

Project ID: **60424**

Project Title: **High Temperature Condensed Phase Mass Spectrometric Analysis**

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This program (in the 20th month as of this writing) was initiated with the goal of designing, constructing and operating a materials analysis instrument capable of obtaining a wide variety of chemical measurements on a material at high temperature. This instrument is being built around a quadrupole mass spectrometer. There are three main modes of obtaining spectra from the high temperature condensed phase material; surface ionization from the condensed phase, secondary ion mass spectrometry (SIMS, both static and dynamic modes) of the condensed phase, and electron impact ionization of vapor phase neutral species. The combination of the data from these three modes will allow the gleaning of chemical information concerning the nature of the chemical species present in both the condensed phase (solid or molten) and the vapor phase. The intended application is the identification of the chemical species present in materials at high temperatures. The logic behind performing these types of studies is that the chemical species present at high temperatures may be quite different from those present at lower temperatures, and may subsequently greatly alter the chemical reactivity and the volatilization of certain species. This has implication for the high temperature processing of various forms of waste.

The example that was presented in the proposal involved the identification of the chemical species of technetium(Tc), some of which are much more volatile at elevated temperatures than others. Specifically, Tc in the +7 oxidation state (the preferred oxidation state) can exist either as Tc_2O_7 or as TcO_4^- . The former is volatile at lower temperatures (mp=393K, bp=584K), and the volatilization of the latter is dependent upon the counter cation, but being an ionic material much higher temperatures are required. The factors that determine the equilibrium between these two species are rather poorly understood, and with the capability to readily measure relative concentrations of these different species it should be possible to gain new insights into this problem and others.

There are important waste management implications related to this chemical system. Tc is present in radioactive wastes that are treated by thermal processes. Because the form of Tc will determine how readily the Tc is released, understanding the chemical equilibrium and processes related to the conversion of TcO_4^- , in both the condensed and vapor phase, to Tc_2O_7 will provide important insights into the development of appropriate waste processing schemes. Rhenium chemistry closely matches that of Tc, particularly in regard to the oxide chemistry (which is the Tc chemistry of greatest importance for waste management), and hence will be used in place of Tc, at least for the initial studies.

Thus far, design and fabrication of the instrument has been the primary focus of the program. During the past year, development and fabrication of the ion optics has been the top priority. Extensive modeling with the ion optics program "SIMION" was performed on many different ion source designs. The preferred design was finalized only after extensive refining. The design was finalized this past April, and the conversion into

engineering drawings was completed in May. This design carefully balances the competing demands of the three main operating modes, which is no simple task. A complete description of this source is beyond what can be included in this report, however, the salient features are as follows. The sample is contained in a small refractory metal tube that is resistance heated. The face of this source is at the focal point of the ion lens that transfers ions into the mass spectrometer. Thermal ions that give important information concerning the more readily ionized species on the surface are transmitted directly from the surface of the source into the instrument. Two different ion guns, one for static SIMS and one for dynamic SIMS, are focused onto this surface. The static SIMS gun will be used to analyze the composition of the top layer. The dynamic SIMS gun will cause significant ablation of the surface and will be used for the analysis of material below the top surface. Since both the thermal and the secondary ions originate from the surface of the sample, the same focusing conditions are able to transmit ions into the mass spectrometer. The neutrals emitted from the surface of the sample are ionized by an electron beam focused from all sides to converge at a point just above the surface of the sample. Ions are produced from the neutral vapor species before they can diverge significantly. The ion optic models suggest that sensitivity for neutrals should be excellent, and it is thought that the analysis of sputtered neutrals should also be possible, although it is recognized that this is much more difficult. The ion optics are optimized to allow highly efficient transmission of ions from all these modes into the mass spectrometer. This source is now being constructed.

The vacuum system and other primary components of the instrument were designed and constructed concurrent with the design of the source. The vacuum lock and high temperature probe have been proven to operate reliably. An ultra high vacuum chamber with turbo, ion, gettering and LN2 pumping houses the instrument. The turbo pump is used to evacuate the main chamber from atmospheric pressure, and is also used to differentially pump the two ion guns and the vacuum lock. After initial evacuation with the turbo, the ion pump is used to maintain vacuum, with the LN2 and sublimator pumps being used to accommodate heavy loads during an analysis. The system pumps into the low 9's without bakeout. The quadrupole mass spectrometer is an Extrel with 0.75" rods and very high sensitivity. The data system is modeled after one developed in our laboratory, and operates the instrument in an efficient fashion.

In the remaining 16 months of this program the plan is to complete the instrument and to test it on a variety of samples. The testing plan has been scaled back to accommodate the level at which the program is funded. The main activity will be to synthesize a variety of materials and to test the factors that force the equilibrium between the various rhenium oxide species (as a surrogate for Tc). We have a variety of ideas to test, such as the extent to which complexation stabilizes the perrhenate anion. We suspect that this is the main factor driving the equilibrium, but this remains to be seen. The various rhenium oxide species are readily differentiated by these methods, as demonstrate by analyses we have performed on various individual instruments. By combining all of these functions (measurement of neutrals, thermal ions and surface analyses by SIMS) into a single instrument, these measurement can be made in rapid sequence on a single specimen, allowing superior interpretation of data.