Gas Analysis
Application Note 254

MS
Quantitative Analysis of Fluorine-Containing Process Streams

Summary

Hiden quadrupole mass-spectrometers are ideal systems for monitoring process chemistry and exhaust gases. The combination of their high precision manufacture and flexible application specific configurations provide the user with a powerful and flexible tool for even the most demanding application. An example of this is the analysis of off-gases from CVD or microelectronics applications which may contain aggressive and / or persistent components such as Fluorine-based compounds. The toxicity and reactivity of these compounds demand the highest sensitivity and response for safe operation. This application note describes measurements of atmospheric-pressure F_2-containing streams and demonstrates the quantitative analysis and optimal dynamic response of the Hiden HPR20 with internal cryopanel at F_2 concentrations from 4-5000 ppm.

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Persistent Component Analysis

Many CVD, PVD and etching methods use Fluorine -containing compounds within their processes. Unfortunately these species can be toxic or react to yield highly toxic fluorine gas. F_2 is one of the most reactive elements known and attacks glass, quartz, most organic compounds and many metals and has a TLV of *ca.* 1ppm. Hence the accurate quantification of trace levels is of great importance but the analysis is equally challenging.

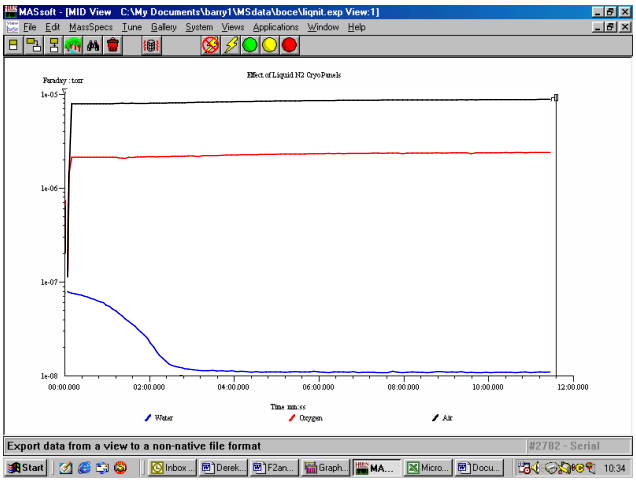


Figure 1. Effect of Cryopanel

To address this application a series of measurements were performed using a gas-mixing manifold fed by thermal mass flow controllers capable of delivering 1-10,000ppm of F_2 in a balance gas (N_2 / Ar). All F_2 concentrations were corroborated via an electro-chemical cell. Prior to any measurement the mass spectrometer internal cryopanels were cooled using liquid N_2 resulting in the adsorption of background H_2O. This was performed to minimise any spectral interference in the m/z 19 region, the data confirms a rapid decrease in the water background of an order of magnitude as shown in Figure 1.

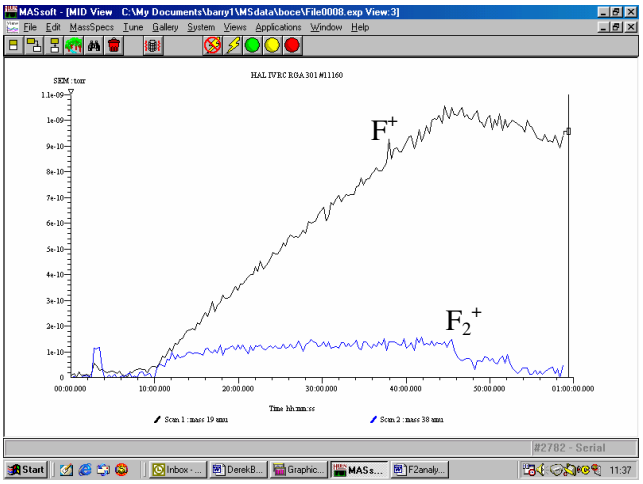


Figure 2. Dynamic Response of F_2^+ and F^+

Next the response of the mass spectrometer to increasing levels of F_2 (2, 10 and 100 ppm) was examined giving the results shown in Figures 2 – 3a,b and c. Surprisingly, the data obtained show an initial lag in response at both m/e 19 (F^+) and 38 (F_2^+) until an apparent F_2 'threshold' concentration was exceeded. This phenomenon is unique to the capillary-MS sampling of Fluorine and is ascribed to its extremely high reactivity and specifically to interactions with the capillary walls which initially adsorb gaseous Fluorine-derived species but then attain an adsorption – desorption equilibrium at which time breakthrough is observed. After this the response for F_2^+ 38 rapidly attained a steady state concentration. In contrast F^+ increased linearly over the duration of the experiment with no apparent plateau. Moreover, upon reduction of the F2 inlet concentration to 10 ppm and subsequently 2 ppm and 1 ppm, there were immediate responses in the F2+ signal. In contrast F+ showed little response and did not return to initial zero values indicating that retention, presumably via adsorption of the F+, had occurred, consistent with the known chemical properties of Fluorine. This retention process resulting in an

increased analyser 'background' at m/e 19, combined with the lack of any dynamic response, confirmed that monitoring of F2+ provided a significantly better process indicator.

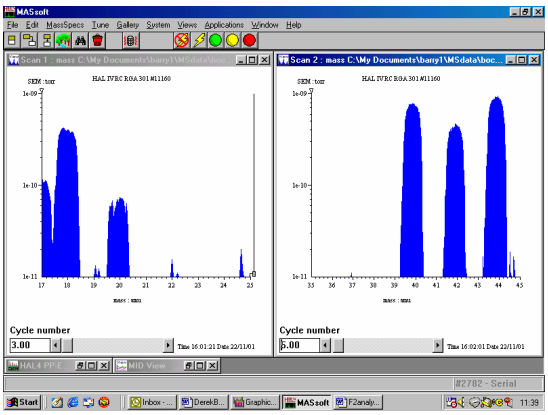


Figure 4. Kr before (a) and after (b) F_2 analyses

Next the dynamic response of F_2^+ was measured in the presence of Ar as the ballast gas to determine whether the presence of Ar^{38} (isotopic abundance ca. 0.3%) resulted in significant spectral interference. The results of this analysis are shown in Figure 5 and showed that in the absence of gaseous F_2 the background response at m/e 38 was negligible whilst introduction of F_2 resulted in the same dynamic response and sensitivity obtained previously.

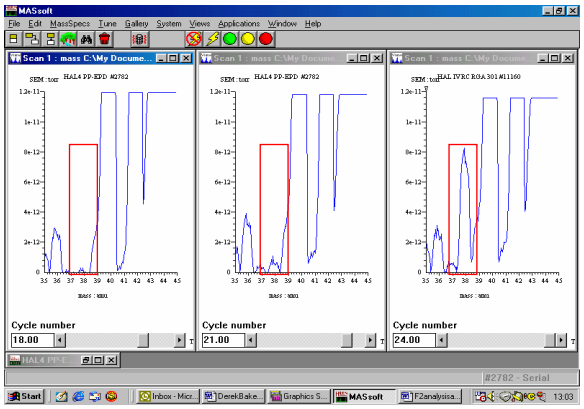


Figure 5. F_2^+ in Ar response

Finally the response of the MS to wide variations in F_2 concentration (1-2,000 ppm) was examined giving the results shown in Figures 6a and b. Again instantaneous step changes in concentration, compared to the residence in the gas manifold were evident, as shown by the step response. However a lower threshold of detection was encountered at below 4ppm. Hence there are marginal differences between the signal at 3,2 and 1ppm. In addition upon increasing the concentration to 4ppm F_2 system recovery was slow as shown in the detail. Further increasing F_2 to 10ppm however restored the instant response. These effects are again ascribed to the unique nature of the Fluorine adsorption / desorption equilibrium within the gas manifold / capillary. However not withstanding this effect the data displayed a good linearity and high reproducibility of response between 4 – 5000ppm F_2.

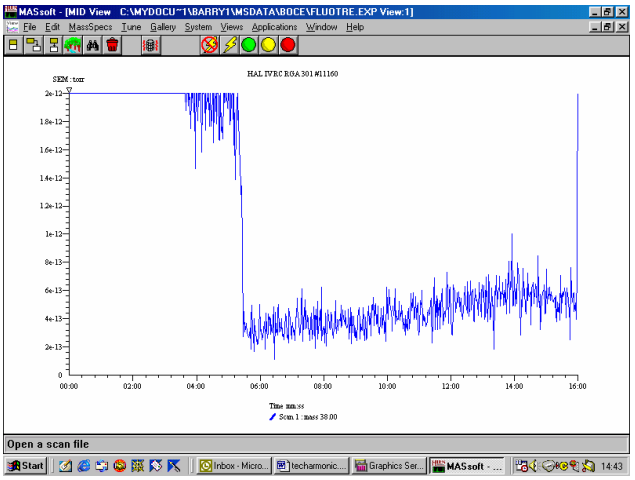
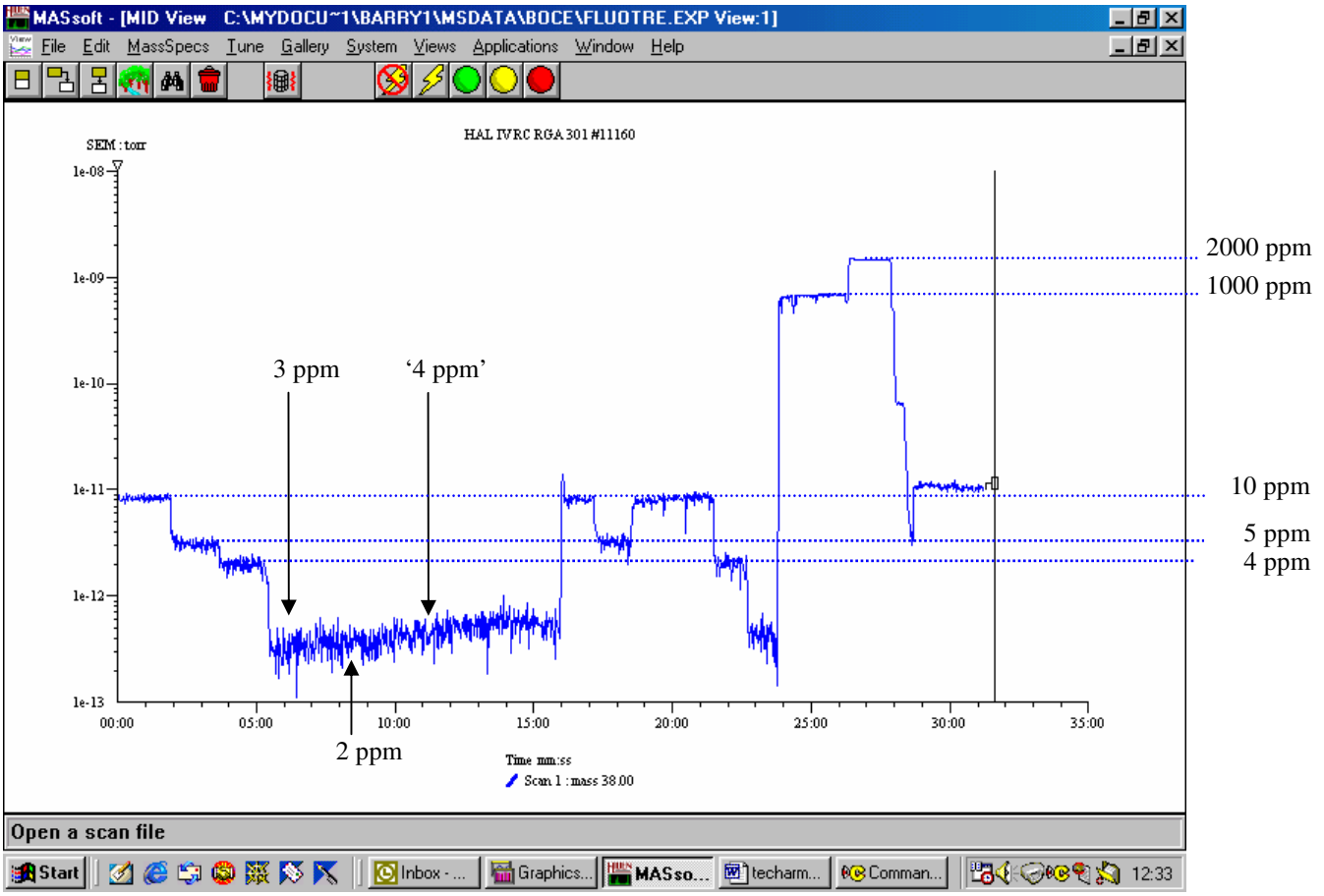


Figure 6a. F_2^+ response 2-4 ppm (detail)

Figure 6b. F_2^+ response 2-2000 ppm.



Conclusions.

The Hiden HPR20 mass spectrometer has been applied to the quantitative analysis of F2-containing streams. The data obtained shows that while analysis of F+ ions yields poor dynamic response and sensitivity, the comparable analysis of F2+ ions shows both high sensitivity and quantitative reproducibility over 4 orders of magnitude concentration confirming the suitability of the MS for this demanding application.