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NOVEL MASS SPECTROMETRIC INSTRUMENT FOR GASEOUS AND PARTICULATE CHARACTERIZATION AND MONITORING

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CONTENTS

EXECUTIVE SUMMARY	1
INTRODUCTION	3
BACKGROUND.....	4
RESULTS AND DISCUSSION.....	7
CONCLUSIONS.....	16

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

The 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

Work was started on tasks 2.1, 2.2, and 2.3 during the month of January, following the project initiation meeting held at METC in December. Task 2.1 has focussed on development of the sample probe and its interface with the ion trap. The design of the inlet to the mass spectrometer is dependent on the particulate concentration anticipated in the stack sample and on the sample processing rate of the ion trap. The air flowrate into the mass spectrometer will also determine the characteristics of the isokinetic sampling probe in the stack of the incinerator.

We have received some information from Dr. William Bostick at ORNL regarding emissions from the K-1425 TSCA Incinerator. This information includes total particulate levels, total hydrocarbons, and some heavy metal emissions from the kiln, and some information on heavy metals in the stack after the ionizing wet scrubber. Table 1 summarizes this information. Based on this information, we estimate that the total particulate emission rate from the stack is about 0.2 mg/l (0.18 mg/l is the regulatory maximum for total particulate). The measured geometric mean diameter of the particulate in the stack is 1.14 μm with a standard deviation of

Table 1 TSCA Incinerator Data

Species	Mass Concentration			
	Kiln	Ref	Stack	Ref
Total particulates	2.0 mg/l	various	0.2 mg/l	calculated assuming 90% removal
Total HCs	100 ppm (vol)	"		
Heavy metals			< 2 mg/l	(1% of total, Bostic)
Arsenic			< 340 ng/l	Shor et al.
Barium			11.8 ng/l	"
Beryllium			0.03 ng/l	"
Cadmium			0.25 ng/l	"
Chromium			20 ng/l	"
Copper			8.4 ng/l	"
Lead			33.3 ng/l	"
Magnesium			57.5 ng/l	"
Manganese			6.4 ng/l	"
Mercury			< 7.6 ng/l	"
Nickel			4.8 ng/l	"
Phosphorus			379 ng/l	"
Selenium			< 342 ng/l	"
Silver			18.0 ng/l	"
Thallium			< 20.6 ng/l	"
Uranium			20.2 ng/l	"
UO ₂	1.5 µg/l	various	Since the scrubber efficiency is not known, the stack levels for these species cannot be estimated at the present time.	
UO ₂ Cl ₂	0.75 µg/l	"		
BeO	0.15 µg/l	"		
PbO	3.0 µg/l	"		
PbCl ₂	0.3 µg/l	"		
Size Distribution				
Geometric Mean Diameter (µm)			1.14	"
U _g (µm)			1.73	"
Mass mean Diameter (µm)			4.82	C. Witham calculation

1.73. Since the size distribution is apparently log-normal, this allows us to compute a mass median diameter of about $4.82\text{ }\mu\text{m}$, and a number concentration (based on mass concentration and log-normal distribution) of approximately $6600\text{ particles/cm}^3$.

The design sample rate of the mass spectrometer is $6\text{ cm}^3/\text{min}$ and the ion trap can respond to a maximum of 20 events/second. (The mass limitation of the ion trap is about 1 ng/sec.) The stack sample will need to be diluted a minimum of 1:33 in order to meet the constraints of the ion trap. A more realistic minimum is 1:100 dilution.

The EPA method 5 particulate sampling train samples at a minimum of $0.014\text{ m}^3/\text{min}$. By using a sample probe as small as 0.32 cm diameter we should be able to achieve isokinetic sampling at a sample rate as low as 3 l/min . This means that the stack sample will require splitting to achieve a representative sample of $6\text{ cm}^3/\text{min}$ for introduction into the mass spectrometer.

The inlet sample splitter/dilutor thus will be a fairly complex design which allows for variable dilution (probably by a factor of 100 to 1000) and for splitting off a sample at a ratio of about 1:2000. We have begun detailed design of this inlet system.

Development of the vapor instrument under task 2.2 is actually broader in scope because it involves adapting the ion trap mass spectrometer to operate in larger, more accessible vacuum system that will be used for both vapor and particulate testing. Based on our extensive calculations of the gas loads, pumping requirements, and resultant operating pressures, we designed and fabricated the main vacuum housings, and completed the remaining design details for component mounting and aligning. All of the optical and vacuum components required to complete the prototype ion trap vacuum housing for tasks 2.2 and 2.3 are now on hand, and the vacuum components have been mounted on a small laboratory cabinet with space for the electronics and pumps, as well as the particle beam sampler and interface. Final assembly of the optical components for the laser light scattering and the ion traps themselves were delayed while the pyrolysis filament tests and particulate trajectory tests (see below) were in progress since these makes use of some of the necessary pumps and other parts.

One important operational aspect of the sampler is the spatial distribution of particulates entering the ion trap. The size of the particulate "beam" will determine the size of the pyrolysis filament, and hence the size of the hole that must be placed in the ion trap electrode. In order to determine this critical parameter, an experiment has been designed to measure the spatial distribution using fluorescent latex particles. These particles have a uniform size, and can easily be visualized by optical excitation. The sampler has been interfaced to a vacuum pump to achieve the 50 Torr operating pressure, and the particle beam impinges on a glass slide coated with vacuum grease. After operation for a fixed length of time with a uniform particle loading (particles/cm^3 in

the sampling chamber), the glass slide is removed and examined. A scanning densitometer will be used to quantitate the spatial distribution. We have also measured the particle flux from the generator (particles/cm³) using 3.7 μ m latex spheres. By combining this information with the carrier gas flow rate, we can estimate the length of time required to deposit a reasonable number of spheres on the target surface. We anticipate that the amount deposited will correspond to much less than a monolayer so that the measured distribution will be due to the actual particle beam distribution and not to redistribution resulting from latex spheres impacting on other latex spheres. In other words, to a high probability, each latex sphere that hits the target surface will strike the vacuum grease coating and stick with unit probability.

Using fluorescent latex spheres, a preliminary test was run. After operation for several minutes (calculated to be sufficient time based on the known particle flux), there was no discernable accumulation of particles downstream of the sampling skimmers. By placing a collection screen near the vacuum pump outlet, it was determined that essentially all of the latex particles were being exhausted through the pump and not being sampled through the nozzle. Minor changes in the sampler design are being made to reduce this split ratio. Once this distribution has been determined for a monodisperse sample, the experiment will be repeated with a mixture of particle sizes to determine if there is a sampling bias as a function of size. The results of these experiments will allow finalization of the pyrolysis filament design.

Testing of pyrolysis filament designs was completed during this quarter. Using an optical pyrometer, we have determined that the tantalum Wood's horn filament can be heated to 1800 degrees Centigrade using 30 amperes of current. Pyrolysis tests have been started, and involve loading the filament with a small amount (a few μ l) of latex beads suspended in water. As the filament is heated in 1 ampere increments, mass spectra are taken of any pyrolyzate produced. The appearance of pyrolysis products is then correlated with the heater current and temperature. Using the latex beads, clear evidence of pyrolysis was seen at very low heater currents (6 amperes). A representative mass spectra is shown in Figure 1. Numerous peaks due to styrene and its fragments are apparent. At that current level, the filament temperature is too low to determine using the optical pyrometer, but is estimated at less than 600 degrees. Subsequent experiments using samples of silver nitrate and silica that require higher temperatures, showed similar results. Figure 2 shows the mass spectra recorded when approximately 3×10^{-9} mol of silver (from AgNO₃) was placed on a tantalum filament and heated with 10 amperes of current. This heating current was previously determined to correspond to a temperature of about 925 deg C, as shown in Table 2.

AP2907 - Latex/Ta filament: 6 A

Figure 1. Mass spectrum of vapors emitted when latex particles are heated on a tantalum filament using 6 amperes of current.

MY1128: AgNO_3 /Ta filament

Figure 2. Mass spectrum of vapors emitted when 3 nanomoles of silver nitrate is heated on a tantalum filament using 10 amperes of current. The approximate filament temperature is 925 deg C.

Table 2. Measured Temperature of Tantalum Pyrolysis Filament
as a Function of Heater Current

Heating Current (A)	Temperature from Optical Pyrometer
10	925
15	1150
20	1350
25	1575
30	1825

Figures 3 and 4 compare the mass spectra recorded with SiO₂ loaded onto the filament at 0 amperes and 30 amperes, respectively. Although the mass assignment for m/z 28 is somewhat ambiguous due to the interference from atmospheric N₂⁺ and CO⁺, comparison with a clean filament heated to the same temperature indicates that the majority of the m/z 28 signal is due to silicon ion fragments produced from vaporized SiO₂.

The final design for the filament will be dictated by several factors: (1) required temperature range and heating rate; (2) particle capture efficiency; (3) physical and electrical compatibility with the ion trap. Assessment of the latter factor will require a combination of computer modeling and actual experimentation with a working ion trap. Therefore, we performed some computer simulations of the effect that various sized holes in the end caps have on the trapping fields. The SIMION calculations indicated that little or no field distortion would result from a 3-4 mm diameter hole placed near the ion exit in the end cap electrode. Since our preliminary design placed the hole in that location, it necessitated moving and shielding the electron multiplier that normally mounts just below the ion exit port. We then made some baseline sensitivity measurements with the ion trap in its normal configuration using both xenon and FC-43 (perfluorotributylamine). Following installation of an electrostatic shield between the electron multiplier and the eventual location of the pyrolysis filament, we repeated the sensitivity measurements and found that moving the multiplier had no measurable effect on the operation of the ion trap.

Although the optimum final diameter for the particle beam entrance channel is not yet known, the position of the channel was established based on the physical constraints of the ion trap geometry. We also determined that the most accurate method of drilling through both end caps is to (1) disassemble the trap, (2) drill through one end cap, (3) reassemble the trap, (4) use a pilot drill through the first hole to located the second hole, (5) disassemble the trap, and (6) drill the

Figure 3. Mass spectrum of background recorded with an unheated tantalum filament loaded with 10 nanomoles of SiO₂.

MY1351: Background spectrum

Figure 4. Mass spectrum of vapors emitted when 10 nanomoles of SiO_2 is heated on a tantalum filament using 30 amperes of current. The approximate filament temperature is 1900 deg C.

second hole. Using this approach, we drilled a 2 mm diameter entrance channel through the ion trap at an 11° angle through the top electrode such that the particle will cross the center of the trap before exiting just to the side of the ion exit apertures. To our knowledge, no one had previously drilled holes of this size or location in both end caps of an ion trap. However, repeating the FC-43 and xenon measurements made earlier, we found no significant degradation in performance as a result of this channel.

CONCLUSION

At the completion of the first nine months of this research effort, overall progress of the effort is 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 tasks 2.1, 2.2, and 2.3. Weekly staff meetings are attended by all personnel so that intertask communication and cooperation is maximized.

During the third quarter of this program, the final designs have been completed for the sampler and its vacuum interface with the ion trap detectors, and fabrication has been started. All of the hardware required to mount both of the ion trap detectors has also been fabricated, and installation in the vacuum test stand will be completed as soon as the particulate trajectory studies are finished. Design, fabrication, and testing of the pyrolysis filament required for particulate analysis will be finalized based on the trajectory results. We have experimentally verified that drilling a 2 mm diameter entrance channel through both end caps of an ion trap has no significant impact on its performance.

During the fourth quarter of this program, the particulate trajectory studies will be concluded, thus allowing for the finalization of both the sampler interface and pyrolysis filament designs. The vacuum test stand used for the trajectory studies will then be converted to its primary function of housing both ion traps. Installation of the newly fabricated prototype sampler and pyrolysis filament will be completed. Installation and testing of the laser light scattering system 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.

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