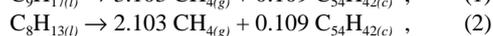
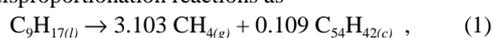


Thermodynamic analysis of pyrobitumen formation during thermal alteration of crude oil in deep hot reservoir and source rocks

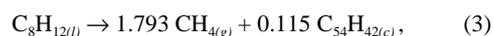
LAURENT RICHARD AND HAROLD C. HELGESON

University of California, Earth & Planetary Science, Berkeley
CA94720, USA., lrichard@uclink4.berkeley.edu,
brogie@socrates.berkeley.edu

Gibbs free energy minimization computer experiments indicate that the oil generated in hydrocarbon source rocks during the incongruent melting of kerogen with increasing depth becomes progressively dominated to an increasing degree by low-molecular weight aromatic species such as toluene and ethylbenzene as temperature increases above ~ 175°C. This increase favors the irreversible disproportionation of crude oil to form natural gas and pyrobitumen in both hydrocarbon reservoirs and source rocks. For example, if we represent the crude oils produced in the computer experiments with average compositions corresponding to C₉H₁₇, C₈H₁₃, and C₈H₁₂ at 150°C, 200°C and, 250°C, respectively, we can write the overall disproportionation reactions as



and



where C₅₄H_{42(c)} stands for a representative pyrobitumen of anthraxolitic composition. It can be deduced from the stoichiometries of these reactions that the formation of pyrobitumen relative to methane is favored to an increasing degree by the concomitant increase in both the temperature and aromaticity of the oil. In fact, for each mole of CH_{4(g)} produced, 0.035, 0.052, and 0.064 moles of pyrobitumen are formed, respectively, with increasing temperature from 150°C to 250°C.

Development of a micro-cavity ion source for enhanced efficiency in thermal ionisation mass spectrometry

L.R. RICIPUTI¹, K.B. INGENERI¹ AND P.M.L. HEDBERG²

¹Chemical Sciences Division, Oak Ridge National Laboratory,
P.O. Box 2008, Oak Ridge, TN 37831-6365
(i79@ornl.gov)

²Safeguards Analytical Laboratory, International Atomic
Energy Agency, Wagramer Strasse 5, A-1400, Vienna,
Austria (P.M.L.Hedberg@iaea.org)

The need to precisely and accurately measure isotope ratios on very small amounts of sample (nanograms to sub-picogram) is of increasing importance in a variety of applications. To improve sample utilization for isotope ratio measurements, we have adapted a micro-cavity source to two sector thermal ionization mass spectrometers (TIMS), a home-built double-focusing instrument equipped with a single pulse-counting detector, and a commercial Finnigan MAT 262 instrument. Unlike traditional TIMS sources which employ a filament design, the sample is loaded into a narrow (0.2-0.5 mm diameter) micro-cavity bored in a tungsten or rhenium rod, which is then heated by electron impact. The source's confined geometry and ability to operate at much higher temperatures (>3000C) provide the potential for enhanced ionization efficiency compared to traditional TIMS sources.

Thus far, our work has focused on uranium and plutonium. On both instruments, efficiencies (ions detected/atoms loaded) measured using the cavity source are an order of magnitude or more higher compared to those measured using filaments. Using single resin beads loaded with ~10ng of U, W cavities on the 262 instrument yielded efficiencies of 0.02 to 0.04%; similar tests on the ORNL instrument using 1ng beads indicated efficiencies of up to 0.4%. Adding a Re/C slurry to W cavities increased efficiencies to 0.1 to 0.2% on the 262. Efficiencies of up to 0.6% were measured on the 262 using Re cavities. In comparison, efficiencies of 0.01 and 0.04% were measured using single Re filaments on the 262 and ORNL instruments, respectively. More limited data has been obtained utilizing resin beads loaded with 30pg of Pu. Efficiencies exceed 0.08% for W filaments, and 0.4 to 1.2% for Re cavities on the 262. Various observations indicate that transmission from the source into the mass spectrometers is far from optimised, suggesting that actual ionization efficiency is significantly higher than the effective efficiency measured in these tests. In spite of this, these results match or exceed many of the best reported TIMS efficiencies. The measurements reported here were not optimised for precision and accuracy of isotope ratio measurements. However, U measurements on the ORNL instrument suggest that accuracy is 0.5% or better, and precision is similar to that obtained using filament measurements.