The EMSP Program "High Temperature Condensed Phase Mass Spectrometric Analysis" was funded in Sep. 1997 for 36 months. The purpose of this program is to address the issues associated with understanding properties and reactions when materials such as glasses and ceramics are heated to high temperatures in a variety of processes. The reason this is important to DOE EM is the fact that many processes are either in operation or are planned that entail the processing of waste materials at high temperatures. These systems have been engineered, but in many cases the actual scientific details of what goes on in these processes are poorly understood. This program was funded to build a high temperature mass spectrometric analysis instrument designed specifically to analyze materials heated to high temperatures that allows the study of materials both held at these temperatures and undergoing chemical reactions at these temperatures. This program is now at the 30 month point, and the end product of this program, a mass spectrometer system with multiple ionization and analysis modes for high temperature samples, is now operational. The instrument is built around a high temperature "Langmuir evaporation source," and has the following ionization modes: a) Static SIMS for cations and anions. b) Dynamic SIMS for cations and anions. c) Surface ionization for cations and anions. d) Electron impact ionization (EI) for cations. These ionization modes are all designed into a single ion source housing interfaced to a high sensitivity quadrupole mass spectrometer.

The operational modes are under computer control and can be operated in a rapidly interlaced fashion to enable the collection of the various types of data for a sample that can be programmed for many types of temperature/time/chemical reaction profiles. The sample can be held at a constant temperature while observing a reaction that may be occurring, while observing changing conditions occurring with a temperature ramp, or some totally arbitrary set of time and temperature conditions. The data system controlling the mass spectrometer and coordinating the ionization modes was custom developed in our lab. The instrument control portion is finished, although there remain programming needs for sequencing through the various ionization modes and for coordinated data storage as the system sequences though ionization modes. We expect to finish these features in the remaining 6 months of the existing program.

The sample is mounted in a small refractory metal tube held in a vertical position with the bottom sealed and the sample in the top. The tube is spot welded onto refractory metal filaments which are in turn supported on the end of a vacuum lock probe. These assemblies are inexpensive and disposed of after a single use. The vacuum lock probe has four electrical feedthroughs, two for power and two for thermocouple connections. The tube can be heated to temperatures that in some cases can be in excess of 1500C, depending upon the configuration. The entire instrument was built in a vertical plane around this configuration so that the sample cannot fall from the holder. The samples are inserted via the vacuum lock that is pumped with a mechanical pump on the first stage and a turbo pump on the second stage. There is a docking mechanism that holds the end of the probe in alignment with the ion source, which in turn aligns the sample collinear with the center axis of the ion lens and the quadrupole mass spectrometer.

The EI mode operates by focusing an electron beam on an area in space just in front of, but not hitting the hot surface, so as to ionize neutrals as they volatilize from the surface. This can be accomplished in a manner that discriminates against ions originating from the sample itself by various biasing voltages. The ion optics have been designed to maximize ion transmission, and the instrument has demonstrated exceptional sensitivity in the EI mode. Since the EI detection of trace condensable species and sputtered neutrals are considered the most important analyses to be performed on this instrument, the EI mode was given the highest priority in the design considerations and in the checkout.

The most important aspect of analyzing the envisioned materials at high temperatures will be of the neutral species volatilizing from the surface. This is due to the fact that the release of vapors from these materials in these processes offers the highest probability of release of hazardous species. These volatilizing species will be analyzed by EI. A complicating factor in these analyses is the extremely wide range of intensities observed from the gases and vapors emitted from the samples. Gases such as water and carbon dioxide will be emitted early in the heating cycle in very large quantities, while later in the heating cycle it will be necessary to measure small quantities of species with low volatilities. We are currently evaluating a variety of alternatives for the extension of the dynamic range while operating in the EI mode, and plan to finish this during the remaining 6 months of the program.

The surface ionization and static SIMS modes have been demonstrated for both cations and anions, with good sensitivity, although at an earlier stage in the testing cycle than the EI mode. The dynamic SIMS mode has not yet been checked out, although the high intensity ion gun is mounted on the system. Since the static SIMS mode requires much higher sensitivity than the dynamic SIMS mode, and the static SIMS mode operates satisfactorily, there is little doubt that the dynamic SIMS mode will operate satisfactorily.

Some ions will be emitted directly from the surface, and these will need to be measured and evaluated, since they will overlay any ions sputtered by the SIMS guns. In some instances these surface ions can be diagnostic for the presence of various species on the surface, and hence can be of importance.

The static SIMS gun is a design of ours and uses the perrhenate anion at mass 250. This gun has proven to be exceptionally efficient for the sputtering of molecular species from surfaces. This will be used for the analysis of chemical species on the top most layer of the surface. This is of particular importance due to the fact that the surface provides the interface for chemical reactions and volatilization of species with the surrounding atmosphere. This gun has been checked out and operates reliably at full voltage (10kV) at currents up to several nanoamperes, although when operating at static SIMS conditions the current is generally held at about 200 picoamperes.

The elemental analysis of the sample will be provided largely with two operating modes of the dynamic SIMS gun. The first is ions sputtered from the sample. These will be representative of near surface materials in the short term, and ions will originate from deeper within the sample the longer the gun operates. In this mode the sample will be biased to maximize ion transmission into the quadrupole. The second operating mode involves biasing against sputtered ions and using the EI source to ionize sputtered neutrals. The dynamic SIMS gun should produce an abundance of neutrals for analysis by this mode. The advantages of analyzing sputtered neutrals instead of ions is a significant reduction in the variation in sensitivity factors for different elements and molecules. This in turn significantly reduces the matrix effects that are observed for different species in a variety of materials. This is due to the fact that in dynamic SIMS the sample is continuously and nearly uniformly sputtered from the surface, and most of these species are neutral rather than ionic. The neutral species are much closer to being in the same ratio as to those in the bulk than the sputtered ions. The sensitivity factors for different gas phase species then only depends upon the ionization probabilities for EI. When ions are analyzed directly from the sputtered surface the ionization probabilities are strongly determined from solid state matrix effects, which are much more variable than the gas phase ionization probabilities.

An example of the evolution of a material as it passes though a heating cycle is illustrated by a silver zeolite sample. First water is given off, and when it has peaked, carbon dioxide evolves in large quantities. When most of these gases have been evolved and the temperature reaches appropriate temperatures, potassium starts being emitted from surface ionization, and at a still higher temperature a small amount of silver ions by surface ionization. About the time that silver ions can be detected, silver neutrals are seen in the EI mode. By this time the water and carbon dioxide have fallen to quite low levels. This is an easy example of how this instrument can be applied. More complex materials, including chemical reactions, are also amenable to this type of analysis. However, considerable study is required prior to the application of this instrument to the more complex problems.

The entire system is approaching the point of being fully operational, although there are a few features that remain to be finished. These have been mentioned previously, and it should not be difficult to finish these items prior to the end of this program in 6 more months.