this species is not normally observed except under cryogenic conditions where it presents a very weak signal [1]. The instability of SF_6^+ is believed to be a consequence of its symmetric electronic structure, although it is equally clear that the highly electronegative F may facilitate fragmentation due to the formation of the favoured F^- leaving group i.e.

$$SF_6 + e^- \quad \rightarrow SF_6^{+*} \rightarrow SF_5^+ + F^-$$

Conversely, there is no corresponding process in electron attachment as any fragmentation results in the formation of neutrals i.e.

$$SF_6 + e^- \quad \rightarrow SF_6^{-*}$$

The excited metastable SF_6^{-*} being stabilised via collision / photo-emission or fragmentation by loss of F^-:

$$SF_6^{-*} + \text{collision} \rightarrow SF_6^+ + \text{energy}$$

$$SF_6^{-*} \rightarrow SF_6^+ + h\nu$$

$$SF_6 + e^- \rightarrow SF_6^{+*} \rightarrow SF_5 + F^-$$

From these processes it becomes evident that in order to detect the presence of SF_6^-, some form of relaxation / energy transfer process must occur. Conversely, any perturbation of the ioniser environment or process which inhibits relaxation / promotes electron detachment would significantly reduce the concentration of the long – lived stabilised SF_6^-.

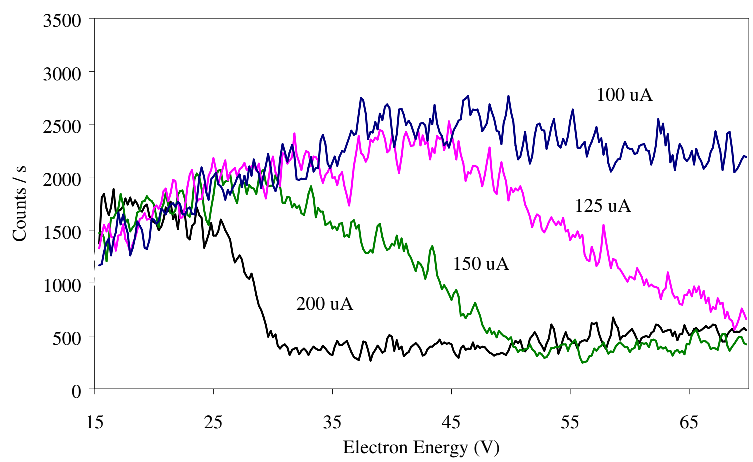
The competition between the relaxation and detachment processes for SF_6^{-*} is illustrated in Figure 3. This indicates that there is a decrease in the concentration of SF_6^- detected as a combination of higher emission currents coupled with higher electron energies. This loss of signal is corroborated in the negative ion RGA profile of SF_6^- and SF_5^- (Figures 4a-4c). Again there is a dramatic decrease, and eventual complete loss in both peak intensities under increasingly extreme ioniser conditions.

These observations are consistent with the enhanced decomposition of the SF_6^{-*}, the common metastable parent of both SF_6^- and SF_5^-. The decomposition / detachment of SF_6^{-*} may occur via either a thermal mechanism or by collision with energetic electrons or photons emitted from the filament. In the case of these studies it is apparent that all mechanisms may be in effect viz: As emission current increases the filament becomes increasingly hot which increases the local temperature inside the ionisation chamber. Concomitant to this localised heating there is an increase in photon flux into the ioniser due to radiant emissions from the filament. Both of these mechanisms would tend to favour decomposition / detachment of the metastable parent. However it is only when the parent ion is also exposed to increasingly energetic electrons that detachment begins to dominate and all signal is lost. Thus it is clear that the use of negative ion detection alone may not be sufficient without due consideration of the stability of the reactive parent species.

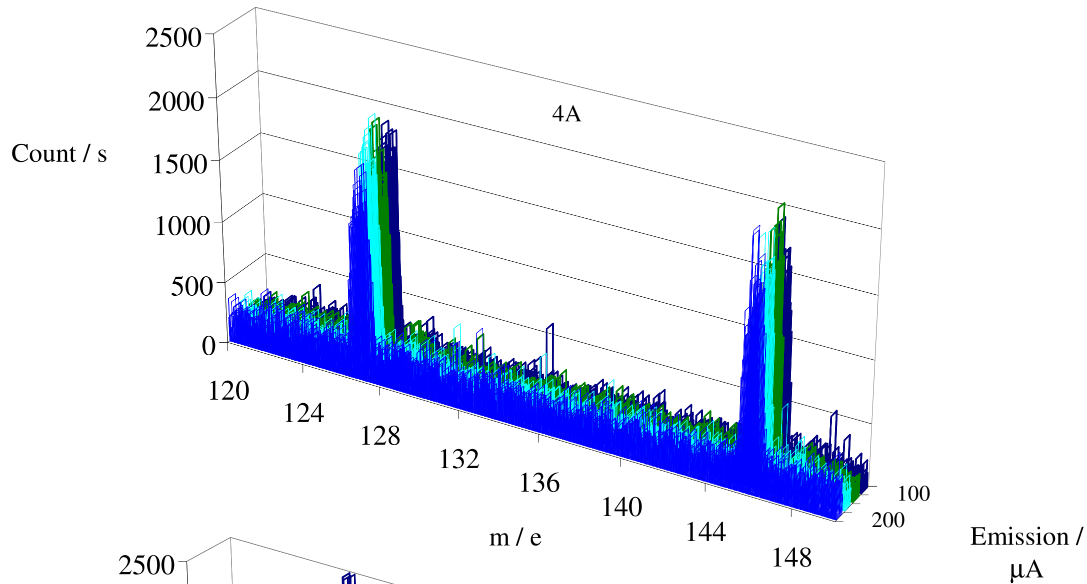
Conclusions

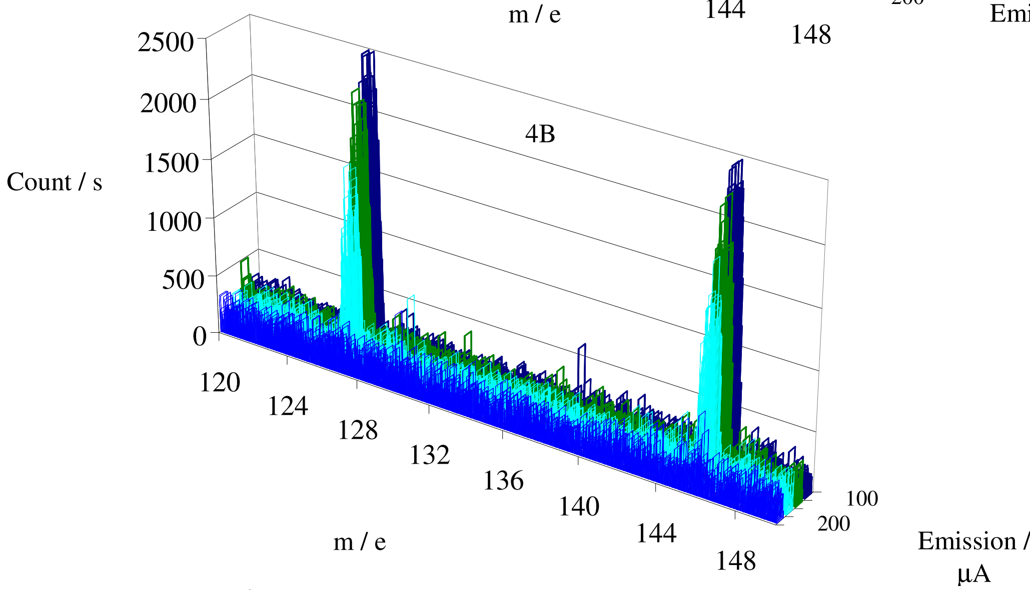
Negative Ion detection / RGA is a simple and powerful method for the detection and analysis of reactive / metastable species not normally seen in conventional RGA. It is particularly useful when analysing electronegative species or molecules with strong electronegative components which act as potential leaving groups under electron impact RGA which facilitate ionisation by decomposition of the parent.

Figure 3. The Effect of Emission Current and Electron Energy on the production of SF_6^-.



1. L.Christophorou and J.K.Othoff, J.Phys. Chem. Ref. Data vol 29, no. 3, p267 (2000)





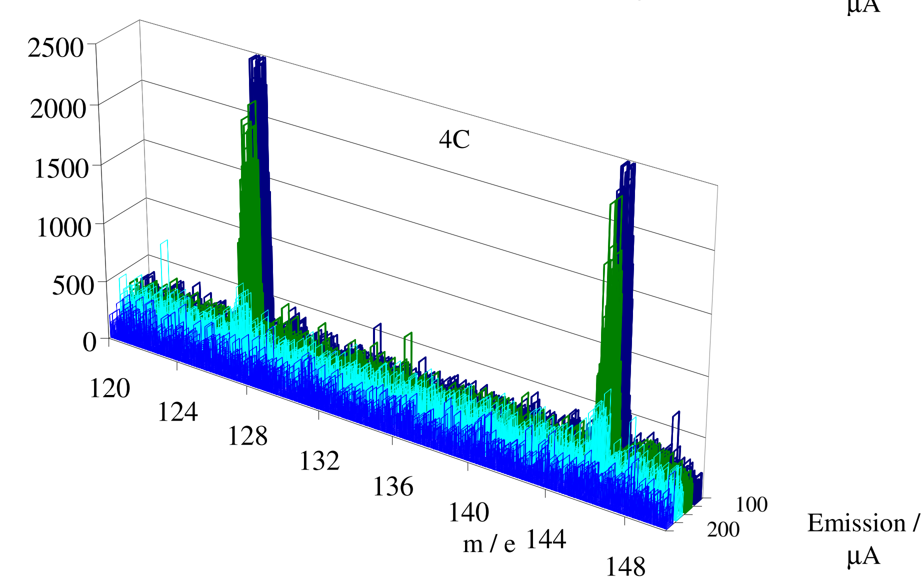


Figure 4 –The Effect of Increasing Emission Current & Electron Energy on the Negative Ion Profile of SF_6
4A. ee = 20 V
4B. ee = 35 V
4C. ee = 50 V