Offgas from Radiolysis – Difficult analysis needing High Resolution Mass Spectrometry

William A. Spencer, Charles L. Crawford, Thomas L. White, Stephen L. Crump, Robert J. Lascola, and Laura L. Tovo, Savannah River National Laboratory, Westinghouse Savannah River Company, Aiken, SC

Many of the current research projects at the Department of Energy Savannah River National Laboratory revolve around the effects of radiation on chemicals and materials required for new processes. The primary concern from radiolysis is the potential for the build up of explosive offgas mixtures. A secondary concern is the development of corrosive gases which might attack the containment vessels being used. Offgas build up rates are generally in proportion to the radiation dose and often become the major design limitation that sets the scale for sizing a new radioactive process. The SRNL analytical chemists, who must support this process development research, are often asked to determine the precise concentrations of offgas mixtures caused by radiolysis as well as from normal thermal and chemical reaction that might occur in the process. Residual gas analysis using small quadrupole mass spectrometers and traditional GC/MS are generally the chosen analytical techniques. However, both have severe limitations in either resolution of isomers, speed of analysis, or required sample amounts. High resolution mass spectrometers offer an attractive alternative analytical technique that overcomes many of the limitations. Co-isomers, which are not resolved in an RGA and ones that are too reactive for gas chromatography, can be determined in these instruments. SRNL has been evaluating two new semi-portable mass spectrometer systems for high resolution of low atomic weight gases. These are the Siemens Applied Automation Division Quantra FTICR system and the JEOL GCMATE II compact sector instrument. Both of these instruments have a modest price compared to traditional high resolution gas mass spectrometers. We will show examples from radiolysis samples that required resolution of CO, N2, C2H4 at mass 28, NH3 and OH at mass 17, O, CH4, and NH2 at mass 16, and CO2, N2O, C3H2O, C3H8 at mass 44. The complex chemistries of oxygen, nitrogen, and water in high radiation fields are well know from the development of both boiling water and pressure based nuclear reactors. Less well known are the slow reactions that occur over time from mainly alpha radiolysis in drums of TRU wastes. The challenge of determining the volatile organic compounds in the TRU offgas mixtures and the difficult determination of the lower flammability limit for the mixture will be illustrated.

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