

Characterization of Shales by Mass Spectrometry during Ion Milling

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A basic principle of science in general, and sample preparation in particular, is to not change the nature of what is being investigated by the improper choice of the method of investigation. Loss of hydrocarbons from oil and gas shales during ion milling could compromise critical dimension measurements of porosity in the organic phase following FIB / SEM.

To assess this phenomenon in situ, measurements were made using mass spectrometry. An Extorr Model XT RGA was installed in place of one of the TrueFocus ion sources of a E.A. Fischione Instruments Model 1060 SEM Mill.[1] The connection from the turbo molecular pumped vacuum chamber was heated to > 190°F to avoid condensation of gas species prior to detection. The ionization energy at the filament was 70 eV. An electron multiplier was used to amplify the ion current when needed. A setting of 2040V was found to give optimal amplification.

Initial mass sweeps were conducted of the residual gas species present at base vacuum, Figure 1. Other than the usual residuals (CO, CO₂, H₂O), no significant hydrocarbons were detected. Common fragments are m15, m29, m43, m57, which are separated by increments of m14 (CH₂). After a raw piece of shale was loaded through the load lock into the vacuum chamber, additional mass sweeps were performed. Hydrocarbons were detectable at mass numbers of m29, m43, m57 as shown in Figure 2.

The instrument's anti – contaminator (dewar) was filled with liquid nitrogen, and after a pause of 20 minutes, an ion milling cycle was started. The process parameters used with one ion source were: 5kV, 45% Ion Beam Focus, no in plane motion for the sample. Mass trends were then acquired to track the outgassing of selected gas species as a function of time.

The trend lines for these species are presented in Figure 3. The initial results indicated that the amplified signals for the hydrocarbons (m29, m43, m57) either remained constant or decreased slightly with processing time. An increase in hydrocarbon levels would have implied an outgassing driven by the sample preparation process. Such outgassing could result in a significant loss of mass and modification of the internal porosity. Additional tests are in progress to confirm and expand these initial results.

References:

- [1] R. R. Cerchiara, P. E. Fischione, M. F. Boccabella, L. M. Marsh and A. C. Robins, "Sample Preparation of Oil and Gas Shales for EBSD/EDX and FIB/SEM", Late Breaking Poster 24, Microscopy and Microanalysis 2012, Phoenix, AZ, Aug. 2012.

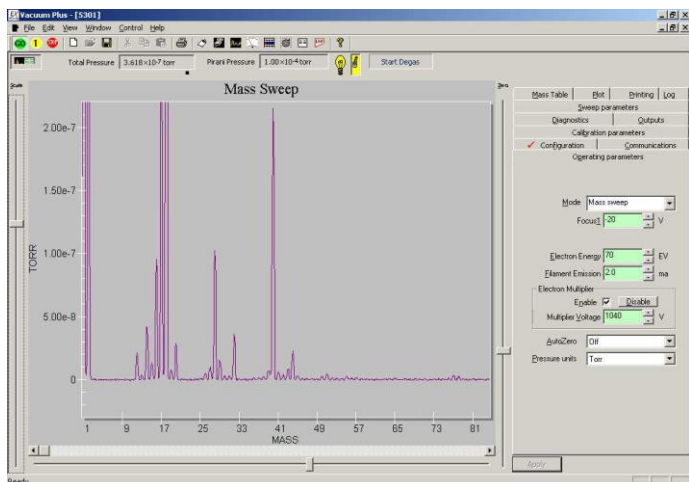


Figure 1 Mass sweep acquired at base vacuum

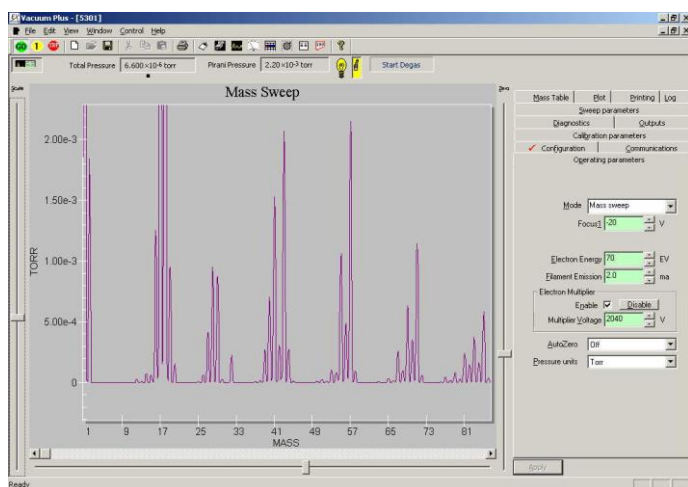


Figure 2 Mass sweep acquired after shale loaded. Hydrocarbons detected at m29, m43, m57.

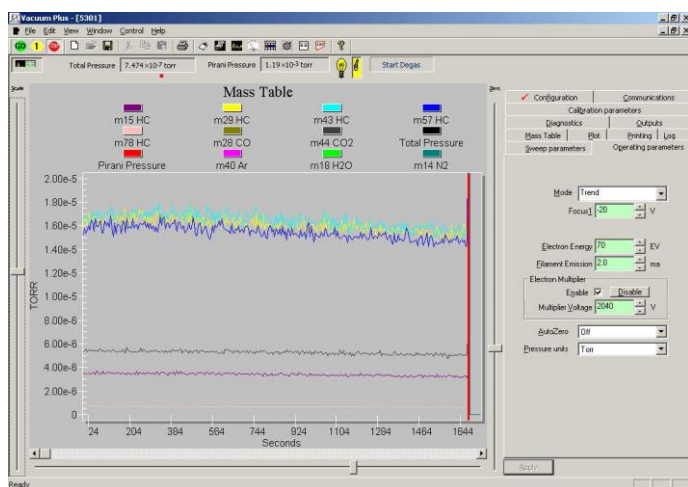


Figure 3 Mass trends acquired as shale ion milled. Hydrocarbons levels (m29, m43, m57) decreased.