

INNOVATIVE TECHNOLOGY

Summary Report DOE/EM-0561

Real-Time Monitor for Transuranics in Glass

Characterization, Monitoring, and Sensor
Technology Crosscutting Program and
Nuclear Materials Focus Area



Prepared for
U.S. Department of Energy
Office of Environmental Management
Office of Science and Technology
January 2001



Real-Time Monitor for Transuranics in Glass

OST/TMS ID 2004

Characterization, Monitoring, and Sensor
Technology Crosscutting Program and
Nuclear Materials Focus Area

*Demonstrated at
Savannah River Site
Aiken, South Carolina*

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Summary Report

Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine whether a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at <http://ost.em.doe.gov> under "Publications."

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SECTION 1 SUMMARY

Technology Summary

This project involved the development of a monitor that can be used to determine the concentrations of certain metals in a glass stream as it flows out of a melter. The monitor is based on the detection of the spectrum of light emitted by a high-temperature object (thermal emission spectroscopy, TES), so the sample is also the source for the spectroscopic measurement. Light emitted by the hot glass stream is focused into an optical fiber, so no direct contact with the sample is required for the analysis. The other end of the optical fiber is coupled to a simple spectrometer with an array detector with no moving parts. Data collection necessary for the determination of several metals requires only a few seconds. The original objective of the project was to develop a near-real-time, on-line process monitor for the determination of plutonium in a molten glass stream, but the monitor may be adapted easily for the determination of several other metals. The most immediate application is the determination of americium (Am) and curium (Cm) in the Americium-Curium Stabilization Project at the Savannah River Site (SRS). The results of the demonstrations of the monitor for that application are described in this ITSR.

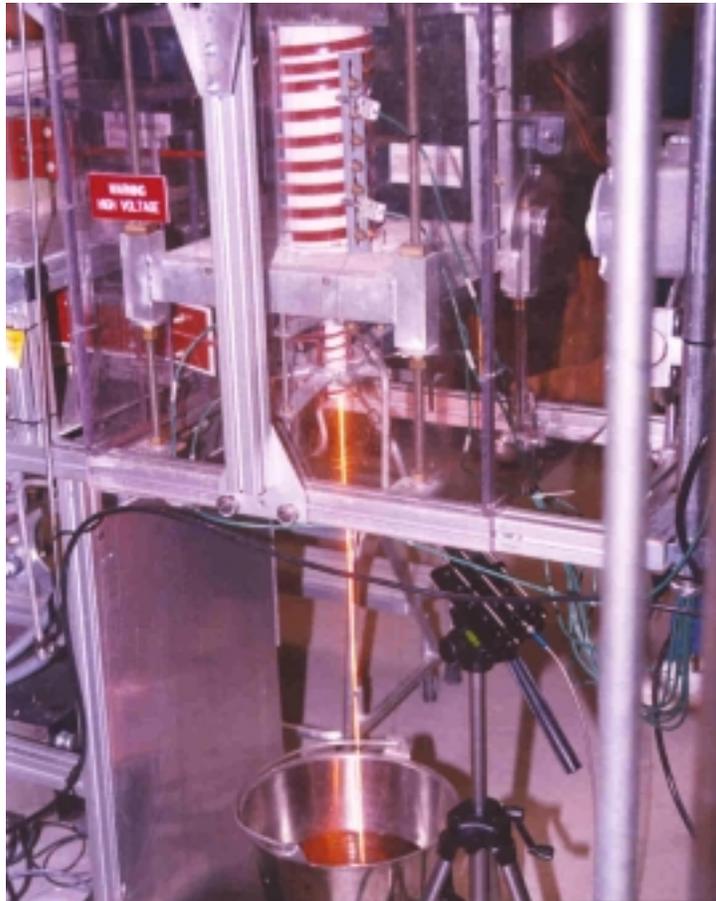


Figure 1. The tripod-mounted light collection head of the monitor can be seen in the lower right portion of this photo taken during a 1998 test at SRS.

Problem. Approximately 14,000 liters of Am-Cm solution reside in an F Canyon tank at SRS. This solution is scheduled to be stabilized by vitrification and stored for later recovery and use. The Am-Cm solution contains about 2.5 kilograms (kg) of Cm and 10 kg of Am. This is a large fraction of the United States' total inventory of these elements. The estimated value is of the order of one billion dollars if these two elements are processed through the DOE Isotope Sales program at the Oak Ridge National Laboratory (Ramsey 1996). Am and Cm are raw materials for the production of californium-252 in the High Flux Isotope Reactor at Oak Ridge, and there are continuing needs for Cf-252 (Defense Nuclear Facilities Safety Board 2000). Due to the extreme radiation levels and elevated temperature of the vitrified product containers, complete remote handling inside high-level cells will be necessary for all operations. A technique for assaying the filled containers for Am and Cm must be developed in order to have a measured accountability value (Savannah River Site Technology Coordination Group 1998). The TES monitor can provide an essentially continuous record of the Am and Cm composition in the molten glass stream as it leaves the melter.

Certain other waste streams can be stabilized by encapsulation into a molten polyethylene stream, and an alternate, related technique (transient infrared spectroscopy or TIRS) can be used as a monitor in such cases as described in TMS #215 (U. S. DOE 1999).

How it Works. The monitor detects the spontaneous thermal emission in the red and near-infrared region of the spectrum. A number of metal ions have electronic transitions in this region of the spectrum, so emission or absorption spectroscopy can be used to determine the concentrations of the metals. For thermal emission spectroscopy to have emission features that are characteristic of the metals and that may be used for quantitative determinations, it is necessary for the emitting species to be in a transparent matrix. This condition is met by transuranic metal oxides that have characteristic emission spectra in a region of the near-infrared spectrum where typical glasses are transparent. As the hot, molten glass stream leaves the melter, emitted light from the hot stream is transmitted through a fiber-optic cable to a simple spectrometer mounted within a personal computer at a sufficient distance from the sample to avoid radiation hazards. The ratio of the emitted intensity due to the analyte to the emitted intensity due to an internal standard can be used to determine the concentration of the analyte.

Potential Markets. The monitor was designed specifically for the Americium-Curium Stabilization Project at SRS, and SRS personnel hosted on-site tests of the monitor and supplied test materials. Progress in the Am-Cm vitrification process development was reported recently (Fellinger et al., 1999). The monitor is intended to be a part of Savannah River's Am-Cm vitrification production facility.

The application of thermal emission spectroscopy to analysis of a vitrification stream is a niche market within DOE. Transient infrared spectroscopy (TIRS), a related technique developed by the same investigators, has been used for determinations of molecular species in non-transparent matrices. A TIRS monitor has been demonstrated on production-scale polyethylene encapsulation lines at the Rocky Flats Environmental Technology Site (RFETS) and at Brookhaven National Laboratory (U.S. DOE 1999). During a "hot" demonstration at RFETS where nitrate-salt waste, molten-salt oxidation waste, and fly ash were encapsulated in polyethylene, the waste loadings as determined by the TIRS monitor had a root-mean-square error of 0.7% relative to the known loadings. Other applications being explored include on-line analyses of wood chips and monitoring the cure of coatings applied to optical fibers.

Advantages over Baseline. The baseline technology for vitrification monitoring requires sampling the glass and transporting the highly radioactive sample to a laboratory for analysis. Typically, the sample is dissolved and then inductively-coupled-plasma-mass-spectrometry (ICP-MS) or ICP-atomic emission spectroscopy (ICP-AES) techniques are used to make the determination of the amount of metal oxide present in the original glass sample (Kinard et al., 1997). Each such sampling and off-line analysis requires about one week to complete, generates secondary waste, and is estimated to cost between \$50,000 and \$100,000. Once installed and calibrated, the on-line TES monitor will provide analyses in less than one minute without contacting the radioactive material. Although it will be necessary to perform some traditional analyses for Am and Cm to calibrate the monitor, the cost of the monitor as well as the research and development expenses will be recouped if only a few baseline-method determinations are avoided as described in Section 5. In addition, the immediate information provided by the monitor will alert the vitrification operators to problems or unexpected conditions during the production process, and the monitor will provide a more detailed archival record of the composition of the vitrified material than can occasional sampling and analysis.

Future Plans at the Savannah River Site. In 1999 Savannah River management began exploring the privatization of the vitrification process. Thus, the future of both the specific vitrification method developed at Savannah River and the use of the monitor in the vitrification are not clear at this writing. A report on the specifications, capabilities, principles of operation, use, and maintenance of the monitor has been provided to Savannah River for use in developing the privatization agreement. As reported by the Defense Nuclear Facilities Safety Board (DNFSB), "The original Implementation Plan foresaw conversion of the dissolved elements by November 1999 to a vitreous form suitable for storage until use. Difficulties with the melter planned for the operation caused deferral of the operation to September 2002 according to the revised Implementation Plan. The most optimistic estimate of a completion date is November 2004." The DNFSB's second-highest priority recommendation was to "Remediate the highly-radioactive solutions of Am and Cm in the F-Canyon at the Savannah River Site. The currently-planned deferral of vitrification of this material is highly undesirable." (DNFSB, 2000)

Demonstration Summary

This report covers the period July 1997 to October 1999. During that interval the monitor was demonstrated three times at the Savannah River Site. The key personnel involved with each of these demonstrations are listed in the Contacts section below. Each demonstration involved the collection of the emission spectra of metal-oxide-containing molten glass as it was poured from a melter into a container. The spectra of actinide surrogates were used to show that the monitor could be used to provide an essentially continuous record of the actinide content in a molten glass stream.

The first demonstration occurred during August 1997 with the Glass Formulation and Vitrification Process Development Task Group for the Plutonium Immobilization Program in Building 774A at SRS. The monitor was used to determine the concentration of ytterbium, a plutonium surrogate, in the molten glass that was poured from a small test melter. This demonstration established the superiority of thermal emission spectroscopy over transient infrared spectroscopy for this application and indicated that the system could be used as a process monitor for plutonium in molten glass. This application was not continued after FY 1997 because of the decision to stabilize plutonium in ceramic instead of glass.

The second demonstration took place in July 1998 with the staff of the Americium-Curium Stabilization Project in Building 701-T at SRS. A revised version of the monitor was set up to determine erbium, a surrogate for Am and Cm, in a molten glass stream produced by a melter similar to the one that will be used for the actual vitrification campaign. Data collection time for each determination was approximately 30 seconds, and this demonstration showed that the monitor could in fact be used to obtain a "real-time" record of the surrogate composition as the glass was poured out of the melter into a container.

The third demonstration occurred in October 1999 with the staff of the Americium-Curium Stabilization Project at the TNX area at WSRS (Building 701-T), the same facility as used for the July 1998 demonstration. The final version of the monitor was used for this demonstration. All major components are available commercially as described in Appendix B. The monitor was used to determine the neodymium content in a molten glass stream in a manner similar to the July 1998 demonstration. The instrument was set to collect data every 10 seconds, but a complete spectrum could be recorded once a second if desired. This demonstration confirmed that reliable spectra could be obtained even when the instrument was not operated with maximum sensitivity. Even though the demonstration was done with a surrogate, the known spectrum of Am suggests that the determination of Am concentrations in glass should be at least as precise of those of the surrogates. Thus, an essentially continuous record of Am and Cm content in the glass should be provided by the use of this monitor along with a few traditional determinations of Am and Cm content for calibrations. As discussed in Section 5, the cost to develop and deploy the monitor will be recovered if only a few traditional determinations are avoided.

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All published Innovative Technology Summary Reports are available on the OST Web site at <http://ost.em.doe.gov> under "Publications." The Technology Management System (TMS), also available through the OST Web site, provides information about OST programs, technologies, and problems. The OST/TMS ID for Real-Time Monitor for Transuranics in Glass is 2004.

SECTION 2 TECHNOLOGY DESCRIPTION

Overall Process Definition

Goals and Objectives. Transuranic metal oxides may be stabilized for long-term storage by incorporating them in glass. In this vitrification process the metal oxides are mixed with glass frit and then melted together. As the glass is poured from the melter into a container, the thermal emission from the glass stream can be used to determine the composition of some components of the glass. The goal of this project was to develop a monitor for transuranics, and the projected deployment is for the determination of Am and Cm at the SRS Americium-Curium Stabilization Project.

Basic Principles of the Technology. All objects that are at a higher temperature than their surroundings emit radiant energy. An object that absorbs all radiation that is incident upon it is called a blackbody, and the emission intensity from a blackbody is well known. The wavelength of the maximum emission intensity is given by $\lambda_m T = 2.898 \times 10^6$, where λ_m is the wavelength in nanometers (nm) of the maximum intensity and T is the temperature of the object in degrees Kelvin. A typical temperature for molten glass is 1450°C or 1723K, and a blackbody at that temperature would have its maximum emission intensity at a wavelength of 1682 nm or a wavenumber, ω , of 5946 cm^{-1} . Thus, the maximum emission intensity is in the near-infrared region of the spectrum, but the emission intensity is equal to or greater than 1% of the maximum from the visible through the mid-infrared regions of the spectrum ($\lambda = 550$ to 11,065 nm or $\omega = 18,180$ to 905 cm^{-1}). The emission intensity of a blackbody is a smoothly varying function of wavelength with no features that are characteristic of the composition of the object. The emission intensity of any object cannot exceed that of a blackbody at the same temperature, and the ratio of the emission intensity of an object to that of a blackbody at the same temperature is called the emissivity of the object. The total radiant power (integrated over all wavelengths) emitted by a blackbody is proportional to its temperature to the fourth power.

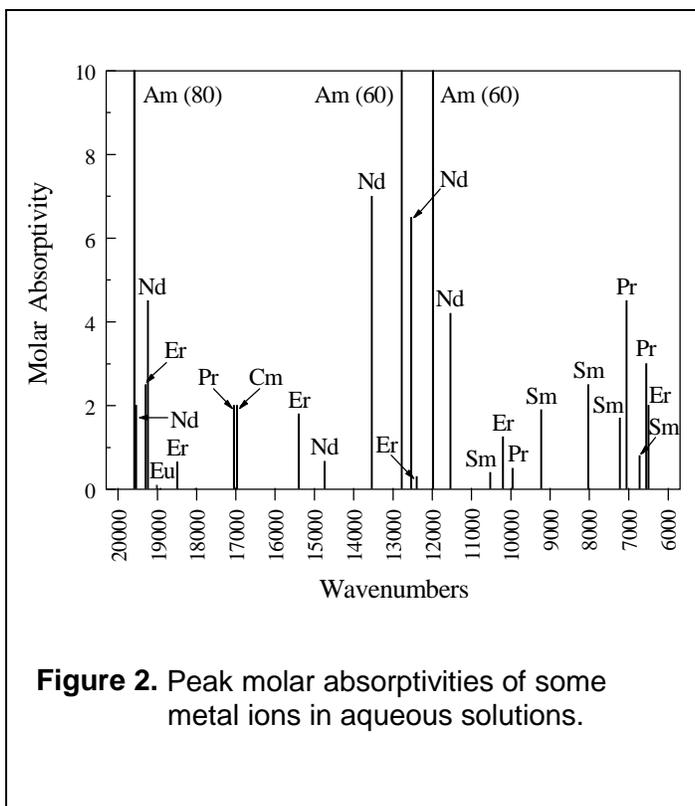


Figure 2. Peak molar absorptivities of some metal ions in aqueous solutions.

Although glass is highly absorbing in the mid-infrared region of the spectrum, typical glasses are transparent in the visible and near-infrared regions of the spectrum. If the glass contains some constituents that are highly absorbing in narrow regions of the near-infrared spectrum, then the dominant thermal emission from the glass in those regions will be due to those constituents. A number of metal ions, including some transuranics, have absorption and emission features in this region of the spectrum. These spectra are due to inner-shell electronic transitions within the ions and are unique for each ionic species. The wave numbers of the maximum absorbances (and emittances) for a number of transuranic and rare-earth metal ions in aqueous solutions are shown in Figure 2. Transitions that occur between an excited electronic state and the ground or lowest energy state can be observed in either emission or absorption spectra. Therefore, absorption spectra of room-temperature glass samples can be determined with conventional near-infrared instruments to determine whether or not a particular component of the glass has a spectrum suitable for use with an

emission monitor. It is also important that the analyte not be in variable oxidation states, and it has been shown that only trivalent americium oxide (Am_2O_3) is present in typical hot glasses (Haire and Stump 1997). Some near-infrared fluorescence spectra of trivalent Am in other glasses have been studied

(Valenzuela and Brundage 1990). The known absorption and emission spectra of Am in various environments suggests that the thermal emission spectrum should be useful for analytical determinations.

The principles underlying determination of metal ions in glass by thermal emission spectroscopy are related to those of gas-phase atomic emission spectroscopy except that the spectral "lines" are much broader due in part to inhomogeneous environments in the vicinity of the ions. Also, there is very little excitation into energy levels sufficiently high to yield emission lines in the blue or ultraviolet regions of the spectrum. But, the general principles are similar:

- At low concentrations, the emission intensity due to the analyte shows a linear variation with the number of atoms present. At higher concentrations, deviations from linearity will occur because of self-reversal; i.e., light emitted by ions in the interior of the glass may be absorbed by ions located nearer to the surface.
- All determinations of composition require a calibration curve obtained using a series of different analyte concentrations with all other variables kept constant. The wavelengths and intensities of the spectral features are dependent on the chemical environment in the vicinity of the ions, so the calibrations must be obtained on standards as close as possible in overall composition to the unknowns. It is also important that the melted glass be homogeneous to avoid complications from light scattering.
- At least two spectral lines in the same spectral region should be used to determine the concentration of a given species. One of these should be due to the analyte and have a simple calibration curve. The other spectral feature should be due to an internal standard, i.e., some other species whose concentration is known. The ratio of the emission intensity of the analyte relative to that of the standard is then used for the analysis. The absolute emission intensities are strongly temperature dependent, but minor source temperature fluctuations will not cause serious errors if an internal standard is used. For example, the emission intensity at 700 nm of a blackbody at a temperature of 1450°C increases by almost 15% if the temperature is increased by 20°C. However, the ratio of the intensity at 700 nm to that at 900 nm decreases by 3% with the same temperature change, so the intensity ratio is much less temperature sensitive than is the absolute emission intensity.

Description of the TEM Monitor. The hardware required to construct the monitor is shown schematically in Figure 3, and a detailed list of parts is given in Appendix B. The three components of the monitor are (1) the collection optics to focus light emitted by the hot glass onto an optical fiber, (2) the fiber-optic cable to transmit the light for a sufficient distance to remove the detector assembly and the operator from a hazardous environment, and (3) the monochromator, detector, and computer assembly to record the spectral information.

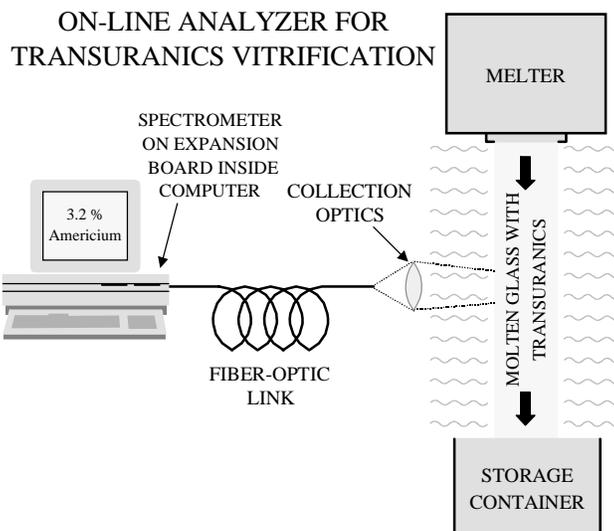


Figure 3. Schematic drawing of thermal emission monitor components.

The early version of the monitor demonstrated in August 1997 used a lens to focus the light from the glass stream directly into the monitor, without a fiber-optic cable. The collection optics used during the later demonstrations consisted of a pair of 1-inch positive lenses with focal lengths of 102 mm and 18 mm arranged to provide a working distance from the glass stream of 254 mm (10 inches). The second lens was fixed to focus the beam onto an optical-fiber bundle with the proper numerical aperture. The lenses and fiber-bundle tip were mounted in an open-cage system, and this light collection head assembly was mounted on a camera tripod to allow easy adjustments of position. For the permanent version that will be installed in the production melter at SRS, a similar, but enclosed, collection head will be fastened to the support structure surrounding the melter.

The fiber-optic cable used for the demonstrations discussed in Section 3 was somewhat different from that expected to be used for the production run. For the July 1998 demonstration a metal-sheathed fiber-optic bundle was used. The cable was five meters in length with SMA 905 connectors on both ends, and it consisted of sixty-seven 100-micrometer diameter fibers, forming a 1/16-inch-diameter bundle that was then jacketed to form the cable. This cable was not radiation hardened. The cable to be used for the production run will have a smaller diameter and could easily be 25 meters in length so that the monochromator (and the operator) can be outside the range of radiation hazards.

Earlier versions of the monitor used an acoustic-optical tunable filter (AOTF). The 1997 and 1998 demonstrations discussed in Section 3 were performed with an AOTF system. A single lens was used to transfer the light from the fiber bundle to the AOTF crystal. After the crystal, an iris blocked all but the selected wavelength band and a lens focused the selected band onto a silicon photodiode detector. To improve the signal-to-noise ratio, the AOTF was driven with a modulated signal, and the detector output was fed to a digital lock-in amplifier. The output was digitized and displayed using an I/O board mounted in a simple personal computer.

Although the AOTF system had no moving parts and gave generally satisfactory results, a CCD-array based spectrometer was selected over the AOTF system in FY99 because it was found to be smaller, faster, cheaper, more robust, and to produce better quality data. This spectrometer has a grating, a 2048-element linear CCD-array detector, and the supporting electronics built into a personal computer expansion card. The resolution of the spectrometer is proportional to the size of the fiber attached to it, so the multi-fiber cable used for the 1998 demonstration would be too large for this spectrometer. The total

hardware cost to assemble this version of the monitor was less than \$5K. A complete parts list for the monitor is given in Appendix B.

The useful spectral range of the AOTF system was from $\lambda = 550$ to 1000 nm (18,000 to 10,000 cm^{-1}), and the PC-card spectrometer has a range of 530 to 1000 nm.

System Operation

Operational Parameters and Conditions. The critical parameters for the use of this monitor are:

- The analytes must have spectroscopic transitions in the near-infrared region of the spectrum.
- The analytes must be incorporated in a matrix that is transparent in the spectral regions where the analytes have spectroscopic features.
- The sample must be at a high temperature, preferably above 1000°C.

The focal length for the light collection head can be adjusted, but it needs to be at a distance of approximately one foot from the sample in the current version. The optical fiber that transmits the collected light to the monochromator needs to be chosen to meet the requirements of the particular task, but commonly available fibers can be used for most situations.

Materials, Energy Requirements, and Expendable Items. A detailed list of component parts required to assemble the monitor is given in Appendix B. The construction of the monitor was discussed in the Overall Process Definition section above. The only energy requirements are the normal 110-volt electrical supply sufficient to operate a personal computer. No expendable supplies are required for operation of the monitor.

Human Resource Requirements. One person can perform all tasks necessary to set up and operate the monitor for a particular application. An operator with some experience in operating laboratory equipment would require several days training for routine operations. Less routine tasks, such as establishing calibration curves and choosing operating conditions, are best performed by persons with advanced training in chemical instrumentation.

Secondary Waste Stream Considerations and Safety Risks. One of the benefits of this monitor is that it has no direct contact with the analyte so there are no secondary wastes. The light collection head can be set in place before pour of the hot glass is begun, so the operator can perform subsequent operations at a sufficient distance from the process to avoid radiation exposure or other contact with hazardous materials.

SECTION 3 PERFORMANCE

Demonstration Plan

The results of three demonstrations at the Savannah River Site are discussed in this section. The first demonstration took place in August 1997 with the Glass Formulation and Vitrification Process Development Task Group for the Plutonium Immobilization Program in Building 774A at SRS. The main objective of this demonstration was to show that the monitor could be used to determine the concentration of a plutonium surrogate in a molten glass stream as it left the melter. The version of the monitor that was used included an acoustic-optical tunable filter (AOTF). It was tested in both the TES and TIRS modes in order to determine which was superior. Although this demonstration indicated that the system could be used as a process monitor for Pu vitrification, the Task Group was not continued after FY 1997 because the decision was made to stabilize Pu in ceramic instead of glass.

The second demonstration occurred in July 1998 with the staff of the Americium-Curium Stabilization Project at the TNX area at SRS (Building 701-T). This demonstration used a revised version of a monitor with an AOTF to show the applicability of the monitor for the determination of Am and Cm in a flowing, molten glass stream. Once again, a surrogate for Am or Cm was used during the demonstration. The demonstration showed that the monitor could be used as a near-real-time, on-line monitor to determine concentrations of actinide metal oxides in a molten glass stream.

The third demonstration occurred in October 1999 at the same site used for the 1998 demonstration. The major objective of this demonstration was to demonstrate a new version of the monitor under conditions as close as possible to those that will be used for the actual Americium-Curium Stabilization Project production runs. The speed, sensitivity, and reproducibility of the CCD spectrometer system were evaluated with the operating parameters expected for the actual production runs, except that a surrogate was used in place of Am and/or Cm in the glass.

Results

Demonstration for the Plutonium Immobilization Program at SRS (August 1997). The process monitor was set up to analyze a molten glass stream as it exited from a small melter. The melter was a small, general-purpose test melter with a capacity of less than one kilogram of glass frit. The monitor used an earlier version of an AOTF for the spectral dispersion and was operated both in the conventional thermal emission spectroscopy (TES) mode and in the transient infrared spectroscopy (TIRS) mode. In the conventional emission mode, the monitor passively observed the near-infrared spectrum emitted by the hot glass stream as it left the melter. In the TIRS mode, a small jet of cooling air blew on the glass stream to create a cooler layer at the surface of the stream. The thin cooled layer acts as filter and absorbs the emission from the bulk of the stream. These spectra are then ratioed against appropriate backgrounds, which are typically obtained using carbon black heated to the same temperature. The TIRS-mode results were inferior to the TES results; so only the conventional emission results are described below.

The lanthanum borosilicate glass frit that was developed for plutonium vitrification was spiked with ytterbium oxide (Yb_2O_3) at levels ranging from 0 to 9.5 mass percent. The composition of the frit is shown in Appendix C. Ytterbium oxide was used as a spectroscopic surrogate for plutonium oxide because the two have spectral features in the same region of the spectrum. The internal standard was neodymium (Nd_2O_3) a component of the frit. The small melter used for this demonstration was not production-size, so if the melter were raised to a temperature at which the frit and Yb_2O_3 thoroughly melted and mixed (about 1500 °C) and then opened, the entire load of molten glass would drain in less than 40 seconds. Although the monitor could collect data for a determination in about 20 seconds, to allow the acquisition of more than one determination per pour the melter temperature was reduced to about 1300 °C prior to starting the pour in order to increase melt viscosity and lengthen pour time to between 2.5 and 4 minutes. The glass stream was roughly 1/8 inch in diameter.

Typical spectra observed with the monitor at four Yb_2O_3 concentrations are shown in Figure 4. The Yb_2O_3 produced a single peak at $10,300\text{ cm}^{-1}$ ($\lambda = 971\text{ nm}$) in the near infrared, and the size of the peak clearly increased as the Yb_2O_3 concentration increased. The other two peaks in the spectrum are due to Nd_2O_3 that is a component of the frit. No other component of the frit had a peak in this region of the spectrum. Each spectrum was acquired in less than 20 seconds, and several spectra are shown just as they were recorded; i.e., they have not been corrected for variations in the sensitivity of the monitor with wavelength. The reduced melter temperature used to prolong the pour time resulted in a glass stream that was smaller and less uniform in size than normal, and the size variation is the major source of noise in the spectra. The spectrum of the 9.51% Yb_2O_3 sample was taken with a high melt temperature and short pour, and that spectrum is noticeably less noisy as a result. Nevertheless, all of the spectra obtained are more than adequate for composition analysis as shown subsequently.

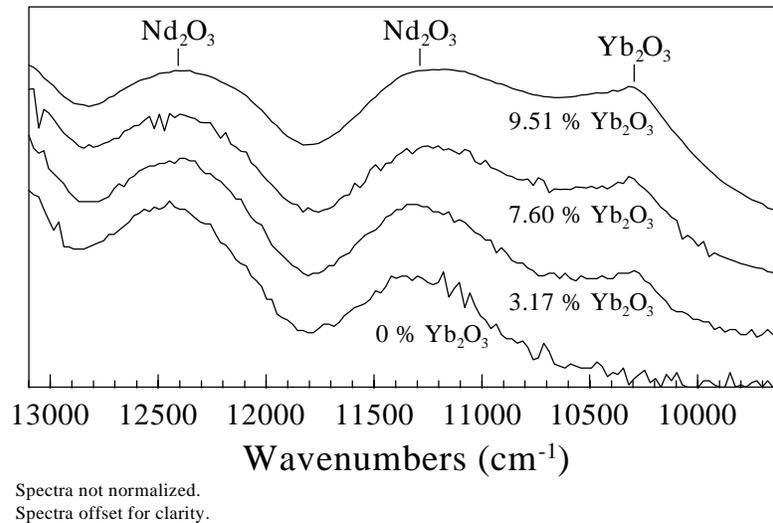


Figure 4. Emission spectra of molten glass containing Yb_2O_3 and Nd_2O_3 .

The Yb_2O_3 composition was determined using the ratio of the peak height of the $10,300\text{ cm}^{-1}$ Yb_2O_3 to that of the $11,300\text{ cm}^{-1}$ Nd_2O_3 peak. The peak-height ratios are plotted versus the known Yb_2O_3 concentrations in Figure 5. The Yb_2O_3 concentrations for this plot were determined by inductively-coupled-plasma spectroscopy methods after the monitor tests were completed. No selection for superior spectra was done for this plot, and only one spectrum obtained at the beginning and one at the end of the pour were excluded because of rapid fluctuations in the amount of glass observed by the monitor at those times. Using a peak-height ratio to determine composition is a relatively unsophisticated method for relating composition and spectra, but even this simple method gave a root-mean-square error of only 0.60 mass percent.

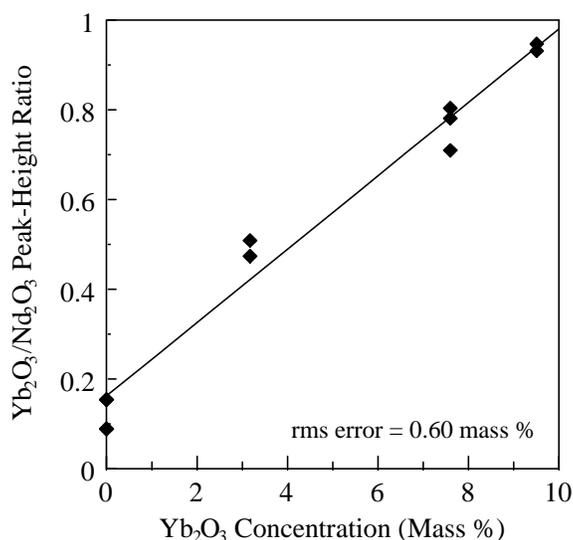


Figure 5. Peak height ratios versus Yb₂O₃ concentrations.

Demonstration for the Americium-Curium Stabilization Project at SRS (July 1998). The system was set up to monitor a molten glass stream as it exited from the Cylindrical Induction Melter (CIM) (Marra et al., 1998). Although the final version of the CIM may not be exactly the same as used for this demonstration, it was operated under the conditions anticipated for production runs. A new version of the monitor was constructed for this demonstration, but the basic components of the monitor were those used for the first SRS demonstration; in particular, the monochromator used an AOTF. Instead of a lens to focus light from the glass stream directly into the monitor, a five-meter optical fiber was used between the light-collection optics and the rest of the monitor.

The composition of the waste surrogate used for this demonstration is shown in Appendix C under the 50SrABS heading. The samples used to prepare the molten glass for this demonstration were prepared by mixing the surrogate (50SrABS) cullet with the SrABS frit to obtain 0, 10, 20, and 30 weight percent of waste surrogate. After the mixture had been mixed, melted, and equilibrated, the glass was poured into a container. The temperature of the poured glass stream was closely monitored with a pyrometer and was around 1520 °C for all pours. The diameter of the glass stream was approximately 1/4 inch, and the pour times ranged from three to five minutes. The collection optic head for the monitor was placed at a distance of 10 inches from the glass stream, and the data collection time was approximately 30 seconds.

The analyte was erbium oxide (Er₂O₃). Typical emission spectra are shown in Figure 6 for the samples with 0, 10, and 20 weight percent of the surrogate; the spectra are offset on the vertical axis for clarity. The Er₂O₃ composition scaled linearly with that of the Nd₂O₃ because both are in the surrogate. As shown in Table 2, there are many other oxides present in the waste surrogate, but the major contributors to the emission spectra in this region are Er₂O₃ and Nd₂O₃. Because the glass temperature was nearly the same for all pours, it was possible to obtain an excellent correlation between peak height and composition without using a reference internal standard. (Of course, all samples had a constant ratio of Nd₂O₃ to Er₂O₃, so the peak height ratios were also constant.) Thus, the ratio of the emission intensity at 655 nm (the peak

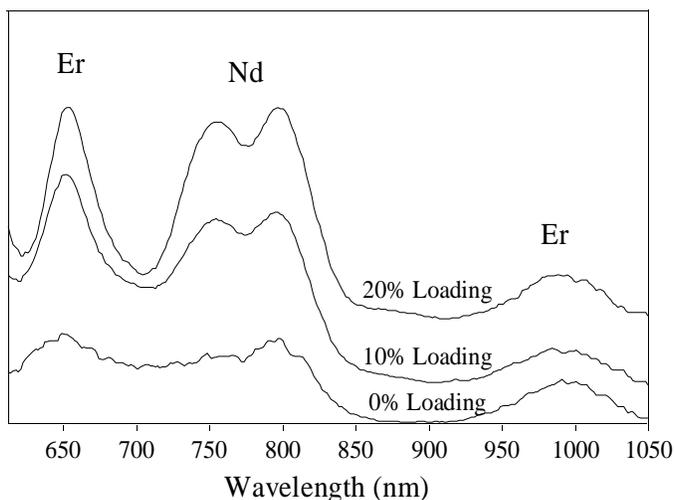


Figure 6. Emission spectra of Er₂O₃ and Nd₂O₃ in glass.

due to Er) relative to the valley at 702 nm was correlated with the surrogate waste loading as shown in Figure 7.

Americium has several peaks in this region that are much stronger than those due to the other constituents. Therefore, the sensitivity for Am should be enhanced relative to the surrogates used in the study reported here.

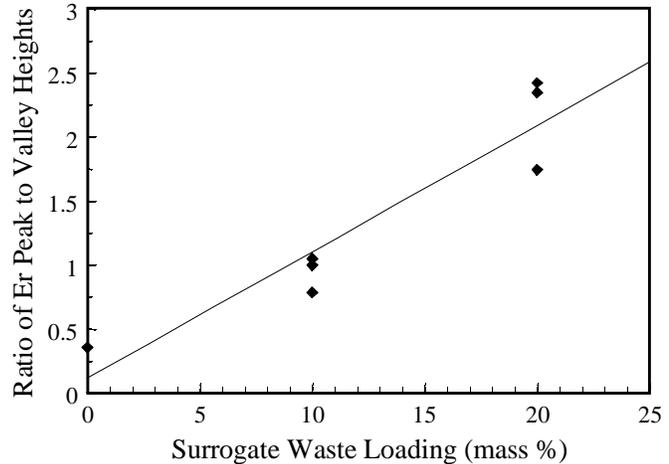


Figure 7. Correlation of spectral height with composition.

Demonstration for the Americium-Curium Stabilization Project at SRS (October 1999). The molten glass samples for this demonstration were prepared in the same melter as used for the 1998 demonstration. The new version of the monitor that used a monochromator with a CCD-array detector was constructed for this demonstration as described in Section 2 and Appendix B. A 5-meter-long multimode single fiber optic with a 200-micrometer (μm) silica core diameter with a polyimide buffer was used with the same light collection optics as used in the 1998 demonstration.

During this test, four different compositions of glass were prepared as shown in Appendix D. Glass frits similar to those described for the 1998 demonstration were used to prepare the glass samples, but the pours were of glass samples with constant Er concentration and variable surrogate waste compositions. Thus, Er was the internal standard used as a reference for the determinations of the variable Nd concentrations. The temperature of the glass was kept constant at 1450 °C for all pours. From 1.1 to 1.7 kg of glass was produced during the pours, and each pour lasted about 4 minutes. The spectrometer was set to acquire a complete spectrum every 10 seconds, so between 20 and 27 usable spectra were collected during the pours. (The spectrometer is capable of acquiring a spectrum every second if desired.)

A typical thermal emission spectrum collected by the TES monitor is shown in Figure 8. The peaks in the emission spectrum are due to rare-earth ions in the glass as shown in the figure. The intensity of each peak increases as the concentration of the corresponding component increases. The Er_2O_3 concentration was kept constant at 3.71% for each of the glass samples prepared for this demonstration. The concentration of Nd_2O_3 , for example, can then be determined using the ratio of the intensity of an Nd peak relative to the intensity of an Er peak along with a calibration curve obtained from samples with known Nd_2O_3 concentrations.

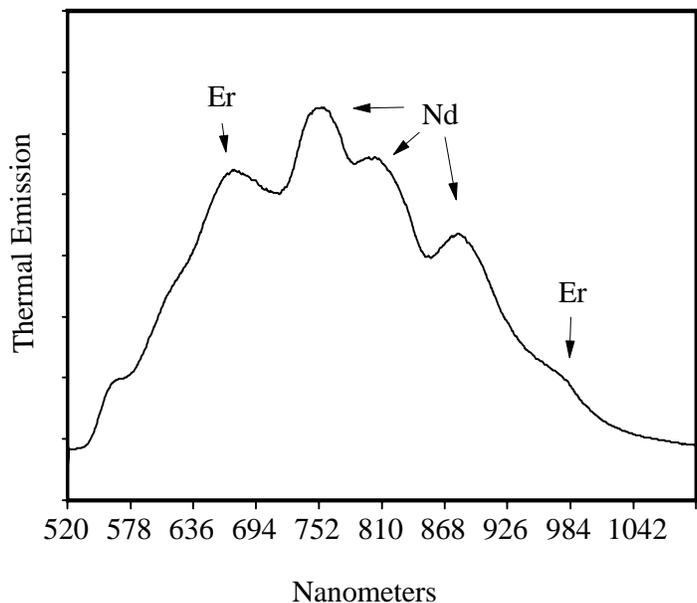


Figure 8. A thermal emission spectrum collected during a glass pour.

The first three pours during the October site test were used to establish a response plot for the TES monitor. This plot is illustrated in Figure 9. The open circles denote the ratio of the Nd peak intensity at 877 nm to the Er peak intensity at 565nm as a function of Nd concentration. The curve is not linear because

at the higher Nd_2O_3 concentration the molten glass stream is starting to become optically thick due to self-absorption of the thermal emission from the lanthanide oxides. This is not expected to cause any

problems because actual waste loadings will be at levels where the molten glass stream is optically transparent and little or no self-absorption occurs. The calibration curve can accommodate a small amount of self-absorption.

The first three runs were done with samples containing 10.56%, 8.80%, and 12.34% Nd_2O_3 , respectively, as shown in Figure 9. The fourth pour was a repeat of the first run where the surrogate waste level was at the anticipated loading for actual waste. The fourth data set was processed in similar fashion and

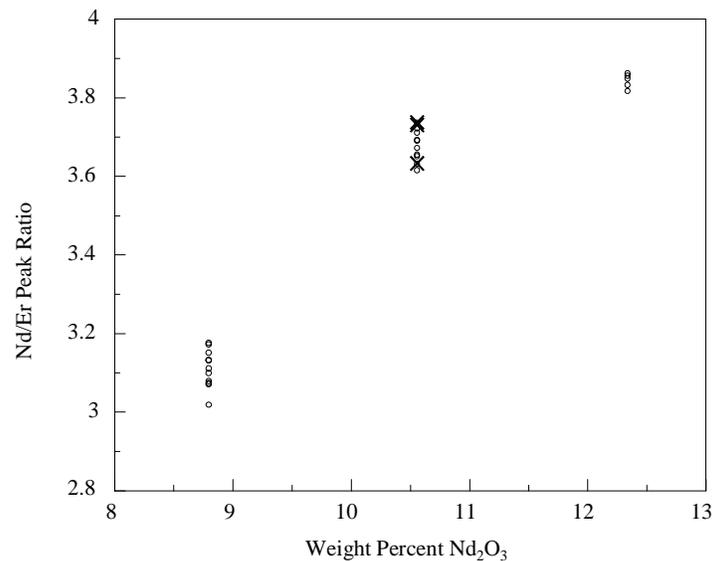


Figure 9. Peak intensity ratios versus Nd concentration.

is shown on the response curve in Figure 9 by the X's. Just prior to the fourth pour the collection head optics

were accidentally bumped resulting in a slight misalignment of the optics. This caused the measured absolute intensity obtained during the fourth pour to be approximately one-sixth of the emission intensities observed during the prior three runs. However, this misalignment did not cause the ratio of peak intensities to be altered, and the data obtained during this run were of similar precision and accuracy to those of the first three. It is expected that other sources of diminished intensity, such as darkening of the fiber-optical cable due to radiation exposure, will be compensated for by this internal standard procedure so long as the intensity is at least 10% of the optimal.

The analysis of the fourth pour data set demonstrates that the TES monitor can accurately track the waste loading during the vitrification process. However, as illustrated by Figure 8, determinations of other components in the waste stream using only peak heights may be complicated by significant overlap of emission bands or by lack of distinctive emission bands for the components. In these cases, more elaborate chemometric analysis methods, such as partial least squares (PLS), may be employed. The data sets from the first three pours during the October 1999 demonstration were analyzed using the chemometric program *PLS plus IQ* from Galactic Industries, Inc. A calibration model was developed with a standard error of prediction (SEP) of 0.5%. Data from the fourth pour were then analyzed using this calibration model with the results shown in Appendix D. This procedure is not necessarily reliable for those components whose concentrations did not vary much in the calibration set, but it was intended to predict the Nd_2O_3 waste loading, which had the largest variations over the four pours. Note that the Nd composition predicted for the fourth pour differed from the known value by only about 0.5 weight percent. The intensities of the emission bands due to Am are stronger than those of Nd as shown in Figure 2, so the accuracy of the predictions for Am should be at least as accurate as those for Nd.

SECTION 4

TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Competing Technologies

Vitrification is the sole option under consideration for stabilizing Am-Cm at SRS, so a technique for assaying the Am-Cm content of vitrified material in the storage containers is necessary for a measured accountability value. "The remote location and adverse conditions under which the Am-Cm product containers will be processed and stored eliminate most traditional non-destructive assay techniques due to the hands-on nature of the measurements" (Savannah River Site Technology Coordination Group 1999). Maxwell and Nelson analyzed the Am-Cm-containing solution at SRS in 1996. They separated Am and Cm from most other metals, and then determined ^{241}Am using gamma pulse height analysis and ^{244}Cm using alpha pulse height analysis. Thermal isotopic ionization mass spectrometry was then used to determine the isotopic composition and thus the total Am and Cm concentrations of 0.671 and 0.181 gram/liter, respectively.

Each of the possible instrumental techniques for glass analyses, including thermal emission spectroscopy, requires an independent determination of Am-Cm concentrations in at least a few samples in order to provide a calibration for the method. A reference procedure for Am-Cm-containing glass samples was outlined by Kinnard et al., 1997. The glass samples were weighed in the Shielded Cell Operations (SCO) facility at SRTC, dissolved, and then diluted so that aliquots could be removed from the SCO. The principal method of determination for ^{243}Am and ^{244}Cm in these aliquots was ICP-MS. Similar mass-spectrometry techniques have been used after chromatographic separations to determine Am in spent nuclear fuels (Chartier, Aubert, and Pillier 1999). ICP-atomic emission spectroscopy can also be used (Huff and Bowers 1990). Of course, these methods also require standards of known composition for calibration, and these standards must ultimately be prepared from pure materials. In the likely event that these standards are not available, instrument response functions for another isotope, such as ^{238}U , would be used for the Am and Cm calibrations. These determinations are expected to cost at least \$50,000 per sample and to require one to two weeks for completion as described in Section 5. So one objective of using alternate techniques is to minimize the number of determinations that must be made by ICP-MS, ICP-AES, or other similar methods.

Alternate on-line techniques for determination of the Am and Cm content of glass might be gamma spectroscopy or laser-induced breakdown spectroscopy (LIBS). High-resolution gamma-ray spectroscopy has been widely used for ^{241}Am and ^{243}Cm determinations, and has been suggested (Wichers et al., 1994) for determinations in reactor fuel. Gamma-ray spectroscopy is sensitive to variations in the detector-sample geometry and would require substantial space around the process stream for shielding due to the extreme radiation levels and elevated temperatures next to the melter in a high level cell.

LIBS would destructively analyze spots only a few micrometers wide and deep along the glass stream, so it would not necessarily reflect the average composition of the whole stream, as would TES. In addition it is difficult to make LIBS sufficiently quantitative and reproducible to use it over a period of several days without numerous calibrations. Equipment and operation costs for both LIBS and gamma spectroscopy would be much greater than for TES.

A calorimetric technique could also be used to estimate Am-Cm content in product containers, but this technique would be neither on-line nor real-time, so it could not be used as a process monitor; i.e., it could not provide a check for the operation of the process during glass pours.

Technology Applicability

Other Potential Applications. Although thermal emission spectroscopy has been used for a wide variety of remote sensing and other analytical applications, the monitor described in this report was developed specifically for the Americium-Curium Stabilization Project. Thus, any potential application would require that the object be at a sufficiently high temperature to yield emission in the near-infrared region of the spectrum, that the analytes have emission in that region, and that the host matrix be optically clear in that

region of the spectrum. Thus, determinations of lanthanide or actinide elements in molten glass are the most likely applications.

The transient infrared spectroscopy (TIRS) version of this technique is also a noncontact, on-line analysis technique that has broader applicability and is particularly useful in cases in which TES is not applicable. With TIRS the surface of a moving stream is heated or cooled to create a thin, non-opaque surface layer for emission or absorption spectroscopy. When used with mid-infrared spectroscopy, it can be used for real-time determinations of molecular species in a moving stream. For example, in 1996 a TIRS unit was installed at the Rocky Flats Environmental Technology Site for monitoring low-level waste in a polymer encapsulation process (DOE 1999).

Patents/Commercialization/Sponsor

Using thermal emission spectroscopy for analyzing transuranics on line is a novel application of TES, but TES is a well-developed technology. Among many examples, remote sensing applications of infrared emission spectroscopy are well known (Christensen and Pearl 1997; Hamilton, Christensen, and McSween 1997), and mid-infrared emission spectroscopy has been used for determinations of thin films of glass (Niemczyk et al. 1999). Since the main components of the monitor developed for the application to actinide-in-glass monitoring are commercially available and the actinide-in-glass monitoring application has a limited potential market, there are no activities toward commercializing the TES monitor.

The transient infrared spectroscopy (TIRS) variant of TES was invented at Ames Laboratory and patented by Iowa State University (McClelland and Jones 1991a, 1991b, 1992) and is available for licensing. As discussed above, TIRS is most useful for monitoring applications in cases where the host matrix is not transparent in the region of the spectroscopic features to be used, such as mid-infrared, vibrational spectroscopic determinations of molecular species in a non-transparent matrix (Jones and McClelland 1990a, 1990b, 1992).

SECTION 5 COST

Methodology

The monitor was developed specifically for the Americium-Curium Stabilization Project at the Savannah River Site, so the cost information presented below was collected from personnel at that site. The following statement from John Marra of SRS provided the basis for the cost analysis:

“The product material contains a variety of constituents in addition to the Am and Cm, namely other actinides, lanthanides, corrosion products, and a spectrum of other elements remaining from the production process. The radiation levels associated with the material are extremely high, necessitating remote operation in a shielded facility. The processing of the Am-Cm material, and the durability of the resultant glass form, is dependent on compositional control during the process operations. Current process plans call for glass sampling and off-line analysis to determine/verify the glass composition. Given the highly radioactive nature of the Am-Cm glass form, sampling and off-line analysis presents worker exposure, transportation, and schedule concerns. [Note: Each canister of Am-Cm glass will read 10,000-15,000 R/hr at contact, resulting in significant personnel exposure to remove samples from the remote facility.] It is estimated that sampling and analysis of a single glass sample will cost in excess of \$50-100K and take ~1-2 weeks to complete.

Due to the hazards and costs associated with sampling the Am-Cm glass, SRTC has been collaborating with the Ames Laboratory on the development of thermal emission spectroscopy. The ability to operate the TES system remotely greatly reduces, and likely eliminates, worker exposure concerns. Further, the real-time nature of the technique would eliminate schedule concerns.

Although currently slated for shipment to ORNL, a portion of the stabilized Am-Cm material may be shipped to a federal repository for long-term storage. Shipment to the federal repository will require detailed compositional information on the vitrified material. This will likely require over a dozen glass samples over the vitrification campaign (~165 canisters, 330 kg of glass). Although a formal sampling estimate has not been developed, using the above sample costs, this will cost the project in excess of \$1,000,000 and result in potential schedule impacts of 12-24 weeks.”

The simplest approach to a cost comparison is to consider the total number of samples that would be analyzed by conventional methods and then calculate the total cost by the conventional and new methods. That approach has been used in the Cost Analysis section below. However, a primary benefit of the TES monitor is that it can provide information that is not obtainable by conventional methods, i.e., a real-time, nearly continuous record of composition that can be used not only for archival purposes but also for monitoring the process during the glass pours. The latter benefit is more difficult to quantify, but as noted in a SRS STCG Need Statement, “Without a defensible measurement of quantities on which to base domestic safeguards, the DOE Orders and prudent judgment require that the quantities be conservatively estimated. This results in a more costly level of safeguards than the material may require if the quantities were known. Investment in a measurement technique would allow the safeguards to be reduced to a level consistent with the material amount and type.” (SRS STCG. 1999) A conservative estimate of cost savings has been used below.

Cost Analysis

The capital costs of the TES monitor used for the October 1999 demonstration are listed in Appendix B. A longer fiber optic cable may be required for production applications, but the total capital cost for a monitor should not exceed \$5000. The costs of power and supplies to operate the monitor are negligible. The only other cost is for one technician to operate the monitor during the pours, and the costs cited in Table 1 assume one full year devoted to this task, which is almost certainly excessive.

Table 1. Estimated total cost for development and use of the TES monitor.

Description	Cost (\$K)
Research and development costs	510
Operating costs	
Capital costs for monitor	5
Operator for one year	60

As noted above, it is anticipated that the Americium-Curium Stabilization Project will produce approximately 165 glass-containing canisters. The TES monitor could provide at least 25 determinations of composition during the filling of each canister, but it was anticipated that only about a dozen samples would be analyzed by the baseline methods as cited above. At least one conventional determination is required to calibrate the TES monitor data, but the comparison of costs shown in Table 2 is based on the use of two conventional analyses for calibration.

Table 2. Comparison of total costs for determination of Am & Cm content in 12 samples.

Use of Baseline Methods	Cost (\$K)	Use of TES Monitor	Cost (\$K)
12 conventional analyses	600-1200	Construction & operation of TES monitor (Table I)	65
		2 conventional analyses	100-200
Total Cost	600-1200	Total Cost	165-265

A comparison of the total costs for obtaining a minimum of 12 up to a maximum of 165 determinations (one per canister) is shown in Figure 10. The costs cited in Figure 10 for the TES monitor **include the total R&D costs** for the development of the monitor, and the average cost per sample was assumed to be \$75K for the baseline analysis method. Note that there is no additional cost for the TES monitor to obtain 25 determinations on each canister.

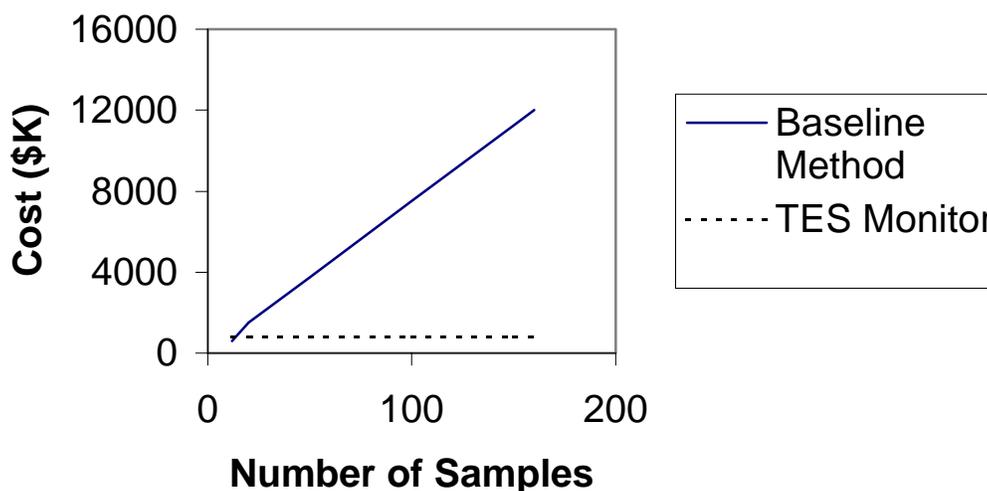


Figure 10. Comparison of costs for baseline and TES methods.

Cost Conclusions

It is highly unlikely that baseline methods would in fact be used to determine Am and/or Cm concentrations in each glass-containing canister. However, even if only ten samples are eliminated from the conventional analysis procedures, the entire cost of the research and development as well as operating costs for the TES monitor will be recouped. In addition, the TES monitor would provide archival records for each canister as well as data useful for quality assurance during the glass pours. These are capabilities that are impossible to achieve with conventional analysis methods that have been proposed for these samples. As noted earlier, each conventional analysis is expected to take one to two weeks to complete, whereas the monitor provides an essentially real-time record of composition. The data collected by the monitor prior to calibration can still be used to determine whether or not the composition is changing during the pour, so it can be used for quality assurance purposes prior to the calibration.

The cost analysis assumed only two calibration samples. This was based on the assumption that the glass composition would be nearly the same for all canisters as planned. If, however, the monitor detected substantial excursions from the average, then additional calibration samples would be required in order to include the range of compositions encountered during the production of the canisters.

There are no current plans for other applications for the monitor, but it could be used at other sites for similar vitrification processes for other legacy materials, such as uranium-233, neptunium-237 or even plutonium if vitrification was again considered for long-term stabilization.

SECTION 6 REGULATORY AND POLICY ISSUES

Regulatory Considerations

Site-Specific Regulatory/Permitting Issues. The monitor itself does not introduce any new health or safety hazards, so no new regulatory issues in addition to those required for the process being monitored should be introduced. Specific applications may require regulatory approval for using the technique for certified analytical results. The monitor has no direct contact with the sample and it generates no secondary waste. Alternate analytical methods require that a sample be obtained for subsequent handling and processing in a laboratory. These methods may generate secondary waste and bring the operators into contact with hazardous materials.

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Criteria.

Because the monitor does not affect the system being monitored in any way and because no secondary waste streams are generated, CERCLA should not apply to the monitor itself. It may, of course, apply to the process being monitored. Following are discussions of the nine CERCLA evaluation criteria:

1. Potential risks to human health and the environment associated with sampling a hazardous waste stream are eliminated because no samples are taken and there is no secondary waste. Some conventional analytical determinations may be required for calibration of the monitor, but the monitor itself introduces no new risks.
2. No issues related to applicable or relevant and appropriate requirements are anticipated.
3. This monitor is in use only during the time glass is poured from the melter into a container, so there are no residual risks attributable to the monitor.
4. The monitor does not affect the toxicity, mobility, or volume of the system being monitored since it has no direct contact with the system.
5. The monitor is designed to replace baseline analytical methods for some of the determinations that would normally be performed during a vitrification process, so there are no impacts on human health and the environment prior (or during) implementation.
6. There are no expendable supplies used during operation of the monitor, and the construction uses components that are available commercially. Implementation is dependent upon the sample being appropriate for thermal emission spectroscopy, but there should be no constraints based on availability of materials.
7. The costs of construction are discussed in Section 5.
8. The most likely applications involve analytical determinations on materials that will remain within DOE control. While there may be issues raised concerning transport and storage of the vitrified materials, they are not intended for release, so there should not be issues raised from state or local regulators concerning the accuracy of the determinations.
9. No issues related to community acceptance are anticipated.

SECTION 7 LESSONS LEARNED

Implementation Considerations

The monitor relies on three properties of the molten glass stream: (1) that it emits brightly because of its high temperature; (2) that it is physically thin enough not to be opaque at the wavelengths of interest; and (3) that the characteristic wavelengths (colors) emitted by the metal being monitored are not obscured by emission at nearby wavelengths from other metals. The first of these is always true as long as the glass is molten, but the other two conditions could prevent the monitor from operating successfully in certain applications. If the molten stream is so thick as to become opaque, the emission intensity is no longer proportional to the concentrations of the components in the glass. In the Am-Cm demonstration at Savannah River, the stream was approximately 5 mm across at the point the monitor observed. Some of the spectra from the final demonstration showed mild effects from the stream beginning to become too thick, so the 5-mm size is probably near the upper limit for the type of glass used (see Appendix D). Because a molten glass stream tends to narrow as it falls, it is possible to locate the monitor farther downstream to observe a small stream diameter; however, the position of the stream could waver from side to side at points well away from the mouth of the melter. Depending on the optics used, this wavering could cause substantial variations in the observed emission intensity, which should be avoided. Whether there will be interferences from metals other than the ones to be monitored depends on what metals are in the vitrification stream, on their concentrations, and on the intrinsic strengths of their emission bands. Figure 2 shows the wavelength locations and intrinsic strengths of the emission bands for metals expected to be in Am-Cm vitrification stream. For this particular application, the great strengths of the Am bands should make the monitoring task straightforward, despite potential interference from Nd bands.

Technology Limitations and Needs for Future Development

As discussed above under Implementation Considerations, the monitor is limited both to glass streams that are not opaque, either because of physical stream size or concentration of light-absorbing components, and to situations where there is not too much interfering emission from metals not being monitored. The unit delivered to Savannah River contained a spectrometer that functions over the 530 nm to 1100 nm range, but this is not an intrinsic limitation of the monitor technology. Molten glass can emit sufficiently strongly at any wavelength from the blue end of the visible spectrum through the near infrared if a metal having emission bands at that wavelength is present in the glass. Commercial spectrometers similar to the one in the Savannah River monitor are available for all of the 200- to 2200-nm range (although no single spectrometer covers the entire range). There are rapid developments in commercial optical spectrometers as the photonic industry explores civilian markets for their formerly military products. A wider range in photodetector arrays for spectrometers continues to become available.

Technology Selection Considerations

The light-collection head of the monitor and the head end of the optical-fiber cable are within the high radiation zone, so the components for these must be chosen with radiation hardness in mind. These components are all optical in nature; there are no electronic components requiring radiation hardening.

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APPENDIX B PARTS LIST FOR THE MONITOR

The items necessary to assemble the complete monitor used for the October, 1999 demonstration at the Savannah River Site are listed below.

Spectrometer Mounted on PC-Expansion Card: Ocean Optics Model PC2000 (with grating for 530-1100 nm range, custom-modified version of OOIBASE32 acquisition and display software, 100 μ m permanently installed entrance slit, 500 nm permanently installed long-pass filter)	\$2624
Desktop Personal Computer: Dell Dimension XPS T450 (with 450 MHz Pentium III processor, 64 MB RAM, 13.6 GB hard disk, 15-inch monitor)	\$1126
Fiber-Optic Cable: Thorlabs M1705 (5-meter long, 200- μ m fiber, SMA patch cable)	\$63
Parts for Light-Collection Head:	
4 Cage Assembly Rods, Thorlabs ER6	\$32
4 Threaded Cage Plates, Thorlabs CP02	\$48
2 Rotating Adjustable-Focus Lens Holders, Thorlabs SM1V05	\$54
1 Optical-Fiber Adapter, Thorlabs SM1SMA	\$17
1 Lens, 1-inch diameter, 20-mm focal length, Oriel 39211	\$50
1 Lens, 1-inch diameter, 100-mm focal length, Oriel 40360	\$29
Mounting for Light-Collection Head:	
Camera Tripod	
Adapter Plate for attaching head to tripod (made in house)	
Total Cost for Parts (excluding mounting for light-collection head)	\$4043

APPENDIX C
COMPOSITION OF GLASS FRITS

Oxide	August, 1997 Demo (Frit for Pu vitrification)	July, 1998 Demo (Frits for Am/Cm vitrification)	
	Frit 30-11.4 (mass %)	SrABS (mass %)	50SrABS (mass %)
SiO ₂	29.1	33.68	21.89
Al ₂ O ₃	21.5	24.87	16.39
B ₂ O ₃	11.7	13.54	8.80
La ₂ O ₃	12.4	25.00	20.18
SrO	2.5	3.10	1.89
Nd ₂ O ₃	12.8		9.57
Gd ₂ O ₃	8.6		1.13
ZrO ₂	1.3		
Yb ₂ O ₃	variable		
Ce ₂ O ₃			4.52
Pr ₂ O ₃			4.52
Sm ₂ O ₃			2.22
Eu ₂ O ₃			0.44
Er ₂ O ₃			4.52
CaO			0.01
Cr ₂ O ₃			0.09
Fe ₂ O ₃			0.77
MnO			2.92
Na ₂ O			0.10
K ₂ O			0.03
NiO			0.03

**APPENDIX D
GLASS COMPOSITIONS FOR
1999 DEMONSTRATION**

Oxide	Glass Composition (weight percent)				PLS Predicted Composition for Run 4
	Run 1	Run 2	Run 3	Run 4	
SiO ₂	22.91	24.71	21.57	22.91	21.43
Al ₂ O ₃	16.93	18.26	15.94	16.93	15.83
B ₂ O ₃	9.18	9.90	8.64	9.18	8.58
La ₂ O ₃	22.47	22.89	22.16	22.47	22.12
Ce ₂ O ₃	4.31	2.98	4.84	4.31	4.92
Er ₂ O ₃	3.71	3.71	3.71	3.71	(Reference)
Eu ₂ O ₃	0.50	0.42	0.57	0.50	0.56
Gd ₂ O ₃	1.28	1.06	1.44	1.28	1.45
Nd ₂ O ₃	10.56	8.80	12.34	10.56	10.05
Pr ₂ O ₃	3.69	3.07	4.15	3.69	4.19
Sm ₂ O ₃	2.48	2.07	2.79	2.48	2.82
SrO	1.70	2.13	1.86	1.70	1.75
	Amount Poured (grams)				
	1315	1702	1100	1315	