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SRI International

Quarterly Report • May 1994

NOVEL MASS SPECTROMETRIC INSTRUMENT FOR GASEOUS AND PARTICULATE CHARACTERIZATION AND MONITORING

Covering the period from January 1, 1994 through March 31, 1994

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Contract No. DE-AC-21-92MC29116

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CONTENTS

EXECUTIVE SUMMARY	1
INTRODUCTION.....	3
BACKGROUND.....	4
RESULTS AND DISCUSSION	7
CONCLUSION	15

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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 work force 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 feed stock, 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.

As described in the last quarterly report, we equipped the instrument with a new pumping system, and developed a new alignment procedure. In January, 1994, we began testing the system with the latex particle beam. Initially, we operated the beam for a short period of time with the pyrolysis filament off to accumulate particle on its surface. The filament was then flash heated while observing the ion trap signal. The reason for using this mode of operation rather than looking for single particle events is our lack of ability to externally trigger the ion trap scan. After collecting latex particles for a minute, we could readily observe their characteristic mass spectrum once the pyrolysis filament was heated above their volatilization temperature. Next, we operated the system in real-time, that is, we observed the mass spectra continuously while allowing latex particles to impact upon a heated pyrolysis filament. Although we were not triggering the mass scans in synchrony with the particle arrival, we anticipated that sufficient accidental coincidences would occur to allow us to directly observe particles. In fact, there were occasional mass scans with clear evidence of volatilized latex particles. The frequency of these observed mass scans was relatively low due to the apparently poor efficiency with which we were transporting the particles through the sampling system and into the ion trap. Nonetheless, we obtained clear proof that the basic concept of in-situ pyrolysis and mass spectrometric analysis of externally sampled particles is a viable means of providing a real time stack monitor.

A continuing weakness of this system is the poor particle sampling/transmission efficiency through the various stages of the instrument. Since an efficient and unbiased sampling system is essential to the ultimate success of this approach, we began a systematic check of each stage of our sampling system. These tests include the collection of particles at different locations throughout the system, and a comparison of the absolute number of particles, their spatial distribution as a function of size (using a mixture of 0.5, 1.0, and 2.0 μm particles), and the uniformity of those distributions.

The first test involved collecting particles using an in-line filter just before the nozzle that generates the "beam". Particles were collected for a fixed period of time, then analyzed using an optical microscope equipped with uv illumination. The particles are color coded using uv absorbing dyes to allow each size particle to be individually counted. Particle counting was done

in quadrants to provide some measure of spatial uniformity. The results of that experiment are given in Table I below.

Table I. Spatial Distribution of Latex Particles Collected Before Beam Formation

Quadrant	2.0 μm (blue)	1.0 μm (green)	0.508 μm (red)	2 μm /1 μm
I	9	24	> 40	1 : 2.7
II	13	40	—	1 : 3.1
III	15	44	—	1 : 2.9
IV	18	53	> 80	1 : 2.9

Note that the density of 0.5 μm (red) particles was so high that it was not possible to accurately determine their number. This result does show, however, that starting with a 1:1:1 mixture of particle sizes, a significant degree of bias is present in the nebulization process used to introduce the particles into the sampled gas stream. This bias is not particularly important, however, since it is an artifact of the particle introduction method and not of the particle sampling method. In a real world situation, the particle generation method is fixed by the process being monitored. Nonetheless, these results show several key features; (1) the spatial distribution is reasonably uniform (at least with respect to the two largest sized particles), and (2) the ratio of 2 μm to 1 μm particles is constant across the particle stream.

The next experiment involved collecting particles 0.6 mm downstream of the orifice plate (0.010" diameter orifice). The result of that experiment is shown in Table II.

Table II. Spatial Distribution of Latex Particles Collected After 0.010" Orifice

Run	2.0 μm (blue)	1.0 μm (green)	0.508 μm (red)	2 μm /1 μm /.5 μm
I	175	487	642	1 : 2.8 : 3.7
II	174	496	655	1 : 2.8 : 3.8

Interestingly, the ratio of 2 μm to 1 μm particles remains approximately the same, showing no sampling bias. However, since the number of 0.5 μm particles is clearly much

smaller than that collected before the orifice plate, there appears to be a significant sampling bias against the smallest diameter particles. Despite this bias, the absolute numbers of smaller particles is large owing to their dominance in the original sample stream.

As a result of the changes in the pumping system described previously, we changed the orifice plate from the original 0.010" diameter to 0.005" diameter to reduce the gas loading on the intermediate pumping region. The smaller orifice plate was used during the real time measurements described at the beginning of this report. Hence, we repeated the particle collection experiment with the smaller orifice in place. Those results are given in Table III, and should be compared with the corresponding results in Table II.

Table III. Spatial Distribution of Latex Particles Collected After 0.005" Orifice

Run	2.0 μm (blue)	1.0 μm (green)	0.508 μm (red)	2 μm /1 μm
I	7	112	$\gg 1 \mu\text{m}$	1 : 16
II	3	68	$\gg 1 \mu\text{m}$	1 : 23

It is apparent that both the number of particles traversing the smaller orifice is considerably less than that can be accounted for by geometry, and a very significant sampling bias has been introduced, allowing far fewer of the larger particles to pass into the next vacuum region. A possible cause is discussed below. A final experiment was performed in which particles were collected after the final skimmer. The result of that experiment is presented in Table IV.

Table IV. Spatial Distribution of Latex Particles Collected After Final Skimmer

Run	2.0 μm (blue)	1.0 μm (green)	0.508 μm (red)	2 μm /1 μm
I	26	~300	$> 1 \mu\text{m}$	1 : 12

It appears that little additional sampling bias is introduced by the skimmer, thus we would conclude from these experiments that the main difficulty lies in the beam formation dynamics associated with the first orifice plate. Following these measurements and the real-time experiments described above, we removed the 0.005" orifice and examined it for particle buildup. This examination showed that a significant deposit of particles had formed on the

inside of the orifice channel itself. The orifice plates have a thickness of approximately 0.010", so that the 0.005" diameter orifice actually is a tube with an aspect ratio (length to diameter) of 2:1. Although nozzles with this aspect ratio are routinely used to efficiently generate gaseous molecular beams, this large aspect ratio appears to result in an early expansion *within* the channel, leading to the observed deposit. On the other hand, since the 0.010" diameter orifice plate has an aspect ratio of ~1:1, it does not appear to suffer from the same difficulty. The major drawback to using the larger orifice is the increased gas load experienced by the intermediate vacuum region. Rather than use the larger orifice, it may prove useful to reduce the thickness of the 0.005" orifice until it also has a 1:1 aspect ratio. We will be pursuing this approach, along with additional studies of the sampling bias and methods to improve the absolute sampling efficiency and transport.

Because our preliminary tests showed both a low sampling efficiency as well as a size bias that discriminated against larger particles, we continued to address this primary weakness of the poor particle sampling/transmission efficiency. An experiment was designed to elucidate which of the various stages of the instrument cause the greatest losses. These tests involved the collection of particles at different locations throughout the system, and a comparison of the absolute number of particles, their spatial distribution as a function of size, and the uniformity of those distributions. Particles were collected for a fixed period of time, then analyzed using an optical microscope equipped with uv illumination. The particles are color coded using uv absorbing dyes to allow each size particle to be individually counted (1.01 μm green, 2.0 μm blue, and 2.87 μm red particles were used). The results of these experiments are described below.

The primary test mixture was made by first placing equal weights of each size particle in separate containers with 100 mL of butanol in each. The particle weight was 1% of the total in each sample. Since the density of each latex particle is the same (0.9 g/cm³), the actual mass of each particle size is given by their volume times their density, as shown below.

Particle Size (μm)	Volume (cm^3)	Mass (g)
1.01 μm - green	5.39×10^{-13}	4.85×10^{-13}
2.0 μm - blue	4.19×10^{-12}	3.77×10^{-12}
2.87 μm - red	1.24×10^{-11}	1.12×10^{-11}

The 1:8:23 ratio of these mass values provides the necessary proportions of each size particle to produce a 1:1:1 mixture. The actual mixture is made by combining 2, 16, and 46 drops of each

solution in 100 mL of butanol. The absolute number of green particles, for example, is thus given by:

$$2 \text{ drops} \times \frac{1 \text{ mL}}{20 \text{ drops}} \times \frac{1 \text{ cm}^3}{\text{mL}} \times \frac{0.01 \text{ g}}{\text{particle}} \times \frac{1 \text{ particle}}{4.85 \times 10^{-13} \text{ g}} = 2.1 \times 10^9 \text{ particles}$$

The corresponding particle delivery rate is found from this value and the flow rate,

$$\frac{2.1 \times 10^9 \text{ particles}}{100 \text{ mL butanol}} \times \frac{0.7 \text{ mL}}{\text{min}} = 1.47 \times 10^7 \text{ particles/min}$$

Our first experiments investigated the relationship between the nozzle diameter and the particle generation bias. The original system design used a 0.127 mm diameter orifice, and produced a sample generation bias between the 1 and 2 μm particles of 10-20. Switching to a 0.178 mm diameter orifice reduced this bias to 1.5, as summarized in the table below.

Orifice Size (mm)	1.0 μm (green)/2.0 μm (blue)	1.0 μm (green)/2.87 μm (red)
0.127	10-20:1	--
0.178	1.5:1	3:1

The use of a larger orifice has a significant effect on the particle generation bias, however, at the cost of increased gas loading on the sample introduction portion of the instrument. While the bias for the 2.87 μm particles is higher than for the 2.0 μm particles, it is unknown if the use of a larger orifice had a measurable effect.

Measurements were next made after the skimmer and after the final orifice plate just prior to entering the ion trap mass spectrometer. Those results are given below.

Particle Size (μm)	Average number entering nozzle/min	Average number collected after skimmer	Average number collected after final orifice plate
1.01 μm - green	2.23×10^3	43	31
2.0 μm - blue	1066	25	10
2.87 μm - red	914	13	1

The corresponding efficiency values are:

Particle Size (μm)	Efficiency after skimmer (%)	Efficiency after final orifice plate (%)
1.01 μm - green	1.9	1.4
2.0 μm - blue	2.3	0.9

These results show that although the particle generation process results in only a modest size bias of 3:1.5:1 for 2.87, 2.0, and 1.0 μm diameter particles, a significant bias (31:10:1) is apparent after the final orifice plate. The reasons for this size bias are unknown at the present time. The beam diameter is estimated to be 4 mm at the point where the particle beam reaches the final 1.5 mm diameter orifice. Thus, approximately 37% of the beam should be transmitted into the final vacuum region based solely on geometric considerations assuming perfect alignment.

It is interesting to note that with the present configuration, $> 10^4$ particles of each size are lost in the generation process, the majority are presumably pumped away. Moreover, given the present configuration, the particle arrival rate at the ion trap mass spectrometer is somewhat less than 1 particle/second (42 particles/minute on average).

Because the laser light scattering system that will be required to trigger data acquisition can also be used to optimize the particle beam alignment, we assembled the necessary optical components to implement this aspect of the laboratory prototype system. The light scattering configuration is shown schematically in Figure 1. Initially, we used only the forward scattered channel to observe particles, however, a relatively high background signal (10-100 kHz count rate) prevented us from observing particles. We subsequently reduced the background signal by careful masking of surfaces and the addition of optical baffles along the incident light path. Even with the background reduced by more than one order of magnitude, we did not observe particle induced light scattering. To further reduce the background, we have incorporated the back scattered light signal in a coincidence configuration. By only gating the counting electronics when both channels measure a time coincident signal, we anticipate the background signal rate should drop to near zero. Since the coincidence electronics are best adjusted with actual signals, we have separated the instrument vacuum housing at the point where the laser light crosses the particle beam and attached a separate particle generator/nebulizer that directs a steady stream of particles across the light path. Once the electronics have been adjusted (pulse height threshold and time coincidence window), the instrument will be reassembled and tested with the normal particle beam generation system.

Testing of the membrane interface used to separate the vapor and particulate streams for independent analysis was also initiated during this reporting period. A second ion trap mass spectrometer was used to test the vapor sampling system. The membrane inlet consists of a small disk of dimethylsilicon supported by a high transmission screen. Vapors at atmospheric pressure are drawn across the surface of the membrane by a small diaphragm pump. Organic

Figure 1. Optical and electrical schematic of the laser light scattering configuration.

vapors preferentially permeate through the membrane, thus giving rise to an enhanced concentration on the back (low pressure) side. These vapors are directly introduced into the ion trap volume, where normal mass scans are performed. The sample vapors are generated using a 1-liter exponential dilution flask. A known volume of organic solvent, such as toluene, is injected into the heated flask where it vaporizes and mixes with a preheated nitrogen or argon carrier gas stream. The resulting homogeneous vapor mixture is drawn across the heated membrane inlet. The membrane temperature is maintained at around 100° C to prevent condensation of vapors and to enhance the permeation rate. For a given constant carrier flow rate, the concentration in the input stream at any time is given by the simple exponential decay function,

$$C = C_0 e^{-(t/t_0)} \quad (1)$$

where C_0 is the initial concentration of the organic vapor and t_0 is the measured time constant of the flask (volume/flow rate).

By measuring the ion signal for the vapor of interest as a function of time, it is possible to obtain an absolute sensitivity value for the combined membrane inlet/ion trap system. Using toluene as a test vapor, we have observed sensitivity values in the range of 25-50 ppb.

During the month of March, the Dr. Michael Coggiola, SRI project leader, met with several members of the EM-50 staff at their headquarters in Germantown, MD. Discussions were held with Al Tardiff, Steve Lien, and Caroline Purdy. In addition to updating the DOE staff on the status of this work, they provided several suggestions of other DOE waste management activities that would benefit from the instrument under development. Primary among those areas were the vitrification program and the storage tank characterization work being performed by PNL at Hanford. At the suggestion of Al Tardiff, we have been in contact with Dr. Steve Coulson of PNL to discuss possible collaborative efforts.

CONCLUSION

With the new pumping and alignment arrangement, we have significantly enhanced the particle beam formation process, allowing us to observe for the first time, the mass spectrum of particles that had impinged on the heated pyrolysis filament. As a result of a comprehensive investigation of the particle sampling system, we have determined that some size bias is evident in both the generation and sampling portions of the instrument. Of more importance, however, we have quantitatively established that the overall sampling efficiency is very low. The reasons for the low sampling efficiency are not yet understood, although they clearly are related to the need to transport particles into a reduced pressure region. The normal particle sampling system operates at or near atmospheric pressure, and hence the majority of designs and related experience upon which we based our preliminary system, is not completely applicable. As a result, we have had to devote a greater share of our time and resources to the design and testing of the particle sampling/inlet system than originally anticipated. While this has caused a slippage in the program schedule, necessitating a lengthening of the Phase I effort, we have encountered no insurmountable difficulties that would render the concept unworkable. On the contrary, we have demonstrated real-time particulate detection, albeit with an as yet low efficiency.

The laser light scattering system that will be required to provide the triggering information has been assembled and tested. The first tests showed that a coincidence approach will be needed to overcome the large background count rates associated with the use of only the forward or backward scattered light signals. Once the coincidence electronics have been adjusted to register only true forward/backward coincident signals, the light scattering system can be used to not only trigger the detection scan, but also to assist with the critical particle beam alignment procedure.

Although most of our effort has been expended on behalf of the particulate detection aspects of the instrument, we have also begun work on the corresponding vapor detection capability. Through these efforts, organic vapor detection limits in the low parts per billion range have been demonstrated. These results were obtained using a simple dimethylsilicone membrane inlet with minimal optimization. In addition to optimizing this membrane inlet, we will also begin interfacing the SRI-developed volcano field ionization source to the ion trap. This combination will then be used to demonstrate the detection and identification of complex mixtures of organic vapors.

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