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NOVEL MASS SPECTROMETRIC INSTRUMENT FOR GASEOUS AND PARTICULATE CHARACTERIZATION AND MONITORING

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EXECUTIVE SUMMARY

Under contract DE-AC21-92MC29116, SRI International will develop a unique new instrument that will be capable of providing real-time (<1 minute), quantitative, chemical characterization of gaseous and particulate pollutants generated from DOE waste cleanup activities. The instrument will be capable of detecting and identifying volatile organic compounds, polynuclear aromatic hydrocarbons, heavy metals, and transuranic species released during waste cleanup activities. The instrument will be unique in its ability to detect and quantify in real-time these diverse pollutants in both vapor and particulate form.

The instrument to be developed under this program will consist of several major components: (1) an isokinetic sampler capable of operating over a wide range of temperatures (up to 500 K) and flow rates; (2) a high pressure to low pressure transition and sampling region that efficiently separates particles from vapor-phase components for separate, parallel analyses; (3) two small mass spectrometers, one optimized for organic analysis using a unique field ionization source and one optimized for particulate characterization using thermal pyrolysis and electron-impact ionization (EI); and (4) a powerful personal computer for control and data acquisition.

The function of the sampler is to obtain a sufficient and representative quantity of air pollutants from a wide range of waste cleanup activities, both vapor and particulate. In addition, the sampler must deliver the vapors and particles to the detection instrument with minimal material loss. The pressure transition region serves multiple functions: (1) it focuses the particles into a "beam" toward the center of the gas flow by momentum separation, (2) it efficiently separates the particulate beam from the vapor stream, allowing independent chemical analyses of particles and vapors, and (3) it provides the first stage of pressure reduction between the ambient atmosphere and the lower pressure (1-2 Pa) region of an ion trap mass spectrometer.

Chemical analysis of the volatile organic species and the polynuclear aromatic hydrocarbons is typically accomplished by first enriching their concentration using a dimethylsilicone rubber membrane separator and then analyzing their composition with field ionization mass spectrometry (FIMS). FIMS is a soft ionization method that is ideally suited to the chemical characterization of complex mixtures of organic compounds. Also available will be an alternative direct inlet of vapors bypassing the membrane and use of EI, for comparisons with the membrane inlet and field ionization. Use of EI will permit monitoring of various small inorganic molecules as well, such as NO_x and SO_x .

Use of a direct sampling method and differential vacuum pumping allows particulate pollutants to be readily introduced into another ion trap mass spectrometer. Volatilization of particles on a heated surface within the volume of the ion trap followed by the complete and quantitative mass spectrometric analysis of the resulting vapors will yield the detailed information required to monitor waste cleanup activity. Based on conservative estimates of the instrument design and performance parameters, a single 0.1- μm -diameter particle will provide a signal level sufficient for complete analysis. All these operations are under the control of the data acquisition computer.

The overall goal of this effort is to develop and demonstrate an instrument that can provide real-time, part-per-billion detection sensitivity for important pollutant species generated by DOE waste cleanup activities. Initially, the instrument will be developed for targeted use in conjunction with the K-1435 Toxic Substances Control Act (TSCA) incinerator at the Oak Ridge National Laboratory K-25 site. Ultimately, the instrument will be designed to operate in the field at any cleanup site, located close to the stack or process vent, providing the plant operations personnel with real-time information and alarm capabilities. In addition, this instrument will be very broadly applicable for cleanup or sampling, for example, any time contaminated soil is moved or disturbed. Because of the versatility and analytical power of this instrument, commercialization for a wide variety of applications in monitoring and control will be important.

The instrument relies on both commercially available technology, including a simple laser scattering particle detector, an ion trap mass spectrometer and a membrane permeator, and unique technologies developed by our organization in the area of field ionization mass spectrometry, and high-temperature sampling. These technologies are now at a Maturity Level of II. The instrument is projected to be easily transportable with minimal utility requirements, making it ideal for deployment at a wide variety of DOE waste sites. Moreover, the straightforward design and use of proven technologies will result in an instrument of very high reliability and sensitivity that can be ready for actual field testing and use within two to three years.

INTRODUCTION

The goals of the Office of Technology Development as outlined by the director of the Environmental Restoration and Waste Management Program (EM), Leo Duffy, in 1991 appropriations hearings include conducting an aggressive technology development program for waste management, waste minimization, waste treatment, storage and disposal of waste. This will be done through the development of more effective remediation technology to reduce occupational and public exposure. We are developing a method to monitor airborne emissions from the TSCA plant at Oak Ridge which will provide real-time, accurate, and inexpensive data on the emission of hazardous organic and inorganic chemicals in both gaseous and particulate form, and to assist DOE in maintaining its ambitious schedules and overcoming significant scientific limitations of its current monitoring technologies.

In May 1988 under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Oak Ridge National Laboratory (ORNL) established a timetable remedial investigation/feasibility study, and a Federal Facility Agreement is being negotiated with the Environmental Protection Agency and the Tennessee Department of Health and Environment. As a result, work has begun on inactive waste sites at ORNL to excavate and isolate wastes in compliance with current standards. In addition, ORNL must comply with the Resource Conservation and Recovery Act (RCRA), which regulates generation, transportation, treatment, storage, and disposal of hazardous wastes and corrective action of releases to the environment of hazardous wastes from active facilities.

Environmental restoration activities at DOE-ORO sites and facilities, such as K-25 and Y-12, are conducted to meet location, contaminant, and action-specific requirements imposed by statutes and regulations and to implement guidance and agreements. These activities typically follow a phased approach with public involvement throughout the process.

A key responsibility of the Oak Ridge Operations Office is for the environmental remediation and restoration activities at the Oak Ridge, Y-12 and K-25 facilities. Support of both the Department of Energy's and the State of Tennessee's commitment to environmental issues is a vital concern of the Oak Ridge site's workforce and management structure. Through advances in technology, the environmental remediation and restoration efforts may be accomplished at less cost, and with a decreased impact on the surrounding communities.

BACKGROUND

The Oak Ridge K-25 site is located 13 miles west of Oak Ridge. Until the summer of 1985, when the gaseous diffusion process was shut down, the mission of the K-25 site was ^{235}U enrichment of uranium hexafluoride (UF_6) for eventual use as a fuel in nuclear reactors. Typical facilities included the feed system and separate systems for collecting the product and the waste (tails) stream. The purging of contaminants from the product stream required the use of large amounts of alumina and sodium fluoride. A number of compounds were used for the clarification of coolant water, and hexavalent chromium, zinc, and phosphate were used to inhibit corrosion of heat transfer equipment. Support facilities produced solutions that required concentration and recovery with some residual that was discarded and buried. Laboratory sample residues and obsolete chemical reagents, spent chemicals, and contaminated equipment were candidates for discard. Sludges from chemical wastes contain hazardous materials, including chromium, copper, lead, mercury, naphthalene, and zinc. Wastes buried at the K-25 site include low-level radioactive solid waste, mixed chemical waste, and radioactive and nonradioactive classified materials. Uranium was released into the air, surface water, and on-site land disposal.

Waste management activities at the K-25 site are increasing. Low-level radioactive waste from other DOE-Oak Ridge Operations (ORO) sites are now being placed in interim storage facilities in the K-25 site building vaults until final disposition strategy is identified. Also, polychlorinated biphenyl (PCB) wastes began arriving from other DOE-ORO sites in 1987 for future incineration in the new K-1435 Toxic Substances Control Act incinerator.

Making an analogy, it is well established that heavy metals are present in the stack emissions of coal-fired power plants. Considerable research in this area has identified every naturally occurring element in coal fly ash, with concentrations ranging from percents to parts-per-million and below. In the case of coal combustion, these heavy metals are present in the feedstock, whereas in the process stream of a waste cleanup facility, many heavy metals will be present at high concentrations as part of the original waste material. Although a number of the naturally occurring elements are of minor concern, many of the heavy metals, such as mercury, lead, cadmium, arsenic, chromium, and uranium, pose significant health risks to humans. Additionally, the transuranic elements such as plutonium, are of particular concern due to their extreme toxicity as respirable particles. Many other elements, both radioactive and nonradioactive, also pose health and safety risks. Included in this category are particles containing beryllium, iodine, and cesium.

By analogy with the known distribution of heavy metals within airborne particles generated by coal-fired power plants, it is reasonable to conclude that significant levels of heavy metals and hazardous inorganic contamination can be unknowingly discharged from process vent stacks in the particulate form. To maintain a high degree of safety and control over cleanup activities at waste sites containing these materials, a monitoring instrument is required that can provide real-time, quantitative measurements of levels of important elements at any point within the process. Particular attention must be given to effluent discharge to the atmosphere via vents and stacks to prevent any release of hazardous by-products of the cleanup activities.

In addition to the heavy metal and inorganic emissions, a very wide range of VOCs will be produced and emitted from any waste cleanup plants, including PAHs, heterocyclic nitrogen and sulfur species, and polychlorinated biphenyls (PCBs). Many of these VOCs are known or suspected carcinogens whose levels must also be controlled. Unlike the metals and inorganic species, many of the organic compounds found in the gaseous effluent of waste cleanup facilities will include materials not initially present in the waste stream. For example, many PAHs are formed during the incomplete combustion of simple organic wastes. As with metals and inorganics, the organic pollutants can be released in both the vapor and particulate forms. Thus, a versatile real-time instrument for determining VOC levels is required to allow plant operators to monitor and regulate stack emissions of these hazardous species.

Any real-time waste cleanup process monitor should be capable of simultaneously measuring numerous important chemical species, both organic and inorganic, present as vapors and particles. Although very sophisticated monitoring technologies are currently under development that make use of optical, electrochemical, and microsensor methods, none yet offers quantitative chemical characterization of both vapor phase and particulate air pollutants. Moreover, most of these sophisticated sensors are capable of detecting only one or two specific chemical species, thereby requiring that many separate sensors be integrated to perform the necessary monitoring and control functions. Such multisensor systems will often be technologically more complex and less reliable than a single, multifunctional instrument, as well as more costly to develop, manufacture, operate, and maintain.

The most universal analytical technique available for monitoring a broad range of chemical species is mass spectrometry. If mass spectrometry is to be used, however, the sampled materials must be vaporized and ionized before analysis. The ionization method must be carefully chosen to prevent preferential, or nonstatistical, ionization while providing adequate and stable signal levels. Even before the effluent can be ionized, it must be sampled and transported from the stack or process stream to the ionizer. In the case of a waste cleanup plant such as the K-1435 TSCA incinerator at the DOE-Oak Ridge Operations site, the sampled effluent will consist of vapors and

particles. Thus, the development of an appropriate sampler will be a critical aspect of this effort. Most of the heavy metals, for example, will not appear in vapor form, but will be incorporated into particles of varying sizes. Not only must these particles be efficiently sampled, they must also be separated from the vapor component and then completely vaporized to provide the requisite composition information. At the same time, the sampled vapors, including the organic species of interest, must be isolated and efficiently detected. No single *instrumental* technique (FTIR, ICP-AES, ICP-MS, GC, GC-MS, LIF) is capable of simultaneously detecting both organic and inorganic species in vapor and particulate forms. However, a single *instrument* consisting of two closely integrated detectors that share a common sampler can provide this critical analytical capability.

RESULTS AND DISCUSSION

To goals of this research program are to develop, demonstrate, and field test a real-time monitoring instrument capable of providing quantitative chemical information on the vapor and particulate emissions produced during the incineration of toxic waste. The Phase I effort is divided into five main tasks and subtasks as follows:

Task 1: NEPA Documentation

Task 2: Instrument Development

Task 2.1: Sampler Development

Task 2.2: Vapor Instrument Development

Task 2.3: Particulate Instrument Development

Task 3: Instrument Testing

Task 3.1: Single Metal Species Testing

Task 3.2: Multiple Metal Species Testing

Task 4: System Design

Task 5: Project Management

A key element of the Task 2 effort is the design of the particle sampler and its interface with the ion trap. This design requires a knowledge of the spatial distribution of the particles as they traverse the sampler and enter the trap. An experiment was designed to quantitatively measure this spatial distribution using a monodisperse beam of latex particles. The basic concept of the experiment is to direct the particle beam at a target coated with an adhesive layer that would trap the particles for subsequent analysis. By using particles dyed with uv sensitive fluorescent colors, we can easily count the number of particles collected in a given exposure time. Our initial plans to utilize the standard vacuum-compatible grease (Apiezon) proved unworkable since the grease itself exhibited strong uv-induced fluorescence that masked the fluorescence from the latex spheres. Therefore, the first results were obtained by using a commercial adhesive-coated material ("spots-o-glue") designed for mounting SEM samples. The initial experiment with these mounts collected particles at the position of the first skimmer, 0.6 cm beyond the end of the particle delivery tube. After a 10-minute run, a 2-mm diameter fluorescent spot was observed under uv excitation.

Attempts to examine the particle distribution using both optical and electron microscopy proved unsuccessful because of the rough nature of the spots-o-glue surface.

Because of the problems associated with the use of the spots-o-glue, we investigated the use of other vacuum-compatible greases, and found that ordinary silicon grease offered a suitable medium for collecting and viewing particles. After installing and aligning the first skimmer, a silicon grease coated slide was placed at the position of the second skimmer. Following a 28-minute exposure to latex spheres, a weak, 4-5 mm diameter spot was observed. A second run produced a smaller spot (3-mm diameter) as a result of reducing the nozzle to skimmer distance from 0.3 cm to 0.2 cm. Examination of the resulting particle distribution using an optical microscope equipped with uv excitation and fluorescence viewing filters, showed a relatively uniform spread across the spot. An example of the distribution observed through a blue filter is shown in Figure 1. The dark region in the lower left corner shows the sharply defined edge of the

Figure 1. Optical microscope image of 2.7 μm diameter fluorescent latex spheres observed under ultraviolet illumination. The dark region in the lower left corner corresponds to the edge of the distribution.

particle distribution. The full image also exhibited a smeared portion in the upper right corner that is not due to particles, but rather appears (under higher magnification) to be due to the spreading of the fluorescent dye into the silicon grease. It is likely that the particle beam retains some small amount of butanol, the solvent used to suspend the latex spheres for nebulization. Any excess solvent that is not removed in the expansion/desolvation region of the particle generator would reach the silicon grease surface and cause small amounts of the dye to "run". We did observe that when the nozzle was rotated, the smearing of the image also rotated, indicating that the source of the smearing is associated with the nozzle itself, and not the skimmers or their alignment. Further investigation confirmed that the smearing is not due to any asymmetry in the particle beam but rather to the method in which it is generated, hence it is not a problem that will be observed with an actual particle beam sampled from a stack.

Based on our estimate to the particle beam size, we drilled a 2-mm diameter entrance channel through the ion trap mass spectrometer electrodes, and found that there was no discernible loss in performance. We then fabricated a Macor support and a tantalum pyrolysis filament, and mounted this unit onto the ion trap. While observing the normal background mass spectrum produced by the trap, power to the pyrolysis filament was slowly increased. No changes in the background spectra were noted until the filament began to glow a dull red. At that point, the baseline of the mass spectra rose sharply, indicating the presence of many more ions that were not mass resolved. The most obvious source of these ions is electron impact ionization within the ion trap volume induced by the copious number of electrons generated by the hot filament. Since the electrons are emitted from the hot filament continually and are not synchronous with the mass scan, the ions appear to be unresolved and lead to a baseline increase. By applying a bias of +250 Vdc to the filament, the thermal electron emission is suppressed, and the no baseline increase is seen until the filament reaches an approximate temperature of 1000-1100 deg C. At the higher power (15-16 amperes) required to reach this temperature, the areas surrounding the pyrolysis filament are heated, resulting in outgassing of adsorbed water vapor and other species. An improved electrostatic shield separating the filament from the electron multiplier has also been added.

Following the experiment described above using a monodisperse beam of latex particles, a second experiment utilizing mixtures of particles was performed in order to investigate any bias in the sampling associated with particle size. By using particles dyed red (0.5 μm), green (1 μm) and blue (3.7 μm), we can easily distinguish their spatial distribution using the fluorescence microscope. The first tests using the mixed size beam were inconclusive because the ratio of 0.5:1:3.7 μm latex particles was not correct. An excess of red particles obscured the fluorescence, and some agglomeration was apparent indicating that the overall concentration was too high. A new mixture was prepared that corrects both of these problems, and another set of experimental

runs was completed. Using the new mixture, runs were made with nozzle-skimmer distances of 1, 5, and 7 mm, each for 10 and 15 minute duration. A detailed microscopic analysis of the resulting distributions is not yet available, however, a preliminary visual inspection shows that the 1 and 5 mm runs produce well focused spots, while the 7 mm run gave a diffuse spot. Also, the overall particle density now appears to be weaker than desirable for particle counting purposes. Based on these preliminary results, we will repeat the measurements with a more concentrated mixture over a narrower nozzle-skimmer distance range of 2-5 mm.

We have also made considerable progress in overcoming the background problems observed when the pyrolysis filament was heated above 1000-1100 deg C. Several sources of outgassing were identified and corrected, as well as improved electrostatic and thermal shielding between the filament and the detector. With these improvements we can now apply 20-24 amperes to the pyrolysis filament for periods of 20-30 minutes with only slight increases in the background signal level. Using thermocouples on surrounding surfaces, we have found that most of the nearby ion trap components do not heat above 200 deg C under these conditions. Since all sources of outgassing have been removed other than normal water desorption, the most reasonable source for the remaining background signal are thermal ions generated directly on the hot filament. We will eliminate this potential background source through appropriate electrostatic shielding at the entrance to the electron multiplier.

Because of both space constraints and safety considerations, we moved the entire ion trap apparatus to a different laboratory. As part of the move, we also enclosed the particle generation region and provided adequate ducting for the vacuum pump exhaust. These precautions were necessary so that when we begin testing with metal oxides, there will be no emission of respirable particles into the laboratory. We had anticipated that during the move, we would modify the vacuum chamber by adding the ion trap mounting platform in preparation for its installation. However, based on the difficulties that we encountered in aligning the particle beam delivery system with the differential pumping skimmers, it was decided that a more elaborate ion trap mounting scheme was required. The final design was dictated by the need to have complete, external adjustability of the ion trap in two dimensions with respect to the particle beam axis. A simple x-y-z translation stage to mount the ion trap was therefore designed and fabricated. The stage allows accurate positioning of the entrance hole in the trap to maximize the transport of the particle beam. The mounting flange that hold the stage was also modified to include three simple, o-ring sealed, rotary feedthrus to provide the necessary adjustment controls.

While the new mounting assembly was being fabricated, we attempted to align the final skimmer with the particle beam in order to complete the spatial distribution measurements. Although we had successfully used a acoustic alignment procedure with the first skimmer, it

proved unsatisfactory for positioning of the second skimmer. Similarly, attempts to use a simple optical alignment method were also unsatisfactory. As an alternative we are constructing a mechanical alignment jig that can provide the necessary positioning accuracy. Using this jig, we can reproducibly align the final skimmer to within 0.1 mm. With the second skimmer aligned, the final particle distribution measurements were completed prior to installing the ion trap assembly.

Final assembly of the pyrolysis-equipped ion trap on the translation stage is also completed, and the entire trap assembly has been mounted within the vacuum chamber. All of the necessary electronics have also been interfaced with the ion trap and pyrolysis filament so that mass spectra of volatilized test particles can be measured. Initial plans are to use the same latex spheres for testing the ion trap as have been used to measure the spatial distribution of the particle beam.

CONCLUSION

At the completion of the first twelve months of this research effort, overall progress of the effort is approximately on schedule, although priorities on individual tasks has been shifted to better match the available resources and personnel. SRI has allocated the appropriate technical staff to continue work on the critical tasks required to complete the effort on schedule. Weekly staff meetings are attended by all personnel so that intertask communication and cooperation is maximized.

During the fourth quarter of this program, the particulate trajectory studies were concluded, thus allowing for the finalization of both the sampler interface and pyrolysis filament designs. The vacuum test stand used for the trajectory studies was then converted to its primary function of housing both ion traps. Installation of the newly fabricated mounting and alignment system and pyrolysis filament were completed. Installation and testing of the laser light scattering system was deferred until the ion trap mounting was finalized, and will be an important task during the next reporting period. The development of a reliable and reproducible trigger signal is critical to the particulate analysis function. Once this trigger signal is available, appropriate modifications to the ion trap hardware/software will be required to initiate a mass analysis scan that is synchronized with the particle arrival and vaporization. Prior to having a particle trigger signal, we will allow the ion trap to operate in a free-run mode that is not synchronized with the particle arrival. The resulting mass spectra will represent an average of many particles rather than single particle spectra, however, the basic operation of the system will be verified.

In the last few months, we have been contacted by several instrument manufacturers and other potential commercialization partners. These companies expressed interest in becoming involved in the latter stages of our development effort with the intent of commercializing this technology. To date, our discussions have served primarily to acquaint them with our program and DOE's needs, as well as to explore how a future cooperative venture might be structured and supported. As this program moves into the next phase, we would anticipate that DOE could become involved in some of these discussions, as well as provide SRI with some guidance in the transfer of this technology to the private sector.

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