
*Instrumentation Development,
Measurement and Performance
Evaluation of Environmental
Technologies*

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Table of Contents

Executive Summary

Characterization of Heavy Metals and Radionuclides . . .	1
Development of Tools for Long-term Monitoring	3
Hanford Tank Waste Chemistry	5
Environmental Control Device Testing	6
Process Monitoring and Control of Toxic Organics	7

TASK 1 *Characterization of Heavy Metals and Radionuclides*

On-line Isotopic Analytical System for Uranium and Other Actinides	9
Laser Probe for Technetium Monitor	13

TASK 2 *Development of Tools for Long-term Monitoring*

Monitoring Plant Physiological Status in Contaminated Environments by High-resolution Spectral Imaging . . .	19
Design, Fabrication and Development of a Portable Miniature Ion Trap Mass Spectrometer	23
Moisture Fiber-optic Diode Laser Sensor.	24
Application of Imaging Techniques	28

TASK 3 *Hanford Tank Waste Chemistry*

Feed Stability and Transport: Solids Formation 38

TASK 4 *Environmental Control Device Testing*

Evaluation of HEPA Filter Performance 52

TASK 5 *Process Monitoring and Control of Toxic Organics*

Dioxin and PCB Studies 55

Toxic Organic Compound Monitoring Using Cavity
Ringdown Spectroscopy 60

List of Figures

FIGURE 1.	Calibration curve for three Mn lines near 403 nm in the presence of a magnetic field	15
FIGURE 2.	Optical arrangement for double-pulse experiment	16
FIGURE 3.	Fiber sensor response against the commercial humidity probe when fiber is coated with CoCl_2 only	25
FIGURE 4.	U-bend probe	26
FIGURE 5.	Variation of the fiber bent probe output as a function of relative humidity, fiber probe is sensitive to all variations in humidity, but the sensitivity varies at different levels of humidity.	27
FIGURE 6.	Image parameters for 512 x 512 pixels with 10-bit pixel depth.	31
FIGURE 7.	Image parameters for 1024 x 1024 pixels with 10-bit pixel depth.	32
FIGURE 8.	Image parameters for 320 x 228 pixels with 12-bit pixel depth.	32
FIGURE 9.	Laser diffraction image acquired by CCD sensor.	33
FIGURE 10.	Optical fiber sizer - intensity profiler and the ROI selection tools	33
FIGURE 11.	Response envelope for the saltwell pumping flow loop for the SX-104 supernatant surrogate and for the surrogate with reduced phosphate loadings	42
FIGURE 12.	Temperatures and phosphate concentrations for the experimental results in this work (red diamonds) and the analysis of the actual SX-104 supernatant by Steen and Herting (red triangle) and for all of the single shell tanks that have not been interim stabilized.	43

List of Tables

TABLE 1.	Limit of detection obtained for all the three lines of manganese for different laser energy having different magnetic field geometry	15
TABLE 2.	Dilution factors for saltwell transfers from the single-shell tanks that have not yet been stabilized . . .	44

Executive Summary

Characterization of Heavy Metals and Radionuclides

On-line isotopic analytical system for uranium and other actinides. During this reporting period, the laser-induced fluorescence (LIF) effort has used DIAL's spectral imaging system to investigate uranium emission as a function of wavelength in an inductively coupled plasma (ICP) atomization source. Different emission transitions were observed in different regions of the plasma. The effect of changing ICP parameters (carrier gas flow rate, moisture content) on the location and intensity of the spectral emission was examined. In addition, a moderately high-resolution dye laser system has been ordered. This dye laser system is required to enable us to have the required spectral resolution for uranium isotopes and not have to rely upon when we can borrow the CRDS group's laser.

Cavity ringdown work in this quarter included collaboration with Dr. Yixiang Duan of Los Alamos National Laboratory (LANL). Dr. Duan transported microwave and discharge plasma systems from LANL to DIAL to be tested with our CRDS system. Tests were carried out using lead for system optimization in preparation for future measurements using uranium. These efforts are directed at continuing to reduce the size, complexity, and power requirements of the CRDS/plasma system for isotopically resolved measurements of uranium.

Additional measurements were also continued using a laser ablation sample introduction system on loan from CETAC Corporation.

Chelation chromatography techniques and chemistry have been marginally successful. Collection of fractions from waste lines and subsequent analysis by ICPES was used to identify method inadequacies. Changes to the methodology have improved performance. Spurious peaks caused from an acid front in the analytical column need to be cleaned up. Method development will continue in order to clean up (eliminate) the extra peaks in the chromatogram. Routine scheduled maintenance and replacement of lamps in the photodiode array detector have been completed. Work with transition metals revealed that samples buffered with large concentration of ammonium acetate gave no detector response during large volume injections. Samples buffered with acetic acid gave a good response. And samples buffered with oxalic acid gave a response, but the peak was very broad.

Laser probe for technetium monitor. Work on the study of the effects of steady magnetic field on various elements in the liquid solution continued. The detection limit of Mn in liquid jet for different laser energy and magnetic field geometries were obtained. A nearly two times lower limit of detection for Mn 403.45-nm line was found in the presence of a steady magnetic field. To evaluate the signal enhancing technique that uses double pulse excitation, initial experiment was set up with two Nd:YAG lasers. This experiment requires two collinear laser beams separated by few tens of microseconds. The optical configurations to combine the two laser beams with different polarizations were evaluated. The optical configurations which use a thin film plate polarizer to align the two lasers having p and s polarization collinearly was later adapted. We will tested this technique with the liquid sample.

Development of Tools for Long-term Monitoring

Monitoring plant physiological status in contaminated environments by high-resolution spectral imaging. The long-term objective of this project is to detect subsurface contamination by remotely monitoring reflectance spectral signatures of vegetation growing at some DOE sites. The outcome of this research could also be applied to monitor the process of phytoremediation of soils contaminated by heavy metals. During this quarter, potted plants of *brassica juncea* were grown and treated with Zn and Cd at different selected concentration levels. Diffuse reflectance spectra of plant leaves recorded with laboratory illumination and with solar irradiation were used to monitor growth and metal treatment processes. Preliminary analysis of spectra of *brassica juncea* plants treated with a “medium” concentration Zn solution (100 micromolar) reveal a spectroscopic feature that is systematically different from the spectra of untreated plants. Preliminary analytical results on leaves from the medium Zn treatment plants show a significant amount of Zn accumulated in the leaves (at the level of approximately 14 g/kg dry shoot weight). Additional spectral data analysis and analytical chemistry tests on harvested leaves from plants of other treatments will be performed during the next reporting period. Further experiments with different plant species and different metal treatments have been planned.

Design, fabrication and deployment of a portable miniature ion trap mass spectrometer. This project was started this month. Preliminary quotes have been investigated for lap top computer. Federal surplus lists are being searched to locate preferred instrumentation at a significant cost saving. Turbo pump reconditioning scheduled.

Moisture fiber-optic diode laser sensor. The aim of this project is to achieve a fiber optic relative humidity sensor. We have been successful in achieving:

- A concept of a bent probe, which leads to larger interaction with the light propagating in the fiber.

- With the help of the bent probe realization of a fiber optic humidity probe which works from 3% relative humidity to above 90% of humidity using a single probe.

Application of imaging techniques. As part of the off-line melter characterization effort, a dialogue with West Valley has been established in order for us to gain information needed to design remote optical and imaging inspection/characterization systems for deployment when the West Valley melter is shut down.

During this reporting period, the spectral imaging system's hardware and software have been upgraded and performance has been optimized. The new spectral imaging system can be used for the off-line melter characterization effort and will be used for the plant monitoring effort (Task 2.1). The spectral imaging system has been tested in our laboratory and has been applied to a spectral imaging study of uranium emission in our inductively coupled plasma (ICP) system in order to aid our Task 1.2 efforts.

Once a spectrum has been obtained at a facility, it is necessary to identify the substance(s) involved by comparison with a library of reference spectra. Therefore, we have identified the need for a tool for selecting a spectrum of interest from a library. Neural networks or a statistical approach, such as principal component analysis (PCA), are possible ways of achieving this goal. Since we have only a very limited number of reference spectra, a neural network is not a viable approach. We have developed many of the program modules for a tool using the PCA method. Currently the modules are being tested. Limitations imposed by the commercial statistical software package will be addressed in the next version of the tool.

The system development for the Fourier transform profilometry (FTP) continued with the completion of the modification of current system packages for the newly installed imaging system drivers.

Efforts continued on the system development for the integration of a higher resolution camera to increase the target sampling frequency.

For the NIR InGaAs camera, the previous obtained bad pixel correction module has been integrated with the system software. Also integrated is the control module of camera exposure time settings. For the PNG file format study, the PNG utility software will now display the PNG image along with the parameters embedded in the PNG file during the imaging file compression process. Work is continued with writing the image format as well with the correct image parameters. The PNG image format is used for DIAL's non-8-bit monochrome cameras. From the spectral survey obtained from the industrial glass furnace, two spectral regions have been selected for system thermal calibration. New version of imaging system drivers has been installed and the modification of current system packages is completed for the thermal imaging system. A new imaging acquisition/display program, featuring user interactive selected line intensity profile display, is developed and installed into Task 2.3's computer. This system is developed to assist studies in the optical fiber sizing measurement.

Hanford Tank Waste Chemistry

Saltcake dissolution. Experimental work continued on determination of the solubilities of double salt and selected single salt systems. Equilibrium liquid phase sulfate and carbonate concentrations were obtained in water at 25 and 50 C. Crystal analysis using the polarizing light microscope was performed. At 25 C only single salts were observed in agreement with model predictions. Data are being compared to the ESP model predictions and also to previous experimental results and to SOLGASMIX calculations performed at ORNL. Studies on the Na-PO₄-NO₃-OH and Na-F-PO₄-OH-NO₃ systems were initiated.

Saltcake dissolution simulations were completed for tanks BY-109, S-110, and U-107 at 50 C. Results have been compared to the experimental data obtained on the actual waste at the site. The FY 01 progress report was prepared and is undergoing review.

Solids formation. Results of additional plug formation experiments using the DIAL saltwell pumping flow loop are combined with previous data to develop an operating envelope for supernatant waste transfers at Hanford. The result is a plot of the temperature at which the plug forms against the heat flux/molar phosphate flow rate. Distinct regimes are identified where a plug will and will not form. Portions of the plot were then extended to compare to the phosphate loadings and waste temperatures of the single-shell tanks that have not yet started the interim stabilization process. The plot allows decisions to be made regarding operations associated with saltwell pumping of these tanks and further transfers that will be performed during saltcake retrieval.

A basic framework is presented for the future development of the fluid dynamics model for establishing safe regimes for slurry transport at Hanford. Initial work to accomplish the development of a three-dimensional surface for use by the operators is described.

Environmental Control Device Testing

Evaluation of HEPA filter performance. Section 4 of the Quality Assurance Test Plan was completed and circulated to members of the HEPA Technical Work Group. A final draft was prepared after review and comment by the NTW. Summary versions of Section 5, "Failure Mode vs. Minimum Detection Limit Testing" and Section 6, "Source Term Testing", were also written to add clarity and completeness to the documentation to be reviewed by the ASME. The entire document which included an introduction, Section 4, which is the calibration section of the HEPA test plan, along with summary versions of sec-

tion 5 and 6, which describe the actual testing, were delivered to the ASME Peer Review Committee.

The HEPA Test Plan is scheduled for peer review by the ASME on October 2, 2001 in Boise Idaho. Preparation for formal presentation of the test plan by The DIAL team was completed. The results of the review should be known by mid October.

Process Monitoring and Control of Toxic Organics

Sampling system for dioxins, furans and other semi-volatile products of incomplete combustion and characterization. The formation of dioxins and furans during combustion processes has become a significant focus of concern over the past few years. EPA has initiated an intensive effort to characterize the different sources of dioxins in the US and to reduce the overall annual rates of emissions. The 1999 MACT for Hazardous Waste Combustors establishes an emission limit for dioxins and furans that will be technically difficult to achieve. Large strides to controlling dioxin and furan emissions from combustion processes will most easily come from an enhanced understanding of their mechanisms of formation. The work being conducted by DIAL will seek to reduce uncertainties associated with the locus of formation of these compounds and factors that contribute to their formation.

Toxic organic compound monitoring using cavity ringdown spectroscopy. Optimization of the diode laser cavity ringdown system for measuring volatile organic compounds has continued throughout this quarter. In addition, two new mathematical routines were evaluated for their effectiveness in removing baseline effects in the system data. Although our previous procedure yielded excellent results as evidenced by the regression coefficient (R²), slight drifts in the baseline were not accounted for properly. This resulted in a day to day variation in the calibration of the system. A new mathematical procedure

has been identified which greatly improves this aspect of the system performance. Also during this quarter, significant system repairs were required after the diffusion pumped failed. The students working on the project successfully rebuilt the pump, and the system is working well again.

Construction of the supersonic jet expansion system for dioxin detection began early in the quarter, although two significant delays have slowed our progress. The primary vacuum chamber was back ordered, but is scheduled to ship at any time. The mechanical vacuum pump for the system arrived, but was damaged in shipment. Discussions with the freight carrier and pump distributor have resolved this issue, and a new pump should ship shortly. The frame for the system is in place near the laser system and the system is being assembled as needed components arrive. Additional laboratory preparations for this new experiment are underway to provide water and power for the laser system and vacuum system.

Characterization of Heavy Metals and Radionuclides

On-line Isotopic Analytical System for Uranium and Other Actinides

D. L. Monts, Yi Su, C. B. Winstead, and T. F. Meaker

Work Accomplished

Laser-induced Fluorescence Spectrometry

During this quarter, the LIF group has focused on upgrading our experimental apparatus. We have placed an order for a moderately high-resolution dye laser system. This dye laser system is required to enable us to have the spectral resolution to resolve the isotopic shifts for selected transitions for uranium. Efforts to purchase a spectrometer and intensified charged-coupled device (ICCD) detector for high-resolution detection of the uranium fluorescence have begun. Two graduate students have joined this effort and have received radiation and safety training during September; during the next reporting period, they will begin actively contributing to this project.

Also during this reporting period, we have studied the effect of ICP operational parameters on uranium emission at different wavelengths. Spectral images were used to investigate the effect of chang-

ing carrier gas flow rate, ICP forward power, and of changing moisture content of the sample carrying gas on uranium emissions in an ICP. Spectral images of uranium emission transitions at 385.9, 393.2, 424.2, and 454.3 nm were recorded with different ICP forward powers and carrier gas flow rates. The OH emission at 307 nm was used to study the effect of carrier gas moisture content. The spatial distribution of uranium emission in an ICP changes at different wavelengths as a function of ICP operational parameters. Among the operational parameters studied, we found that changing the carrier gas flow rate had a great effect on the spatial distribution of uranium emission. Spectral images of OH emission at 307 nm from the ICP did not reveal any significant changes when we raised the cooling temperature of the ultrasonic nebulizer (USN) (which was used for sample delivery) and hence attempted to increase the moisture content of the sample gas stream. This may be because the ultrasonic nebulizer still removed moisture from the gas stream efficiently even when we raised the cooling temperature to the highest allowed point.

Cavity Ringdown Spectroscopy

The potential for using a microwave induced plasma (MIP) system as an atomization source for cavity ringdown spectroscopy was investigated during this quarter. This work was carried out as part of an effort to evaluate the use of MIP for reducing the size, cost, and complexity of a portable or fieldable isotopic analysis unit. These experiments were carried out in collaboration with Dr. Yixiang Duan of Los Alamos National Laboratory. MIP units were transported from Los Alamos to DIAL for two weeks of testing. This initial testing was carried out using lead to avoid the use of radioactive materials during system optimization and to provide for comparison with our lead data obtained using CRDS coupled with an inductively coupled plasma system. Although the detection limit for lead determined using MIP-CRDS (1 ng/ml) was slightly worse than the limit achieved using ICP-CRDS (0.3 ng/ml), some potential advantages for MIP-CRDS were readily apparent. First, the power supply size and electrical

requirements (standard 110 VAC) for operating the MIP are more conducive to field use. In addition, the operating gas requirements are approximately one-quarter of those required by the ICP. Collaborative efforts with Dr. Duan are planned for the future to better optimize the MIP system for coupling with CRDS and improve detection limits even further.

Analytical Method Development

Chelation chromatography techniques and chemistry have been marginally successful. Collection of fractions from waste lines and subsequent analysis by ICP-ES was used to identify method inadequacies. Changes to the methodology have improved performance. Spurious peaks caused from an acid front in the analytical column need to be cleaned up. Method development will continue in order to clean up (eliminate) the extra peaks in the chromatogram. Routine scheduled maintenance and replacement of lamps in the photodiode array detector have been completed. Work with transition metals revealed that samples buffered with large concentration of ammonium acetate gave no detector response during large volume injections. Samples buffered with acetic acid gave a good response. And samples buffered with oxalic acid gave a response, but the peak was very broad.

Work Planned

Laser-induced Fluorescence Spectrometry

During the next reporting period, we plan to continue our study of the effect of ICP operational parameters on uranium emission. We plan to remove the cooling of the USN channel in an effort to increase the moisture content of the gas stream. Delivery and installation of the moderately high-resolution dye laser system is anticipated toward the end of the next reporting period; this will enable us to concentrate

on isotopic resolution experiments and on the effect of matrices on detection limits.

Cavity Ringdown Spectroscopy

Upon further evaluation of our previous results for uranium, we have decided to modify our research plan slightly. Thus far, the 286.6, 358.4, and 409-nm uranium transitions have been isotopically resolved, yielding detection limits of approximately 140, 300 and 230 ppb, respectively for U-235. This work has been directed at strong absorption transitions in the ultraviolet and blue region of the spectrum. In our original research plan, we targeted transitions accessible to blue diode lasers as being of primary interest. However, before purchasing an external cavity blue diode laser, we have decided to evaluate the system using a red transition and our pulsed laser. Although the transitions in the red region of the spectrum are not as strong, we can easily obtain better cavity mirrors for these wavelengths, possibly offsetting any loss in sensitivity. In addition, the technology for red diode lasers is much more advanced and less expensive than for blue diodes. A small fieldable isotopic analysis system based on a red diode would be far less expensive and likely more robust than a comparable system based on a blue diode. After evaluating selected red transitions using our pulsed laser, we will select either the red or blue diode technology for further system development. This is also part of an overall effort to continue to reduce the cost, size, and complexity of the system without overly sacrificing system performance.

Analytical Method Development

The next quarter experiments are planned to assess compatible mobile phases for rare earth elements. These will first be attempted with large volume injections. Continued method development on chelation chromatography will continue using transition metals.

Laser Probe for Technetium Monitor

V. N. Rai, F. Y. Yueh and J. P. Singh

Introduction

Technetium is a product of the nuclear power cycle. The most stable Tc isotope is ^{99}Tc . It has a half-life of 2.1×10^5 years and decays via β -emission. Due to the long half-life and the relatively high yield from uranium decay, DOE desires to separate technetium from non-radioactive and short life components of the tank waste. They plan to isolate it with other long life radionuclides in a geologically stable waste form for long-term safe storage. An on-line monitor for technetium is needed for this waste processing. On-line monitoring during the waste processing will ensure Tc is properly removed from the processed effluent. The on-line Tc monitor should be able to measure Tc below the 100- $\mu\text{g/L}$ levels. The technique should achieve at least a 10% confidence interval at 1000 $\mu\text{g/L}$.

This technical task focuses on the development and application of laser-induced breakdown spectroscopy (LIBS) to monitor Tc in effluent of Tc processing waste facility. LIBS is a laser-based, non-intrusive, and sensitive optical diagnostic technique for measuring the concentration of various atomic and molecular species in test media.^{1,2} It uses a high-power laser beam to produce a laser-induced plasma at the test point. The plasma atomizes and electronically excites the various atomic species present in the test volume in a single step. The intensities of the atomic emission lines observed in the LIBS spectrum are used to infer the concentration of the atomic species. LIBS has been successfully demonstrated its real-time monitoring capability in various field tests.³⁻¹⁰ We will evaluate various techniques, which can improve LIBS' sensitivity for Tc measurements.

Work Performed

An enhancement in the visible emission from the plasma in the presence of steady magnetic field has an important implication in the trace element analysis from solid and liquid samples with LIBS. The LIBS spectrum of manganese in liquid solution were recorded in the absence and the presence of magnetic field. It was found that LIBS signal enhances by 1.5 - 2 times in the presence of magnetic field. This enhancement was attributed to the confinement of laser-produced plasma in the presence of magnetic field, which increases the effective density of plasma. This increase in plasma density due to confinement and decrease in plasma temperature as a result of plasma expansion will enhance the rate of recombination, which will lead to an enhancement in the emission. LIBS spectra were recorded by changing the concentration of manganese (1 - 10 ppm) in the solution as well as at different laser energy. The calibration curves for the manganese were obtained in the absence as well as in the presence of magnetic field for different laser energy. Figure 1 shows the calibration curve for three Mn lines near 403 nm in the presence of magnetic field. These calibration curves were used to calculate the limit of detection (LOD) for manganese in order to see the effect of laser energy and other experimental parameter on it. The limit of detection obtained from these calibration curves is presented in Table 1. Comparison of data in Table 1 indicates that the LOD improves with an increase in laser energy as well as in the presence of magnetic field. Particularly, the LOD was found better in the case when magnetic fields were having cusp geometry (same pole of magnets facing each other). A nearly two times lower limit of detection for Mn 403.45-nm line was found in the presence of a steady magnetic field.

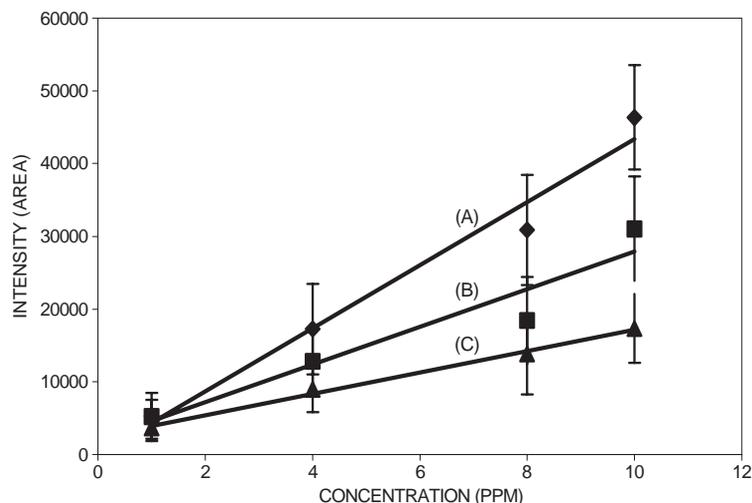


FIGURE 1. Calibration curve for three Mn lines near 403 nm in the presence of a magnetic field: (B = 5 KG) (A) Mn 403.076 nm, (B) Mn 403.307 nm, (C) Mn 403.449 nm.

TABLE 1. Limit of detection obtained for all the three lines of manganese for different laser energy having different magnetic field geometry. Some of the notations in the table are defined below.

Mn Lines (nm)	Limit of Detection (LOD)					
	Laser Energy of 140 mJ			Laser Energy of 280 mJ		
	No Mag.	N-S Mag.	N-N Mag.	No Mag.	N-S Mag.	N-N Mag.
403.076	1.74	0.83	0.72	0.87	0.8	0.63
403.307	2.47	1.53	1.47	2.17	1.45	1.08
403.449	6.23	2.21	2.02	4.24	2.04	1.83

*No Mag. - In the absence of magnetic field.
 *N-S Mag. - N pole of one magnet is facing the S pole of the other magnet (linear field line).
 *N-N Mag. - N pole of one magnet is facing the N pole of the other magnet (cusp geometry).

On the basis of the above results it is expected that the combination of magnetic field with double pulse excitation technique may be useful in enhancing the sensitivity of the system manifold. For this purpose we have started setting up double pulse excitation experi-

ment. This experiment uses two frequency-doubled Nd:YAG lasers. One laser beam is p-polarized whereas another is s-polarized. Both the laser beams were made collinear with the help of a thin film polarizer separator. The optical arrangement made for this experiment is shown in Figure 2. Along with optical alignment, synchronization of both the lasers is also important. This experiment requires two laser beams separated by few tens of microseconds. An electrical delay generator was modified in order to control the arrival of both lasers to the liquid jet at a certain interval of time. The first laser beam initially creates the plasma, which expands in air with time. The second laser beam interact with this expanding plasma and observe a better absorption, which lead to an increase in number of excited atoms. Finally, it provides an enhancement in the emission signal, which leads to an improved value of LOD. The initial testing of the alignment and timing of the laser beams for the double pulse experiment has completed.

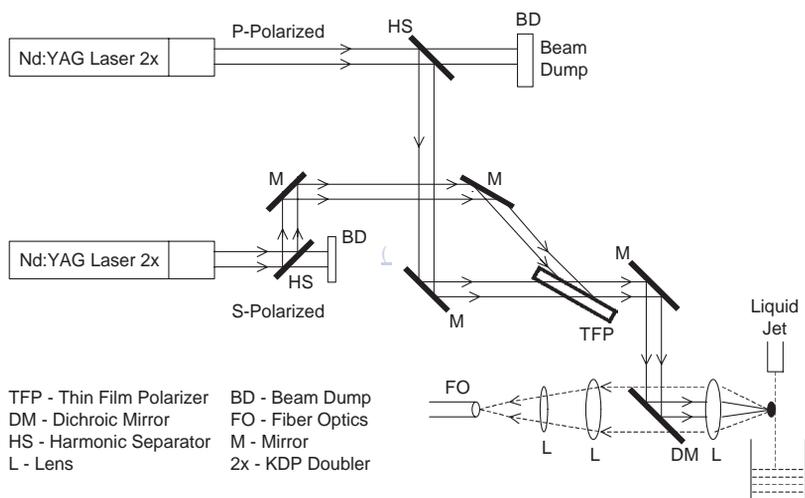


FIGURE 2. Optical arrangement for double-pulse experiment.

Work Planned

The combination of magnetic field and double pulse excitation will be tested after completion of this double pulse experiment, which is in progress.

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Monitoring Plant Physiological Status in Contaminated Environments by High-resolution Spectral Imaging

Yi Su and David Monts

Introduction***Purpose***

The goal of this project is to use remotely sensed data to monitor the physiological status of plants growing on contaminated DOE sites. The physiological status will be used as an indicator of the presence of pollutants, such as heavy metals or radioactive species, in the growing environment. This capability will enhance DOE's capability for cost-effective long-term monitoring of contaminated sites.

Plant reflectance is governed by leaf surface properties and internal structure, as well as by the concentration and distribution of biochemical components, and thus remote analysis of reflected light can be used to assess both the biomass and the physiological status of a plant. Particular spectral bands and band combinations (often referred as reflectance indices) for monitoring crop stress resulting from nitrogen deficiency, water deficiency, etc. have been reported using remote

sensing. We propose to monitor the impact of contamination, such as by heavy metals, on plant physiological status. A computerized spectral imaging system will be applied to take images of plants growing in a controlled environment with known concentrations of heavy metal contamination. Spatial and temporally distributed information extracted from images of different spectral bands will be part of this plant physiology study. The focus of this project is to search for indices (signatures) that indicate the impact and the content of heavy metals in the leaves and canopies of live plants. This ground-level study will also help to determine whether the physiological reflectance signals are stronger than disturbances introduced by factors such as the position of the sun, heterogeneity of the landscape, or atmospheric interference. The resulting information will be essential to determine whether remote sensing technology can be used for long-term monitoring of the spread of pollutants at some of the DOE closed sites.

Methodology

A portable spectroradiometer system and a spectral imaging system will be applied to monitor plant physiological status in contaminated environment. The spectroradiometer will be used to record reflectance spectra from the plant throughout the growing process. The spectral analysis will provide us the impact of the contamination on the plant physiology, and also will help determine the key spectral band(s) (signature) related to specific contamination. A spectral imaging system, which is based on the outcome of Task 3.2 (On-Line Multispectral Imaging of Thermal Treatment Process) of last year's Cooperative Agreement, will provide the spatial analysis. The spectral imaging system will help us overcome problems related to mixtures in the field of view, such as soil, dry leaves, stems, and shadows. The information extracted from spectral images will also be used to study plant canopy structure change during the growing process.

This is a multi-year project. First year will be devoted to a laboratory study: a laboratory-size plant bed will be used to study the

impact of selected metal species on plant physiology status. The second and third years will be devoted to study plants grown under a controlled natural environment for conditions similar to those that pertain to selected DOE sites; the plants affected by contamination will be studied in a potted-plant growing facility in a natural environment. The following years will be devoted to DOE site-specific studies.

Work Accomplished

During this reporting period, we have conducted a series of experiments with *brassica juncea* planted in pots. These experiments were conducted in the natural environment outside the DIAL building at ambient temperature and illuminated with natural light. *Brassica juncea* were seeded in potting mix for four weeks prior to metal treatments. After the first three weeks, the plants were thinned, leaving two plants in each pot. Water and nutrient solutions were applied to the potted plants daily until the plants were harvested. After four weeks of growing, the plants were treated with metal solutions of Zn and Cd daily. Eight pots (16 plants total) of *brassica juncea* were kept as untreated, five other subsets of eight pots (16 plants) each were treated with medium concentration Zn solution (100 μM), high Zn solution (300 μM), medium Cd solution (50 μM), high Cd solution (100 μM), and medium Zn (100 μM) plus medium Cd (50 μM) solution. The plants treated with high Zn concentration and both Cd solutions exhibited signs of severe toxicity immediately after the start of the treatments. The plants with medium Zn treatment, the plants with Zn plus Cd treatment and the untreated plants were harvested ten days after the start of the treatment. The harvested plants were then dried at 80 C for 48 hours. Dry plants were ground and weighed for the analytical chemistry tests.

Diffuse reflectance spectra of plant leaves recorded with laboratory illumination and with solar irradiation were used to monitor growth and metal treatment processes. A portable spectroradiometer

were used to collect the reflectance spectra of the plants inside a laboratory with artificial illumination. The plants were transferred back to the natural environment immediately afterward, and reflectance spectra of the plant with solar irradiation were acquired on non-raining days. Preliminary analysis of diffuse reflectance spectra of *brassica juncea* plants treated with a “medium” concentration Zn solution (100 μM) reveal a spectroscopic feature that is systematically different from the spectra of untreated plants. The spectroscopic feature appeared about three days after the start of the treatment. Preliminary analytical results on leaves from the medium Zn treatment plants show a significant amount of Zn accumulated in the leaves (at the level of approximately 14 g/kg dry shoot weight). A typical untreated plant may accumulate about 100 mg of Zn/kg dry shoot weight and 1 mg of Cd/kg dry shoot weight. Additional spectral data analysis and analytical chemistry tests on harvested leaves from plants of other treatments will be performed during the next reporting period.

Work Planned

We have already started another sets of pot experiments. Lower concentration of Cd treatments will be applied to potted plants of *brassica juncea* in this period. Another lower Zn concentration will be applied in addition to the 100 μM Zn subset. The same spectral monitoring procedure and analytical chemistry tests will be conducted on this new batch of plants.

Design, Fabrication And Development Of A Portable Miniature Ion Trap Mass Spectrometer

Thomas Meaker

Introduction

Current research performed by the principle investigator has successfully reduced the size of a mass spectrometer to a few millimeters in diameter. This accomplishment has eliminated the need for large rf voltages associated with ion traps (IT). Furthermore, the vacuum manifold needed for the mini-IT is significantly reduced, requiring considerably less power demands to maintain a suitable vacuum. The short-term goal revolves around incorporating these two major advancements of miniaturization into the design and fabrication of an ITMS. This would allow for a portable instrument to be in place within 12 to 18 months. The long-term objective would continue to improve on the prototype by further reducing electrical energy demands by incorporating a field emitter array as the ionization source. To further reduce the overall size and power needs, we would assess the potential use of Fourier transform (FT). This, if successful, would effectively allow the elimination of electron multiplier detection devices. The FT of a time domain signal will produce a frequency spectrum that can easily be correlated to mass. This would have a two-fold affect. First, this would eliminate the external electronics of the electron multiplier, further miniaturizing the instrument. Second, it would allow for the non-destructive analyses of a particular sample, allowing for significantly lower detection limits. Current IT technology uses a mass selective instability scan to eject ions out of the trap to an electron multiplier. Once the electrons are ejected, they are lost (and only one-half of the ions reach the detector). Using FT, all ions are analyzed and the signal can be integrated for extremely long times, effectively lowering detection limits.

Work Accomplished

This project was started in September. Preliminary quotes have been investigated for a lap top computer. Federal surplus lists are being searched to locate preferred instrumentation at a significant cost saving. Turbo pump reconditioning the scheduled.

Work Planned

This quarter should see delivery of the instrument package and data station to begin experimentation of the miniature ion trap. A vacuum manifold will need to be fabricated or procured during this period.

Moisture Fiber-optic Diode Laser Sensor

R. Jindal, S. Tao and J. P. Singh

Introduction

Moisture fiber optic sensors can be used for monitoring of the harsh environment such as down hole drill, factories with electromagnetic noise unacceptable for regular capacitance-based moisture gages, radioactive waste storage places etc. Several U.S. DOE waste tank storage sites such as Hanford site has needs to monitor water in subsurface rear storage. The main purpose of this study is to prove the concept of the sensor, make preliminary samples as well as experimentally find a way for improvements of their performance. The present study of the sensor is based on the absorption of the evanescent tail of the light propagating in fiber.^{14,15} To increase the interaction with the light propagating in the fiber a bent probe was tried³ and found to give very desirable results.

Work Accomplished

The approach in this period has been mainly based on evanescent wave absorption as it was found to be faster and repeatable. To go to lower relative humidity it was tried to coat the bare portion of the fiber with an aqueous solution of just CoCl_2 , as it was thought that probably PVA is stopping a better interaction between the light guided by the fiber and CoCl_2 . Various CoCl_2 concentrations were tried. It was found that with high CoCl_2 concentration the sensor responds to relative humidity above 60% (Fig. 3).

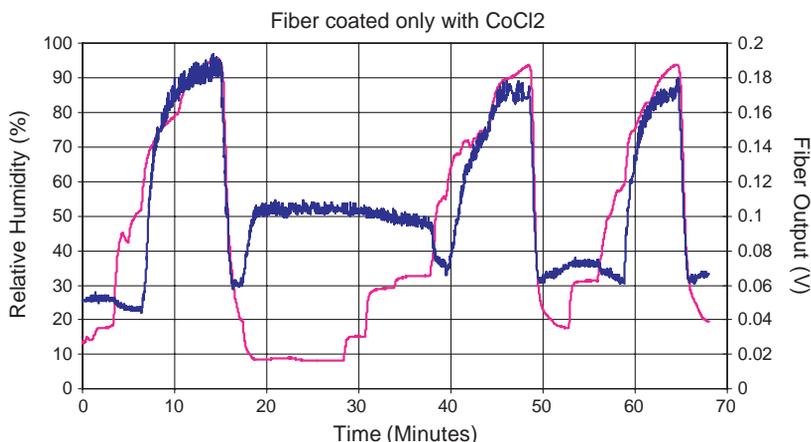


FIGURE 3. Fiber sensor response against the commercial humidity probe when fiber is coated with CoCl_2 only.

The response time was very little and was reversible too. But the pure CoCl_2 coating was found to be very brittle and could be easily taken off the fiber by the touch of hand. Also the insertion loss of the fiber increases with a pure CoCl_2 coating as there is more scattering loss from the fiber surface. These two property rules out pure CoCl_2 for a long term monitoring. So it was decided to continue with the coating of a solution of PVA and CoCl_2 . To have a larger interaction with the light propagating in the fiber a bent fiber loop was then tried by bend-

ing the exposed portion of the fiber in a circular loop with the help of a scotch tape. The bend loop shows very good effects, as with coating this loop with PVA and CoCl_2 solution shows the output change in humidity from 30% and above. This is a significant improvement on the previous results. Though the bending does increase the insertion loss of the probe because of the radiation loss but the effect is not very significant. Further methods to make a bent probe were also explored as it was found that the scotch tape gets loosen after some time thus making a change in bending diameter and in turn changing the behavior of the probe. One of the effective ways found was to take off the fiber jacket and heat the fiber at a high temperature (about 500 - 700 C) and simultaneously bending the fiber results in a U-bend probe, which works quite effectively (bent probe is shown in Fig. 4).



FIGURE 4. U-bend probe.

Bent probe were tried with different core diameter fibers and it was found that smaller core diameter fiber is more sensitive. It was found that with a 200-micron fiber bent sufficiently we could measure a change in output of the fiber for a relative humidity change from 3% to above 90% using a single probe (Fig. 3). Only draw back is that the behavior is non linear with respect to change in humidity. Also the amount of coating variation can lead to significant changes in the out-

put behavior. We are trying to look up at the reason for this non-linear behavior and possibilities to make it linear if possible. Also other parameters like different bending diameters and coating thickness are also being tried.

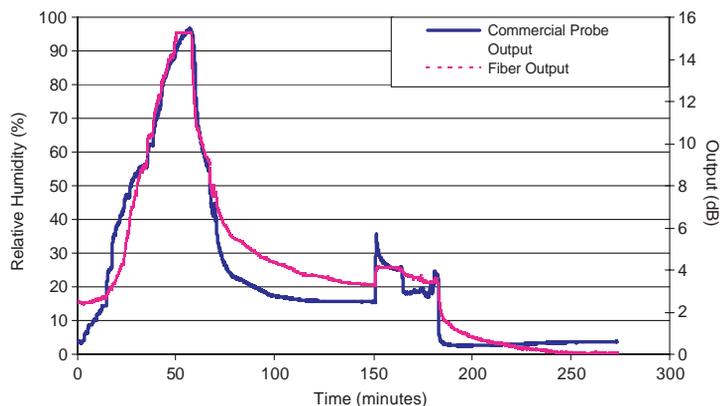


FIGURE 5. Variation of the fiber bent probe output as a function of relative humidity, fiber probe is sensitive to all variations in humidity, but the sensitivity varies at different levels of humidity.

Work Planned

The primary requirement in this period is to find an effective way of making the behavior of the sensor linear and also looks for possible sources of a false signal.

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Application of Imaging Techniques

David Monts, Yi Su, Ping-Rey Jang, and Thomas Philip

Introduction

Purpose

Imaging techniques can be utilized to provide solutions to a wide variety of issues facing DOE, ranging from process control to off-line melter inspection to long-term monitoring. This effort will develop the techniques and instrumentation needed to address these needs.

Spectral images are obtained by positioning a narrow-bandwidth band pass filter in front of a camera. The band pass spectral region of the filter is selected to coincide with the emission of an atomic or molecular species of interest or to coincide with regions of the spectrum containing only blackbody emission. By proper selection of wavelengths, information about the spatial distribution of species present or about temperature distribution can be derived from these images. Spectral and thermal imaging can provide DOE with information crucial to its decision-making processes.

There is a commonality to the data collection hardware, data and analysis software, and to the data sifting techniques necessary for applying imaging techniques. This effort expands on existing expertise to develop imaging collection and analysis systems that address a wide variety of DOE's needs. Our efforts this grant year concentrate on (but will not be limited to) inspection of off-line Joule-heated

melters to determine where and how much exceptional wear occurred, and also to determine where deposits are located, how big the deposits are, and a preliminary identification of the materials deposited.

Methodology

Our efforts will concentrate on DOE needs for inspection of off-line Joule-heated melters to determine wear patterns and the location and composition of deposits; this information can be utilized in the design of the next generation of HLW melters. Narrow band pass filters will be combined with block cameras to enable spectral imaging within the melter. DIAL's imaging capability will be extended to the near-infrared spectral region. Diffuse reflectance spectroscopy will permit selection of proper observation wavelengths. Means of quantitative determining the extent of wear or amount of deposition will also be developed based on two techniques: Fourier transform profilometry (FTP) and stereo vision. DIAL has previously demonstrated that its FTP system can quantitatively determine the volume and depth of removed material to high accuracy. Improvements will include: (1) improvement of the fringe pattern projection system, and (2) improvement of the phase unwrapping algorithm—this upgrade will resolve the 2π -phase discontinuity associated with abrupt changes in surface height. A second imaging technique, stereo vision, will also be developed as a means of determining the depths/heights of surface features. Stereo vision provides determinations of depths/heights by combining images simultaneously recorded by two cameras. Knowledge gained from and techniques developed for characterization of off-line melters can also be applied to characterization of on-line melters. A collaborative arrangement has been established with SRS's DWPF facility to inspect their melter at an appropriate time. Efforts are underway to establish a similar relationship with West Valley.

Techniques have been developed to detect hot spots, thermal distribution, characterization of vegetation, detection of uneven surfaces, etc. from imaging data. This year's effort also aims at enhancing the techniques already developed here and to develop new techniques and capabilities utilizing statistical as well as intelligent system approaches. While statistical methods provide linear relationships, artificial neural networks are apt to deal with non-linear relationships inherent in the data. Besides these, rule-based techniques would derive heuristic relationships. The existing capabilities will be extended to characterize soil, melters, and vegetation from uni- and multi-spectral images. This will enable long-term monitoring to detect the presence and variation of trace elements, especially hazardous ones in plants. The ability to classify regions of interesting characteristics will provide valuable information regarding contamination in soil and other media. One of the objectives of this effort is to go beyond typical data analysis methods in pursuit of discovering new relationships and thereby sifting information hidden in the data.

Work Accomplished

Profilometry

Modification of the current FTP system with the newly installed imaging system drivers has been completed. As part of the off-line melter characterization effort, a dialogue with West Valley has been established in order for us to gain information needed to design remote optical and imaging inspection/characterization systems for deployment when the West Valley melter is shut down.

Thermal Imaging

For the NIR InGaAs camera, efforts concentrated on integrating the previously obtained bad-pixel correction module with the system software. The control module of camera exposure time settings was also integrated into the system software. Images acquired by the

acquisition system are corrected with the bad-pixel mask along with the non-linear image median filter. Raw image acquisition and corrected image display can be achieved in near-real time.

The Portable Network Graphic (PNG) image format utility software will now display the PNG image along with the parameters that were embedded in the PNG file during the imaging file compression process. As shown in Figures 6, 7 and 8, the image parameters are accessed and displayed for the images with various resolutions as well as in 10- and 12-bit pixel depth. The PNG image format is used for DIAL's non-8-bit monochrome cameras.

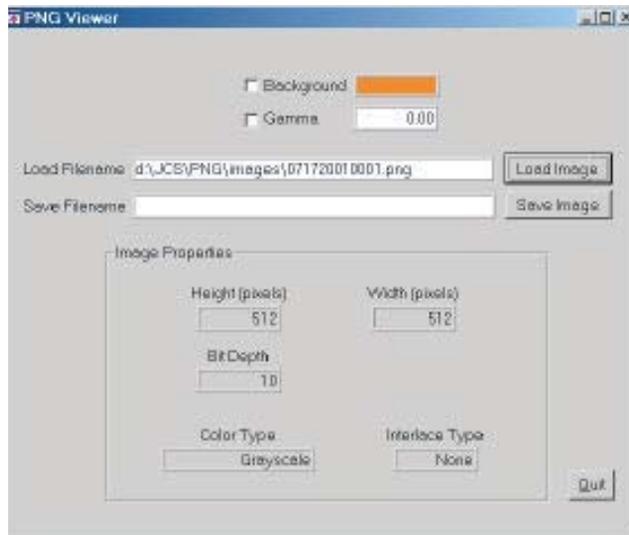


FIGURE 6. Image parameters for 512 x 512 pixels with 10-bit pixel depth.

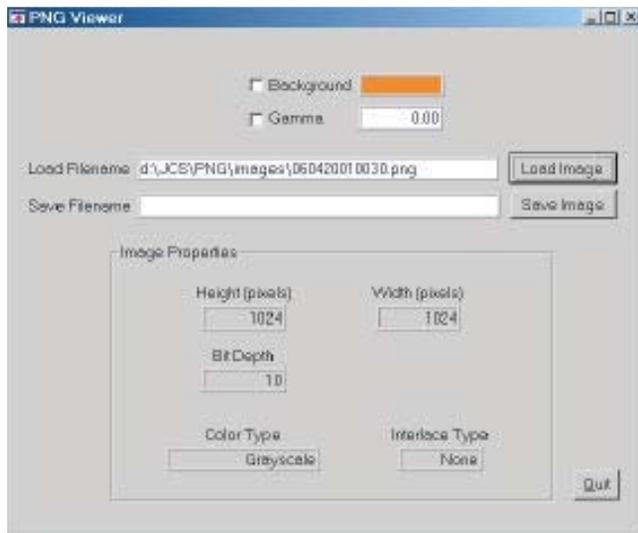


FIGURE 7. Image parameters for 1024 x 1024 pixels with 10-bit pixel depth.

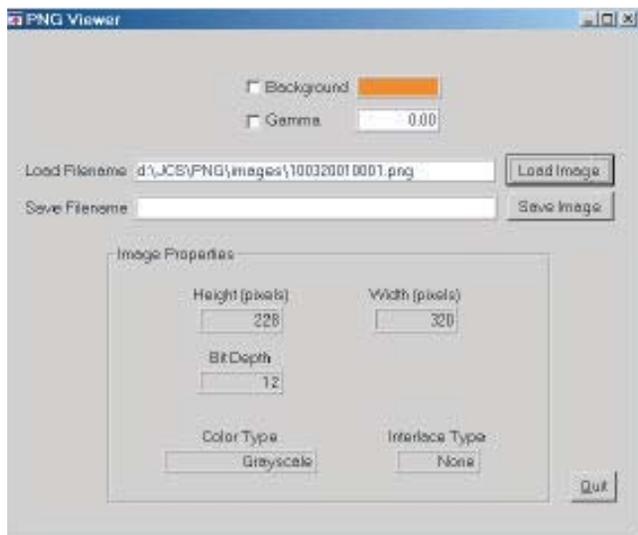


FIGURE 8. Image parameters for 320 x 228 pixels with 12-bit pixel depth.

A new imaging acquisition/display program, featuring an interactive, user-selected line intensity profile display as shown in Figures 9 and 10, has been developed and installed into Task 2.3's computer. This system was developed to assist studies in optical fiber sizing measurement. Further development of this technique is expected.

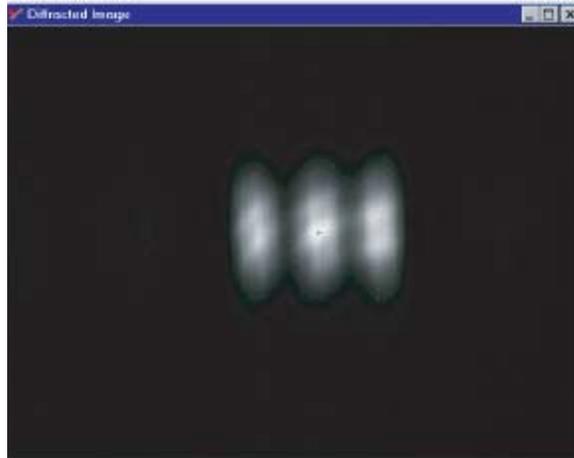


FIGURE 9. Laser diffraction image acquired by CCD sensor.

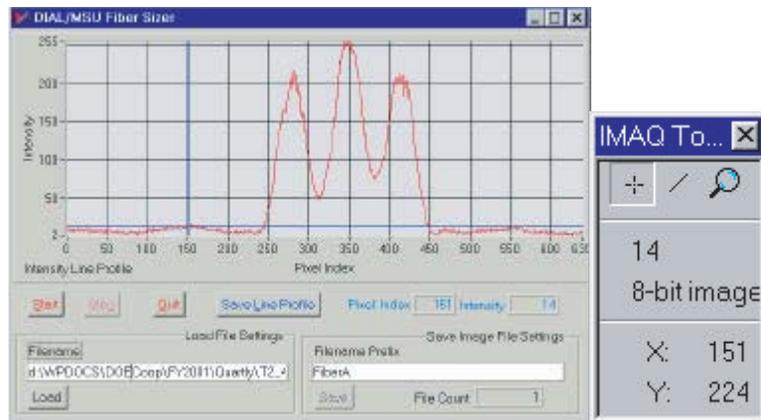


FIGURE 10. Optical fiber sizer - intensity profiler and the ROI selection tools.

The capabilities of the thermal imaging system have been upgraded by addition of new imaging system drivers and by the ability to acquire thermal images in two newly selected spectral regions (selected from spectral surveys obtained in an industrial glass furnace). The thermal imaging system is in the process of calibrating the thermal image intensities. The system now utilizes a high-resolution (1 K x 1 K and 10 bits pixel depth) digital camera. Thermal calibration efforts should be completed during the next reporting period.

Spectral Imaging

During this reporting period, the spectral imaging system's hardware and software have been significantly upgraded and performance has been optimized. Hardware components upgraded include: (1) a new frame grabber board for the computer in order to improve data acquisition time and intensity resolution, and (2) two new illumination systems. The first one is a new fiber optic light source with a ring of sufficient diameter that a collection lens and/or a camera can be positioned inside the ring, permitting uniform illumination of the target. The second illumination system consists of two high-intensity, DC-powered quartz-tungsten-halogen lamps. The new light sources will be used with the off-line melter characterization effort and with the plant monitoring effort (Task 2.1). Computer software upgrades include updates of the commercial data acquisition and analysis software platforms and also computer software (written by us) to expand our capabilities and enhance performance. The spectral imaging system has been tested in our laboratory and has been applied to a spectral imaging study of uranium emission in our inductively coupled plasma (ICP) system in order to aid our Task 1.2 efforts.

Information Sifting

During this quarter, our efforts were focused on developing software procedures to evaluate principal component analysis (PCA) as a viable approach to match an unknown spectrum to one in a reference

spectral library. We selected twenty-five different spectra from the EPA library to use them as reference spectra. Separate procedures were developed to test out various segments of the algorithm. The algorithm essentially consists of data preprocessing, principal component analysis, and post processing. Only the first two steps are used to train the software with the reference spectra. All three steps are applied to identify an unknown spectrum. This approach identifies a spectrum when there is a close match with one in the library.

In the current version, spectral data are given to different modules manually, which makes it prone to errors during processing. Therefore the entire training and identification processes need to be automated and integrated as much as possible. This is a task to be accomplished during the next quarter.

Work Planned

Profilometry

Works continues on studying and developing phase unwrapping algorithms^{1,2} for target areas that have large height discontinuities and/or surface isolations. Efforts to integrate a higher resolution digital camera into the FTP system in order to increase the target sampling frequency will continue.

Thermal Imaging

For the NIR InGaAs camera, development of a false-color image display based on assigned pixel intensity (12-bit) bins will continue. The software module for reading parameters within PNG image files will be integrated with the current imaging system so that exact interpretation of PNG images can be achieved. We will continue the thermal calibration and system software modification for the new thermal imaging system with the newly selected spectral regions and the high-resolution camera.

Spectral Imaging

Works continues on developing and improving the image acquisition and processing software package. An acousto-optic tunable filter (AOTF) telescope video adapter has been ordered and will be integrated into the spectral imaging system upon arrival of the adapter. This will enable us acquiring spectral images at any desired wavelength in the visible and near infrared regions with very short wavelength switching times. The spectral imaging system will be applied to monitoring plant stress resulting from heavy metal contamination (Task 2.1).

Information Sifting

- Automate the spectral identification process and test it thoroughly.
- Integrate the modules into a system with training and identification functionalities.
- Validate the software with data from the DIAL test facility.
- Acquire hardware and software for efficient processing.

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15. Mitsuo Takeda, *et al.* August 1997. Frequency-multiplex Fourier-transform profilometry: a single shot three-dimensional shape measurement of objects with large height discontinuities and/or surface isolations. *Applied Optics* 36:22.

Acronyms

CCD charge-coupled device

DWPF	Defense Waste Processing Facility
EPA	Environmental Protection Agency
FTP	Fourier-transform profilometry
ICP	inductively coupled plasma
InGaAs	indium gallium arsenide
NIR	near infrared
PCA	principal component analysis
PNG	Portable Network Graphics
ROI	region of interest
SRS	Savannah River Site

Feed Stability and Transport: Solids Formation

J. S. Lindner, V. Raju, R. K. Toghiani and H. Al Habbash

Introduction

Tank farm operations at Hanford include the interim stabilization program where the supernate and interstitial liquor in the single-shell tanks is reduced. Benefits from this process include the minimization of leakage from aging tanks, thereby limiting migration of waste into the soil, and the temporary reduction of waste within the tank. The process consists of jet-pumping the liquid in a given tank, obtained through a screen or salt well to a double-shell holding tank and then to an evaporator. Dilution water is added at the pump head. Recently, solids formation and plugging have been noted during transfers from tanks 241-SX-104, 241-U-103, and 241-BY-102.¹⁶ The primary solid responsible for the plugs from the first two tank wastes has been tentatively assigned, through experiments conducted on the waste liquid in the laboratory, as $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$.

The plug formed during salt well pumping of BY-102 was believed to arise from sodium carbonate.

Other solids may participate in the plug formation process and this will largely depend on the solid-liquid equilibrium of the species contained in the waste stream. Little information, aside from the laboratory screening experiments is known regarding the mechanisms of plug formation and, more importantly, the required change in pressure that would indicate the beginning of plug formation. From operations measured records, the time needed for a plug can be determined and by knowing the pressures and flow rates the approximate location of the plug can be estimated; however, prevention of inadvertent plugs may be possible based on a suitable engineering tool that will allow operators to tailor waste transfers.

Development of an engineering tool that can describe slurry transfers and salt well pumping is also an objective of this program. In the case of slurry transport experimental data is being obtained at Florida International University and information on solids behavior, size, and growth rates is being measured at AEA Technologies. A test loop for obtaining data on supernate transfers does not currently exist. The lack of a test loop for salt well pumping, the need to understand the process in greater detail, and provide the fundamental data for development of the engineering tool provided the basis for the work described below.

Work Accomplished

Salt Well Pumping Flow Loop Experiments

Previous work on the evaluation of saltwell supernatant transfers has centered on evaluation of the effects of the SX-104 surrogate flow and cooling rates on particle and agglomerate growth, sedimentation, and plug formation.¹⁷ Results indicated that at the same cooling water flow rate the time necessary to form a plug increased with an increase in the surrogate flow rate. Imaging experiments on a section of the channel provided particle and agglomerate dimensions, growth rates, velocities, and insight into sedimentation behavior. The results were

evaluated in terms of an equation for the critical particle velocity or size developed by Duran. In all of these experiments the particles were found to grow at a similar rate of 2 mm²/sec. The longer times necessary to form a plug were then found to depend on the difference between the initial particle or stream velocity and on the critical velocity. The effect of decreasing the cooling rate while keeping the initial surrogate flow rate constant was observed to result in reduced particle growth rates. The time for a plug to develop increased accordingly.

The experiments provided valuable information regarding the mechanisms involved in the formation of a plug for a surrogate composition at a given phosphate concentration of 0.22 M. Additional experiments at different phosphate concentrations were deemed necessary to formally establish an operating envelope that could be applied to actual saltwell liquor transfers. For these tests all of the constituents of the SX-104 surrogate remained constant except for the initial phosphate loading. Two other concentrations, 0.15 and 0.11 M were investigated.

A lowering of the phosphate concentration required larger cooling water flow rates to achieve the temperatures necessary for particle nucleation and subsequent growth. For the 0.15 M phosphate surrogate cooling water flow rates of 1.2 and 1.8 gpm were not sufficient to generate a plug. A plug was formed with a cooling water flow of at the maximum flow rate of the heat exchanger, 3 gpm. Development of a plug at the 0.11 m phosphate concentration required the use of a cooler circulating water at 10 C.

Results from all of the experiments are collected in Figure 11 where the temperature at which the plug formed is plotted against the ratio of the heat flux to the phosphate concentration. The heat flux was determined from the heat lost by the surrogate ($q = mC_p\Delta T$) over the area of the heat exchanger. This quantity was then divided by the molar flow rate of phosphate. Solid symbols correspond to those con-

ditions where a plug was formed. The experimental data for the 0.22 and 0.15 M phosphate concentrations were fit to linear expressions. For the higher concentration the data was described by

$$\text{Temperature at Plug } PO_4 \text{ 0.22 M} = (-6.5e - 03)(\text{normalized heat flux}) + 49.6 \quad \text{(EQ 1)}$$

At the 0.15 M phosphate concentration the following expression was obtained:

$$\text{Temperature at Plug } PO_4 \text{ 0.15 M} = (-4.2e - 03)(\text{normalized heat flux}) + 49.4 \quad \text{(EQ 2)}$$

Both regressions provided intercepts within 0.2 C. A further relationship between the phosphate concentration and the slopes was determined. This allowed estimation of the slope for the 0.11 M phosphate concentration and it is seen that the estimate agrees with the actual experimental point to within 1.8 C. The data demonstrate that plug formation can occur at temperatures as high as 43 C. A decrease in the phosphate concentration moves the plug temperature to lower values.

An estimate of the region that defines plug formation was obtained from the data points where a plug was actually observed. In the case of the two lowest phosphate concentrations this regime is subject to slight uncertainty owing to the number of experiments performed and the fact that not all possible values of the cooling water flow rate were investigated. Thus, the demarcation may be closer to a temperature of 39 C for the 0.15 M phosphate condition. Nonetheless, the operating envelope can be used for specifying saltwell transfers.

To date confirmed plugs have arisen during transfers from three tanks, SX-104, U-103, and BY-103.¹⁶ The plug from the saltwell supernatant from the later tank occurred within a pipeline following a stop work order related to a flammable gas safety issue. The fluid remained in the pipeline for a period of months during which the plug formed. Attempts to remediate the plug were unsuccessful and the

transfer line was abandoned. Plugs for the transfers from SX-104 and U-103 occurred in junctions located in diverter boxes. The routing pipes are not heat-traced and the diverter boxes are not insulated. The temperature drop encountered by the fluid corresponds to the initial waste temperature in the tank and the temperature in the diverter box that is limited by the ambient conditions. In using this plot the mass flow of the fluid is a measured quantity and the heat capacity can be obtained from ESP calculations. The area of the jumper is known and an estimate for the change in temperature the normalized heat flux can be calculated. Most importantly average phosphate concentrations are available from analysis of the supernatant of the tanks as is routinely performed during interim stabilization operations.¹⁸⁻²⁰

Assuming that the temperatures in the diverter boxes were measured or even estimated, the response envelope in Figure 11 can be used to determine the amount of dilution water necessary to avoid a plug.

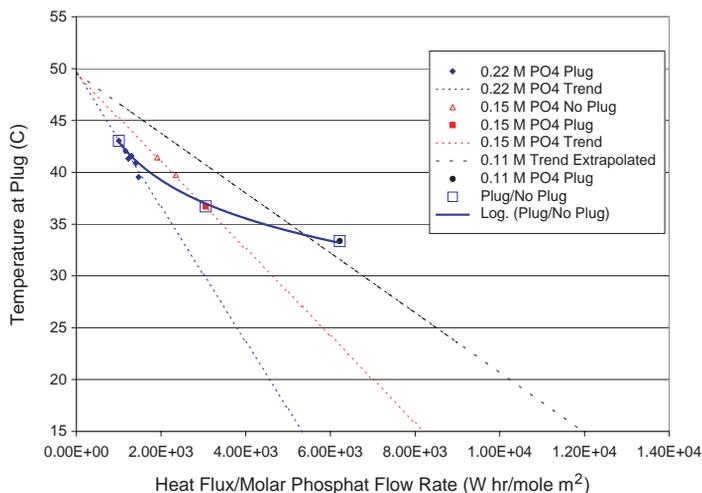


FIGURE 11. Response envelope for the saltwell pumping flow loop for the SX-104 supernatant surrogate and for the surrogate with reduced phosphate loadings.

A second representation of the data is provided in Figure 12 where the temperature is plotted against the phosphate concentration.

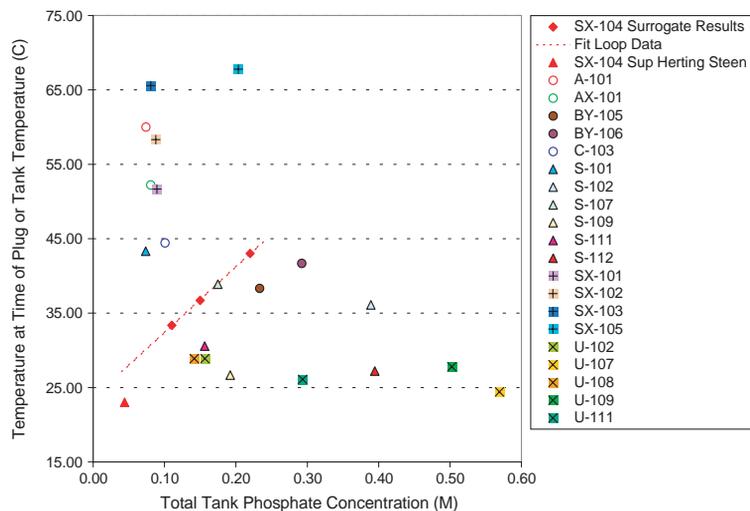


FIGURE 12. Temperatures and phosphate concentrations for the experimental results in this work (red diamonds) and the analysis of the actual SX-104 supernatant by Steen and Herting (red triangle) and for all of the single shell tanks that have not been interim stabilized. The plug and gel temperatures are given for the flow loop and Hanford laboratory experiments respectively. Phosphate concentrations from the BBI relate to the total phosphate loading and do not reflect partitioning into the solid phase at temperatures less than 43 C.

The phosphate concentration for the actual SX-104 saltwell liquor was determined to be 0.044 M.¹⁸ The gel temperature was determined by following the formation of solids as the solution was cooled from 50 C using a polarized light microscope.¹⁹ Extrapolation of the flow loop data to the 0.44 M phosphate concentration results in a difference of about 4 C. This difference is thought to reflect the composition of the actual saltwell liquor as compared to the surrogate employed in the flow loop experiments. Additional solids were present in the waste that may participate in the sedimentation process leading to plug formation.¹⁹

Waste temperatures and phosphate concentrations for the single-shell tanks were gathered from the Best Basis Inventory.²⁰ The initial SX-104 phosphate concentration (not shown as the tank has been stabilized) was found in the BBI to be 0.077 M at a temperature of 50 C. The decrease of the phosphate concentration to that obtained in the laboratory arose from either dilution of the liquid in the saltwell pump and/or heterogeneity within the tank. For a plug to form during transfer a temperature drop of around 25 C had to have occurred. Insulating or heating the diverter boxes to an elevated temperature is expected to reduce the possibility of plugging for the SX tanks (Fig. 12) and for A-101, AX-101, C-103, and S-101.

For those wastes at temperatures above 43 C dilution ratios can be determined based on the response data and the anticipated temperature drop, Table 2.

TABLE 2. Dilution factors for saltwell transfers from the single-shell tanks that have not yet been stabilized.

Tank Name	Temp. (C)	[PO ₄] BBI (M)	Dilution Factor [PO ₄] = 0.044 M (%)	Dilution Factor [PO ₄] = 0.022 M (%)
241-SX-105	67.8	2.03E-01	462	925
241-SX-103	65.6	8.05E-02	183	366
241-A-101	60.0	7.39E-02	168	336
241-SX-102	58.3	8.77E-02	199	398
241-AX-101	52.2	8.07E-02	183	367
241-SX-101	51.7	8.95E-02	203	407
241-C-103	44.4	1.01E-01	229	457
241-S-101	43.3	7.36E-02	167	335

The dilution factors necessary to achieve a 0.044 M phosphate concentration would form a plug at 23 C. Further dilution of the liquid to 0.022 M phosphate would be expected to decrease the temperature at which the stream will plug. Combining the experimental data

resulted in an expression for the gel or plug temperature as a function of the phosphate concentration

$$\text{Temperature} = (112 * [\text{PO}_4]) + 19.35 \quad (\text{EQ 3})$$

A plug temperature of 21.8 C is expected at the 0.022 M phosphate loading. Such temperatures and heat fluxes may be possible in the transfer routes; however, heating and/or insulating the junction boxes would provide actual temperatures that could further narrow the dilutions required.

At waste temperatures less than 43 C the phosphate will be partitioned between the aqueous phase and the sodium phosphate dodecahydrate solid. For these tanks it should be noted that increasing the temperature of the waste would result in dissolution of some fraction of the phosphate solids thereby increasing the phosphate ion concentration in the transfer stream. The data in Figure 12 indicate that raising the waste temperature in these tanks using hot dilution water or steam may lead to transfer problems. Here it is remarked that the interim stabilization program is aimed at reducing the supernatant and interstitial liquid in the tank; however, the dissolution of any phosphate solids will need to be considered during retrieval operations.

The specific tank phosphate concentrations presented in Figure 12 represent the total phosphate loadings in the tanks. Some preliminary ESP calculations were carried out for the compositions from 241-U-107 and 241-S-109 to provide estimates for the solid/aqueous phase partitioning for phosphate. Cation and anion masses were taken from the BBI and were converted into concentrations using the total waste volume in the tank.

The water analyzer module was used to for charge reconciliation according to the method described in an earlier report.²² The stream was then routed to the ESP Process Module where a single separation block was used.

The waste in U-107 contains, according to the BBI, the largest phosphate concentration of all of the remaining single-shell tanks. Initially this concentration is 0.57 M. The equilibrium calculations predicted that at the 24.4 C temperature of the tank the aqueous phase phosphate concentration was 0.049 M. For this tank, therefore, some dilution will be required to transfer the saltwell liquor without forming additional solids in the stream.

On the other hand, the composition for 241-S-109 is predicted to contain a total phosphate concentration of 0.19 M at a temperature of 26.7 C. ESP simulations indicated that the liquid phase concentration for the phosphate in this tank was 4.9×10^{-4} M. Difficulties were encountered in these calculations. The reported water loading in this tank is 9% and ESP calculations would not converge at this low amount. In addition, the pH for this waste was determined to be 9.4. The model predicted the formation of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, a solid that has not yet been investigated. Additional ESP calculations are needed to evaluate the dilution factors necessary for the transfer of saltwell supernatants from the low temperature tanks.

Feed Stability and Prevention of Solids Formation Model

Previous sensitivity study results

Earlier simulations have illustrated the importance of the flow velocity, the solids density and the slurry viscosity.¹⁷ These simulations clearly indicated that accurate properties values are necessary. The effects of solids particle size distribution was seen to be not be critical; however, the size and amount of the heavier particles tended to dominate the model predictions. This is due to the fact that the flow velocity must be able to suspend the largest particles if sedimentation is to be prevented. The initial results of the sensitivity analysis can be summarized as follows:

- Viscosity, density are important to waste transfer so accurate values are needed.

- Target velocity should be towards high end.
- Required pump pressure will depend on velocity and solids density.
- Shape of particle size distribution not very important, but amount of large particles is important.

Operating envelope for reliable waste slurry transfer at Hanford

The main goal of the remaining work is to develop a three dimensional operating surface that describes slurry waste transfers at Hanford for a given (or assumed) PSD and solids volume fraction. The three major axes in the three dimensional space would be the velocity, density and viscosity. The points on the surface are generated by performing simulations (for the given PSD and volume fraction) at different but bounded combinations of velocities, densities and viscosities. The choice of variables on the axes was based on the initial sensitivity analysis in which it was found that the major parameters that can affect a safe waste slurry transfer are composed of characteristics of the waste stream such as density, viscosity, solids volume fraction, and particle size distribution, and on operational parameters such as velocity and turbulence levels, pipeline geometry (recirculation zones elbows etc.), and local environment which effects waste stream parameters.

All of the above are important to determine if a planned transfer can be executed reliably, but the first three parameters are probably the most critical to the transfer and to the site operators since they represent measurable, and therefore controllable quantities.

Development of the operating surface has begun by concentrated on an assessment of the available literature related to Hanford slurry transfers and to the models and correlations currently considered by operations, establishing the limits for the waste parameters listed above, and running additional simulations on a longer section of transfer line.

The literature search was conducted on waste transfer at the site and the Replacement Cross Site Transfer System (RCSTS).²¹⁻²³ The information available on the design of the RCSTS stated that the pipeline is 6.2 miles long with two booster pumps. The channel is a 3.0-inch schedule 40 (304 stainless steel) pipe. The transfer line was designed to attain a maximum pumping pressure of ≤ 230 psig with Reynolds numbers ≥ 20000 . The density and viscosity of the slurry mixture were originally taken as $\rho = 1.0$ kg/l at $\mu = 0.4665$ cP and $\rho = 1.5$ kg/l at $\mu = 30.000$ cP.

The lower bound on the velocity will come from the calculated critical velocity for the largest and heaviest particles in the PSD using available empirical or mathematical correlations. This value will be augmented with a 30 to 50% increase in the velocity to accommodate for pressure losses through the pipeline. Bounds on densities and viscosities will come from the available data above based on the design and analysis documents. Another source could be from ESP simulations for the given waste composition.

The remaining portion of this work will be based on further defining the parameters for the simulations, running the code and interpreting the results. A letter report will be developed and reviewed by site operators. This document will compare the results of the simulations with the predictions of the correlations employed at the site.

The amount of time needed to generate these surfaces will greatly depend on the computer time required to complete each full-scale simulation (represent one point on the surface) and also the solution convergence behavior of the code when performing these simulations. The information available about the RCSTS indicates that the transfer line can be divided into approximately three 2.1 miles long sections. The simulations performed in the sensitivity study required between 1 to 2.5 hours of (CPU) computer time for an 11-meter long section. This should give a rough idea about the CPU time required to perform a simulation for 3.3 km pipeline section. This is also without

counting other problems that the CFD code might encounter because of convergence difficulties due to the huge increase in grid cells required. These issues will be assessed soon after conducting test runs using the new version of the code that has been received. This version incorporates a new program that should help to accelerate solution convergence and minimize computer time. Additional methods for extrapolating pressure drops determined from shorter simulations to longer pipe sections will be investigated.

Project Status

Work on the prevention of solids formation is continuing in FY 02 with emphasis on waste transfers planned for Hanford tank 241-S-112 and for Savannah River Site Tank 37. Additional computational calculations will be performed to further define slurry transfer operating regimes and to assess the assumptions employed in the correlations currently used in establishing operating conditions for Hanford transfers. Additional waste slurry simulations will be conducted to assess the feasibility of the use of CFD flow analysis over the long transfers envisioned at the site.

Conclusions

Flow loop experiments have been reduced to an operating envelope that can be used by Hanford operators to assess the tendency of salt well supernatant waste streams to form a plug during transfer. The available data has been compared to the phosphate concentrations of the wastes in the single-shell tanks that have not yet begun the interim stabilization process. Results contained in the Best Basis Inventory indicate that many of the tanks in the U and S farms contain high phosphate concentrations and are at low temperatures. ESP calculations indicate that the supernatant phase will contain phosphate loadings that can form a plug at these temperatures. Increasing the waste temperature, by, for example, diluting the waste with elevated

temperature water or steam, would tend to increase the supernatant phosphate loading thereby increasing the potential of plug formation.

A framework for completing the CFD flow sensitivity studies is being developed and literature studies related to the RCST have been completed. Additional work is needed to streamline the simulations such that numerical convergence can be attained in a reasonable time period.

Work Planned

Evaluation of the formation of the sodium dodecahydrate in the presence of additional particles of sodium nitrate is in progress. These studies will allow an assessment of the effect of solution structure on the gel formation process.

Further evaluation of the new version of the code is in progress. Familiarity with the multi-grid optimization algorithm is a priority as well as establishing an extrapolation from a small section of pipe to those similar in use at Hanford.

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Evaluation of HEPA Filter Performance

J. A. Etheridge

Introduction

In 2000, the U.S. Department of Energy (DOE) and the Environmental Protection Agency (EPA) signed a Memorandum of Understanding to combine research efforts to the maximum extent possible to resolve important questions of common interest. One of these revolved around the issue of assuring the performance of HEPA filters used in off-gas systems. As a result, this Technical Working Group was chartered to provide methodology to ensure that HEPA filters provided adequate protection throughout their service life. The work proposed here is a direct result of the efforts of the NTW.

One of the major parts of this project is a survey of what has already been done, what is currently being done, and what the priorities are for additional work that needs to be completed. At present there is a lot of confusion and misinformation concerning HEPA filters, filter testing, and filter applications. There appears to be a strong need for a HEPA filter test bed for the purposes of challenging the filter medium as well as for development of instrumentation. We plan to construct a

filter test bed (HEPA Filter Challenge Facility). It will be capable of DOP/PAO testing as well as handling a variety of other challenge agents including water, smoke, heat, and particles from particle generators. It will be instrumented and monitored in much the same way as the combustion test stand and will also be useful for instrument development and CEM testing. Modeling of the results of specific types of failures will also be done along with testing, where practical, to verify that the model is useful. This is important for understanding both DOP testing and online failure of HEPA filters.

One of the major needs related to HEPA filters is the need for a “break through” detector. Testing of the cavity ring down system for possible use as a break through detector is also planned. It is also proposed to acquire an “electrostatic impactor” (ELPI) for use as both a measure of input challenge agents and for measuring after the HEPA filters. If this unit is successful in measuring very low particle concentrations (or low mass loading) it will allow us to test the limits of detection of other particle measuring techniques.

The scope of this project could be amended depending upon the results of the NTW’s review of our Data Quality Objectives and the evolution of the NTW’s HEPA Filter Performance position paper. However, it is believed that the activities described below accurately represent the magnitude of the effort, and the equipment and supplies required for the program.

Work Accomplished

Section 4 of the Quality Assurance Test Plan was completed and circulated to members of the HEPA Technical Work Group. A final draft was prepared after review and comment by the NTW. Summary versions of Section 5, “Failure Mode vs. Minimum Detection Limit Testing” and Section 6, “Source Term Testing”, were also written to add clarity and completeness to the documentation to be reviewed by the ASME. The entire document which included an introduction, Sec-

tion 4, which is the calibration section of the HEPA test plan, along with summary versions of section 5 and 6, which describe the actual testing, were delivered to the ASME Peer Review Committee.

The HEPA Test Plan is scheduled for peer review by the ASME on Oct. 2, 2001 in Boise Idaho. Preparation for formal presentation of the test plan by The DIAL team was completed. The results of the review should be known by mid October.

Dioxin and PCB Studies

C. A. Waggoner and C. B. Winstead

Introduction

Selected congeners of the families of dioxins and furans (D/F) are potentially some of the most carcinogenic compounds known to exist. Recognition of the potential risk to the U.S. population spurred the conduction of a national inventory of D/F sources. A significant outcome of this initiative has been the establishment of a strategy to reduce emissions in a targeted fashion. One of the centerpieces of the D/F reduction strategy is the Maximum Achievable Control Technology (MACT) standard just issued for hazardous waste combustors (HWC). Each of the DOE hazardous or mixed waste incinerators falls subject to this new standard and there are stringent emission levels that will need to be met in the near future.

The 0.2-ng/dsm³-emission standard called for under the HWC-MACT stresses the technical limits of operational control and emissions testing. Uncertainties associated with USEPA reference method stack sampling accuracy and method quantification limits for the 17 D/F congeners that have non-zero toxicity equivalence factors invite

skeptical review of the measurements that will be made by facilities to demonstrate compliance with this new standard.

Of the six needs listed on the DOE EM-Needs web page related to dioxin/furan problems, three (ID-3.2.32, ID-S.1.02, and SR00-1021) recognize the lack of knowledge associated with the specific locus of D/F formation, the distribution of D/F congeners between adsorbed and gaseous phases at temperature, and/or the behavior of these classes of compounds in the sampling train. This lack of knowledge is an impediment to minimizing emissions by process control or design/operation of pollution control devices. Additionally, a much fuller understanding of the phase behavior in off-gases is essential to development of a functional continuous emission monitor or verifying the accuracy of extractive sampling methodologies. Finally, a clearer picture of the gas phase chemistry is the best hope of identifying a dependable analytical surrogate, if one exists.

Intensive research has been undertaken throughout the past two decades to gain a more complete understanding of the mechanism(s) of dioxin/furan formation in combustion processes. The majority of controlled mechanistic studies of D/F formation tend to be carried out using bench top and micro-scale apparatus. A significant body of data has also been accumulated from off-gas samples collected from solid waste incinerators and industrial processes. However, the large number of variables associated with fuel feed and operational history of incinerators makes it difficult to extrapolate from bench to full scale. A series of studies is proposed to take advantage of bench scale results and, in a two-stage manner, extend these investigations to pilot scale.

The primary focus of this effort will be to determine the behavior of D/Fs associated with fly ash particulates in an isothermal off-gas environment for the temperature range of 300 to 800 F. This will include analysis of samples for D/F homologues to determine the

extent of formation, destruction, and dechlorination under test conditions.

All of the results from these investigations will be utilized, along with literature information, in the initial development and evaluation of a hybrid artificial intelligence system (combination neural network-expert system) to project D/F formation, identify areas of needed research, and search for analytical surrogates.

Work Accomplished

Progress has been made over the past three months in the development of the small-scale test stand and the sampling system that will connect it to a near real-time instrument. The test stand has been modified to position a sequence of thermocouples up throughout the full length of the flight tube for mapping temperature profiles and facilitating establishment of the smallest possible delta T for test conditions.

An appropriately scaled particle feeder has been developed for introduction of fly ash into the small-scale test stand. However, problems were encountered when the nitrogen carrier gas flow rate was reduced to acceptable levels (with regard to dilution of off-gas products of incomplete combustion or temperatures). A variety of changes have been made to the feeder to enhance the consistency of feed rate and reduce the volumetric flow rate of the carrier gas. The target flow rate of one liter per minute has not been achieved without clogging, but tubing with a smaller inside diameter has been fitted to the feeder and should produce more favorable results. Additionally, the unit has been permanently fitted with a new gas flow indicator to more accurately monitor the flow rates.

The bottom of the flight tube has been modified to facilitate attachment of either the high loading capacity impactor or the filter assembly that will be employed for removal of particulate matter.

This allows continued use of a GC oven that had been mated to the bottom of the test stand to serve as the isothermal chamber for PM removal.

The initial design of a filter housing that will be placed on the front end of the sampling system proved to be unacceptable due to the length of time required to reach thermal equilibrium. Restek was consulted once again regarding the types of metals that could be coated with Sulfinert. An updated version of the filter assembly has been developed that is physically smaller in size, constructed from a material of lower density, and should reach thermal equilibrium more quickly. This smaller unit has been evaluated for performance for pressure drop across the filter at various flow rates and time required to reach thermal equilibrium.

Work has also continued on refining the trap portion of the sampling system. The original set of Peltier thermoelectric cooling units were fan cooled and proved to have insufficient cooling capacity. Higher capacity water cooled Peltiers have been acquired and cooling jackets fabricated. Preliminary tests have been conducted and results indicate a significantly enhanced heat removing capability.

Work Planned

DIAL will continue to develop its small-scale test stand for D/F research and the evaluation of its isokinetic and isothermal sampling system. During the next three months efforts will be made to make the full length of the flight tube as isothermal as possible. This testing will include the full range of operating temperatures from 250 to 700 F.

Efforts will also be undertaken to enhance the functional status of the sampling system. Data will be collected to evaluate volumetric flow rates, pressure drops, and temperature profiles for each element of the sampling system at a benchmark test stand operating tempera-

ture of 300 F. The search will continue to identify a set of valves necessary to complete the sampling system ensemble and allow testing of the assembled system with regard to its chemical performance.

Efforts will also be directed toward reducing the carrier gas flow rate for the particle feeder to a level that is functional with regard to particle transport and nominal with regard to perturbing the off gas chemistry and temperature profile in the region downstream of particle injection. Data will be collected to evaluate the stability of carrier gas flow rate and PM feed rate.

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Toxic Organic Compound Monitoring Using Cavity Ringdown Spectroscopy

C. B. Winstead

Introduction

Several US DOE science and technology needs are based upon the need for high-sensitivity and robust monitoring devices for various organic species. For example, the following needs are all related to the monitoring of volatile or semi-volatile organic compounds (VOCs or SVOCs) in combustion or thermal treatment systems.

- Continuous Emissions Monitor for Offgas Analysis (ID-2.1.18, Priority 1)
- Develop Thermal Treatment Unit Offgas CEM Monitors (ID-3.2.32, Priority 2)
- Volatile Organic Compound Monitoring and Detection (ORHY-04, Priority 3)

The effort reported here is a continuation and combination of two separate tasks from DIAL's previous cooperative agreement (Task 1.1 *Volatile Organic Compound Monitors Using Diode Lasers* and Task 1.3 *Sensitive Detection of Toxic Chlorinated Compounds*). Together, these projects have demonstrated the first sensitive detection of VOCs such as benzene and chlorobenzene using diode laser CRDS and obtained the first CRDS spectra for dioxin (an SVOC). While the emission of dioxins and furans are important risk and regulatory drivers, significant research will be required prior to full development of a dioxin/furan continuous emission monitor (CEM). Questions such as how dioxin is partitioned in the gas stream between gas and particulate phases must be investigated and appropriate sampling systems developed before truly quantitative analysis can be carried out on-line. In addition, monitoring dioxin precursor or indicator molecules

such as chlorobenzene may prove to be a viable alternative to dioxin monitoring.²⁹ Thus, it is beneficial for the development of VOC or SVOC monitors for thermal applications to be coupled with an overall investigation of formation and monitoring of dioxin. Such instruments likely will have value in research efforts to understand dioxin formation well before reaching a level associated with an industrial CEM, a role that may ultimately prove more important for reducing dioxin emissions than a commercial CEM.

The approach taken here includes continuing the development of advanced CRDS techniques using both ultraviolet pulsed and near-infrared diode lasers for the detection of VOCs and SVOCs at atmospheric or reduced pressures. CRDS is based upon the measurement of the time required for light to decay in a stable optical cavity.³⁰ This light may be injected into the cavity using either pulsed or continuous wave lasers. A small quantity of an absorbing species present in the optical cavity will absorb and thus remove some light from the cavity, reducing the decay time. This change in ringdown time can be directly related to the number density of absorbing atoms or molecules in the cavity. The extreme sensitivity of the CRDS techniques is achieved due to the extremely long effective pathlength (up to several kilometers) for the light recirculating in the cavity to interact with a sample gas.

The efforts described here are focused on improving the sensitivity and selectivity of our previous measurements and participating in collaborative efforts to develop appropriate sampling systems for dioxin species. Slit jet expansion techniques will be incorporated with CRDS to cause narrowing of molecular spectra by decreasing the population in excited vibrational and rotational energy levels.³¹ This narrowing will reduce the spectral overlap between different VOCs or SVOCs, thus enhancing detection selectivity. The slit jet expansion will initially be tested with VOCs prior to a demonstration of the detection of dioxin. The expansion cooled spectra will be directly compared to our other room temperature dioxin data to quan-

tify the change in detection limit due to the expansion. These efforts are designed to be complementary to those underway by EPA researchers who are using resonantly enhanced multiphoton ionization (REMPI) for dioxin detection.³² Continued development of CRDS should ultimately provide a technology complementary to the REMPI system. CRDS sensitivity should not be strongly impacted by increasing chlorination of dioxin molecules, in contrast to expected sensitivity reductions for REMPI.

Finally, small yet ultra sensitive sensor systems could no doubt play a significant role in monitoring and/or process control for a number of remediation activities related to clean-up of volatile organics. For example, a number of subsurface and ground-water remediation efforts could benefit from on-line “process” monitoring for VOCs. These include efforts utilizing soil heating, in-well vapor stripping, passive soil vapor extraction, and other in-situ clean-up technologies where simple, real-time VOC monitoring could be used to indicate or monitor system performance. Low-power sensing technologies for VOC monitoring will be required for long-term monitoring efforts both for atmospheric and subsurface monitors, e.g. for continuous monitoring of subsurface reactive barriers or VOC plumes. Systems have already been demonstrated that utilize underground piping to collect soil gas and transport it to a surface monitoring system.³³ For long-term monitoring, diode-based VOC monitoring systems could significantly simplify the analytical equipment required for monitoring while reducing power consumption, features important for use in remote locations. Our continued development of diode laser CRDS may impact these areas in addition to thermal or combustion system monitoring.

Work Accomplished

Very significant progress was achieved this quarter in improving the reproducibility and accuracy of organic species measurements using the diode laser cavity ringdown system. Although linear cali-

bration curves were obtained reproducibly in previous analyses, the slope of the calibration curve tended to drift from day to day or sometimes even hour to hour. Our initial efforts to discern cause of this behavior centered on minimizing physical changes in the system. However, these results were only minimally successful. Far more successful were efforts to improve the mathematical treatment of our data. The original data processing procedure involved a manual subtraction of a baseline DC voltage always present in the data. Although this procedure resulted in near perfect exponential fits to our ring-down waveforms, it was not accurate enough to allow for correct determination of the ringdown time. When this procedure was replaced by a mathematical procedure that automatically included this baseline voltage as part of the fitting routine, the calibration drift virtually disappeared. We have been re-analyzing our previously obtained data and compiling all results obtained to date in order to better characterize the actual performance of the system.

Two different mathematical procedures were evaluated as part of this effort. One procedure used only selected points on the waveform to determine a value for the offset voltage in the data. Although significant improvement was noted, this method still resulted in occasional deviation from a stable calibration. The most successful procedure was to use a full three-parameter fit to the equation,

$$I = A + Be^{-t/\tau} \quad (\text{EQ 4})$$

where τ is the ringdown time and A is the DC offset voltage. This results in a much higher accuracy determination of the offset voltage than otherwise obtainable. A commercial software package was used to obtain the fit values. In addition to these efforts focused on data analysis, significant system repairs were required after the diffusion pumped failed. The students working on the project successfully rebuilt the pump, and the system is working well again.

Construction of the supersonic jet expansion system for dioxin detection began early in the quarter, although two significant delays

have slowed our progress. The primary vacuum chamber was back ordered, but is scheduled to ship at any time. The mechanical vacuum pump for the system arrived, but was damaged in shipment. Discussions with the freight carrier and pump distributor have resolved this issue, and a new pump should ship shortly. The frame for the system is in place near the laser system and the system is being assembled as needed components arrive. Additional laboratory preparations for this new experiment are underway to provide water and power for the laser system and vacuum system.

Work Planned

As soon as possible, construction of the supersonic jet expansion system for dioxin will begin. As noted above, problems in acquiring needed equipment and supplies has slowed our progress somewhat. We anticipate that these problems have been resolved and that soon we will be able to begin construction and vacuum testing. The resolution of calibration issues with the DL-CRDS system will allow us to move on to evaluating the system for additional volatile organic compounds and initiating plans for coupling to a sampling system.

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G.P. Miller and C.B. Winstead. 2000. cavity ringdown laser absorption

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