IMPROVED METHODS FOR PAH COMBUSTION SOURCE SAMPLING

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1.0 ABSTRACT

Benzo(a)pyrene (BaP) and other polycyclic aromatic hydrocarbons (PAH) are classified as toxic air contaminants in California under the classification polycyclic organic matter (POM). More accurate sample collection, extraction and analysis methods are needed in order to make assessments of stationary combustion sources that emit PAH.

To this end, a new Reduced Artifact Dilution Sampler (RADS) has been developed which consists of an isothermal/isokinetic stack probe, an automated dilution system and a reduced artifact sampling system for the collection of both vapor phase and particulate PAH. A primary advantage of dilution volume sampling over the current Modified Method 5 (MM5) system, is that chemical reactions between the condensing constituents occur under physical and chemical conditions similar to those at the stack exit. The RADS system is designed to collect PAH from the dilution system without significant artifact formation from acidic combustion gases or volatility loses from the particulate matter collected on the filter. The reduced artifact sampling train includes an acid gas denuder, and a Teflon filter followed by a series of polyurethane foam (PUF) plugs.

A prototype Photoelectric Aerosol Sensor (PAS) was investigated for use as a real-time PAH aerosol monitor. The PAS is designed to be small enough for field usage and is equipped with a stack sampling probe with an internal dilution system. Although the instrument is known to respond to the PAH aerosol concentration in some combustion sources, a performance evaluation was necessary for the mixture of emissions present in different stationary incinerator sources.

A simplified well controlled combustion source for polycyclic aromatic hydrocarbon (PAH) aerosols was constructed in the

laboratory to evaluate the performance of a prototype Photoelectric Aerosol Sensor (PAS) and to develop the new Reduced Artifact Dilution Sampler (RADS). Fresh combustion generated aerosol provided a realistic particulate matrix to evaluate the collection efficiency of the reduced artifact sampling train, and the recovery efficiency of the associated PAH analytical method. Monitoring the laboratory combustion source with the real-time PAS provided a convenient method for determining the stability, and the relative level of PAH aerosol produced under different combustor operating conditions.

New more efficient analytical methods, including Pulsed Ultrasonic Extraction (PUE) of the combustion particles and Simple Compression Extraction (SCE) of the PUF plugs, were developed to improve the speed and accuracy of PAH determinations by gas chromatography / mass spectroscopy (GC/MS). A new simplified single step clean-up technique was also used to remove interfering substances co-extracted from the sample matrix. The new PAH extraction and single step clean-up techniques, as well as, supercritical fluid extraction (SFE) were evaluated using standard reference materials of urban particulate matter and diesel emissions.

In field trials, the RADS system successfully maintained isokinetic and isothermal sampling conditions for diesel exhaust stack velocities over 11 m/s (36 ft/s) at standard temperature and pressure conditions (STPC, 20°C and 760 mmHg) and temperatures exceeding 200°C (392°F). A dilution factor of 35:1 was automatically maintained to reach near ambient temperature conditions for sample collection. Dilution to ambient air temperature conditions was a necessary operating condition, so that chemical reactions between condensing constituents occur under physical and chemical conditions similar to those at the stack exit. For this field study, the RADS was utilized in the simplified high volume dilution sampler configuration without particle size segregation. Intended

for routine monitoring applications, this configuration was the most suitable choice for the intermethod comparison with MM5.

Utilizing the PAS as a source survey tool, the Combustion Emissions Research Laboratory (CERL) at EHLB successfully determined that the optimum time for sampling was relatively short, on the order of 10 minutes, due to the high levels of PAH containing particulate matter in the generator exhaust. The analytical results of the side-by-side comparison indicate that the CERL method using the RADS reported substantially higher PAH levels than found with Method #429 using the MM5 sampler. For example, over six times more BaP was determined by the CERL method than reported for Method #429. A correlation between enhanced PAH collection by the RADS and the carbon number of the individual PAH species suggests that sampling artifacts which act to reduce the PAH collected in MM5 occur in both the XAD-2 resin bed and on the heated filter.

Together the PAS and RADS provide a promising integrated approach to determining the PAH emissions from stationary combustion sources. Although the PAS cannot be considered to be specific for individual PAH compounds, calibration with combustion aerosol has demonstrated the usefulness of the PAS as a total PAH aerosol monitor. This is useful for field screening source emissions to determine the necessity of collecting samples for chemical analysis using the RADS system. Depending on the level of PAH present, the RADS can be used as a high volume dilution sampler without particle size segregation or as a low volume reduced artifact sampler for respirable PAH. In either configuration, the PAS can be used as a RADS loading monitor to ensure sufficient sample is collected for the level of detailed chemical analysis required at a particular source.

2.0 SUMMARY AND CONCLUSIONS

2.1 Program Summary

Airborne polycyclic aromatic hydrocarbon (PAH) emissions from sources represent an important component of the toxic substances released into the environment. Benzo(a)pyrene (BaP) and other PAH are considered as toxic air contaminants in California. The EPA Modified Method 5 (MM5) sampling procedure currently used to monitor 16 priority PAH compounds from combustion sources is known to produce an underestimate of the PAH originally present due to sampling artifacts. A more comprehensive assessment of the nature of these toxic emissions, especially from combustion sources, has been hampered by the absence of suitable techniques for field screening emission sources, and for the collection of source samples for more detailed laboratory chemical analysis.

In this research, existing advanced technologies where combined and modified in innovative ways to develop monitoring and analytical tools to replace PAH source monitoring methods recognized to be inefficient and/or inaccurate. Promising new monitoring technologies have been identified by maintaining a close association with other international scientists, and through the development of laboratory reference techniques for evaluating and improving the performance of candidate PAH monitoring instrumentation.

In order to make accurate assessments of combustion sources that emit PAH, the original project objective centered on the development of a Reduced Artifact Dilution Sampling (RADS) system to provide a more representative measurement of the chemical and physical form in which PAH are emitted into the environment. During the course of the research, the scope was expanded to include the development of more advanced PAH analysis techniques, the evaluation of the Photoelectric Aerosol Sensor (PAS) as a real-time PAH monitor, and the design of a laboratory PAH combustion source

to evaluate sampling techniques.

Side-by-side comparisons of a new integrated method for the measurement of combustion source PAH, and the Modified Method 5 (MM5) sampling technique, currently used as a part of the California Air Resources Board (CARB) PAH Method #429, were conducted on a 500 kilowatt diesel generator stack. The intent was to perform a source test under field sampling conditions which would provide a realistic setting for a preliminary comparison of the two methods. The new integrated source method consisted of the Reduced Artifact Dilution Sampling (RADS) system and the prototype real-time Photoelectric Aerosol Sensor (PAS). The real-time photoelectric aerosol sensor (PAS) was tested as a potential source survey tool and loading monitor for the sampling of PAH combustion aerosol. The RADS was tested as a new sample collection technology, designed to provide a more representative measurement of the chemical and physical form in which air toxics are emitted from combustion sources.

2.2 Technical Developments

Several new PAH monitoring techniques and reference methods have been developed in the CERL. Some of these developments were specifically included in the original CARB contract and others have evolved naturally as the product of a flexible mission driven association with CARB Research Division.

(1) Micro-capillary Combustor (MCC) is a compact laboratory scale reference source for combustion derived vapor and particle phase PAH. Development of the MCC was not specifically included in the original CARB grant but evolved from the desire to model the PAH fingerprint of different combustion sources in the laboratory. In this way, the MCC has allowed the evaluation of the sensitivity of PAH detectors to changes in chemical fingerprint for a realistic matrix of combustion products.

(2) Photoelectric Aerosol Sensor (PAS) is a real-time solid state device for measuring the concentration of PAH on the surface of combustion aerosols by detecting the amount of charge produced by ultra-violet illumination. The sensor represents a good example of an international cooperative effort between governmental research organizations, which developed the basic sensor operating principle and private industry, which engineered a standardized prototype instrument for field testing. Although the PAS is not specific for individual PAH compounds, calibration with combustion aerosol from the MCC has demonstrated the usefulness of the PAS as a total PAH monitor for field screening source emissions. The technology of the PAS could also be applied to monitor other classes of organic compounds as well as trace metals.

(3) Photoelectric Vapor Sensor (PVS) uses a technology similar to the PAS but is designed to monitor total vapor phase PAH in combustion source emissions in conjunction with the PAS. The first prototype of the PVS was constructed in the laboratory to demonstrate the feasibility of the device, but evaluation of the instrument was beyond the scope of the current project.

(4) High Temperature Velocity Sensor (HTVS) is a real-time solid state mass flow probe to be used to determine the volumetric emission rate of combustion products from a source at temperatures up to 260°C (500°F). When used in conjunction with the PAS, real-time emission rates for PAH from sources may be measured directly.

(5) Reduced Artifact Dilution Sampler (RADS) developed in the CERL laboratory is a new emission source sample collection technology designed to provide a more representative measurement of the chemical and physical form in which air toxics are emitted from combustion sources. The RADS utilizes the HTVS technology coupled with microprocessor driven controllers to automatically maintain both isokinetic sampling and a preselected dilution ratio for the

sampled combustion products. Dilution of the sampled combustion products before collection allows condensation driven chemical and physical transformations to occur under similar conditions to those which occur on emission to the environment. Acid gas removal denuder technology, previously developed for atmospheric sampling (Wall et al., 1988), is utilized to minimize chemical artifact formation in the collected sample.

(6) Pulsed Ultra-sonic Extraction (PUE) of PAH from filter collected combustion particles and Simple Compression Extraction (SCE) of PAH vapor collected on polyurethane foam (PUF) are new technologies developed to simplify and improve sample preparation for GC/MS analysis. Supercritical fluid extraction (SFE) technology is another promising alternative; however, initial results suggest that the extraction yield for PAH is matrix dependent.

(7) PC-486DX computer based work and instrument control station to revitalize the Finnigan 4500 GC/MS underwent final testing at CERL. The operational software for data acquisition and data reduction was designed in a cooperative effort with Sysnet Inc., a custom scientific work station company. Suggestions to Sysnet during each phase of the system design allowed the incorporation of features such as flexible user defined libraries for target compound analysis, and a convenient menu driven windowing environment.

2.3 Field Testing

In these first field trials, the RADS system successfully maintained isokinetic and isothermal sampling conditions for diesel exhaust stack velocities over 11 m/s (36 f/s) at standard temperature and pressure conditions (STPC, 20°C and 760 mmHg) and temperatures exceeding 200°C (392°F). A dilution factor of 35:1 was automatically maintained to reach near ambient temperature conditions for sample collection. Dilution to ambient air temperature conditions was a necessary operating condition, so that

chemical reactions between condensing constituents occur under physical and chemical conditions similar to those at the stack exit. For this field study, the RADS was utilized in the simplified high volume dilution sampler configuration without particle size segregation. Intended for routine monitoring applications, this configuration was the most suitable choice for the intermethod comparison with MM5.

Utilizing the PAS as a source survey tool, CERL successfully determined that the optimum time for sampling was on the order of 10 minutes due to the high levels of PAH containing particulate matter in the generator exhaust. Forced to base sampling time estimates on previous experience with other diesel generator emission sources, CARB elected to sample for unnecessarily long periods. Accordingly, MM5 samples had to be diluted by up to a factor of 100 before analysis. The response of the real-time PAS for diesel combustion derived PAH aerosol was sufficiently consistent with calibrations conducted on other combustion source types to be useful as a loading monitor during sample collection.

The CERL pulsed ultrasonic extraction and a micro-column clean-up procedure proved to be a simplified and rapid analytical approach for the determination of PAH in the complex diesel combustion particle matrix. Simple Compression Extraction (SCE) of the PUF plugs and the same simplified single step clean-up technique provided efficient extraction of vapor phase PAH without interference form other substances co-extracted from the collection matrix.

The analytical results of the side-by-side comparison indicate that the CERL method using the RADS reported substantially higher PAH levels than found with Method #429 using the MM5 sampler. For example, over six times more BaP was determined by the CERL method than reported for Method #429. The CERL method levels were higher by up to a factor of 10 for all 16 priority PAH compounds except

naphthalene. Naphthalene is expected to be primarily in the vapor phase and to deposit in the polyurethane (PUF) foam plugs behind the Teflon filter in the RADS. Unlike the filter, the PUF plugs were not changed during a sampling run and may have suffered break through for the highest vapor pressure PAH, naphthalene.

A correlation between enhanced PAH collection by the RADS and the carbon number of the individual PAH species suggests that sampling artifacts, which act to reduce the PAH collected in MM5, occur in both the XAD-2 resin bed and on the heated filter. These results are consistent with the artifact arguments made in the original research proposal which prompted the development of the RADS system.

Together the PAS and RADS provide a promising integrated approach to determining the PAH emissions from stationary combustion sources. Although the PAS cannot be considered to be specific for individual PAH compounds, calibration with combustion aerosol has demonstrated the usefulness of the PAS as a total PAH aerosol monitor. Field screening of emission sources using the real-time PAH sensor provides an efficient approach to identifying sources with sufficiently high levels to warrant a more extensive chemical characterization. Depending on the level of PAH present, the RADS can be used as a high volume dilution sampler without particle size segregation or as a low volume reduced artifact sampler for respirable PAH. In either configuration, the PAS can be used as a RADS loading monitor to ensure sufficient sample is collected for the level of detailed chemical analysis required at a particular source. With a proper source specific calibration, the PAH sensor could also be utilized as continuous source monitor for regulatory purposes.

3.0 RECOMMENDATIONS

The mission of this project has been to identify, develop and evaluate improved methods to measure PAH emissions from stationary combustion sources. Initial evaluation of these proposed PAH methods was conducted in the laboratory under well controlled conditions designed to simulate a limited set of source emission compositions and sampling environments. Field testing has demonstrated the operational feasibility and advanced performance of the new CERL integrated method for PAH source sampling. The results of limited side-by-side sampling with MM5 have illustrated the importance of the artifact reducing features of the RADS. These features were designed to provide a more representative measurement of the PAH emitted from the stack exit.

Further research is required to assess the new methods performance under a more extensive range of emission source conditions. Accordingly, the following specific recommendations are made for future laboratory research and source sampling trials to validate the proposed PAH methods for routine use in the field:

(1) Extend the intermethod comparison of the new integrated CERL method and the conventional CARB Method #429 to other large scale stationary source types. Conduct these side-by-side field trials in conjunction with the CARB routine source sampling program to gain experience operating in different stack environments. Explore the Photoelectric Aerosol Sensor (PAS) response and the Reduced Artifact Dilution Sampler (RADS) performance for the PAH source signatures representative of different common combustion processes.

(2) Employ the side-by-side field trial results to expand the PAS universal calibration curve to include a greater variety of distinctive source signature types. Attempt to use the Micro-capillary Combustor (MCC) to match these source

signatures and to conduct a more extensive span calibration of the PAS response. Evaluate the performance of the PAS as a source survey tool and loading monitor for general use in the field.

(3) Expand research on the Micro-capillary Combustor (MCC) as a candidate PAH calibration source by exploring techniques for controlling particle size, particle/gas phase PAH partition, nitro-PAH generation, and the PAH emissions fingerprint to model large scale combustion sources. Utilize knowledge of the micro-capillary combustor (MCC) operational modes to investigate sampling artifact formation for a variety of different chemical and physical emission fingerprints using stable ^{13}C labeled PAH. Continue development of the real-time Photoelectric Vapor Sensor (PVS) for use with the PAS.

(4) Utilize the combustion samples collected as a part of the PAS/RADS evaluation to further refine the newly proposed PAH analytical methods, including Pulsed Ultrasonic Extraction (PUE), micro-column clean-up and Simple Compression Extraction (SCE). Also explore promising methods to utilize supercritical fluid technology to combine sample extraction, clean-up fractionation and on column injection into a single step. Explore full scan GC/MS techniques to elucidate the large differences in PAH collection efficiency between the RADS and MM5 based on known chemical artifacts.

(5) Field test the low volume Reduced Artifact Sampler (RAS) attachment to the RADS including an acid gas denuder and particle size segregation. Develop and investigate the performance of a proto-type vapor phase PAH denuder in conjunction with the RAS to accurately determine the partition between vapor and particle phase PAH. Explore the use of inertial impactors to provide detailed PAH species-specific

particle size distributions to investigate the combustion aerosol formation history.

(6) Explore the use of bioassay analysis in conjunction with the current CERL sampling, extraction, and chemical analysis techniques to determine the mutagenic activity of different PAH fractions. Utilize bio-directed chemical analysis to investigate the PAH fractions which account for most of the mutagenicity for source samples collected with the RADS.

4.0 INTRODUCTION

4.1 Background

Benzo(a)pyrene (BaP) is considered as a toxic air contaminant (TAC) under the provisions of AB 1807 and AB 2728. Other polycyclic aromatic hydrocarbons (PAH) or polycyclic organic matter (POM) are currently being evaluated for consideration based their short term potencies relative to BaP. The CARB is required to develop an assessment of those combustion sources that emit polycyclic aromatic hydrocarbons (PAH), specifically benzo(a)pyrene (BaP). Polycyclic aromatic hydrocarbons (PAH), and other semi-volatile organic species are emitted into the atmosphere primarily from stationary combustion source as the result of incomplete combustion. These compounds are emitted from incinerators used to burn hazardous commercial waste and municipal refuse. The complex and heterogeneous nature.of the waste used as incinerator fuels can promote the production of these toxic compounds. The potential in California for a large increase in the number of private municipal and commercial incinerators burning heterogeneous waste to produce energy, demonstrates the need to develop more accurate techniques for sampling these toxic compounds emitted into the atmosphere. The need for more accurate source monitoring techniques is expected to increase, due to new toxics legislation (e.g. AB 2588, Air Toxics Hot Spots Information and Assessment Act) and the requirements for the site selection and permitting of new incinerator facilities.

The current sampling procedure for monitoring the sixteen criteria PAH compounds from combustion sources, as prescribed in CARB Method #429, utilizes EPA Modified Method 5 (MM5) as shown in Figure 4-1. MM5 is recognized to be an inadequate sampling method for PAH due to artifacts produced by irreversible chemical reactions. In Modified Method 5, combustion products sampled from the stack are passed through a heated filter at 120°C to collect particles and the vapor phase components are collected by a resin trap at atmospheric

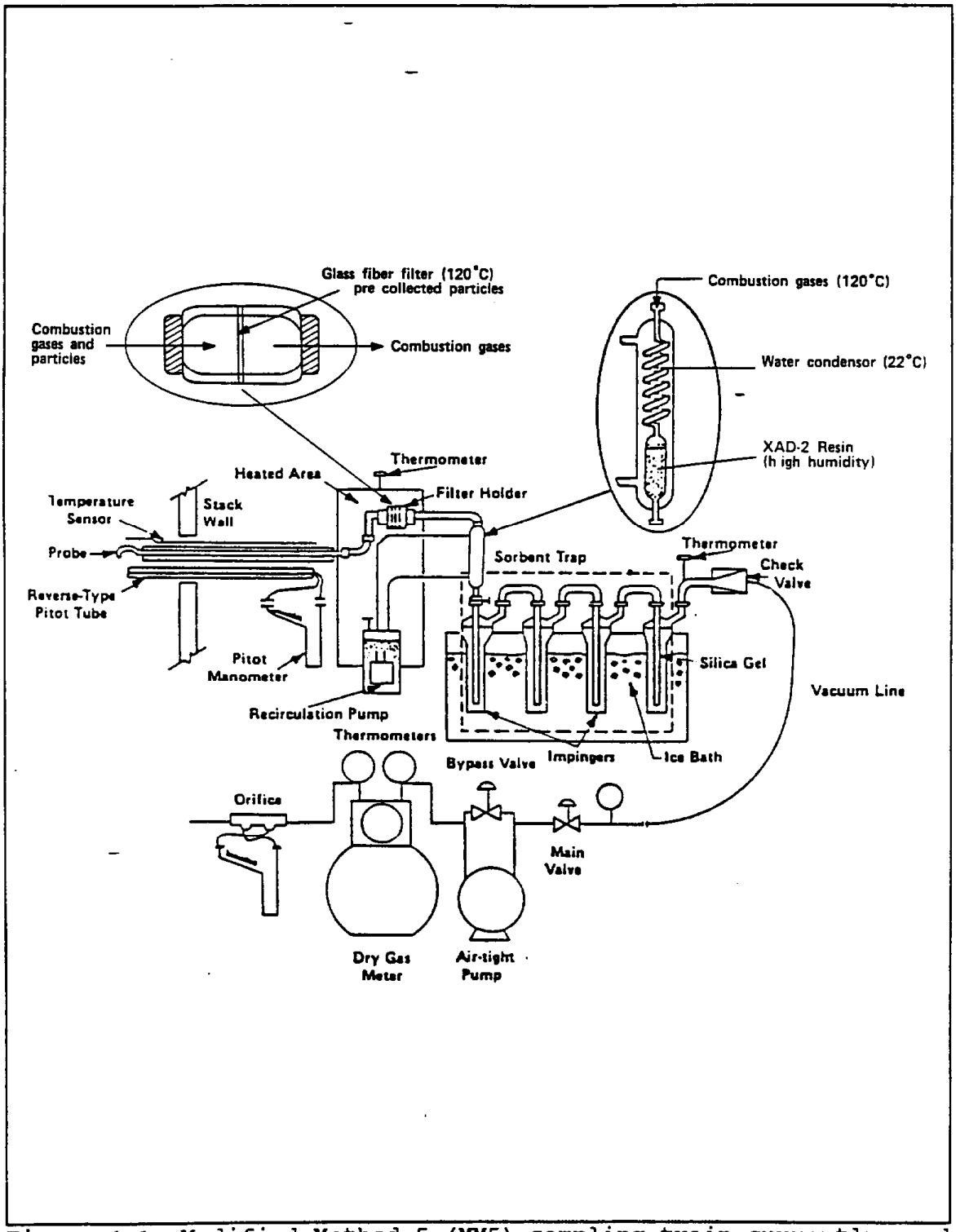


Figure 4-1. Modified Method 5 (MM5) sampling train currently used to sample PAH from stationary combustion sources.

temperature (22°C) placed downstream of the particulate filter. Hot stack gases (including HNO_3 and HCl) have been found to react with both particle phase PAH compounds collected on the filter and gas phase PAH compounds collected in the resin adsorbent downstream of the filter. Gas phase organic compounds can also react irreversibly with precollected particles and the glass fiber filter matrix. Artifact-forming reactions can be expected to be significantly promoted by the high temperature at which particles are collected and the high humidity under which the gas phase components are collected from the undiluted stack gas. Artifacts known to occur under the artificial environment created by the sampling conditions of MM5 are summarized in Table 4-1. The effect of these chemical artifacts is to produce an underestimate of the amount of criteria PAH pollutants present. In some cases the chemical derivatives formed (e.g. nitro-PAH compounds) are significantly more toxic than the parent PAH compound initially present. CARB has acknowledged that such artifacts can occur in the Method #429 sampling train and constituents a negative interference in the method (CARB Method #429, 1995).

The atmospheric fate and potential adverse health effects are determined by the form in which these toxic organic materials are emitted after the initial atmospheric dilution at the stack exit. The current sampling method (EPA Modified Method 5) is designed to determine the total concentration (particles and gas phase combined) of PAH present in the hot combustion products in the stack, before the cooling and dilution which occurs on emission to the atmosphere. Although particles and gases are collected separately, the partition between particle and gas phase cannot be expected to reflect the partition that exists either in the stack or after emission into the atmosphere. This is due to the large differences which exist between the conditions in the stack, at the stack exit and in the MM5 sampling train.

Table 4-1. Potential Chemical Artifacts in Source Sampling with Modified Method 5.

PAH Phase	Artifact Former	Mechanism	Investigator(s)
High Temperature Filtration (gas-solid phase reactions)			
Particulate	Reactive gases (HNO_3, HCl...)	Derivative formation (*nitro – PAH*)	Gorse et al (1983)
Vapor	Fly ash particles	Chemical conversion Irreversible adsorption	Korfmacher et al (1981) Lee, Peters (1980)
Vapor	Filter matrix (*glass/quartz*)	Chemical conversion	Griest et al (1980)
Resin Vapor Adsorbent (high humidity, aqueous reactions)			
Resin bound	Aqueous inorganics (HNO_3, HCl...)	Derivative formation (*nitro – PAH*)	Johnson et al (1982)
Condensed	Condensed organics	Chemical conversion (*catalyzed*)	Johnson et al (1982)
No PAH	Aqueous inorganics (HNO_3, HCl...)	Chemical reaction (*with resin*)	Lochmuller et al (1980)

One improved sampling approach, as first recognized by both California Air Resources Board (Draft Method #429, 1988) and the US Environmental Protection Agency (Johnson, 1982), may include dilution of the combustion products to inhibit chemical artifacts, but in a manner that reflects the actual conditions of emission into the ambient atmosphere. A comparison of the physical conditions which the particles are exposed to under MM5 and dilution volume sampling is shown schematically in Figure 4-2.

4.2 Approach

In MM5, the extracted stack combustion products are not diluted but undergo cooling from the stack gas temperature (typically 250°C) to the particulate filter temperature (120°C) during transport in the sampling inlet (Figure 4-2, Panel 1). Under these conditions, nucleation of new PAH containing particles, and condensation of PAH vapors on pre-existing combustion particles as well as the inlet walls would be expected. After subsequent collection on the filter, these particles are constantly exposed to reactive gases which pass through the filter matrix throughout the sampling period.

In dilution volume sampling, the sampling conditions are designed to reflect those at the stack exit to the atmosphere (Figure 4-2, Panel 2). The undiluted combustion products are maintained at the stack temperature in the sampling inlet until emission into the dilution tunnel where the temperature, particulate, and vapor levels decrease rapidly with the addition of large volumes of dilution air. In contrast to MM5, condensation of PAH vapors, reactive gases and water occur together on the surface of airborne combustion particles at near ambient temperature. Chemical reactions between the condensing constituents occur under physical and chemical conditions similar to those at the stack exit rather than under the artificial environment of MM5.

PAH compounds are expected to occur in both the gas and particle phase, after emission from a stack under atmospheric conditions,

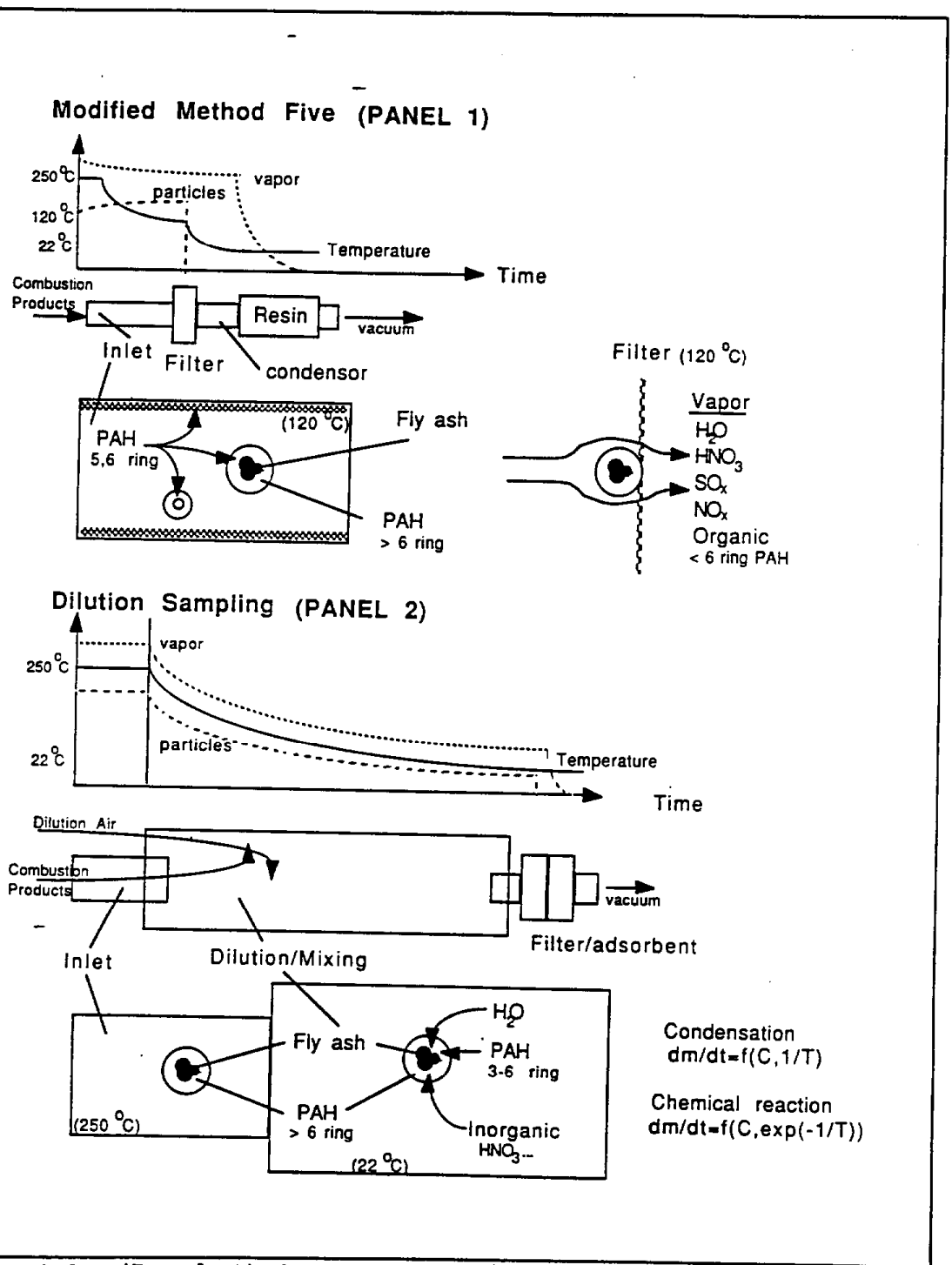


Figure 4-2. (Panel 1) A representation of transformations which occur under artificial environment of Modified Method Five Sampling. (Panel 2) A similar representation of dilution source sampling for comparison.

with the ratio of gas to particle phase increasing with temperature and decreasing with molecular weight within a homologous series. This ratio is based on atmospheric sampling using a filter to collect particle phase components followed by an adsorbent to collect gas phase components (Yamasaki et al., 1982). However, these experimental results are subject to sampling artifacts, since volatile loss of these compounds from the collected particulate matter would cause an overestimate of the gas phase contribution (Coutant et al., 1988). A similar sampling artifact also occurs with the current Modified Method 5 sampling system. Source sampling techniques designed to reduce sampling artifacts are required which determine the partition of the compounds between the gas and particle phase exiting the stack under ambient conditions.

Currently, the most feasible approach to the artifact problems inherent in MM5 is to develop a new dilution volume sampling system designed specifically for stationary combustion source sampling. Dilution systems were first used extensively to reduce artifacts in the sampling of automobile exhaust, but the early automotive dilution tunnels lacked the portability required to sample stationary sources (Carpenter, 1978; Foster et al., 1972). Although compact dilution tunnels have been developed for engine exhaust sampling (Gnuschke et al., 1988), field portability has not been a primary design feature. More portable dilution systems have been developed which are designed to sample non-volatile organic compounds from stack emissions. These samplers can employ the particle collection devices, including the Air and Industrial Hygiene Laboratory (AIHL) cyclone (John and Reischl, 1980) and the dichotomous sampler, originally developed for atmospheric monitoring (Hildeman et al., 1988). Recently, more sophisticated atmospheric sampling methods have been developed to determine the gas particle partition of semi-volatile inorganic compounds, such as nitrate (Wall et al., 1988; John et al., 1988), without significant artifacts. Similar methods can be applied to sampling PAH from combustion sources after dilution of the stack gases.

Despite recent advances, the currently available dilution sampling systems do not incorporate all the necessary design features to sample PAH and other semi-volatile organics in a manner which is representative of the physical or chemical form in which these compounds are emitted into the atmosphere. The design criteria for the development of an improved stationary source sampling system, as well as the sampler features required to meet these criteria, are listed in Table 4-2.

Table 4-2. Dilution Sampling System Design Criteria.

Design Criteria	Design Feature
Simulate Atmospheric Dilution	Highly adjustable dilution factor Cooled to ambient temperature Well mixed system (length and *Re*)
Minimize Sample Contamination	Non-outgasing surface materials Easily cleaned surface materials Temperature resistant materials
Model Gas/Particle Interaction (*nucleation and condensation*)	Well controlled mixing Sufficient residence time
Minimize Particle and Vapor Loss	Large diameter tunnel (*small surface/volume*) Optimize flowrates to prevent deposition
Minimize Artifacts in Sample Collection	Remove acid gases Collect organic vapors separately Teflon filter Filter back-up adsorbent

5.0 REDUCED ARTIFACT DILUTION SAMPLER

5.1 Design Overview

A schematic diagram of the Reduced Artifact Dilution Sampling (RADS) system, which consists of (1) a dilution sampling system and (2) a reduced artifact PAH sampler, is shown in Figure 5-1. The dilution volume system incorporates a heated stack probe for isokinetic/isothermal sampling of the combustion products, and a dilution tunnel in which the combustion products are rapidly mixed with large volumes of clean dilution air. The reduced artifact PAH collection system is comprised of a residence chamber, in which the diluted combustion products are aged to allow phase partition to go to completion, and up to four low volume sampling trains which collect the PAH particle and vapor phase components from the residence chamber without significant artifacts. Depending on the level of PAH present, the RADS can be used as a high volume dilution sampler without particle size segregation or as a low volume reduced artifact sampler for respirable PAH.

The RADS system is designed to be highly portable and occupies a space less than 46 cm (18 in) in diameter and 1.8 m (6 ft) in height. Major components including the dilution tunnel and residence time chamber are constructed from thin wall polyvinyl chloride (PVC) pipe for durability and are lined with a removable polytetrafluoroethylene (PTFE) Teflon adhesive film. The Teflon lining provides an inert surface for the interior of the sampler which may be solvent washed to recover PAH after sampling or replaced when severely contaminated. This design also reduces the system weight to less than 23 kg (50 lbs.), with two sections of 11.5 kg each, and avoids the corrosion problems from attack by acidic gases (i.e. HCl), inherent in previous designs which employ thick wall stainless steel.

5.2 Isothermal Stack Probe

An improved probe design was also developed for the RADS to allow

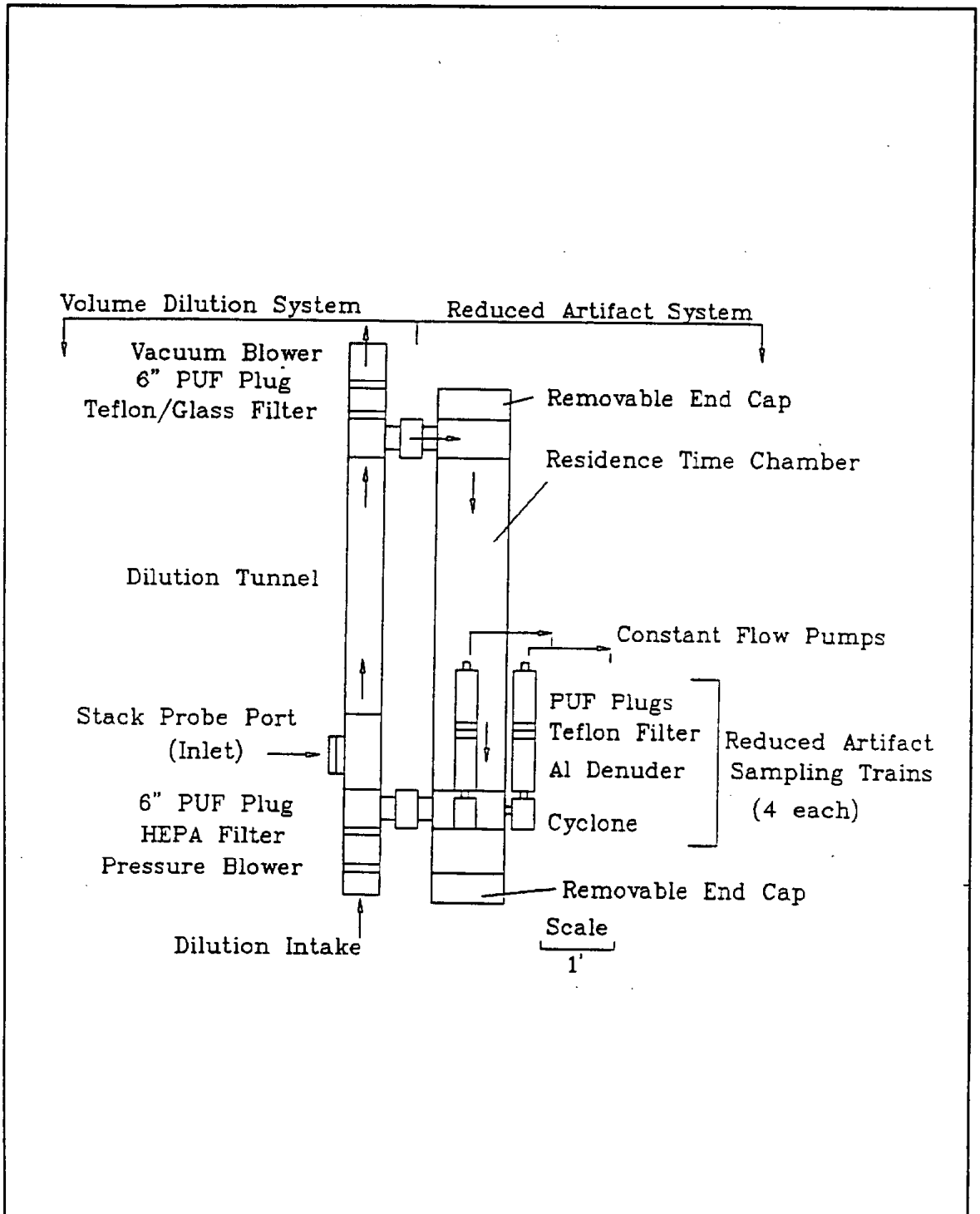


Figure 5-1. Major components of the Reduced Artifact Dilution Sampler (RADS) including the Volume Dilution System (VDS) and the Reduced Artifact Sampler (RAS).

true isothermal stack sampling, to reduce particle losses in the probe nozzle, and to facilitate cleaning the interior of the probe after sampling. The redesigned probe shown in Figure 5-2 utilizes three individually controlled heating zones each with an Platinum Resistance Thermometer (Pt-RTD) temperature sensor which is continuously compared with the stack Pt-RTD mounted on the end of the probe. Unlike the single heat zone design of the MM5 probe, the triple zone design allows the probe interior to be maintained at the stack temperature even during radial traverse sampling. Previously, radial traverse sampling with a single zone probe caused uneven heating due to the changes in the proportion of probe length inserted into the stack. To allow free movement of the probe during positioning in the stack, the probe is connected to the dilution tunnel with a flexible heated hose which is also maintained at stack temperature.

In the new design, a simplified probe nozzle with a single 90° bend and a 5.1 cm (2 in) radius replaces a much sharper 1.3 cm (0.5 in) radius triple bend "button-hook" style nozzle in order to reduce particle losses. Also the probe inner diameter has been increased from 0.95 cm (0.375 in) to 1.9 cm (0.75 in) and incorporates a one piece removable thin-wall Teflon tube as a liner to facilitate cleaning after sampling. PTFE Teflon tubing was employed to achieve a temperature rating in access of 260°C (500°F). The modular design of the probe allows repairs to be accomplished in the field.

Flow through the probe is monitored with a small solid state High Temperature Velocity Sensor (HTVS) mounted in the nozzle which blocks less than 8% of the flow cross-section. The free stream stack velocity is continuously measured by an identical sensor mounted along side the probe nozzle inlet. Isokinetic sampling from the stack is automatically maintained by matching the sampling velocity in the inlet of the probe with the free-stream velocity in the stack. The sampling velocity in the probe is adjusted by

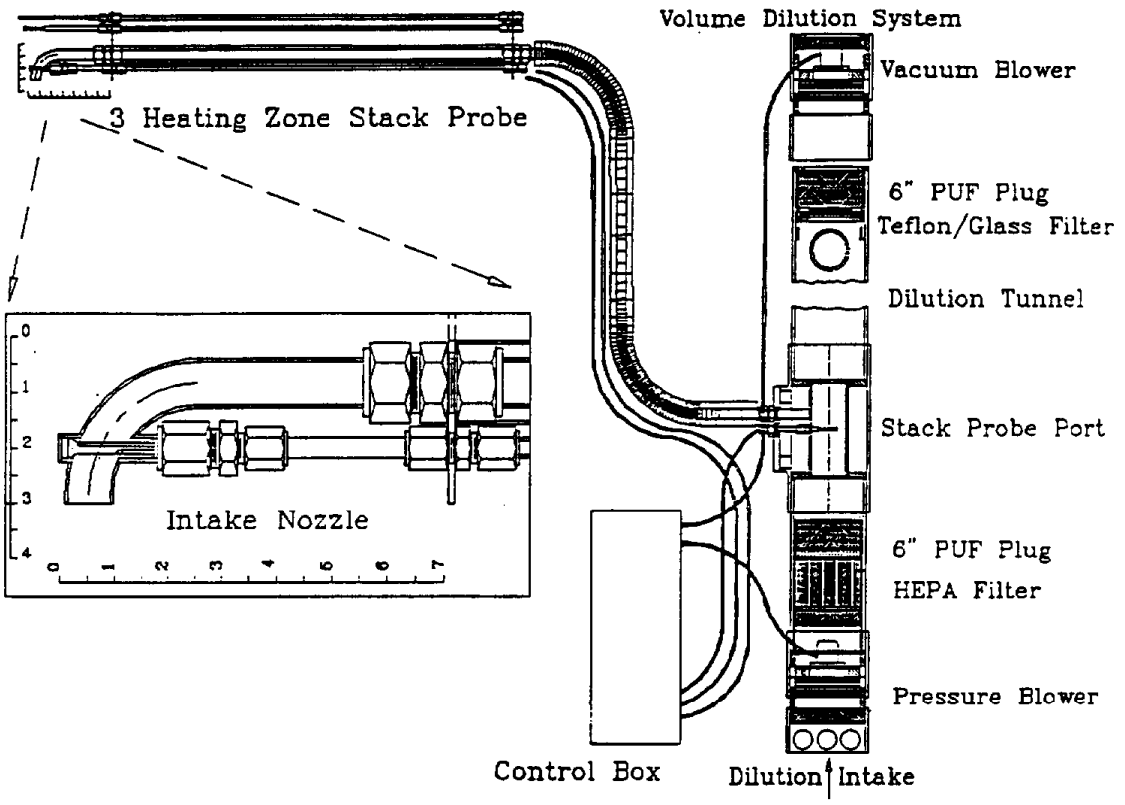


Figure 5-2. The Volume Dilution System (VDS) sampler portion of the RADS system showing the redesigned probe and the internal structure of the dilution system.

controlling the relative speeds of the blowers in the dilution sampling system as discussed in the next section.

5.3 Dilution Sampling System

The cut-away diagram of Figure 5-2 shows the internal structure of the dilution sampling system design. A high volume pressure blower housed in the base of the dilution tunnel supplies dilution air which is forced through a thin 2.5 cm (1 in) x 15 cm (6 in) diameter polyurethane foam (PUF) prefilter to remove coarse particles, a HEPA™ filter to remove > 99.97% of the remaining particles, and a thick PUF plug 15 cm (6 in) x 15 cm (6 in) in diameter to remove semi-volatile organic vapors including PAH. The rate at which the combustion products are introduced into the dilution air is controlled by adjusting the flowrate of a vacuum blower housed in the top of the dilution tunnel.

The difference between a larger air volume exhausted from the dilution tunnel with the vacuum blower and a smaller air volume supplied to the dilution tunnel from the pressure blower, determines the flowrate of the combustion products drawn into the dilution tunnel through the stack probe. The two High Temperature Velocity Sensors (HTVS), one mounted in the probe nozzle and the other in the stack free stream are monitored by the microprocessor based control system depicted in Figure 5-3. The control system continuously matches the probe inlet sampling velocity to the stack free stream velocity by automatically adjusting the speed of a high volume vacuum blower mounted on the exit of the dilution tunnel. Using this control technique, the inlet sampling velocity of the stack probe can be continuously matched with the stack free stream velocity to maintain isokinetic sampling.

The velocity of the clean dilution air entering the 15 cm (6 in) diameter dilution tunnel through a reduced 7.6 cm (3 in) diameter mixing section is monitored by a third High Temperature Velocity

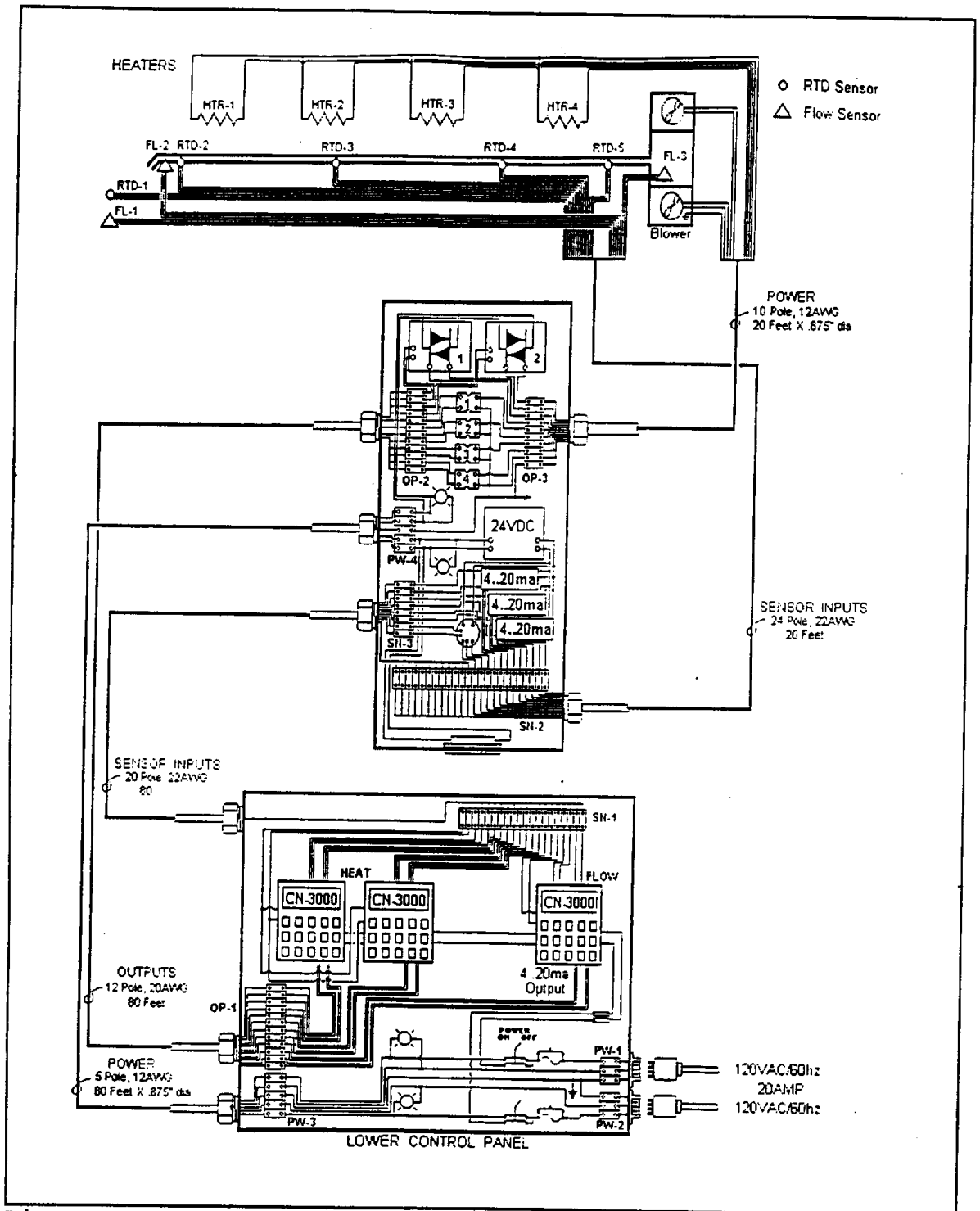


Figure 5-3. The micro-processor based control system used to maintain isothermal and isokinetic stack sampling at a selected dilution ratio.

Sensor (HTVS). The sensor is located just upstream of the port through which the combustion products from the probe are introduced. The dilution factor is calculated from the ratio of the dilution air velocity and the free stream stack velocity sampled by the probe nozzle, after corrections are made for the differences in flow cross-section for the two velocity sensors.

The sampler control system contains three microprocessor based dual loop controllers with full software programming and graphics display capability. Two of the controllers are utilized to automatically maintain the three heat zones of the probe and the flexible heated hose connection to the dilution tunnel at stack temperature. The third dual loop controller serves two functions: (1) to automatically maintain isokinetic sampling from the stack and (2) to automatically maintain the sampler dilution factor selected by the operator at the initiation of sampling. A custom real-time data logging system is built into the controllers to continuously monitor, record, and graphically display the performance of the RADS system during sampling runs.

In addition to the multiple low volume samples collected by the Reduced Artifact Sampler (RAS), the Volume Dilution System (VDS) can be used to collect a high volume sample. This is accomplished with a removable filter pack which precedes the vacuum blower on the outlet of the dilution tunnel. A Teflon coated glass fiber filter 13 cm (5 in) in diameter is used to collect the combustion particles and a large PUF plug 15 cm (6 in) x 15 cm (6 in) in diameter collects semi-volatile organic vapors before the excess dilution air is vented to the atmosphere.

5.4 Reduced Artifact Sampler

In the Reduced Artifact Sampler (RAS) system, a fixed portion, from 2 L/s (4 CFM) to 2.5 L/s (5 CFM), of the diluted combustion products are sampled from the dilution tunnel and pass through a residence time chamber. This allows additional time to establish

chemical and physical equilibrium before the combustion products are collected by four separate reduced artifact PAH sampling trains connected to base of the chamber. Using four separate trains sampling in parallel from the same dilution sampler, allows the flexibility of combining the extracts from several trains. Sufficient sample can be obtained in this way to allow accurate PAH chemical analysis. Otherwise the PAH collected by each train can be analyzed separately to estimate the uncertainty of the measurement. In future, a single high flowrate sampling train could be designed to replace the four separate sampling trains, and be sized to fit inside the base of the residence time chamber.

The reduced artifact sampling trains shown in Figure 5-4 are designed to operate at 30 L/min and consist of previously tested air sampling components including: an AIHL cyclone to remove non-respirable particles (<2.5 μm diameter), an aluminum denuder to remove acidic gases (Wall et al., 1988) followed by a Teflon filter to collect the respirable combustion particles, and a PUF plug to collect vapor phase PAH. Combined extracts of the filter and PUF backup provide a measure of the total PAH present.

The purpose of the cyclone developed at AIHL (John and Reischl, 1980) is to remove coarse particles in order to prevent deposition of these particles in the diffusion denuder. In the denuder, acidic gases are collected by diffusion to the anodized aluminum surfaces of a long annular cavity, without significant deposition of the fine particles (<2.1 μm diameter). Fine particles are collected on an inert Teflon filter directly downstream of the denuder. The acid gas denuders have an active adsorption surface of black anodized aluminum and have been shown to remove more than 90% of the nitric acid gas sampled (Wall, et al., 1988). A high efficiency denuder is necessary to remove acidic gases which can react with PAH compounds previously collected on the filter and backup sorbent producing chemical artifacts.

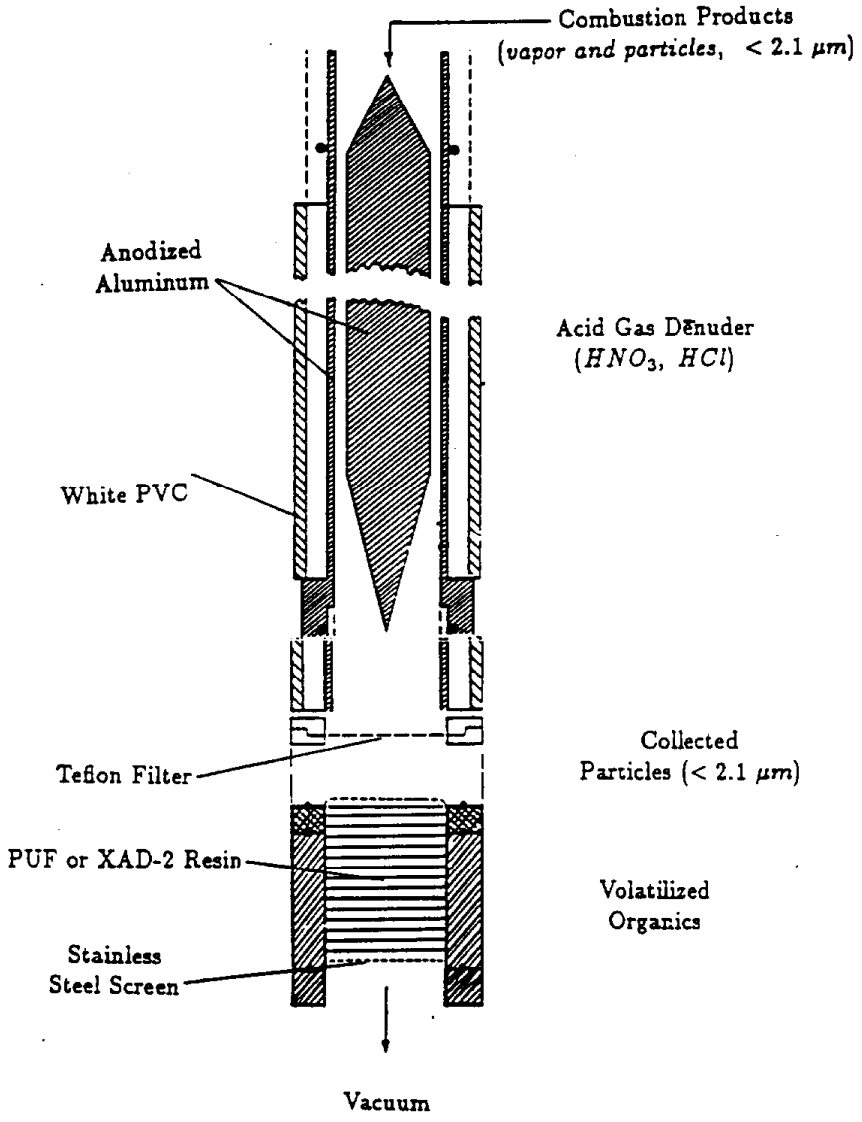


Figure 5-4. Reduced Artifact Sampler (RAS) trains used to collect vapor and particle phase PAH after aging in the residence time chamber.

The 30 L/min flowrate required by each of the four sampling trains is provided by two dual-channel constant-flow pump systems developed in our laboratory. These pumps are designed to operate unattended and maintain a constant flowrate for pressure drops up to 330 mm (13 in) Hg.

6.0 REAL-TIME MONITOR

6.1 Description

A real-time PAH aerosol monitor manufactured by Gossen of Germany was received for evaluation from the local U.S. representative (EcoChem, Inc.). The Photoelectric Aerosol Sensor (PAS) is designed to be small enough for field usage and is equipped with a stack sampling probe with an internal dilution system. The instrument utilizes the principle of photoionization to measure the PAH adsorbed on the surface of combustion particles. A flow scheme and the primary components of the instrument are shown in Figure 6-1.

Combustion products entering the heated stack probe are diluted with clean filtered air monitored with a mass flowmeter to allow accurate dilution ratios up to 100:1. To remove residual charge from the combustion generated particles and gases, the sample stream passes through an electrostatic precipitator before entering the ionization chamber. The ionization chamber consists of a low pressure mercury UV lamp (λ>180 nm) and a quartz irradiation tube aligned in the focal axis of an elliptically grooved aluminum block as shown in Figure 6-2 (after Niessner, 1986). The instrument operates by ionizing the PAH adsorbed on particle surfaces with UV light and measuring the resulting electric charge as the particles are collected on a filter housed in a Faraday cage. A sensitive electrometer (10^{-15}amp) continuously records the current necessary to neutralize the charge on the particles, which has been demonstrated to be a linear function of the aerosol PAH concentration for some combustion sources (Zajc et al.,1990).

For field use, the PAS is housed in a self-contained case and can sample stacks continuously at temperatures up to 500°C (932°F). The instrument flowrate is automatically maintained at 8 L/min and the mass flow sensor design allows the selection of a series of preset dilution factors up to 100:1. With the dilution capability, the PAS

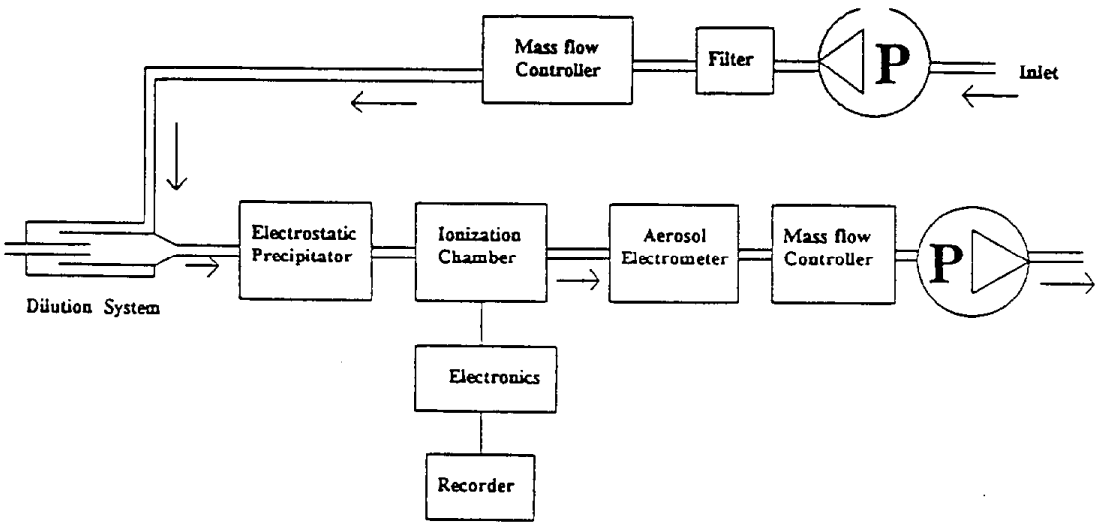


Figure 6-1. Flow diagram of the Photoelectric Aerosol Sensor (PAS) indicating the major system components.

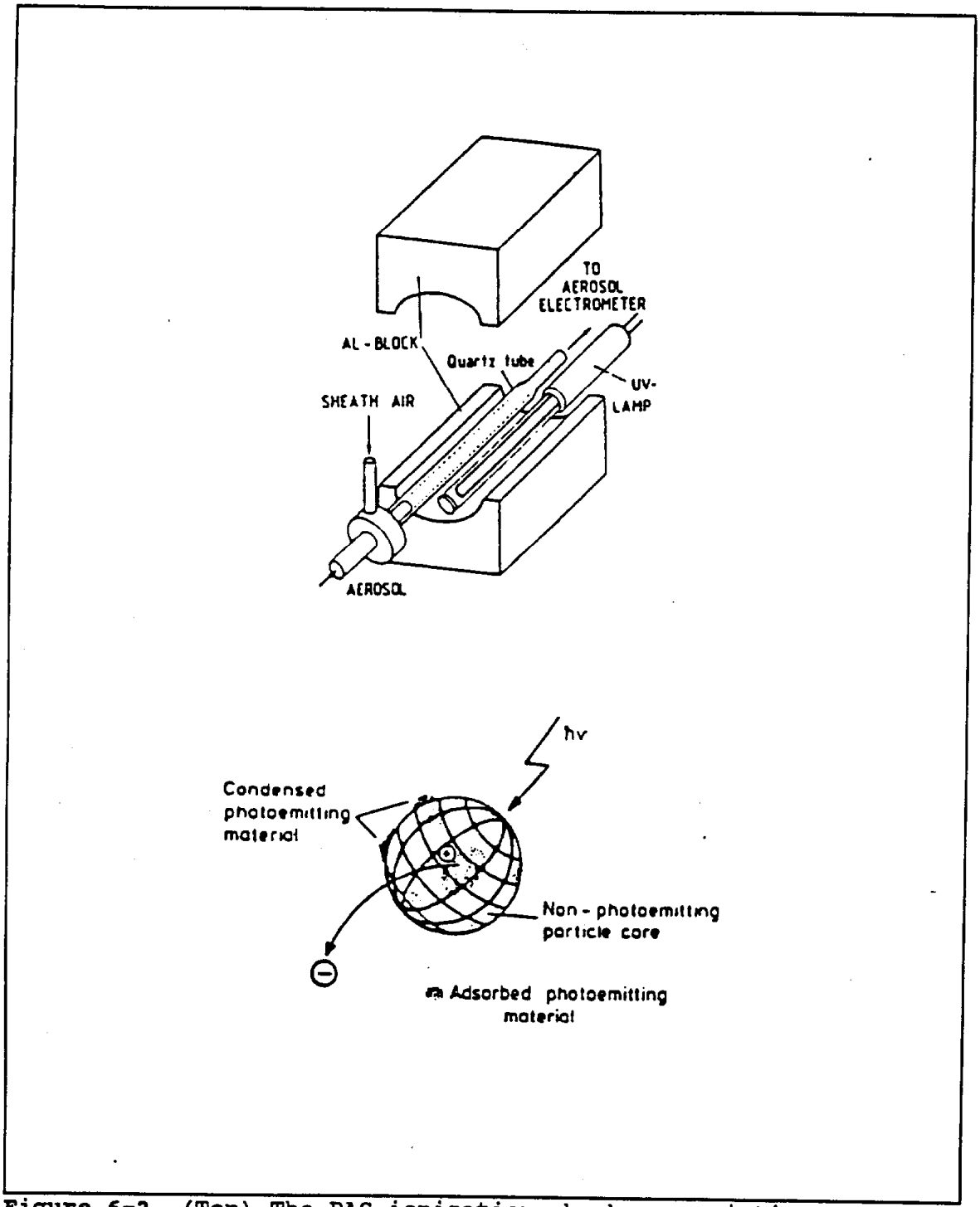


Figure 6-2. (Top) The PAS ionization chamber consisting of a low-pressure UV lamp and a quartz irradiation tube with sheath air ducted aerosol flow. (Bottom) The principle of photoemission charging for ultrafine combustion aerosols.

concentration range is from 1 ng/m^3 to 50 μg/m^3 measured as total particle phase PAH.

6.2 Function

Since photoionization is a surface technique, the performance of the analyzer depends on the composition and surface properties of the sampled aerosols. In general, the combustion of organic materials produces ultrafine (< 1 μm diameter) particles with less than a monolayer of PAH adsorbed on the surface as depicted in Figure 6-2(Bottom). Since PAH compounds adsorbed on carbon particles are more readily photoionized and ultrafine particles are efficient photoemitters, the PAS is very sensitive to combustion generated PAH aerosol. Operating the PAS mercury lamp to yield only emission wavelengths greater than 180 nm, produces ionization of adsorbed PAH while avoiding the ionization of vapor phase PAH.

The instrument has been shown to be the most sensitive to BaP in diesel exhaust (Niessner, 1990), but the device must be evaluated for the different mixture of emissions present in stationary incinerator sources. Since the instrument cannot measure the concentration of individual PAH species, the value of the PAS would be as a source survey tool, and as a loading monitor during the collection of integrated filter samples for laboratory analysis. A linear relation between the PAS signal and CO concentration (as an indicator of incomplete combustion) has been observed by Burtscher et al. (1988). Initial qualitative tests by CERL with a kerosene flame suggest that the PAS signal increases (more PAH on the surface of the combustion particles) as the combustion occurs under more fuel rich conditions. A more complete evaluation required the development of a laboratory scale PAH calibration source.

7.0 PAH CALIBRATION SOURCE

7.1 Requirements

The development of new monitoring methods requires a well controlled combustion source with well characterized particle and vapor phase PAH components. Previously PAH methods development studies have been conducted using artificial aerosol/vapor systems generated in the laboratory without combustion or using a specific type of full size industrial or research combustion system.

Artificial laboratory generated PAH aerosol/vapor systems are useful in exploring specific questions concerning PAH monitoring performance; however, they lack the complexity of the chemical and physical transformations which occur in the combustion process. Full size industrial and research combustors offer the advantage of a "real-world" combustion source, but they are expensive to operate and usually offer a limited set of fuels and operating conditions for generating PAH products.

The Micro-capillary Combustor (MCC) is a compact laboratory scale reference source for combustion derived vapor and particle phase PAH. Development of the MCC was not specifically included in the original CARB Interagency Agreement but evolved from the desire to model the PAH fingerprint of different combustion sources in the laboratory. In this way, the MCC has allowed the evaluation of the sensitivity of PAH detectors to changes in chemical fingerprint for a realistic matrix of combustion products.

7.2 Development

A simple combustion source was constructed in the laboratory to evaluate the performance of the prototype Photoelectric Aerosol Sensor (PAS) and the chemical artifact reducing portion of the RADS system (Wall, 1992). As shown in Figure 7-1, the MCC device consists of a modified catalytic kerosene combustion source, Pyrex emissions stack, dilution system, and a residence time chamber. The

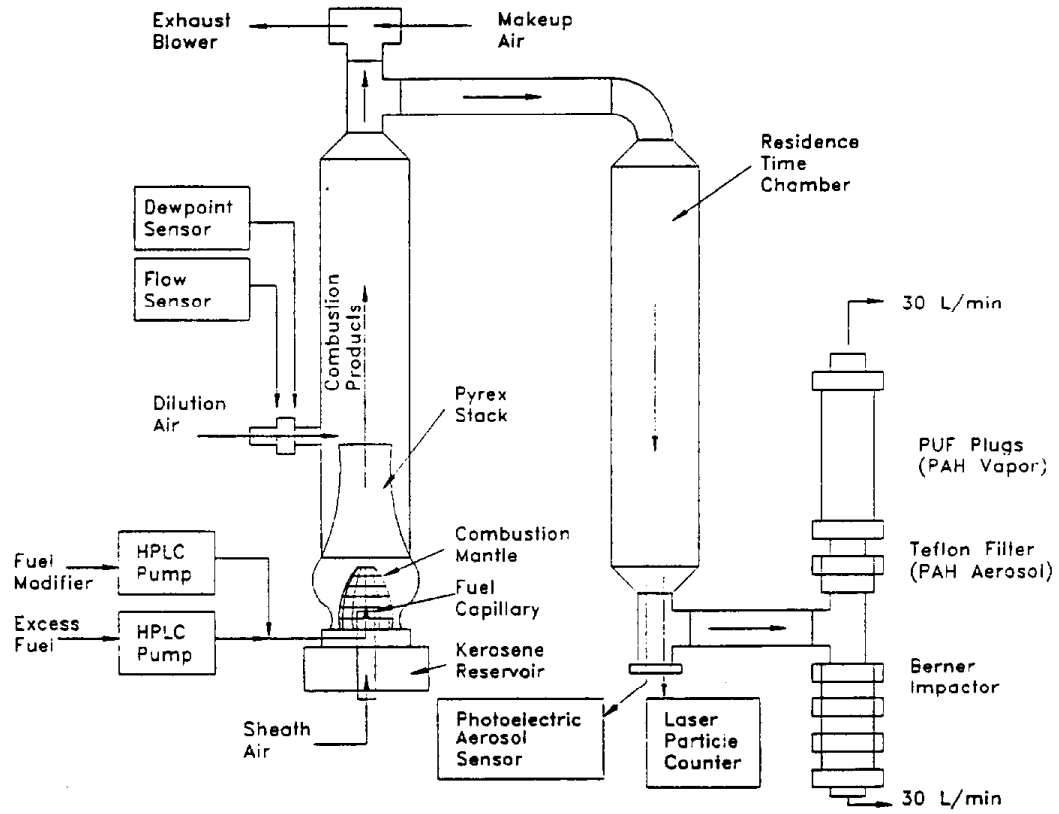


Figure 7-1. The Micro-capillary Combustor (MCC) system used to generate particle and vapor phase PAH for methods development.

residence time chamber is equipped with ports to simultaneously sample with the PAS, the Reduced Artifact Sampling train of the RADS system, and a Berner impactor (Berner et al., 1988). As a developmental tool, the dilution system and residence time chamber were designed as simplified, scaled-down versions of the RADS system equivalents.

Initially, the MCC was operated to burn kerosene which was "wicked-up" to the combustion mantle from a large reservoir by simple capillary action. When operated to produce maximum luminescence from the combustion mantle without sooting, very little PAH was detected in the combustion products. Generation of stable levels of PAH are achieved by introducing an accurately metered flow of kerosene from an HPLC pump to a fine capillary inside the mantle. The resulting jet of fuel ignites to form a standing laminar diffusion flame which issues from the top of the highly efficient combustion zone of the glowing mantle. Provision is also made for the metered addition of a fuel modifier to the kerosene which enters the fuel capillary.

Monitoring the laboratory combustion source with the real-time PAS provides a convenient method for determining the stability and the PAH aerosol output level under different MCC operating conditions. An optical particle counter interfaced to a multichannel analyzer provides a measure of the combustion aerosol size distribution for particles greater than 0.1 μm. The Berner impactor allows the collection of size segregated samples for particles $\geq$ 0.063 μm.

This laboratory combustion source provides freshly generated particle and vapor phase PAH compounds to be used to evaluate the collection efficiency of the reduced artifact sampling train and the recovery efficiency of the new PAH analytical method. The PAS response to particle phase PAH for the different mixture of emissions present in the MCC laboratory source under different combustion conditions can also be investigated.

8.0 ANALYTICAL METHODS DEVELOPMENT

8.1 Particulate Samples

8.1.1 Extraction

The conventional Soxhlet extraction technique has the disadvantages of requiring a very long extraction time (>16 hours) and the need to concentrate the sample from large quantities of solvent (sample volume is reduced to 1 mL from 700 mL). One alternative to Soxhlet extraction is ultrasonic extraction as suggested by the US EPA. The PAH extraction efficiency of a recently developed ultrasonic instrument is comparable to the conventional Soxhlet extraction technique for SRM #1649 (urban particulate matter). Based on the successful preliminary results, an ultrasonic extraction instrument (NEY # 40-PRO-0506N) was purchased for use in the extraction of PAH from incinerator particulate samples.

The short well-conditioned high energy bursts produced by the instrument can be adjusted to optimize extraction and minimize the potential for sonochemistry. The differences in signal waveform between a conventional ultrasonic generator and the Process Control Ultrasonic (PCU) instrument are shown in Figure 8-1. A major advantage of the PCU instrument is the precise control of the duration and shape of the ultrasonic pulse which exceeds the cavitation threshold (C_t) of the extraction fluid. The ultrasonic signal parameters, which include: 40MHz burst duration (Burst t), time between bursts (Quiet t), time for a burst train (Train t) and time between burst trains (Degas t), were optimized to yield uniform cavitation throughout the ultrasonic bath. Cavitation uniformity was determined by observing the surface pitting caused on aluminum foil strips placed in the solvent filled extraction vials. Up to twelve samples, each in a capped 50 mL vial containing 35 mL of solvent, can be extracted simultaneously in the water bath of the PCU instrument.

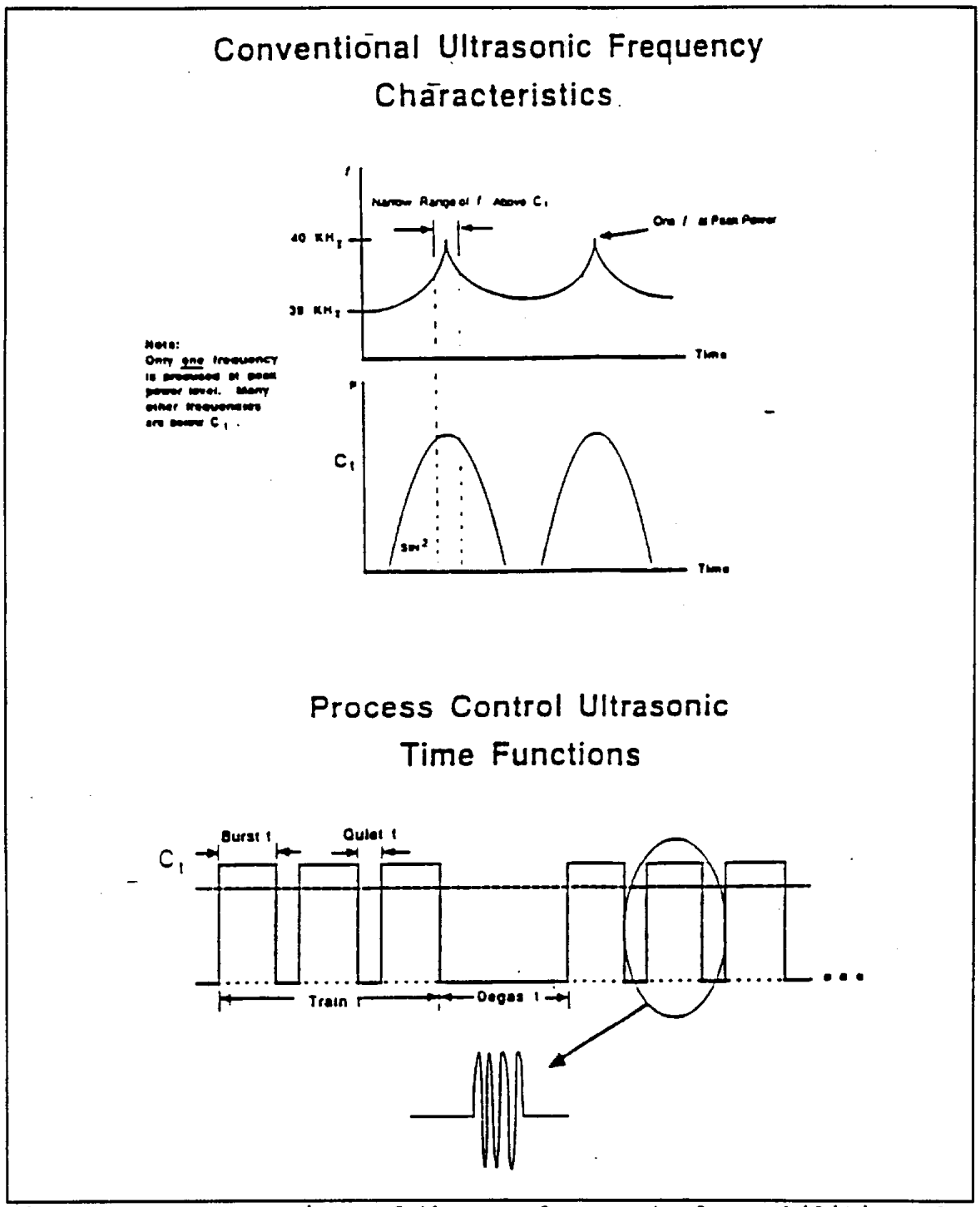


Figure 8-1. A comparison of the waveform control capabilities of a conventional ultrasonic bath and the Process Control Ultrasonic (PCU) device used in the new Pulse Ultrasonic Extraction (PUE) method for particulate bound PAH.

Extractions of particulate samples were performed in a 4:1 mixture of cyclohexane/dichloromethane (CH/DCM). This slightly polar solvent has been shown to give good recoveries of PAH and nitro-PAH from SRM #1650 (diesel exhaust particulate matter) without extracting large quantities of the very polar material extracted with a pure DCM solvent. When pure DCM was used, the large quantity of polar accompanying substances co-extracted with the PAH compounds was found to interfere with the column chromatography clean-up procedure used to concentrate the PAH and nitro-PAH into separate fractions. A detailed stepwise procedure for this new Pulsed Ultrasonic Extraction (PUE) method is given in Appendix B.

8.1.2 Clean-up Fractionation

The entire combustion sample analysis method developed over the first two quarters of the project is shown in Figure 8-2, and a complete evaluation of this analysis scheme is given in section 10.4. As part of the method, a simplified single step clean-up technique was used to remove interfering substances co-extracted from the sample matrix. The procedure has been adapted from a method recently developed in Germany (Zajc et al., 1991), and consists of solid-liquid chromatography on a micro-column containing two silica gel packings of different mesh size. The technique has been reported to give clean separations into fractions containing PCB, PAH, and nitro-PAH compounds, by eluting the sample as indicated with increasingly more polar solvents. The technique has been further refined to increase sample throughput and decrease the potential for sample contamination. A detailed outline of the method is also given in Appendix B.

A brief preliminary evaluation of supercritical fluid extraction (SFE) as a combined PAH extraction and clean-up technique was also conducted using standard reference materials. The mechanical problems previously experienced with the commercially available SFE instrument (ISCO model #1200) were solved by redesigning the capillary restrictor. A restrictor is required to withdraw the

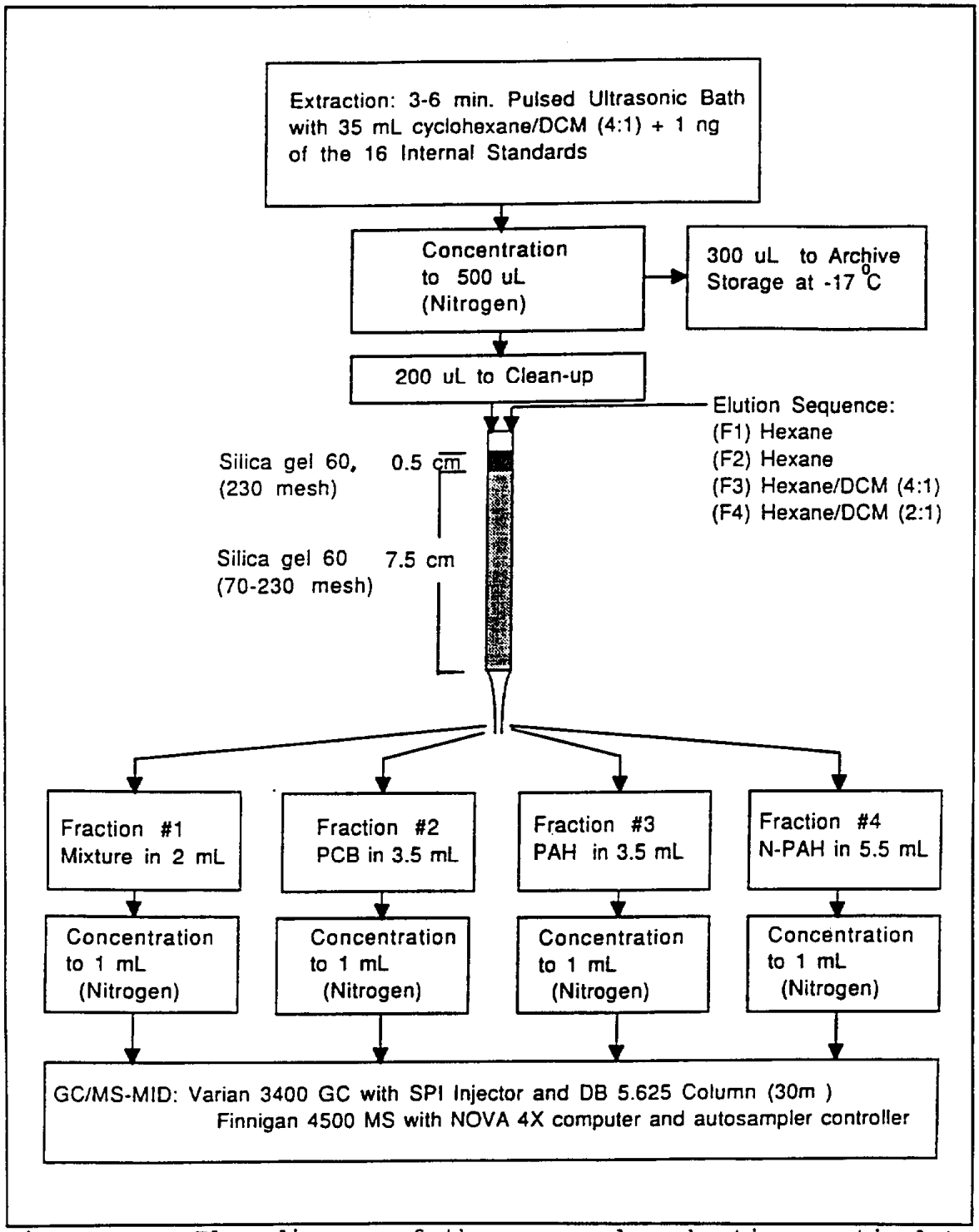


Figure 8-2. Flow diagram of the proposed combustion particulate sample analysis method for PAH including extraction, clean-up fractionation, and GC/MS analysis.

supercritical fluid containing PAH from the high pressure extraction vessel. In the redesigned restrictor, a very short (1 cm) length of capillary tubing is attached to a 19 cm length of stainless steel microbore tubing. This configuration avoids the mechanical stress which produced repeated fractures in the original 20 cm long capillary restrictor design.

Initial attempts were made to utilize SFE as a single step extraction and clean-up technique by collecting a series of extract fractions at increasing SFE pressures. Although the solubility of PAH increases with supercritical fluid extraction pressure, a pressure fraction could not be identified which gave a sufficiently selective extraction of PAH to avoid the necessity of sample clean-up before analysis.

8.2 Adsorbed Vapor Samples

The polyurethane foam (PUF), was chosen as a filter backup adsorbent to capture volatile loss of PAH from the filter particulate catch in the Reduced Artifact Dilution Sampler (RADS). Although PUF was found to require pre-cleaning to remove chemical interferents, a simple compression rinsing clean-up procedure for PUF which requires only one hour was found to be an effective pre-sampling treatment.

The XAD-2 resin trap currently used to collect vapor phase PAH in the conventional Modified Method Five (MM5) combustion source sampling system has several disadvantages. XAD-2 resin requires extensive clean-up treatment including sequential Soxhlet extraction for 22 hours with methanol, dichloromethane (DCM), and then hexane in order to remove chemical interferences before sampling. The XAD-2 trap also has the potential for reduced collection efficiency due to channeling of the sample flow through the resin bed. One alternative to XAD-2 resin for the collection of vapor phase PAH is a monolithic polyurethane foam (PUF) plug, which has been recommended by the US EPA for high volume atmospheric

sampling.

Polyurethane foam (PUF) was also found to require pre-cleaning to remove chemical interferents; however, unlike XAD-2, simple compression in solvents can be used as the clean-up procedure (Chuang, Bresler and Hannan, 1985). A new Simple Compression Rinsing (SCR) procedure has been developed which involves repeatedly compressing the PUF 30 times each in toluene, acetone and then hexane/DCM (4:1). A syringe was used to simultaneously rinse as many as four PUF plugs 5 cm (2 in) x 7.6 cm (3 in) in diameter by operating the syringe plunger. This PUF cleaning procedure requires only 1 hour and was found to be as effective as Soxhlet extraction in DCM for 16 hours.

An automated system has been designed to conduct unattended Simple Compression Rising (SCR) of PUF plugs using timed applications of pressure and vacuum. A similar procedure is used to extract adsorbed PAH vapor from the PUF plugs after sampling, and is termed Simple Compression Extraction (SCE). The details of the SCR and SCE procedures are given in Appendix B.

8.3 Chemical Analysis

The sample extracts are analyzed for PAH by capillary GC/MS using a Finnigan 4510 system operating in the Multiple Ion Detection (MID) mode. Improvements in the GC/MS system for this study include a new high resolution gas chromatograph (Varian 3400), with a special temperature programmed injector (SPI), and the modification of the low resolution mass spectrograph electronics with the addition of a variable high voltage dynode power supply to improve sensitivity. The fast programmed heating of the SPI injector acts to concentrate the sample which condenses on the end of the cold column. With these improvements, method detection limits less than 5 pg/μL (5 ng/sample) are possible for standard solutions. This is more than an order of magnitude improvement over the limit reported in CARB Method #429 for sampling combustion source PAH. However,

several problems had to be overcome to achieve the increased sensitivity.

A source of multiple mass contamination in the mass spectrometer was traced to the outgasing of the injector septum, produced by the rapid injector heating. The contamination was eliminated by increasing the septum sweep gas flow and maintaining the injector at the highest programmed temperature until cooling just before injection of the next sample. A peak splitting problem in the GC was eliminated by the addition of a 2 meter deactivated guard column installed between the injector and the activated analytical column.

An autosampler has also been added to better control the sample injection process. In conjunction with a guard column, the autosampler allows up to twice the current 1 μL injection volume without degrading the quality of the chromatographic separation. This allows analysis of PAH levels less than 5 pg/μL and unattended operation of the GC/MS to increase sample throughput.

Changes in the mass spectrometer data reduction software subcommand parameters were also made to allow more accurate mass peak identification and integration at low PAH concentrations. These parameters, which included the subcommands for detecting mass peaks and setting the baseline for peak integration, were optimized using raw mass chromatograms from a series of previously analyzed standard reference materials.

The GC/MS computer control and data storage device was also upgraded to the Sysnet 486DX PC-based Galaxy 2000™ System. The Galaxy 2000™ System replaced the original NOVA System for the chemical analysis of the field trial samples. Early in the project, data reduction was achieved by importing the raw chromatographic peak area data from the Finnigan NOVA computer into an IBM

compatible personnel computer. Final concentrations were calculated in a Lotus spreadsheet using an internally developed macro-program.

9.0 QUALITY ASSURANCE AND CONTROL

9.1 Sampling Methods

The Reduced Artifact Dilution Sampler (RADS) employed a variety of sensors which provided measurements of the stack sampling conditions as inputs to the on-board microprocessor control systems and real-time data logger. These sensors including the Platinum Resistance Temperature Detectors (Pt-RTDs), used to maintain isothermal sampling, and the High Temperature Velocity Sensors (HTVS), used to maintain isokinetic sampling at a fixed dilution ratio, were calibrated with instruments traceable to the National Institute of Standards and Technology (NIST). An example of the mass flow HTVS calibration has been given in Figure 10-2. Similar NIST traceable calibrations were performed to validate the performance of the high volume blowers and the low volume constant flow pumps as shown in Figures 10-1 and 10-3 respectively. Periodic recalibrations were performed to verify that the performance of these devices was within the manufactures specifications (typically ± 2%).

Performance checks were also instituted to ensure proper operation of the RADS after assembly in the field. Prior to sampling, the integrity of the isothermal control system was established by monitoring the electrical power requirements of each probe heating zone necessary to maintain a preset temperature near 200°C (392°F). The integrity of the isokinetic sampling and dilution systems were verified in a similar manner by monitoring the electrical power requirements of the high volume blowers to maintain a preset probe nozzle velocity near 11 m/s (36 f/s) at STPC. As shown in Figure 11-2, a performance index was available during sampling to monitor the operation of all RADS control systems.

Detailed performance index data for each sampling period of the three field trials conducted on the 500 kW diesel generator are included in Appendix E. The in-place calibration of the flow

sensors, as well as, the methods used to calculate the probe nozzle velocity, and the RADS performance index from the sensor data are discussed. Equations used to calculate the total air volume sampled from the stack and the total elapsed time for each sample, using the output of the RADS data logger, are also presented.

9.2 Analytical Methods

Method blanks, performance evaluation standards, and laboratory control samples were routinely included in the new analytical scheme employed by CERL for combustion derived PAH. Method blanks for both the Teflon coated glass fiber filters and the previously cleaned PUF plugs were determined for each set of RADS samples. Methods blanks for the Teflon coated filters and the PUF plugs used in the field study to sample the exhaust of the 500 kW generator are given in Appendix D. Blanks were taken from the same filter batch and the pre-cleaned PUF plug batch used in the field study. PUF Blank levels were consistent with those previously reported in Table 10-4 for the initial simple compression rinsing (SCR) method development tests. Typically PAH blank levels were not detected for the Teflon coated glass fiber filters or the pre-cleaned PUF plugs. Accordingly, method blank levels were reported as less than or equal to the method detection limit (MDL). The MDL for the 16 priority PAH were determined independently for the two collection media using spiking solutions as recommended by CARB.

Performance evaluation samples consisting of Standard Reference Materials (SRM) from NIST were analyzed on a triennial basis. SRMs for both urban dust (NIST #1649) and diesel particulate matter (NIST #1650) underwent extraction, clean-up, and GC/MS analysis by the same methods used in the field sampling. Representative results obtained for analysis of each of these SRMs have been presented in Table 10-2 and Table 10-3. Routine analysis of SRM #1649 was chosen as the performance evaluation sample for the field study, due to the large variety of certified priority-PAH compounds compared to SRM #1650. Results of the most recent performance evaluation and a

discussion of the performance criteria developed to trigger corrective action, are included in Appendix D.

Laboratory control samples (LCS) were routinely prepared by spiking pre-cleaned PUF plugs with between 1-2 μg of the 16 priority PAH compounds. Expected recoveries for the new CERL analytical method utilizing Simple Compression Extraction (SCE) were typically greater than 90%, similar to the results for deuterated PAH shown in Table 10-5. Results for the LCS analyzed for the 500 kW diesel exhaust sampling field study are included in Appendix D. Recoveries for all 16 priority PAH were well within the acceptance criteria adopted by CARB in Method #429, which requires a relative recovery difference of less than 50% and a percent recovery of between 50% and 150%.

Routine performance checks of the gas chromatography/mass spectroscopy (GC/MS) system were conducted on a daily basis before the initiation of sample analysis. The spectrometer mass assignments were checked using the standard FC43 calibration gas which was introduced directly into the ionization volume. PAH response factor variability, and the recovery standard reproducibility for the GC/MS system were checked by analyzing standard PAH solutions prepared for isotope dilution. These standards covered the range from 5 pg/μL to 5 ng/μL for all 16 priority PAH. These standards contained 1 ng/μL of the 16 corresponding deuterated PAH as internal standards and 1 ng/μL of the 2′,2′-difluorobiphenyl as a recovery standard.

10.0 LABORATORY RESULTS

10.1 Overview

The scope of the original research design, to develop an improved combustion source PAH sampler, has evolved over time to include the development of advanced PAH analytical methods, real-time PAH sensor technology and a laboratory combustion source for PAH method evaluation.

Early in the project, considerable effort had to be expended to develop more efficient, sensitive, and accurate PAH analytical techniques. These improved techniques were required to conduct the extensive testing necessary to assess the feasibility of new candidate combustion source sampling methods. Conventional PAH analysis methods suffered from a high potential for chemical artifacts and were found to be unnecessarily labor intensive and time consuming.

With the advent of the PAS photoelectric aerosol sensor (PAS), the research effort concentrated on developing an integrated approach to PAH source sampling. This approach consists of a utilizing the real-time PAS as a source survey tool, and the RADS to collect PAH samples for laboratory analysis. At low level PAH sources identified by the PAS, the simplified RADS configuration could be used to collect a high volume dilution tunnel sample. At higher level sources, a more detailed characterization could be performed using the complete RADS low volume sampling configuration.

10.2 Reduced Artifact Dilution Sampler

A summary of the design features of the Reduced Artifact Dilution Sampler (RADS) which satisfy the original design criteria for measuring combustion derived PAH are listed in Table 10-1. The RADS system consists of three major operational components: (1) the heated stack probe system, (2) Volume Dilution System (VDS) and (3) the Reduced Artifact Sampler (RAS) system, which were redesigned

Table 10-1. Design Features of the Reduced Artifact Dilution Sampler (RADS).

Design Criteria	New System Design Feature
Simulate Atmospheric Dilution	Dynamic dilution factor ($10X - 100X$) Cooled to ambient temperature Well-mixed system (high $Re \geq 10,000$) Well-developed flow ($length \geq 10\ Diam$)
Minimize Sample Contamination	PTFE Teflon lined inlet (*replaceable*) Stainless Steel stack probe exterior PTFE Teflon coated dilution system Replaceable interior surface components
Model Gas/Particle Interaction (*nucleation, condensation*)	Automatic dilution and mixing control Adjustable condensation residence time
Minimize Particle and Vapor Loss	Large diameter tunnel (*small surface/volume*) Optimized flowrates to prevent deposition Inlet heated above stack temperature All interior surfaces Teflon coated
Minimize Artifacts in Sample Collection	Aluminum Denuder (*acid gas*) Teflon filter (*inert substrate*) PUF plug back-up adsorbent (*volatile loss*)
System Conveniences	Small, lightweight, portable Automatic isokinetic sampling Sampler flows set automatically No maintenance during operation Corrosion resistant

Velocities in the RADS system are monitored using solid state High Temperature Velocity Sensors (HTVS) designed to operate at temperatures up to 260°C. The HTVS were calibrated using precision mass flowmeters to determine the correlation between the sensor output (millivolts) and the gas velocity. A highly accurate and reproducible calibration was obtained for all three sensors as shown in Figure 10-2. An especially important result was the nearly identical calibration curves observed for the two 0 to 15 m/s (0 to 3000 ft/min) sensors as shown in Figure 10-2 (top frame). The output of these sensors is used by the flow control system to match the stack probe inlet sampling velocity and the free stream stack velocity to maintain isokinetic sampling. The output of the third sensor is used to control the dilution rate of the isokinetic stack sample.

The initial design concept for the isokinetic sampling system used differential pressure from a pitometer to measure stack velocity, similar to the current MM5 probe. Design changes were made to incorporate the solid state HTVS technology after early testing confirmed that pitometer measurements were unreliable at the lower velocities, < 4.6 m/s (15 ft/s), found in many stacks. This finding suggests that a large portion of the historical data base for MM5 sampling may not have been collected under isokinetic conditions due to inaccurate stack velocity measurements.

In designing the sampling trains for the Reduced Artifact Sampler (RAS), polyurethane foam plugs (PUF) were chosen as the vapor phase PAH collection media. PUF plugs are more convenient to handle and require substantially less pretreatment before sampling than the XAD-2 resin used for PAH vapor collection in MM5. As shown in section 10.4.3, trace background PAH levels, which require 66 hours of Soxhlet reflux pretreatment for XAD-2 resin, can be achieved in one hour for PUF plugs using a solvent compression extraction method detailed in Appendix B.

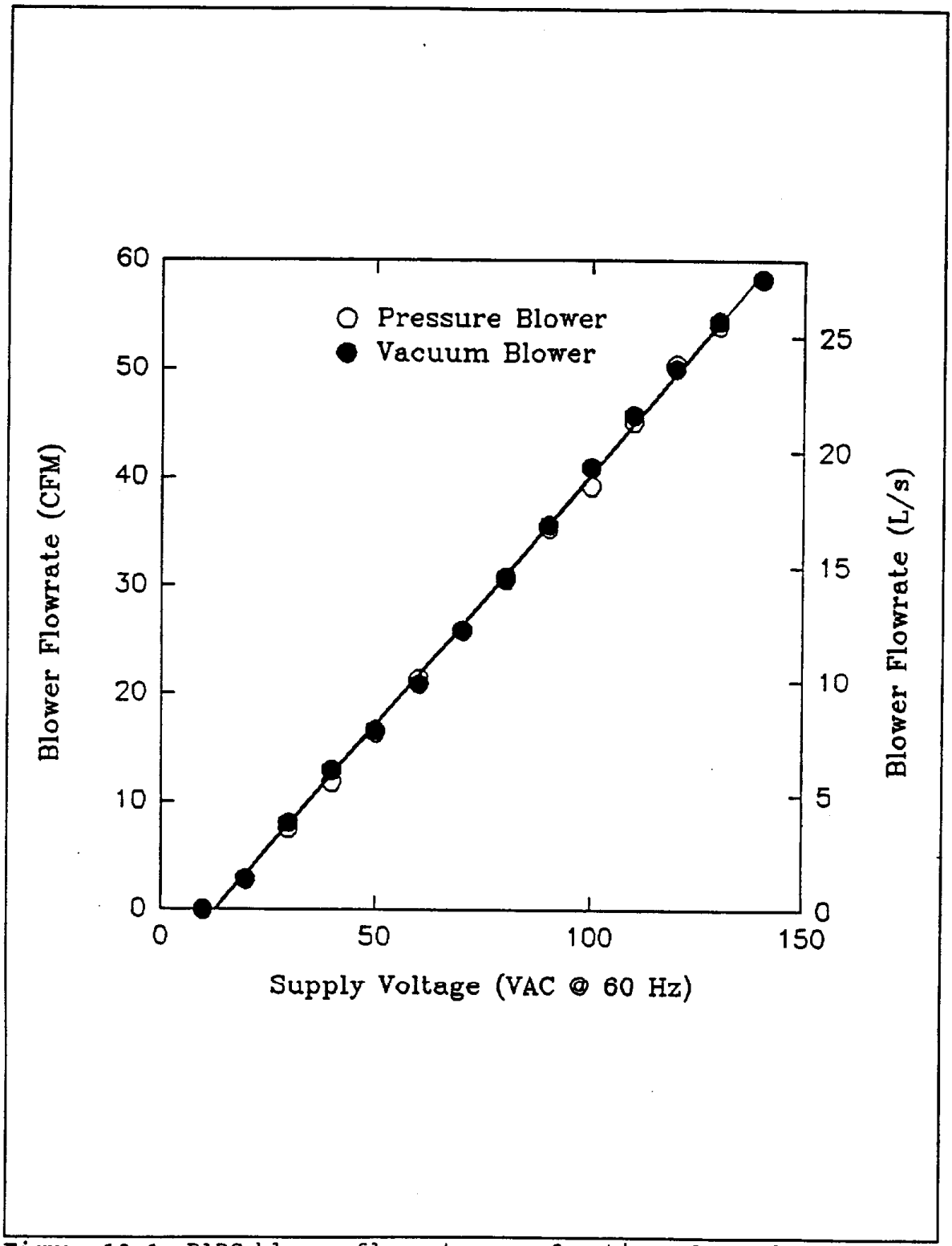


Figure 10-1. RADS blower flowrate as a function of supply voltage.

Under the low flowrate (30 L/min) and small sampling volume conditions employed in the Reduced Artifact Dilution Sampler (RADS), PUF is expected to be an efficient collection media (You and Bidleman, 1984). PUF has been successfully applied in atmospheric sampling (Thrane and Mikalisen, 1980; Chuang, Hannan and Wilson, 1987). Initial laboratory studies employing segmented PUF plugs to sample vapor phase PAH from the Micro-capillary Combustor (MCC) indicate no breakthrough for even the most volatile PAH, naphthalene.

Each of the four reduced artifact sampling trains attached to the residence time chamber is designed to operate at 30 L/min. Two compact dual-channel pump modules have been developed to provide the necessary constant flow features for unattended operation. A complete laboratory calibration has demonstrated that the new dual-channel pump system automatically maintains each separate flow channel at a constant flowrate of 30 L/min ±10%. This flowrate is independent of filter pressure drop (from particulate loading) up to 330 mm (13 in) Hg as shown in Figure 10-3.

The reduced artifact sampling trains have been used to sample the PAH produced by the Micro-capillary Combustor. These samples have been used to evaluate new analytical techniques and to characterize the PAH emissions produced by the MCC under a number of operating conditions. Typical PAH chemical fingerprints for several different MCC combustion conditions are shown in Figure 10-4. Notable are the MCC operating conditions which allow shifts in the relative distribution of high and low molecular weight PAH species.

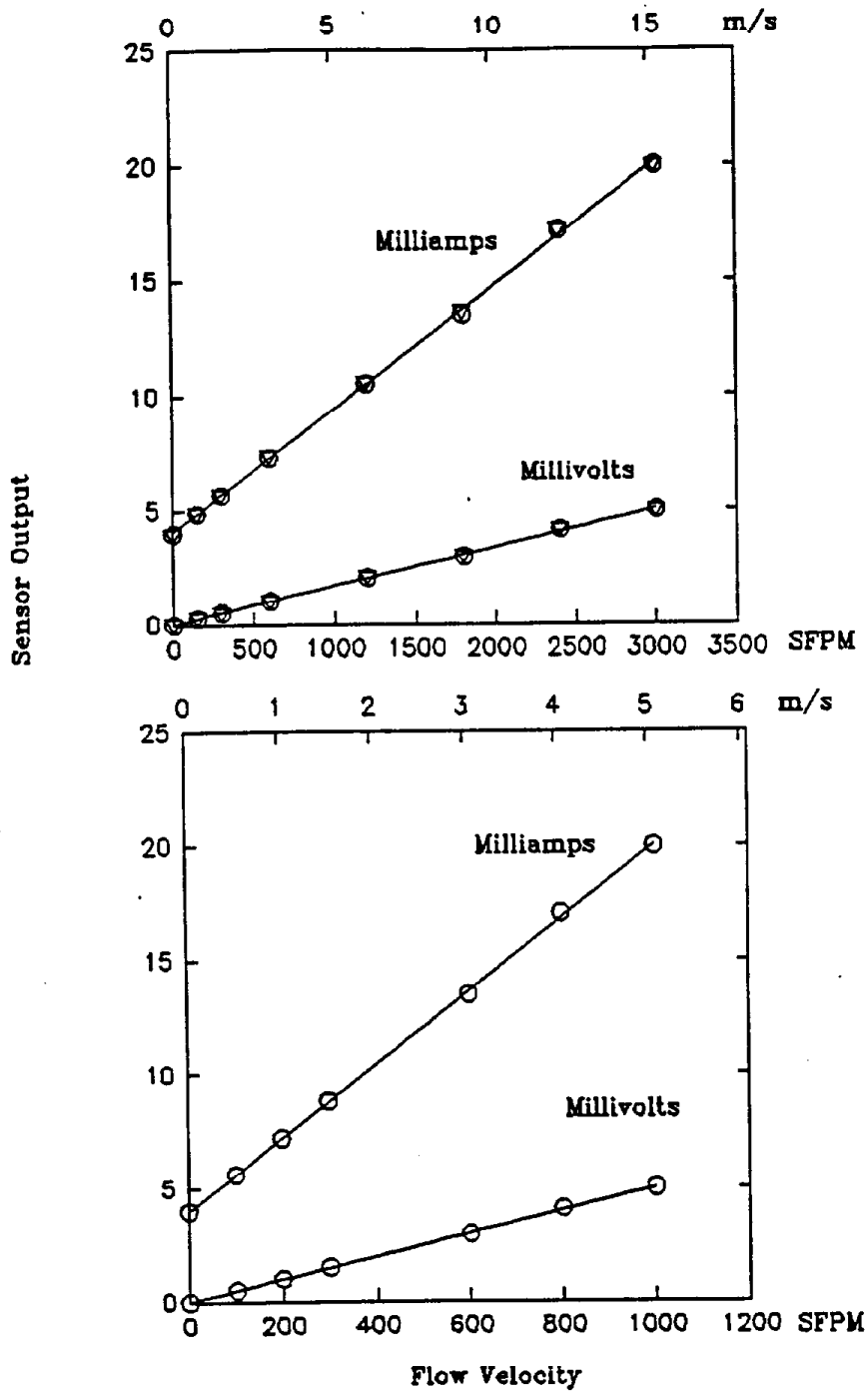


Figure 10-2. Calibration of High Temperature Velocity Sensor (HTVS) outputs for: (top frame) the two isokinetic sampling system probes, and (bottom) the dilution rate probe.

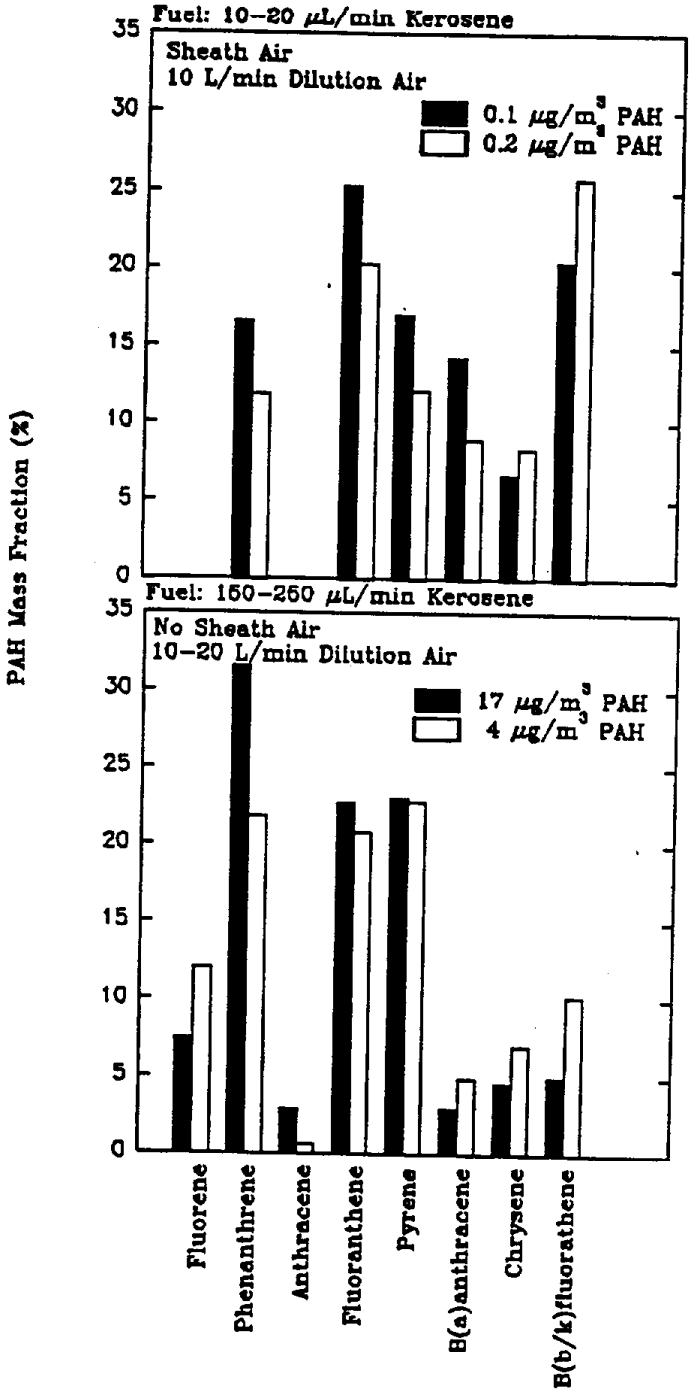


Figure 10-4. A typical PAH chemical fingerprint determined with the Reduced Artifact Sampler (RAS) train for different Micro-capillary Combustor (MCC) operating conditions.

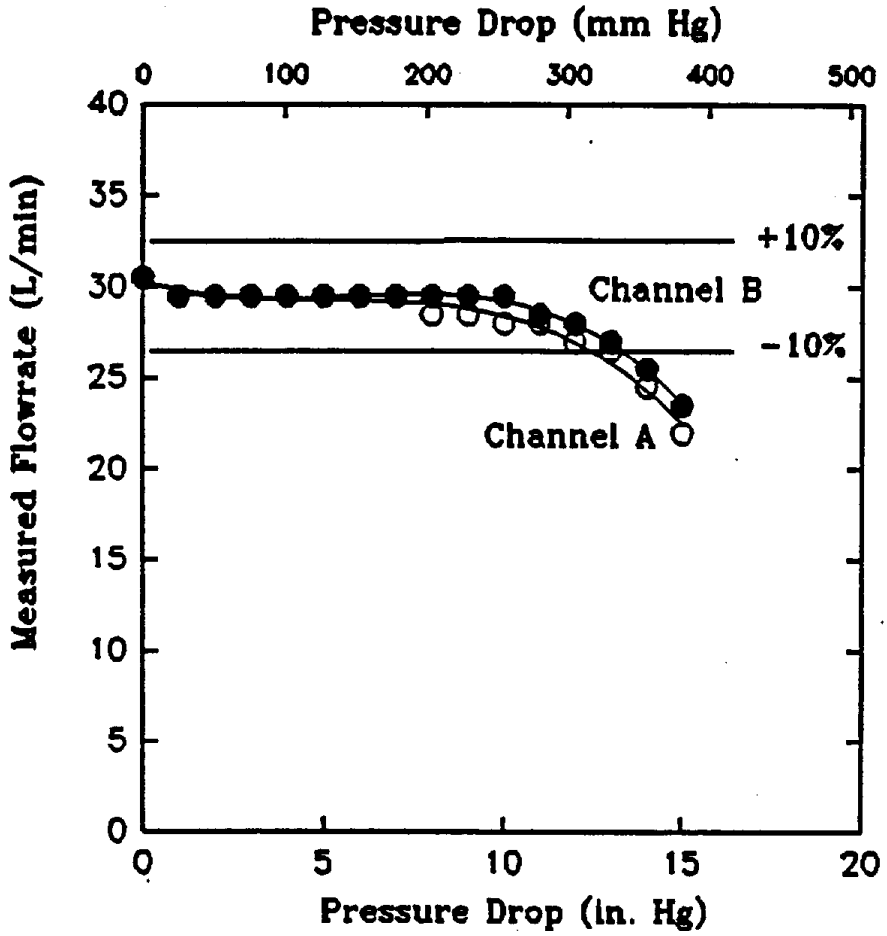


Figure 10-3. Calibration of the new dual-channel constant flow pump system for the Reduced Artifact Sampler (RAS) train at high pressure drops.

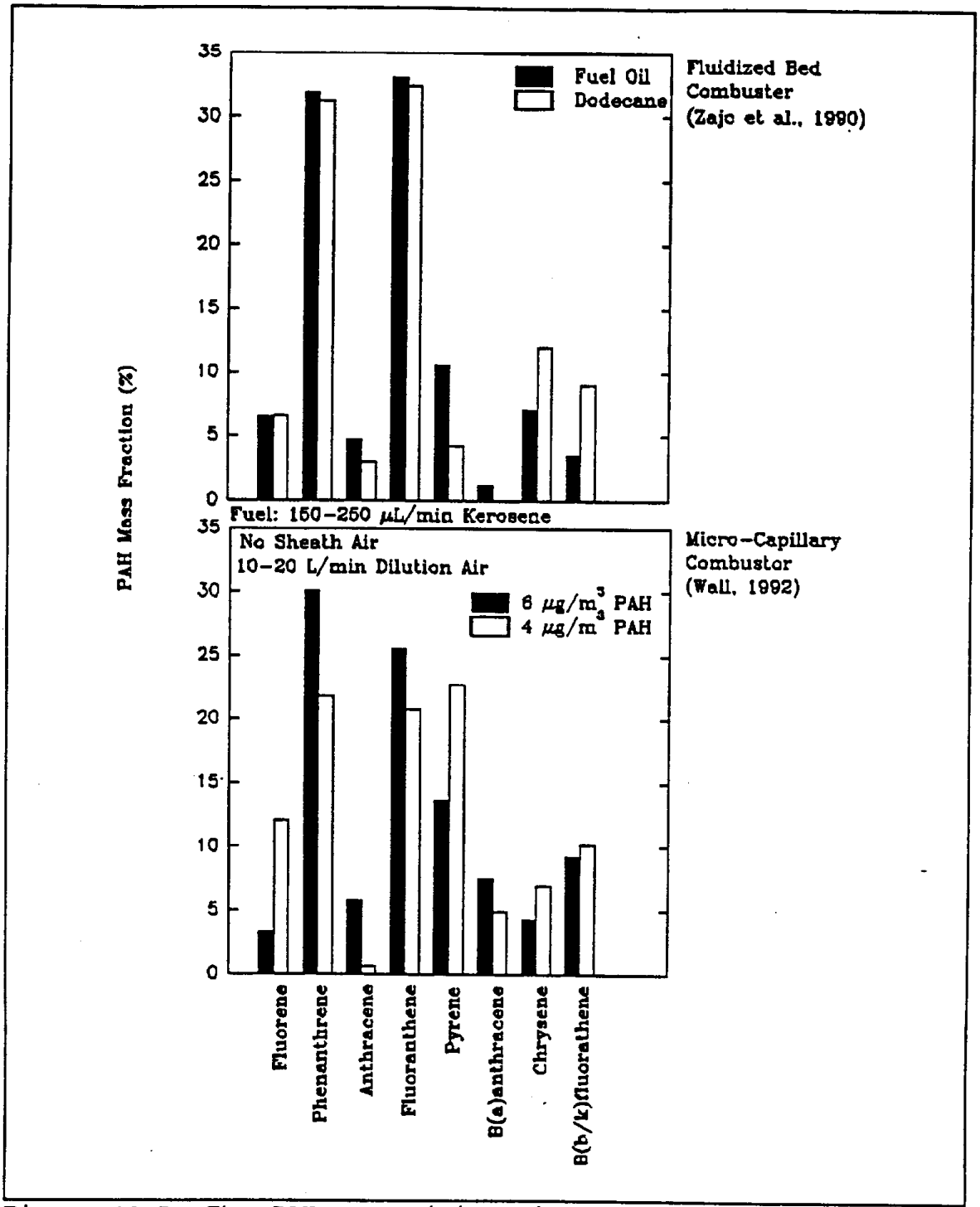


Figure 10-5. The PAH composition signature for (top frame) the fluidized bed combustor of Zajc et al. (1990), and (bottom frame) the Micro-capillary Combustor (MCC) operated to produce a similar signature.

10.3 Photoelectric Aerosol Sensor

The operating principle of the Photoelectric Aerosol Sensor (PAS) is the photoionization of PAH adsorbed on the surface of the airborne particles and the measurement of the residual charge after photoemission. Since the threshold for photoemission depends upon the specific PAH and the adsorption surface composition, the PAS must be evaluated using a realistic matrix of well characterized combustion products. Reproducible levels of freshly generated particle and vapor phase PAH compounds in the $\mu g/m^3$ range can be produced with the laboratory scale Micro-capillary Combustion (MCC) source.

Previously, the only known detailed calibration of the PAS was conducted by Zajc et al. (1990) using a small research scale fluidized bed combustor burning fuel oil to generate PAH aerosol. The PAH composition signature determined by Zajc for the aerosol phase component produced by the fluidized bed combustor is shown in Figure 10-5 (upper frame). Although Zajc found a linear relationship between the PAS response and the concentration of each PAH species in the source signature, the sensitivity of the PAS to changes in the source signature has not been thoroughly investigated.

After investigating a number of different MCC operating conditions, a source signature similar to that for the Zajc fluidized bed combustor was successfully generated as shown in Figure 10-5 (lower frame). Calibration of the PAS response for specific PAH compounds under these conditions yield linear relationships with slopes very close to those determined by Zajc. However, these relationships are not necessarily preserved when the combustion source signature is changed. The sensitivity of the PAS response to these changes in source PAH signature is currently under investigation using the MCC.

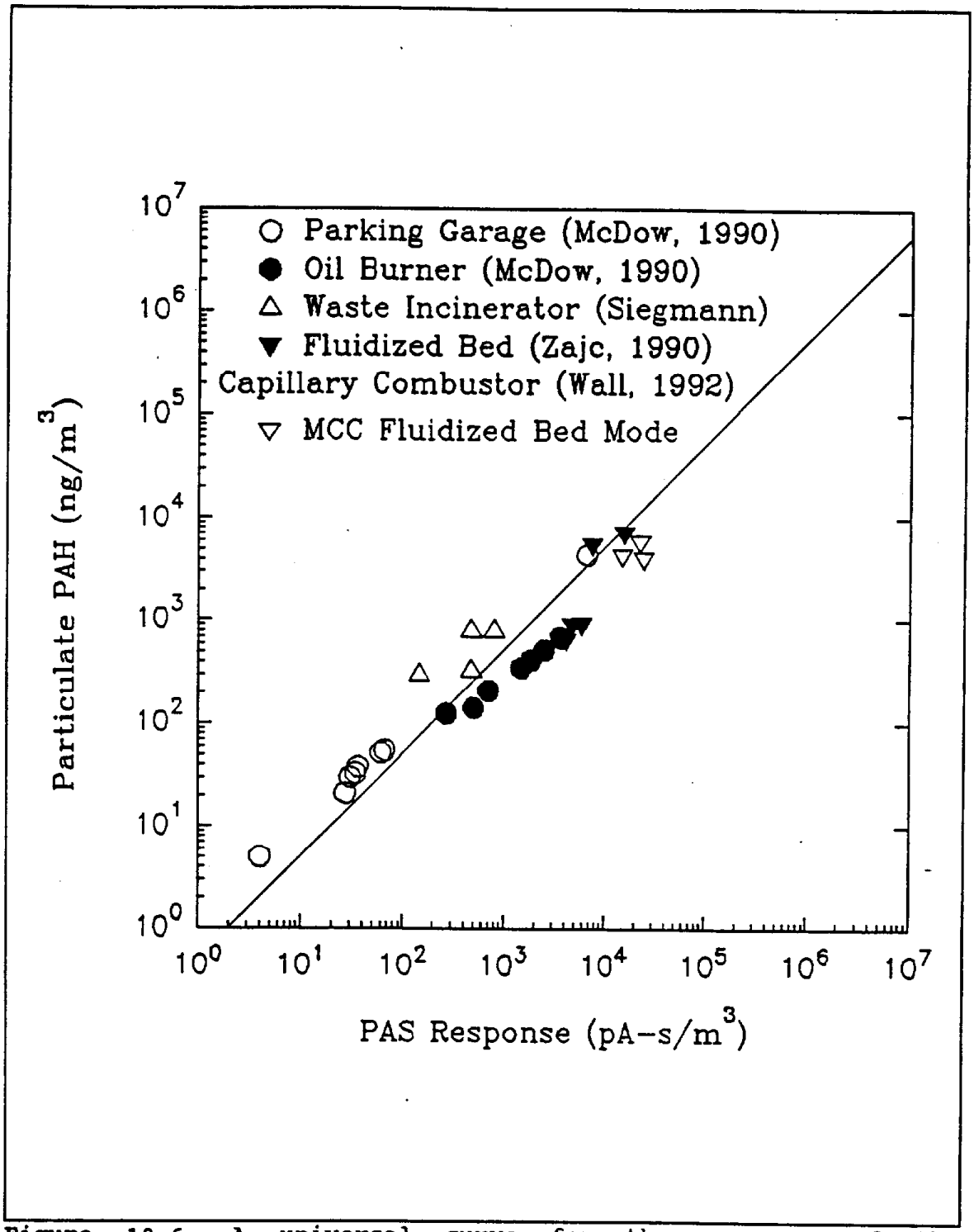


Figure 10-6. A universal curve for the response of the Photoelectric Aerosol Sensor (PAS) to the total PAH present in a number of different combustion sources.

Although the PAS response was correlated with the level of a series of different PAH compounds present in the combustion aerosol, the PAS technique cannot generally be considered to be specific for individual PAH compounds. Monitoring the laboratory combustion source with the real-time PAS proved to be a convenient method for determining the stability and the PAH aerosol output level under different MCC operating conditions. Accordingly, the PAS could be valuable as a source survey tool, or as a loading monitor during the collection of integrated filter samples for chemical analysis of specific PAH compounds.

A universal calibration curve comprised of the PAS response to the level of total PAH present for a wide range of source signatures is shown in Figure 10-6. Here total particle phase PAH is defined as the sum of the 16 priority PAH compounds collected by a filter sample. Although the data are from PAH sources as diverse as automobile exhaust, laboratory combustors, and waste incinerators, a general relationship between total aerosol phase PAH has been established.

Table 10-2. Comparison of Extraction Methods for PAH from NIST Standard Reference Material #1649 (Urban Dust/Organics).

PAH Species	NIST Value[α] (*ng/sample*)	Pulsed Ultrasonic[β] (*% recovered*)	Soxhlet[η] (*% recovered*)
Phenanthrene	1125 ± 75	63 ± 5	83 ± 4
Fluoranthene ‡	1775 ± 125	71 ± 9	84 ± 6
Pyrene	1575 ± 100	69 ± 9	81 ± 5
Benz(a)anthracene ‡	650 ± 75	98 ± 12	105 ± 8
Chrysene	875 ± 25	104 ± 14	124 ± 10
Benzo(b)fluoranthene ‡	1550 ± 75	97 ± 10	124 ± 8
Benzo(k)fluoranthene	500 ± 25	95 ± 10	87 ± 9
Benzo(a)pyrene ‡	725 ± 125	97 ± 13	103 ± 13
Indeno[1,2,3-cd]pyrene ‡	825 ± 125	63 ± 7	87 ± 17
Benzo(ghi)perlyene ‡	1125 ± 275	72 ± 7	101 ± 6

α. Total ng/sample extracted. The actual aliquiot analyzed was 1/350 of this amount.

β Pulsed Ultrasonic extraction for 12 min. using Cyclohexane/DCM (4:1).

η Soxhlet for 16 hours using DCM.

‡ Values certified by NIST for these species.

10.4 Analytical Methods

10.4.1 Particulate PAH Extraction

Preliminary results of a comparison of the ultrasonic technique with the currently recommended Soxhlet extraction using DCM (CARB Method #429) are shown in Table 10-2. The levels reported by NIST for the ten target PAH in SRM #1649, which are considered here to represent the 100% target values, were determined using 48 hour Soxhlet extraction with benzene/methanol (1:1).

For five of the ten PAH species (including benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(a)pyrene), the efficiency of a single 12 minute ultrasonic extraction in CH/DCM (4:1) was greater than 95%, and closer to the SRM reference value than the results for the 16 hour Soxhlet extraction using a much more polar solvent (DCM). Of the remaining five PAH, ultrasonic extraction efficiencies for fluoranthene and pyrene were within experimental error of those obtained by Soxhlet extraction. Ultrasonic extraction efficiencies for phenanthrene, indeno[1,2,3-cd]pyrene, and benzo(ghi)perylene were approximately 25% lower than by Soxhlet extraction. Multiple ultrasonic extractions with CH/DCM (4:1), or a single ultrasonic extraction with a slightly more polar solvent, are expected to further improve the ultrasonic extraction efficiency relative to Soxhlet extraction. CH/DCM (4:1) was chosen for the ultrasonic extraction, since more polar solvents (i.e. DCM and benzene/methanol) have been found to extract large amounts of non-PAH accompanying compounds, which can make sample clean-up much more difficult.

Efforts were directed toward optimizing the ultrasonic generator wave form and the extraction duration to achieve the maximum extraction efficiency for PAH. The optimum time for the extraction of the priority PAH compounds from SRM #1649 was determined by measuring the extraction efficiency as a function of time. As shown for selected PAH in Figure 10-7, the maximum extraction efficiency for the PCU instrument occurs near three minutes as compared with

up to 24 hours for the conventional Soxhlet method. At less than three minutes, the extraction efficiency drops dramatically with decreasing time in a different way for each PAH species. Further investigation of this effect could provide information on how strongly different PAH compounds adhere to the surface of particles. For extraction times longer than six minutes, the efficiency drops with little difference between PAH species. Extraction efficiency reaches a constant value nearly 20% less than the maximum valve for extractions longer than 20 minutes. The decrease in SRM #1649 extraction efficiency for these longer times, would be consistent with reabsorption of PAH on freshly created surfaces produced by the breakup of the particulate matter. It is interesting to note that surface pitting damage was observed in the aluminum foil strips used to evaluate cavitation uniformity. This pitting was complete after 20 minutes under the same PCU instrument conditions.

At the optimum PCU instrument extraction time of three minutes for SRM #1649, the extraction efficiency relative to the NIST target value is greater than 95% for benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(a)pyrene; 86% for indeno[1,2,3-cd]pyrene; 80% for benzo(ghi)perlyene; and 72% for fluoranthene. Multiple ultrasonic extractions with CH/DCM (4:1) or a single ultrasonic extraction with a slightly more polar solvent are expected to further improve the ultrasonic extraction efficiency relative to Soxhlet extraction.

Following the new method procedure, Process Control Ultrasonic (PCU) extractions of the SRM #1650 were performed for 3, 6 ,and 12 minutes in the same 4:1 mixture of cyclohexane/dichloromethane (CH/DCM) solvent used for SRM #1649. This slightly polar solvent has been shown to give good recoveries of PAH and nitro-PAH from combustion source particulate matter without extracting large quantities of the very polar material, which interfere with the column chromatography clean-up portion of the new analytical

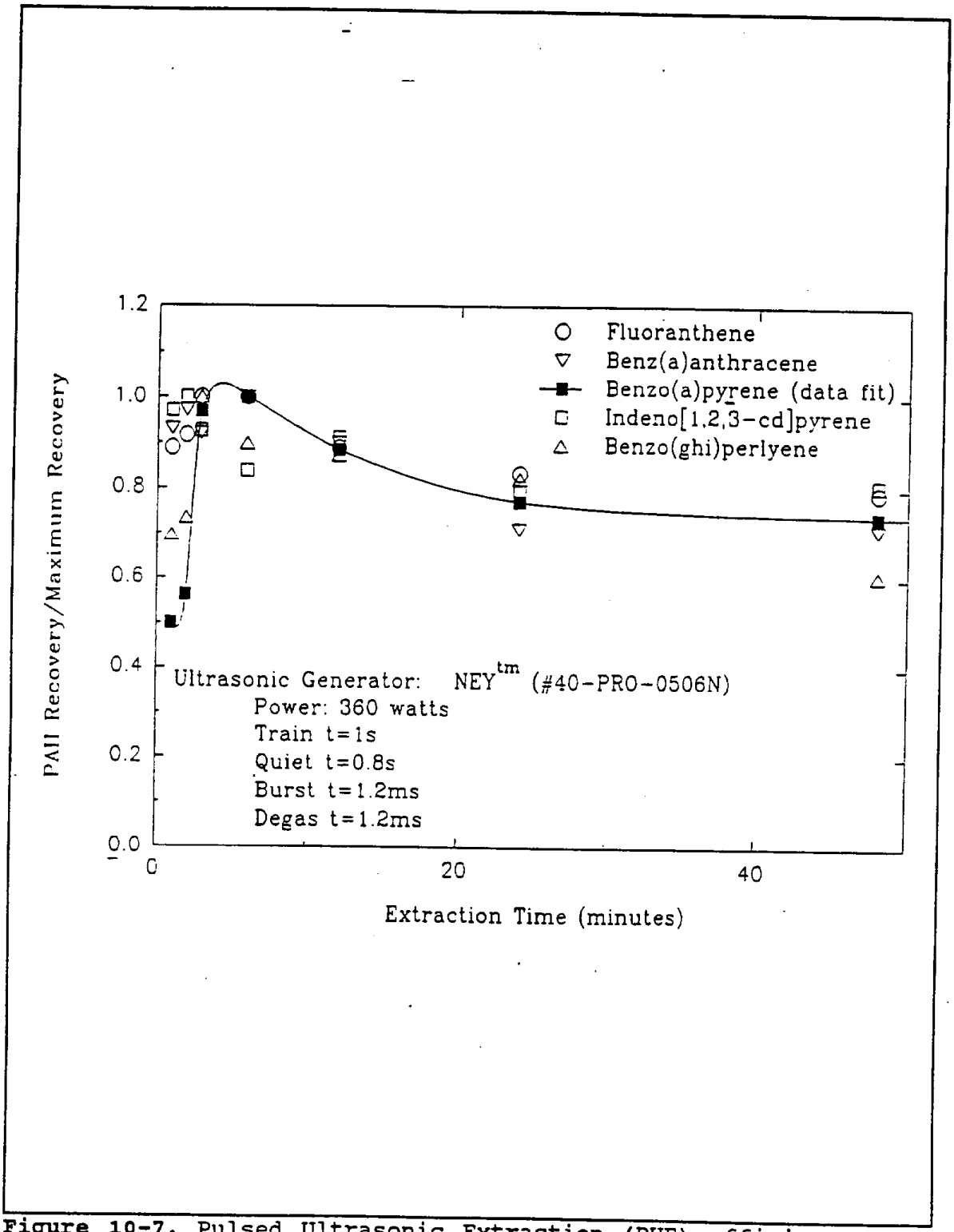


Figure 10-7. Pulsed Ultrasonic Extraction (PUE) efficiency as a function of time (NIST) Standard Reference Material #1649.

Table 10-3. Extraction Efficiency for PAH from NIST Standard Reference Material #1650 (Diesel Particulate Matter).

PAH Species	NIST Value (ng/sample)	Pulsed Ultrasonic[α] (% recovery)	
		3 *min.*	3 − 12*min.*[β]
Fluoranthene	2780 ± 218	70	70 ± 4
Pyrene	2616 ± 218	69	70 ± 2
Benz(a)anthracene	354 ± 60	83	88 ± 5
Benzo(a)pyrene	65 ± 16	nd	63[γ]
Benzo(ghi)perlyene	131 ± 33	128	110 ± 21
1-Nitropyrene	1036 ± 109	93	104 ± 11[δ]

α Corrected for PA^{2}H internal standard losses.
β Mean ($\pm\sigma$) recovery for 3, 6 and 12 minute extractions.
γ B(a)P not detected (nd) in 3 and 6 min. extraction.
δ 1-Nitropyrene not detected in 12 min. extraction.
1-Nitropyrene clean-up recovery assumed to be 97 %.

method. Unlike the atmospheric particulate matter SRM (#1649), the diesel particulate matter SRM (#1650) must be run through the simplified single step column chromatography clean-up technique, in order to remove the interfering substances co-extracted from the complex combustion matrix.

In Table 10-3, recoveries of the certified PAH and nitro-PAH levels in SRM #1650 are shown for the new analytical method using the three minute PCU extraction time established as optimum for SRM #1649. These PAH recovery efficiencies are similar to those reported for a 24 hour Soxhlet extraction of SRM #1650 using the same cyclohexane/DCM (4:1) solvent (Zajc, 1991).

Recovery of 1-nitropyrene by the three minute PCU extraction was significantly higher (93%) than that reported by Zajc et al. (1991) for the 24 hour Soxhlet technique (46%). Unlike the other PAH compounds, no deuterated form of 1-nitropyrene is commercially available to be included as an internal standard to correct for losses in the extraction and clean-up procedures. The nearly complete recoveries obtained for 1-nitropyrene, without the internal standard correction, is consistent with low losses of nitro-PAH compounds in the micro-column clean-up procedure as previously reported by Zajc (1991).

Recoveries determined by averaging the results for the 3, 6, and 12 minute extractions are also included in Table 10-3 for comparison. Except for the 12 minute extraction time required to quantify the relatively low level of BaP in SRM #1650, no significant improvement in recoveries were achieved by extending PCU extractions for longer than three minutes. Furthermore, although nearly complete recovery of 1-nitropyrene was obtained for a PCU extraction time of three minutes, 1-nitropyrene could not be detected for extractions extended to 12 minutes. A six minute extraction time period may provide the pragmatic compromise necessary to achieve optimum recoveries of both PAH and nitro-PAH.

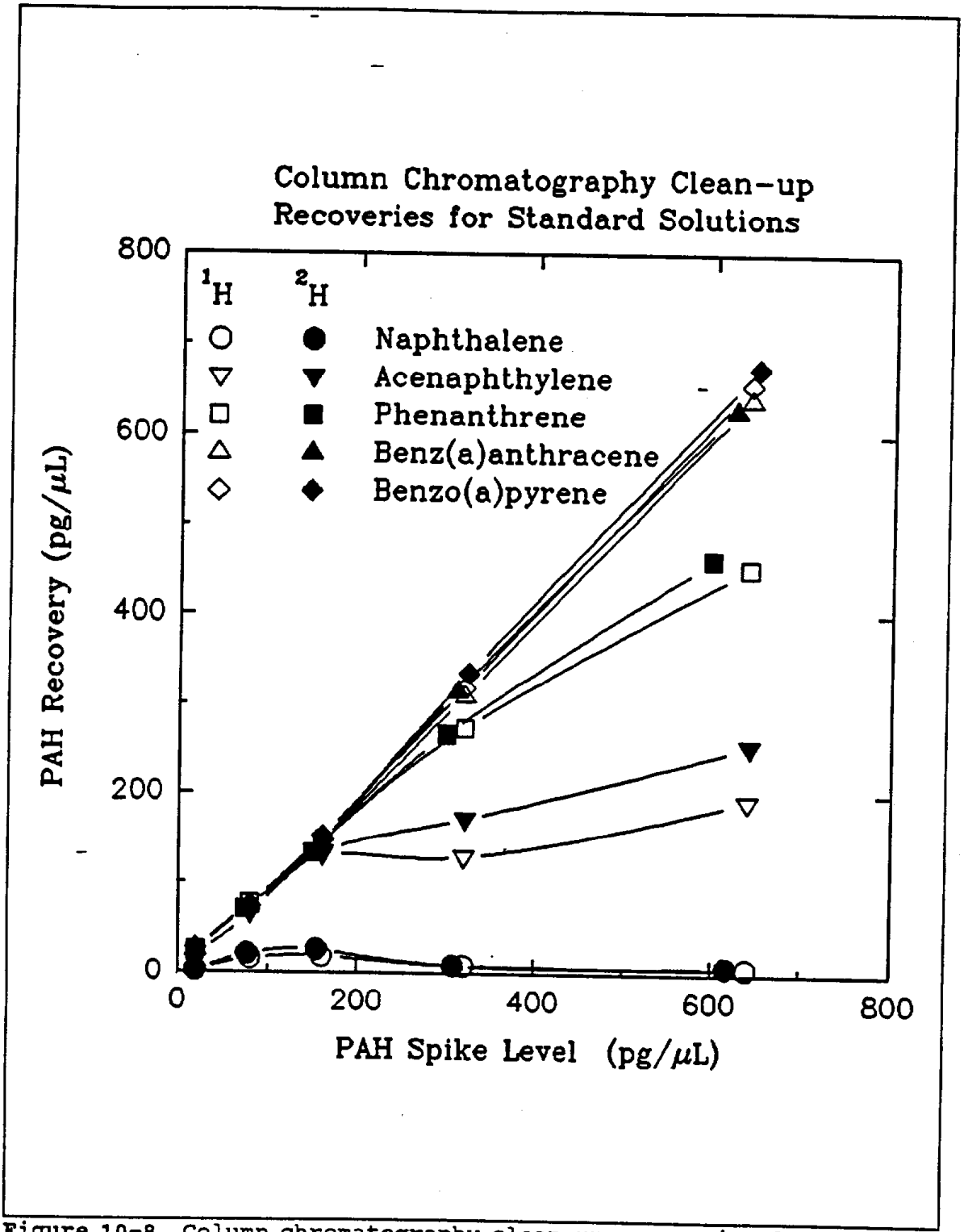


Figure 10-8. Column chromatography clean-up recoveries for standard solutions.

10.4.2 PAH Clean-up Fractionation

In order to evaluate the losses in the clean-up procedure, column chromatography was performed on deuterated and native forms of all 16 priority PAH, which were delivered as a standard solution spike of 200 μL. It is important to evaluate the recoveries of both the native and the deuterated PAH; since, in the isotope dilution procedure used for quantitation in GC/MS, the losses for a native PAH is assumed to be equivalent to that for the corresponding deuterated PAH.

In Figure 10-8, the clean-up recoveries for selected native and deuterated PAH are shown for the range of PAH concentration levels expected for real combustion samples. If 100% recoveries were obtained for all tagged and untagged PAH, the experimental points would lie along a 45° angle line through zero. Nearly complete recoveries were observed for both the native and deuterated PAH with greater than three member rings, as represented by benz(a)anthracene and benzo(a)pyrene. Very poor recoveries were observed for the lowest molecular weight PAH, naphthalene. For the intermediate PAH compounds represented by phenanthrene and acenaphthylene, nearly complete recoveries were obtained below a threshold spike concentration level, which was specific to each PAH. Incomplete recoveries were found to be due to a portion of the less-than-four-ring PAH eluting in the second fraction (containing PCB compounds), rather than in the third fraction as expected. This may not represent a serious difficultly; since, under the atmospheric temperature conditions employed by the Reduced Artifact Dilution Sampling System (RADS) the particulate filter catch is expected to contain PAH greater than three rings. Initially both the second and third fractions of the particulate matter extract will be analyzed for PAH to verify this assumption. If clean-up on the vapor phase PAH species ($\leq$3 rings) collected on the PUF adsorbent downstream of the filter is necessary, the column chromatography elution scheme will be modified to recover most of

Table 10-4. Comparison of PAH Background Levels for Pre-Cleaned PUF and XAD-2 Resin Sorbents.

PAH Species	PUF Plug† (ng/sample)	XAD-2 Resin‡ (ng/sample)
Naphthalene	5 ± 5	≤ 42000
Acenaphthylene	13 ± 0.5	≤ 13
Acenaphthene	25 ± 0.5	≤ 24
Fluorene	54 ± 7	≤ 49
Phenanthrene	587 ± 13	≤ 740
Anthracene	14 ± 1	≤ 16
Fluoranthene	102 ± 5	≤ 120
Pyrene	73 ± 2	≤ 30
Benz(a)anthracene	26 ± 3	≤ 13
Chrysene	21 ± 3	≤ 22
Benzo(b)fluoranthene	27 ± 4	≤ 44
Benzo(k)fluoranthene	29 ± 3	≤ 22
Benzo(a)pyrene	45 ± 3	≤ 99
Indeno[1,2,3-cd]pyrene	54 ± 20	≤ 16
Benzo(ghi)perlyene	40 ± 18	≤ 50

† PUF is 2x3 in. plug cleaned by compression for 25x with: toluene, acetone and then cyclohexane/DCM (4:1).

‡ XAD-2 is 30 gm of resin cleaned by soxhlet for 22 hrs. with: MeOH, DCM and then hexane.

≤ indicates the quantitation limit reported by CARB for XAD-2 resin.

the PAH in the third fraction.

Supercritical fluid extraction (SFE) was conducted on both SRM #1649 (atmospheric particulate matter) and SRM #1650 (diesel particulate matter) at pressures from 300 to 500 atm and temperatures from 35 - 65 °C using a series of commonly investigated supercritical fluids including: carbon dioxide, carbon dioxide with 5% methanol, nitrous oxide, and nitrous oxide with 5% methanol. Non-polar carbon dioxide was the least effective in extracting PAH from either standard reference material. The addition of 5% methanol, to increase the polarity of the carbon dioxide supercritical fluid, was more effective in extracting most of the certified PAH compounds than nitrous oxide (N_2O) and only slightly less effective than nitric oxide with 5% methanol modifier. In general, SFE extractions for 60 minutes using carbon dioxide with 5% methanol recovered significantly less PAH than a three minute extraction with the Process Control Ultrasonic (PCU) technique. For example, SFE using CO_2 with 5% methanol at 300 atm and 65°C recovered less than 55% of the BaP from SRM #1649 compared with 97% BaP recovery for PCU extraction. Micro-column chromatography clean-up was necessary on the SFE extracts due to the large quality of accompanying substances co-extracted with the PAH.

10.4.3 Adsorbed PAH Vapor Extraction

A comparison of background levels of 15 priority PAH compounds in pre-cleaned PUF and XAD-2 resin sorbents is included as Table 10-4. Pre-cleaning of the PUF was performed using the Simple Compression Rinsing (SCR) technique and the XAD-2 resin was pre-cleaned by Soxhlet extraction for 22 hours with MeOH, DCM, and then hexane. Background levels were determined by extracting pre-cleaned 5 cm (2 in) x 7.6 cm (3 in) diameter PUF plugs with 40 mL of DCM by SCR, and 30 grams of pre-cleaned XAD-2 resin with 700 mL toluene by the Soxhlet procedure. In each case, the sample size chosen for extraction and GC/MS MID analysis represents a typical quantity of

Table 10-5. Simple Compression Extraction Recoveries from PUF for Standard Solutions (2000 ng/sample PA^2H spike).

PAH Species	Extraction Solution Spike† (% recovery)	Direct Foam Spike‡ (% recovery)
Acenaphthylene	93 ± 3	85 ± 5
Acenaphthene	89 ± 3	80 ± 5
Fluorene	114 ± 12	100 ± 4
Phenanthrene	93 ± 5	90 ± 5
Anthracene	94 ± 4	92 ± 5
Fluoranthene	93 ± 5	91 ± 4
Pyrene	91 ± 3	91 ± 3

† Internal Standards (PA^2H) added directly to the DCM extraction solution before foam compression.

‡ Internal Standards added directly to the foam before compression in the extraction solution.

sorbent to be used in sampling vapor phase PAH.

As shown in Table 10-4, the background levels measured by GC/MS for the priority PAH compounds were comparable for both XAD-2 and PUF, with the exception of naphthalene. Naphthalene and alkylated derivatives of naphthalene are known to be high level contaminants commonly found throughout the XAD-2 resin matrix (Hunt, 1986). High residual levels of naphthalene (as well as benzene and toluene) are not uncommon in resin cleaned by the current Soxhlet extraction procedure, and can preclude accurate quantitation of these species in combustion source emissions.

In order to evaluate the potential losses of PAH during the PUF extraction procedure, the deuterated forms of all 16 priority PAH compounds were introduced as internal standards before Simple Compression Extraction (SCE) of pre-cleaned PUF plugs. For comparison, 2000 ng of each internal standard was introduced either as an indirect spike to the DCM extraction solution or as a direct spike to the interior of the PUF plug. After SCE, the extract volumes were concentrated to 1 mL and analyzed by GC/MS following the same isotope dilution technique employed for extracts of particulate samples.

In Table 10-5, the SCE recoveries are shown for those deuterated PAH compounds (less-than-five-rings), which are expected to be present in the vapor phase under the dilution volume sampling conditions of the RADS system. Nearly complete recoveries were observed for most of the PAH compounds with somewhat greater losses occurring when the internal standards were spiked directly into the PUF plug. Direct spiking of the PUF plug after field sampling could be used to determine volatile loss of PAH during field storage and transportation back to the laboratory for analysis. In general, the recoveries for internal standards extracted from pre-cleaned PUF plugs by SCE at the 2000 ng/sample level were significantly higher (factor of 2) than the recoveries

11.0 FIELD TRIAL RESULTS

11.1 Overview

Side-by-side comparisons of a new integrated method for the measurement of combustion source PAH, and the Modified Method 5 (MM5) sampling technique, currently used as a part of the CARB PAH Method #429, were conducted on a 500 kilowatt diesel generator stack in Berkeley. The intent was to perform a source test under field sampling conditions which would provide a realistic setting for a preliminary comparison of the two methods. Since the RADS system had not yet been field tested, performance optimization of the sampler had to be conducted on the diesel source before the side-by-side sampling. This required a significant additional research effort. Accordingly, in lieu of planning additional tests at an second source site, tests were conducted only at the Berkeley Way site with the addition of the real-time PAH monitor to the comparison. The source test trials were conducted over a period of two days and consisted of three side-by-side sampling runs. A more extensive field comparison including other types of combustion sources was beyond the scope of the current project.

The new integrated source method consisted of the Reduced Artifact Dilution Sampler (RADS) and the prototype real-time Photoelectric Aerosol Sensor (PAS). The PAS was tested as a potential source survey tool and loading monitor for the sampling of PAH combustion aerosol. The RADS was tested as a new sample collection technology, designed to provide a more representative measurement of the chemical and physical form in which air toxics are emitted from combustion sources.

CARB provided all the equipment, cleaned sampling media, and staff to conduct the MM5 sample collection. CERL provided the corresponding items for the RADS and PAS instruments. The CARB contract laboratory (Alta Analytical) performed the sample extraction, preparation and analysis for all MM5 filter samples and

routinely reported for pre-cleaned XAD-2 by the Soxhlet extraction technique employed in CARB method #429 (CARB Source Test Report #C-87-001, 1989).

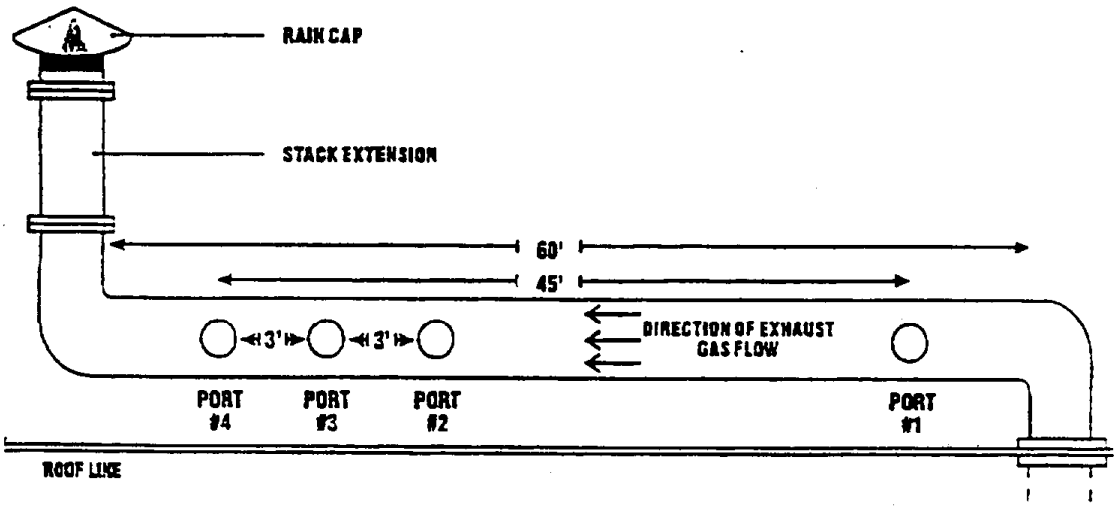


Figure 11-1. A schematic of the 500 kW diesel generator exhaust duct and sampling port configuration for the intermethod comparison field trials.

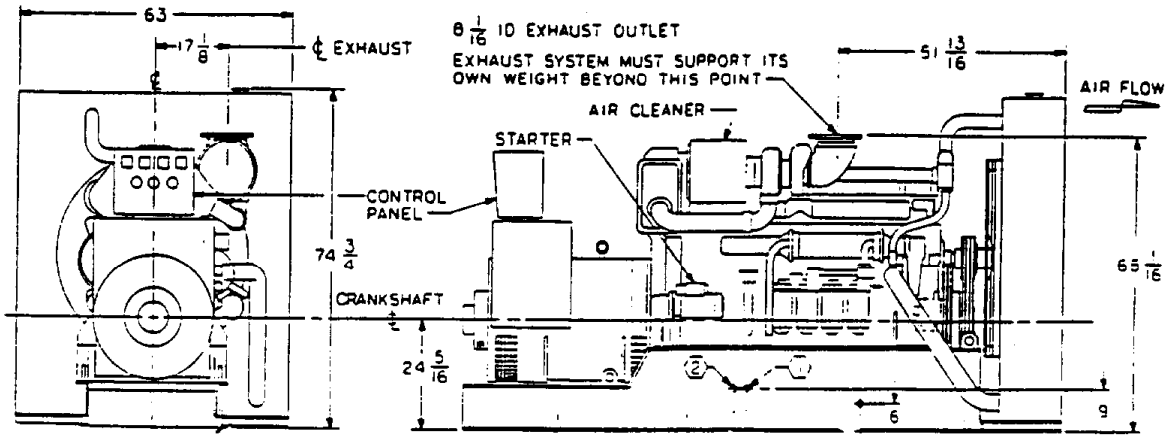
XAD-2 resin collected samples. This included prescreening the sampling media for PAH blank levels. Half the sample extract was to be archived for subsequent CERL analysis. CERL performed the sample extraction, preparation, and analysis for all RADS collected samples using the techniques as described elsewhere in the final report. Half the sample extract was to be archived for subsequent analysis by CARB.

11.2 RADS Stack Operation

The site for the intermethod comparison was the 500 kilowatt emergency diesel electrical power generator located in the basement of the Department of Health Services Laboratory building at 2151 Berkeley Way, in Berkeley, California. The exhaust stack from the diesel generator passed through the basement ceiling and extended for 18 m (60 ft) parallel to the roof line at 1 m above the cement slab style roofing surface. A new 2 m vertical exhaust stack extension was added to elevate the plume away from the sampling platform. The 25 cm (10 in) diameter stack was also outfitted with 10 cm (4 in) diameter sampling ports to accommodate probes from the RADS, PAS, and MM5 for side-by-side sampling on the roof as shown in Figure 11-1. Ports 2 and 3 were used to introduce sampling probes from the RADS and PAS respectively, while the MM5 probe was introduced through Port 4. The Engineering and Laboratory Evaluation Branch (ELB) of the Monitoring Laboratory Division (MLD) of the California Air Resources Board operated the MM5 sampler as part of the standard PAH Method #429. The Combustion Emissions Research Laboratory (CERL) of the Environmental Health Laboratory Branch operated both the RADS system and the PAS instrument. Less than two person hours were required to assemble the RADS in place, test all control systems, and have the system ready for stack operation.

The emergency generator was operated by the building Facilities Management Engineers to maintain a no-load steady state condition throughout the sampling trials. The generator specifications and

Table 11-1. Specifications of the 500 kW Diesel Generator Source and the Stack Sampling Conditions for the Intermethod Comparison.



500 kW Diesel Generator Source

Specifications	
Generator Engine	Type: 4 Cycle, Diesel Turbocharged/Aftercooled Displacement: 21.7 liters Bore x Stroke: 16 cm x 18 cm Number of Cylinders: Six Combustion air: 837 L/sec
Sampling Conditions	
Exhaust Stack	Diameter: 25.4 cm Temperature: 203 (C) Velocity: 11.4 m/s @ STP
Reduced Artifact Dilution Sampler (RADS)	Nozzle diameter: 6.35 mm Probe flowrate 21 L/min Sampling velocity: Isokinetic Dilution ratio: 35 to 1
Photoelectric Aerosol Sensor (PAS)	Nozzle diameter: 8.3 mm Probe flowrate: 8 L/min Sampling velocity: 7.6 m/s

exhaust stack sampling conditions, as measured by the solid state sensors on the RADS probe, are shown in Table 11-1. Radial profiles of the stack indicated a flat velocity distribution and uniform temperatures for all three of the intermethod sampling ports which were located near the stack exit. Specially designed Tedlar covered glass wool batts wrapped around the probes functioned as port seals to prevent leakage of diesel exhaust and to avoid disturbance of the stack flow profile. The cross-flow dimension of the probes was determined to be less than 3% of the stack cross-section and the probe ports were placed more than 70 probe diameters apart to minimize upstream flow effects.

The RADS microprocessor driven controllers were designed to automatically maintain both isokinetic sampling and a preselected dilution ratio for the sampled combustion products. Table 11-1 lists the nominal RADS probe operating conditions for isokinetic sampling as well as the sampling conditions for the PAS. The RADS system successfully maintained isokinetic and isothermal sampling conditions for stack velocities over 11 m/s (36 fps) at STPC and stack temperatures exceeding 200°C (392°F). Under these conditions, dilution factors approaching 35:1 were necessary to reach near ambient temperature conditions for sample collection. Dilution to ambient air temperature conditions was a necessary operating condition, so that chemical reactions between condensing constituents occur under physical and chemical conditions similar to those at the stack exit.

A performance index for the microprocessor control system, which maintained the isokinetic stack sampling conditions at a specified fixed dilution ratio, is shown for a two run sampling sequence in Figure 11-2. Isokinetic sampling occurs when the ratio of the probe inlet nozzle velocity to the freestream stack velocity is unity. Except for a momentary spike at the beginning of a run as the blowers were started, isokinetic sampling was maintained within 5%

over the course of the run until high filter loadings caused a flow decrease just before the end of the run. Similar performance was observed for the dilution system which maintained the required 35:1 dilution ratio within 5% except for the momentary spikes at the beginning and end of each run. These performance index traces (Figure 11-2) were available in real-time as a feature of the RADS internal data logger graphics display.

11.3 PAS Performance

The real-time Photoelectric Aerosol Sensor (PAS) was tested as a potential source survey tool and loading monitor for the sampling of PAH combustion aerosol from the 500 kW diesel generator. The usefulness of the PAS as a survey and/or loading monitor stems from the low cost and portability of this device. Although the PAS measures total particle phase PAH, a universal calibration has been obtained which encompasses a large variety of source types. As used in this field trial, benzo(a)pyrene (the analyte of interest for CARB) was estimated as a fraction (4%) of total particulate PAH measured by the PAS. The total particle phase PAH was determined from the PAS signal employing the new revised version of the original PAS universal calibration curve as shown in Figure 10-6. The universal calibration curve was revised from an earlier version to conform more closely to the slope recommended by the manufacture.

Using the PAS as a source survey tool on test day, CERL used the observed signal ($6x10^4$ pA-s/m^3) to estimate the diesel generator stack concentration to be near 40 $\mu g/m^3$ total particulate phase PAH or 1.6 $\mu g/m^3$ benzo(a)pyrene. From an estimated RADS stack probe flowrate of 21 L/min (0.74 CFM), required to achieve isokinetic sampling, and a target analytical level of 350 ng/sample (350 pg/μL at GC/MS injection), CERL determined the optimum time for sampling was on the order of ten minutes. This surprisingly short sampling time requirement, was due to the very high levels of PAH containing particulate matter in the generator exhaust.

ELB elected to sample for considerably longer times of up to 100 minutes based on previous experience with diesel generator emissions and a pre-test PAS stack concentration estimate of 5$\mu g/m^3$ total particulate PAH. This pre-test PAS value of 5 ug/m^3 was based on an early unrefined universal calibration curve employed in the initial stages of field test planning. Using the revised curve of

Figure 10-6, available the first day of field sampling, the PAS pre-test measurement would have yielded a value closer to 20 ug/m^3 total particulate PAH.

Subsequent chemical analysis of sample extracts demonstrated that, as predicted by the PAS real-time monitor, a ten minute sampling period was more than sufficient to collect PAH for chemical analysis. Accordingly, MM5 samples had to be diluted by up to a factor of 100 before the high resolution mass spectrometer analysis could be conducted by Alta Analytical.

PAS measurements of the total PAH aerosol level in the stack during sampling were also successfully used to provide a continuous record of the PAH loading over time. A comparison of the PAS record with the analytical results of the stack samples collected indicate that Method #429 and RADS particulate PAH values were 0.7 and 4.7 times the PAS value respectively. After recalculation of the universal curve, including the results from this diesel generator exhaust field study and diesel PAH signature laboratory combustor data (see Figure 11-4), these ratios become 0.4 and 2.7 respectively.

The PAS is not specific for individual PAH compounds; however, the device does measure the charge produced by UV irradiation of the PAH chemical signature adsorbed on combustion aerosol. Accordingly the PAS signal may display some sensitivity due to differences in the PAH signature between combustion sources. Currently the only full span calibration of the PAS consists of a universal curve based on a number of different combustion source types as shown previously in Figure 10-6. Unfortunately this calibration does not include measurements of PAS response for any diesel generator sources. A more definitive calibration requires PAS measurements to be performed on aerosol with the diesel generator PAH signature. This underlines the necessity of gaining further field and laboratory experience with the response of the PAS.

Recently the Micro-capillary Combustor (MCC) system developed in our laboratory (see Figure 7-1) was tuned to produce a PAH composition signature similar to the 500 kW diesel generator. A comparison of the particulate PAH source signatures of the 500 kW diesel generator and for the MCC operating in the diesel signature mode are shown in Figure 11-3. The ability to tune the MCC to model different PAH sources provides a convenient method for studying the sensitivity of the PAS to changes in particulate PAH composition. As a well controlled laboratory PAH source, the MCC also offers the promise of allowing a source specific full span PAH concentration range for PAS calibration. A full span calibration is often unfeasible on real-world sources due to operational restrictions on the concentration range of PAH stack emissions. Together the PAS and MCC provide a powerful means for rapidly investigating the combustion conditions that lead to PAH aerosol formation.

An updated universal calibration curve including the points derived from the 500 kW diesel generator intermethod comparison is included as Figure 11-4. Also shown are new points obtained by operating the MCC in a mode to produce a PAH chemical figure print similar to the 500 kW diesel generator. The universal curve includes all of the PAS measurements currently available for a variety of diverse combustion sources. A straight line relationship between PAS signal and the aerosol phase PAH concentration was obtained for all sources within a factor of two.

The purpose of constructing a universal curve is to provide a general guideline for interpreting PAS source survey measurements, within the uncertainty of the PAS response to a change in combustion source PAH aerosol signature. Routine continuous monitoring of PAH aerosol emissions from a particular combustion source, as is contemplated by the new United States Environmental Protection Agency Enhanced Monitoring regulations, would require an insitu calibration with chemical analysis of collected samples to establish the PAH signature.

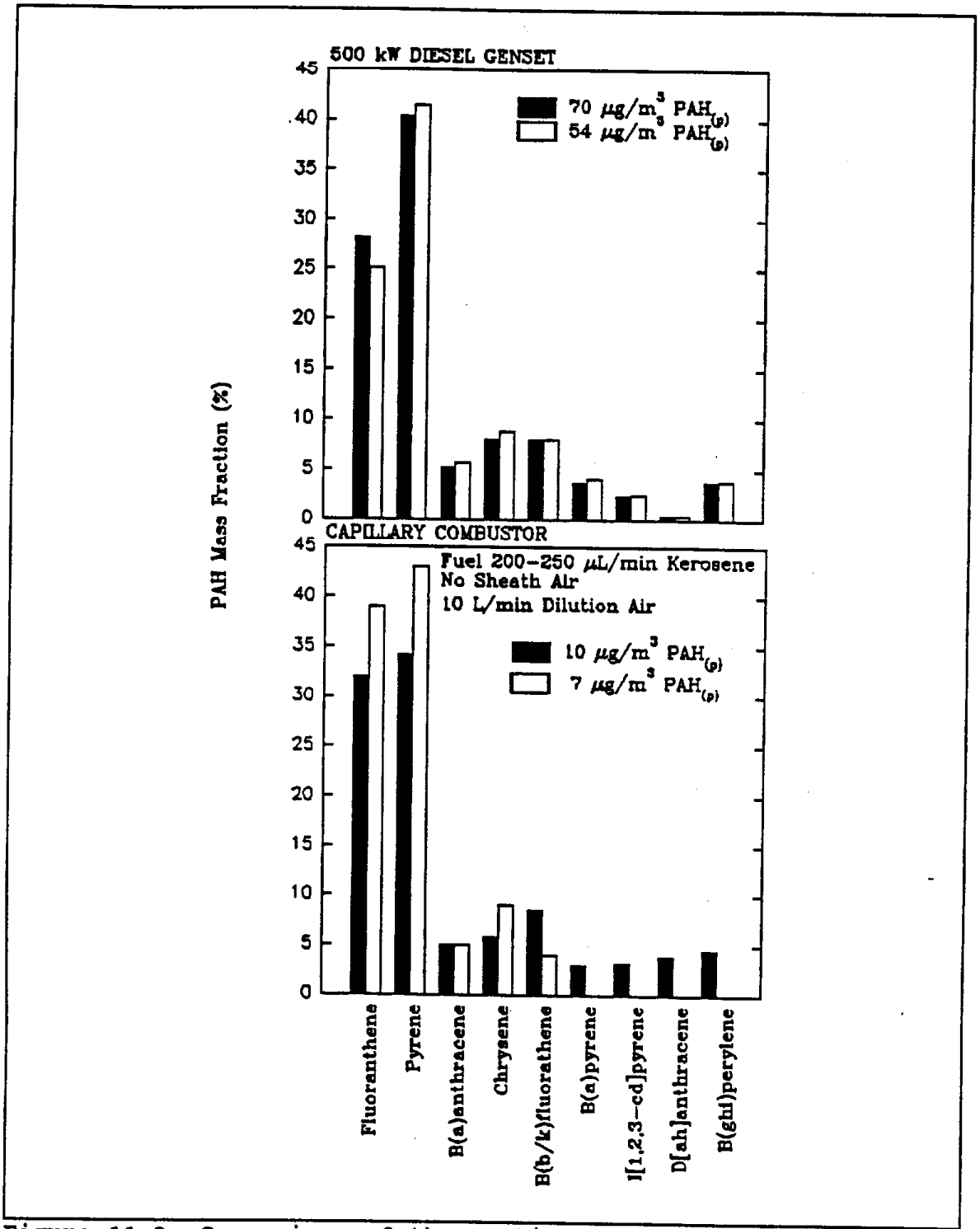


Figure 11-3. Comparison of the particulate PAH source signatures for the 500 kW diesel generator and the MCC operating in diesel signature mode.

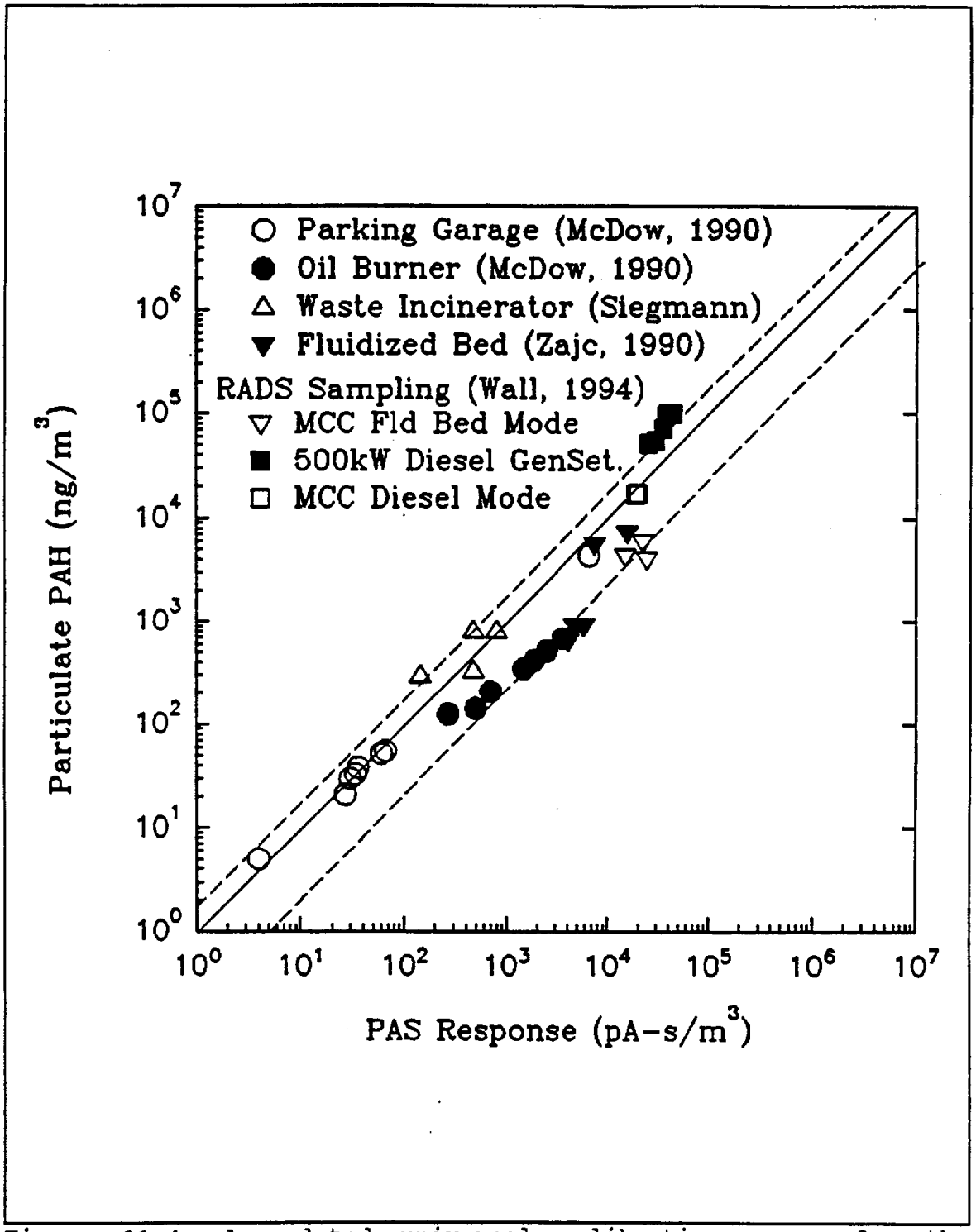


Figure 11-4. A updated universal calibration curve for the Photoelectric Aerosol Sensor (PAS) including measurements from the 500 kW diesel generator.

The usefulness of the PAS as a continuous source monitor relies on the applicability of the universal curve or a site specific calibration conducted at the source. As a continuous monitor, the PAS is best suited as a leading indicator to signal when a source requires additional testing. In order to obtain more detailed information on specific PAH compounds, further research is required to determine the sensitivity of the sensor to a change in PAH fingerprint, and the variability of the PAH fingerprint within a source type. Modifications to the basic instrument also need to be investigated in an effort to make the device more specific for PAH species of interest.

11.4 Analytical Method Comparison

In order to conduct the side-by-side method comparison, the MM5 sampler was operated to collect sample only during the 8-12 minute periods used to collect successive samples with the RADS. Three sampling runs were conducted, generating three PAH samples from the MM5 trains which were analyzed by the CARB's Engineering and Laboratory Branch's (ELB) contract laboratory (Alta Analytical) using the standard CARB Method #429 procedure. The samples from the RADS were carefully extracted and composites made to yield three samples which could be directly compared to those collected by MM5. The new CERL analytical method including Pulsed Ultrasonic Extraction (PUE) of the combustion particles and Simple Compression Extraction (SCE) of the PUF plugs was used to determine the PAH concentration by GC/MS. This method is outlined in section 8.0 and presented as a detailed protocol in Appendix B.

As agreed in the original protocol for the field tests, the ELB contract laboratory (Alta Analytical) analyzed the RADS composite samples previously analyzed by CERL to verify the results. The composite scheme for extracts of the RADS samples is shown in Figure 11-5. Composites for both CERL and Alta Analytical were prepared by combining equal aliquot volumes from each of the filter and PUF sample extracts. The aliquot volumes (A_i) were chosen to yield the same undiluted sample volume (V_t) and internal standard concentration as the individual extracts. Alta Analytical conducted the standard CARB Method #429 PAH clean-up and high resolution GC/MS analysis on the composite extracts, with modifications to account for different internal standards (I.S.) used by CERL for a few of the 16 priority compounds. By design, the extraction procedure for each sample was conducted by the standard protocol described in section 8.0 and listed in detail in Appendix B. The only modification for this field trial was to combine a constant volume aliquot from each extract to yield a composite sample with a volume and internal standard concentration equivalent to the standard CERL method. The purpose was to utilize the proposed

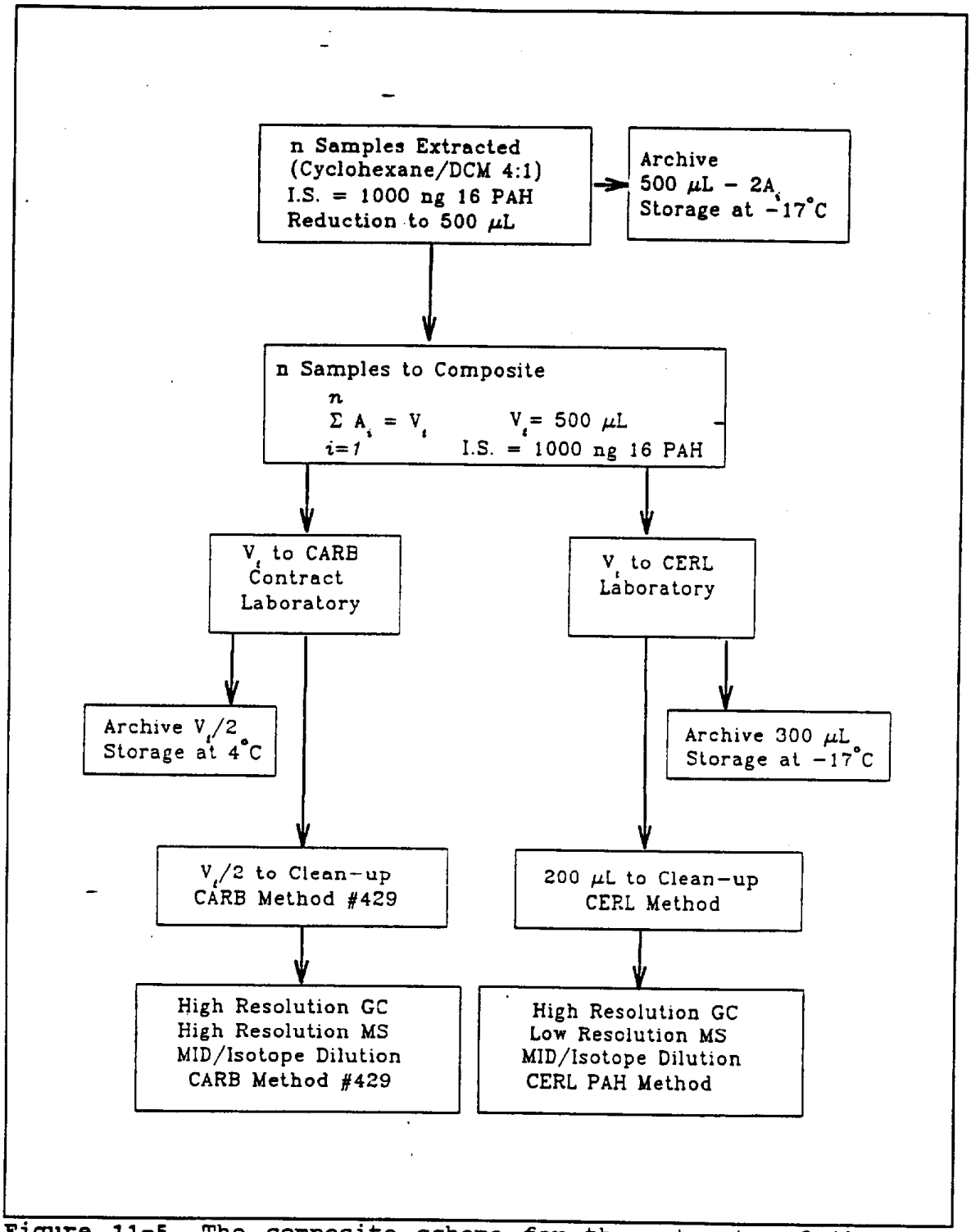


Figure 11-5. The composite scheme for the extracts of the RADS samples analyzed by both CERL and CARB, where the aliquot volume was chosen to yield the total volume of the original extracts.

analytical method in a form that was as close as possible to the detailed protocol included as Appendix B.

The 500 kW diesel generator stack concentrations for 16 priority PAH compounds determined by the new CERL sampling (RADS) and chemical analysis method are listed for each of the three trial runs in Tables 11-2, 11-3, and 11-4. Included for comparison are the ratios between the new CERL method and the CARB Method #429 analytical results for CERL composite extracts of the RADS samples. In general, as evidenced by ratios near 1.0, Method #429 analysis performed by Alta Analytical verified the CERL analytical results.

Significant differences in the results for the two laboratories, as determined by the t-test ($p<0.01$, two tailed, paired) were noted for naphthalene, acenaphthlene, fluorene, phenanthrene, benz(a)pyrene and dibenz[ah]anthracene. The primary concern here is that the internal standard recoveries reported by Alta for acenaphthlene, fluorene, anthracene, and phenanthrene were less than 25% and substantially lower (an order of magnitude lower for D_8-phenanthrene) than those reported by CERL. The inherit error in correcting for these large PAH losses may partially explain the difference.

One possibility for these low internal standard recoveries is a clean-up column capacity mismatch between the Method #429 and CERL methods. The CERL method uses a less polar extraction solution (cyclohexane/DCM 4:1) to reduce the necessary cleanup column capacity by an order of magnitude from the 250 x 10 mm column required for the pure DCM extractions of Method #429. The less polar extraction solvent utilized by CERL requires a proportionately larger amount of hexane (3.5 cleanup column volumes) to elute the less polar PAH fraction. Method #429 uses only 1.2 cleanup column volumes of hexane, which may be better matched to the higher proportion of polar compounds extracted with

Table 11-2. Sampling Trial Number 1: Comparison of Analysis Methods for PAH Collected by the RADS Sampling a 500 kW Diesel Generator Stack.

PAH Species	RADS† (ug/m^3)	CERL/CARB‡ (ratio)
Naphthalene	154.5 ± 0.9	0.5
Acenaphthylene	235.7 ± 5.8	1.2
Acenaphthene	50.5 ± 2.5	0.4 §
Fluorene	160.6 ± 7.7	0.3 §
Phenanthrene	544.7 ± 24.2	0.3 §
Anthracene	54.4 ± 1.0	0.2 §
Fluoranthene	55.1 ± 5.8	1.0
Pyrene	91.6 ± 0.3	0.8
Benz(a)anthracene	14.9 ± 0.3	0.7
Chrysene	20.4 ± 0.8	1.0
Benzo(b)fluoranthene	14.7 ± 0.1	1.4
Benzo(k)fluoranthene	4.2 ± 0.01	0.7
Benzo(a)pyrene	7.4 ± 0.4	0.6
Indeno[1,2,3-cd]pyrene	4.1 ± 0.2	0.8
Dibenz[ah]anthracene	0.62 ± 0.02	0.6
Benzo(ghi)perlyene	10.6 ± 0.2	1.3

† Combined extracts of Stack Probe, Teflon filter and PUF plugs.
‡ Extract composites of 5 sampling periods were split and analyzed by the CERL method and CARB Method 429.
§ Accurate quantitation by the CARB may have been complicated by low recoveries of the internal standard.

Table 11-3. Sampling Trial Number 2: Comparison of Analysis Methods for PAH Collected by the RADS Sampling a 500 kW Diesel Generator Stack.

PAH Species	RADS† (ug/m^3)	CERL/CARB‡ (ratio)
Naphthalene	210.6 ± 2.7	0.6
Acenaphthylene	273.6 ± 16.2	1.3
Acenaphthene	62.3 ± 8.0	0.5§
Fluorene	160.5 ± 2.5	0.3§
Phenanthrene	620.6 ± 10.1	0.3§
Anthracene	63.7 ± 2.4	0.2§
Fluoranthene	62.4 ± 8.8	1.2
Pyrene	96.4 ± 3.0	1.0
Benz(a)anthracene	15.2 ± 0.10	0.8
Chrysene	19.7 ± 0.5	0.9
Benzo(b)fluoranthene	13.6 ± 0.04	1.4
Benzo(k)fluoranthene	4.5 ± 0.4	0.7
Benzo(a)pyrene	7.5 ± 0.02	0.6
Indeno[1,2,3-cd]pyrene	3.7 ± 0.1	0.8
Dibenz[ah]anthracene	0.5 ± 0.1	0.6
Benzo(ghi)perlyene	10.3 ± 0.1	1.3

† Combined extracts of Stack Probe, Teflon filter and PUF plugs.
‡ Extract composites of 5 sampling periods were split and analyzed by the CERL method and CARB Method 429.
§ Accurate quantitation by the CARB may have been complicated by low recoveries of the internal standard.

Table 11-4. Sampling Trial Number 3: Comparison of Analysis Methods for PAH Collected by the RADS Sampling a 500 kW Diesel Generator Stack.

PAH Species	RADS† (ug/m^3)	CERL/CARB‡ (ratio)
Naphthalene	145.5 ± 0.6	0.5
Acenaphthylene	259.8 ± 3.5	1.2
Acenaphthene	60.5 ± 1.1	0.5 §
Fluorene	125.4 ± 20.4	0.2 §
Phenanthrene	571.3 ± 0.4	0.3 §
Anthracene	56.3 ± 0.7	0.3 §
Fluoranthene	51.6 ± 0.6	0.8
Pyrene	86.0 ± 0.2	0.8
Benz(a)anthracene	13.9 ± 0.2	0.8
Chrysene	19.6 ± 0.3	1.0
Benzo(b)fluoranthene	14.0 ± 0.4	1.6
Benzo(k)fluoranthene	3.9 ± 0.2	0.7
Benzo(a)pyrene	6.8 ± 0.003	0.6
Indeno[1,2,3-cd]pyrene	3.8 ± 0.05	1.0
Dibenz[ah]anthracene	0.5 ± 0.01	0.5
Benzo(ghi)perlyene	10.0 ± 0.2	1.4

† Combined extracts of Stack Probe, Teflon filter and PUF plugs.
‡ Extract composites of 5 sampling periods were split and analyzed by the CERL method and CARB Method 429.
§ Accurate quantitation by the CARB may have been complicated by low recoveries of the internal standard.

the pure DCM solution required by the CARB method. Since column cleanup methods must be optimized for the polarity of the extraction solvent used, it is not surprising to discover large differences in the internal standard recoveries when extraction and cleanup techniques are taken from different methods.

CERL had also agreed to verify the CARB analytical results for the MM5 samples. Unfortunately the archive extracts of the MM5 samples, normally saved as part of the Method #429 analytical procedure, were mistakenly discarded by the CARB contract laboratory (Alta Analytical). These archive samples would have afforded the opportunity to conduct the new CERL cleanup and analytical protocol on samples extracted by the conventional CARB Method #429 Soxhlet procedure. The possibility of re-analyzing the remaining extracts that had already undergone clean-up and analysis by Alta Analytical was eliminated due to uncertainties about the effect of their storage history. Apparently, these extracts lost up to 40% of their volume during several months storage by Alta Analytical at 4° C. No measurable volume change have been noted for RADS samples stored by CERL at -17° C in similar septum capped vials for periods exceeding three years.

11.5 RADS Performance

11.5.1 PAH Collection

The RADS system incorporated microprocessor-controlled isokinetic stack probe and dilution sampling systems for the collection of both vapor phase and particulate PAH. For this field study, the RADS was utilized in the simplified Volume Dilution System (VDS) sampler configuration without particle size segregation as shown in Figure 5-2. Intended for routine monitoring applications, this configuration was the most suitable choice for the intermethod comparison with MM5. In this configuration, the combustion products from the 500 kW diesel generator stack were sampled isokinetically and traveled 5 m through the 1.9 cm (0.75 in) diameter Teflon-lined probe at stack temperature to reach the dilution tunnel. Rapid mixing with clean dilution air occurred during transit through the Teflon lined dilution tunnel to the filter pack, where both particle and vapor phase PAH were collected. The interior of the stack probe and dilution tunnel represented unintended collection sites of some concern. Although not quantified for PAH, CARB has determined probe losses to represent over half of the particulate mass collected by the MM5 sampler (CARB Source Test Report #C87-072, 1989).

For the purposes of the intermethod field comparison, extracts of the sampling probe liner, dilution tunnel liner, filters and PUF plugs were combined to yield measurements of the total quantity of the 16 priority PAH collected. However, separate measurement of each deposit site was made during ten minute sampling runs prior to the intermethod comparison. These sampling runs were designed to develop new rapid and efficient methods for recovering PAH from the RADS interior surfaces. PAH losses to the stack probe and dilution tunnel liners were recovered using PUF plungers saturated with the standard CERL extraction solvent of cyclohexane/DCM (4:1) and pushed through the bore of each of these sampler sections. For the probe, the plunger consisted of 60 mL of solvent confined between two 2.5 cm (1 in) x 1.3 cm (0.5 in) diameter PUF plugs attached to

a flexible 0.32 cm (0.125 in) diameter polyvinylidene fluoride (PVDF) rod. The dilution tunnel plunger consisted of the same 2.5 cm (1 in) x 15 cm (6 in) diameter PUF plugs used as the RADS filter pack backup adsorbent, which were attached to a 0.64 cm (0.25 in) stainless steel tube and saturated with 125 mL of solvent. Each liner section was recovered twice, the extraction solvent collected and combined with the Simple Compression Extraction (SCE) of the PUF plunger.

Stack probe and dilution tunnel PAH deposition, for those species expected to be primarily in the particle phase at ambient temperature, are compared with the quantity collected on the Teflon filter during a ten minute run in Figure 11-6. Sampling losses to the 5 meter stack probe liner represented less than 15 percent of the filter deposit for most PAH aerosol including BaP. Losses to the dilution tunnel liner were an insignificant fraction of the filter deposit for most of these PAH including BaP. The measurable deposition of fluoranthene and pyrene to the large surface area of the dilution tunnel may reflect a significant vapor phase component for these compounds, which was absent for the higher molecular weight PAH as shown in the next figure.

The distribution of these PAH species between the particulate deposit on the Teflon filter and the vapor adsorbed in the PUF plug downstream of the filter is shown in Figure 11-7. As expected, only the higher vapor pressure PAH constituents were detected in the PUF plugs. Less than 25% of the fluoranthene and pyrene were present in the PUF backup adsorbent consistent with previous atmospheric sampling results for the same collection substrates (L. Van Vaeck et al. 1984). Various other deposit sites in the RADS were also analyzed for the more volatile PAH, to determine losses to locations other than the PUF backup adsorbent. No detectable levels of those PAH expected to be almost completely in the gas phase at STPC (including naphthalene, acenaphthylene and acenaphthene) where found in the inlet probe, dilution tunnel or on the Teflon coated

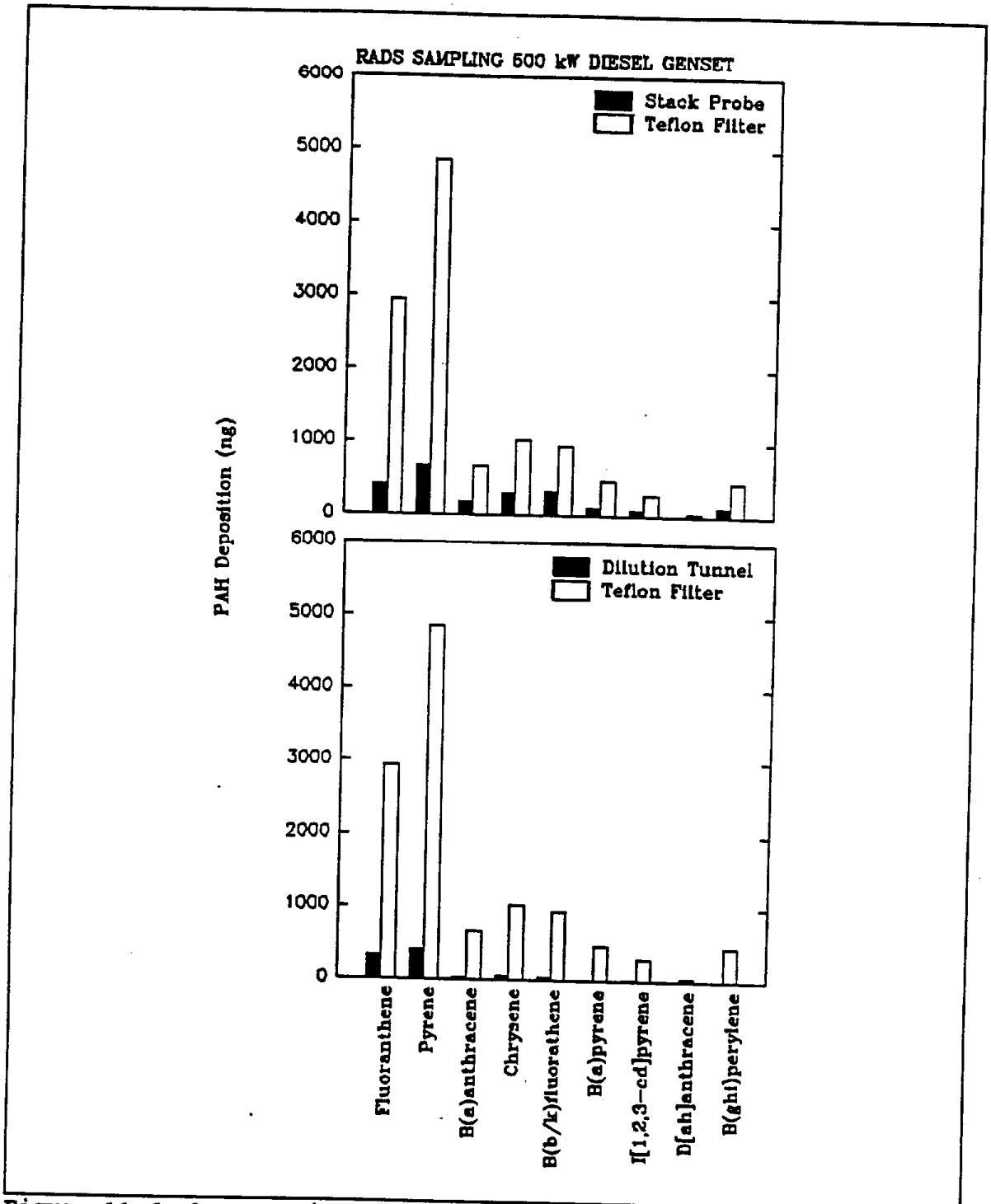


Figure 11-6. A comparison of the PAH collected by the Teflon filter with the unintended deposition to the stack probe (top frame) and to the dilution tunnel (bottom frame) for species primarily in the particle phase.

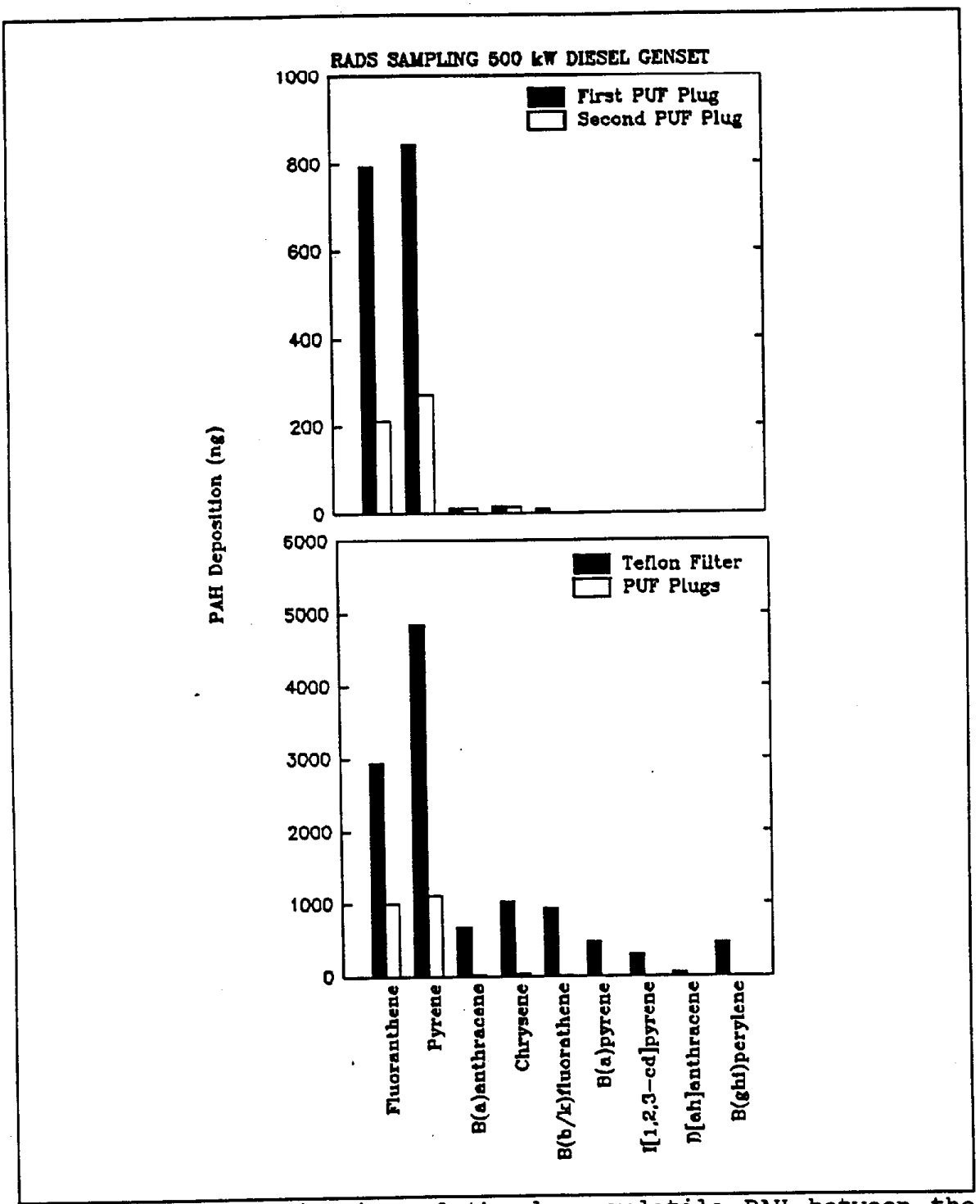


Figure 11-7. Distribution of the less volatile PAH between the particulate deposit and the vapor adsorbed in the PUF plug (bottom frame). The distribution of the same PAH between the different segments of the PUF plug (top frame).

filter. These PAH were found only in the extractables from the PUF plugs.

The absence of higher molecular weight PAH in the PUF extracts was also consistent with atmospheric sampling results, and indicated that no breakthrough of particles had occurred due to improper sealing of the filter cassette. The 15 cm (6 in) diameter PUF backup adsorbent for the filter cassette consisted of three 2.5 cm (1 in) thick plug segments, which were extracted and analyzed separately. The vapor phase PAH was collected in the first two PUF plug segments (5 cm thickness) with nearly 80 % captured in the first plug segment. No significant levels of PAH where found in the third plug segment, indicating sufficient adsorbent capacity to prevent breakthrough losses for these PAH for 10 minute sampling periods.

11.5.2 Comparison with MM5

Side-by-side field sampling trials of the new CERL method and the conventional CARB Method #429 conducted on the 500 kW diesel generator stack were intended to provide an intercomparison of these completely different methodologies. CARB Method #429 and the new CERL source method utilized substantially different techniques for stack sampling, sample handling, PAH extraction, cleanup, and analysis. The new CERL methods were devised to reduce artifacts inherent in the current CARB method which could produce an underestimate of the PAH present in the stack emissions.

The results of the side-by-side comparison indicate that the CERL method using the RADS reported substantially higher PAH levels than found with Method #429 using the MM5 sampler, as shown for all three field trials in Tables 11-5, 11-6, 11-7. For example, over six times more BaP was determined by the CERL method than reported for Method #429. The CERL method levels were higher by up to a factor of 10 for all 16 priority PAH compounds except naphthalene which was under-reported relative to Method #429. Naphthalene was expected to be primarily in the vapor phase and to deposit in the polyurethane foam (PUF) foam behind the Teflon filter in the RADS. Unlike the filter, the PUF plugs were not changed after each 10 minute period during a sampling run and may have suffered breakthrough for the highest vapor pressure PAH, naphthalene.

A comparison of the PUF air sampling volumes with the calculated breakthrough volumes has been made for all three field sampling runs. The breakthrough volume of the RADS PUF plugs was computed for those PAH expected to be in the vapor phase as shown in Appendix F. These theoretical calculations suggest that the PUF plug collection efficiency was nearly 100% for all vapor phase PAH, except for acenaphthylene (70-90%) and naphthalene (<10%). Low PUF plug collection efficiencies for naphthalene have been observed before for long duration high volume atmospheric sampling by Chuang, Hannan and Wilson (1987). When compared with XAD-2,

Table 11-5. Sampling Trial Number 1: Comparison of the PAH Collected by the RADS and the MM5 Methods Sampling a 500 kW Diesel Generator Stack.

PAH Species	RADS† (ug/m^3)	RADS/MM5‡ (ratio)
Naphthalene	154.5 ± 0.9	0.2
Acenaphthylene	235.7 ± 5.8	19.1
Acenaphthene	50.5 ± 2.5	3.1
Fluorene	160.6 ± 7.7	3.5
Phenanthrene	544.7 ± 24.2	7.2
Anthracene	54.4 ± 1.0	7.2
Fluoranthene	55.1 ± 5.8	7.3
Pyrene	91.6 ± 0.3	7.8
Benz(a)anthracene	14.9 ± 0.3	7.5
Chrysene	20.4 ± 0.8	7.2
Benzo(b)fluoranthene	14.7 ± 0.1	4.7
Benzo(k)fluoranthene	4.2 ± 0.01	4.7
Benzo(a)pyrene	7.4 ± 0.4	5.7
Indeno[1,2,3-cd]pyrene	4.1 ± 0.2	2.2
Dibenz[ah]anthracene	0.62 ± 0.02	2.8
Benzo(ghi)perlyene	10.6 ± 0.2	4.4

† Combined extracts of Stack Probe, Teflon filter and PUF backup absorbent.

‡ RADS values are composites of 9 sampling periods, each of approximately 9 minutes duration. The MM5 train collected one continuous sample over the same 9 sampling periods.

Table 11-6. Sampling Trial Number 2: Comparison of the PAH Collected by the RADS and the MM5 Methods Sampling a 500 kW Diesel Generator Stack.

PAH Species	RADS† (ug/m^3)	RADS/MM5‡ (ratio)
Naphthalene	210.6 ± 2.7	0.3
Acenaphthylene	273.6 ± 16.2	6.2
Acenaphthene	62.3 ± 8.0	3.7
Fluorene	160.5 ± 2.5	3.5
Phenanthrene	620.6 ± 10.1	8.3
Anthracene	63.7 ± 2.4	6.2
Fluoranthene	62.4 ± 8.8	9.2
Pyrene	96.4 ± 3.0	9.3
Benz(a)anthracene	15.2 ± 0.10	8.5
Chrysene	19.7 ± 0.5	10.0
Benzo(b)fluoranthene	13.6 ± 0.04	6.6
Benzo(k)fluoranthene	4.5 ± 0.4	7.1
Benzo(a)pyrene	7.5 ± 0.02	7.3
Indeno[1,2,3-cd]pyrene	3.7 ± 0.1	2.2
Dibenz[ah]anthracene	0.5 ± 0.1	2.7
Benzo(ghi)perlyene	10.3 ± 0.1	4.6

† Combined extracts of Stack Probe, Teflon filter and PUF backup absorbent.

‡ RADS values are composites of 5 sampling periods, each of approximately 10 minutes duration. The MM5 collected one continuous sample over the same 5 sampling periods.

Table 11-7. Sampling Trial Number 3: Comparison of the PAH Collected by the RADS and the MM5 Methods Sampling a 500 kW Diesel Generator Stack.

PAH Species	RADS† (ug/m^3)	RADS/MM5‡ (ratio)
Naphthalene	145.5 ± 0.6	0.2
Acenaphthylene	259.8 ± 3.5	24.6
Acenaphthene	60.5 ± 1.1	4.6
Fluorene	125.4 ± 20.4	2.7
Phenanthrene	571.3 ± 0.4	5.4
Anthracene	56.3 ± 0.7	6.9
Fluoranthene	51.6 ± 0.6	6.5
Pyrene	86.0 ± 0.2	7.1
Benz(a)anthracene	13.9 ± 0.2	11.4
Chrysene	19.6 ± 0.3	6.0
Benzo(b)fluoranthene	14.0 ± 0.4	4.8
Benzo(k)fluoranthene	3.9 ± 0.2	4.8
Benzo(a)pyrene	6.8 ± 0.003	8.5
Indeno[1,2,3-cd]pyrene	3.8 ± 0.05	2.1
Dibenz[ah]anthracene	0.5 ± 0.01	2.5
Benzo(ghi)perlyene	10.0 ± 0.2	4.0

† Combined extracts of Stack Probe, Teflon filter and PUF backup absorbent.

‡ RADS values are composites of 9 sampling periods, each of approximately 8 minutes duration. The MM5 collected one continuous sample over the same 9 sampling periods.

Chuang et al. found PUF to collect less than 10% of the naphthalene present during 24 hr. high_volume sampling. Comparable levels of all other vapor phase PAH were found in side-by-side sampling with the two collection media.

Although only somewhat less volatile than naphthalene, levels reported by CERL for the more reactive PAH acenaphthylene were up to 20 times higher than determined by Method #429. Substantial decomposition of acenaphthylene collected on XAD-2, without a decrease in other PAH including naphthalene, has been previously reported for atmospheric sampling by Chuang, Hannan and Silvon (1987).

The range of intermethod ratios observed for the 16 priority PAH can be compared between runs for similar compounds, and between compounds within a sampling run. For example, the enhancement factor (CERL/M429) for acenaphthene and fluorene, expected to be in the vapor phase, was consistently between three and five. Factors of between two and five were consistently noted for the highest molecular weight PAH, expected to be in the particulate phase, including indeno[1,2,3-cd]pyrene, dibenz[ah]anthracene, and benzo(ghi)perlyene. Enrichment factors for intermediate molecular weight (three and four ring) PAH, expected to be in both the vapor and particle phase, ranged from seven to eight for the first run, from six to ten in the second run and from five to ten for the third run samples.

This side-by-side field test was only a preliminary intermethod comparison and the limited sample size does not allow an evaluation of the significance for the smaller enhancement factors. The factor for BaP over all three sampling runs was 7±1, and clearly represents a significant enhancement for the RADS samples. A more extensive field comparison satisfying the US EPA method 301 criteria for the minimum number of collocated samples would be necessary to confirm the significance of the enhancement factors.

Although this field comparison was not designed to elucidate the reasons for the disagreement between complete methods (including sampling and analysis), several fundamental points can be made to help clarify the significance of these results as follows:

(1) Both the CERL and CARB #429 analytical methods, including sample extraction, cleanup and chemical analysis, have been validated using Standard Reference Materials (SRM) for PAH on particulate matter from National Institute of Standards and Technology (NIST).

(2) There is general agreement between the CERL and Method #429 analytical methods for RADS samples collected from the 500 kW diesel generator and extracted by the CERL method. This agreement occurred despite a mismatch between the CERL extraction and the CARB Method #429 cleanup procedure.

(3) An SRM for PAH in particulate matter (NIST SRM #1649) analyzed by CERL using Method #429 extraction procedures, followed by CERL cleanup and chemical analysis (GC/MS), yielded results in good agreement with the NIST certified values (see Table 10-2).

These observations suggest that the different approaches used by the CERL and Method #429 analytical procedures cannot alone account for the substantially higher PAH levels determined by CERL when the complete methods (sampling and analysis) are compared.

In an attempt to understand the relatively large differences in PAH levels measured by the two source sampling methods, the PAH collection enhancement factor (RADS/MM5) was examined as a function of carbon number for each of the 16 priority PAH in Figure 11-8. Carbon number was chosen as an indicator for the magnitude of the conjugated π-electron ring structure which characterizes PAH chemistry on surfaces. The same parabolic trend with carbon number was seen for each of the three different sampling runs conducted for periods ranging from 50 to 80 minutes. The smallest enhancement factors occurred at both the lowest and highest carbon numbers, with maximum factors observed at the intermediate carbon numbers of

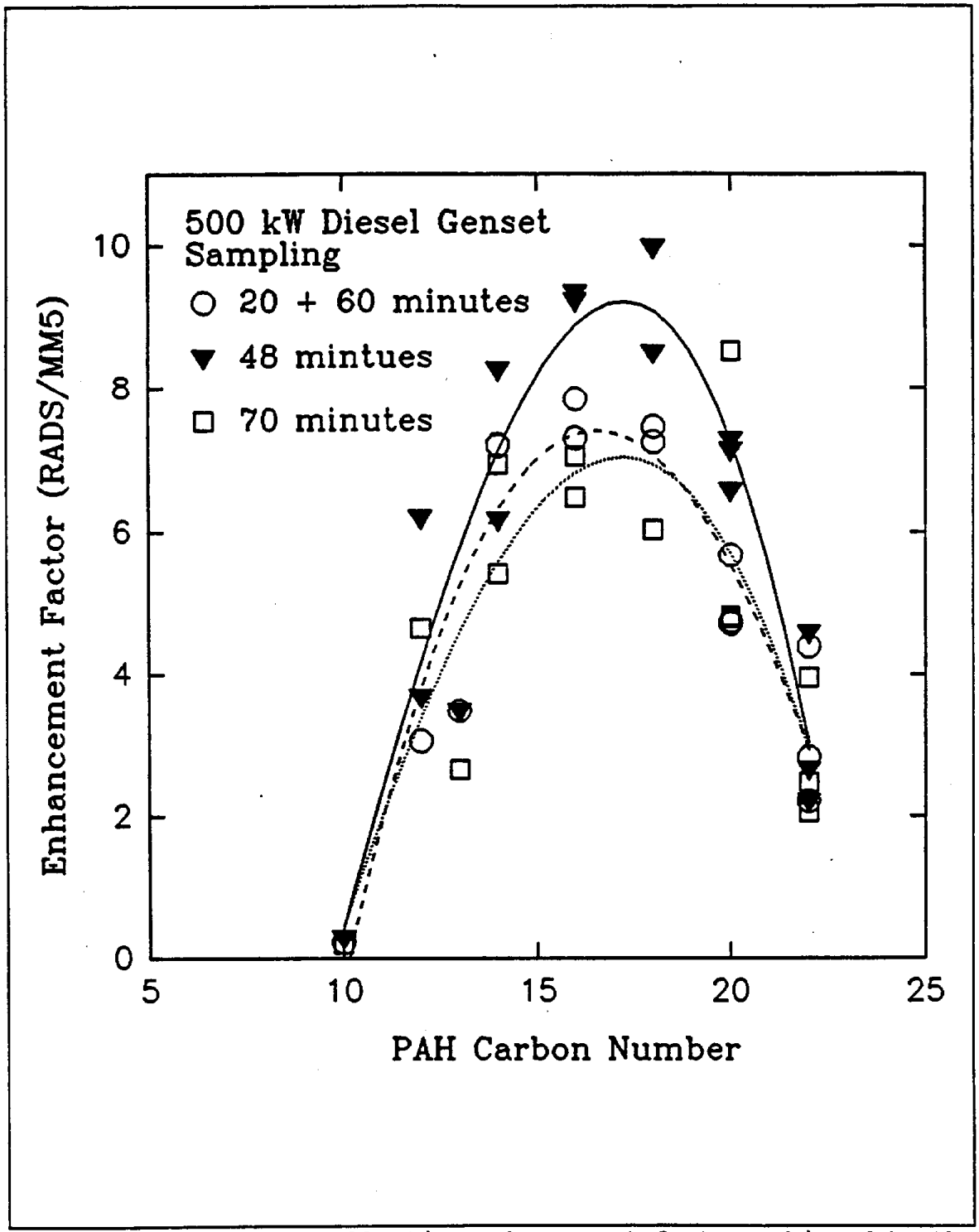


Figure 11-8. The PAH collection enhancement factor achieved by the RADS system over the conventional MM5 method as a function of the carbon number for each of the 16 priority species.

four member ring PAH (e.g. pyrene).

Previously, concern has been expressed that chemical artifact reactions can occur both in the heated filter section and the XAD-2 resin bed section of MM5 during sampling (see Table 4-1). These chemical reactions, which occur under the artificial sampling environment of MM5, are considered negative artifacts that act to produce an underestimate of the PAH present. Collection enhancement ratios > 1 for both the lower carbon number PAH, collected in the vapor absorbent behind the filter, and the higher carbon number PAH, collected on the particulate filter, were consistent with negative artifacts for both MM5 collection substrate environments. Intermediate carbon number PAH, with both vapor phase and particulate phase components, were subject to negative artifact formation in both the heated filter and XAD-2 adsorbent sections. This is consistent with the higher enhancement factors observed for these intermediate carbon number PAH.

This comparison of enhancement ratios as a function of carbon number (Figure 11-8), provides a starting point for a discussion of the relationship between potential chemical artifacts and collection site within the sampler. In order to identify possible artifacts, established indicators were explored for evidence of artifact mechanisms including electrophilic substitution (e.g. nitration) and decomposition (e.g. oxidation). One well-known indicator of PAH chemical transformation, the ratio of specific PAH compounds to benzo(e)pyrene (BeP), has been utilized by Daisey, Cheney and Lioy (1986) to catalog the available data on PAH fingerprints for specific source types. BeP was chosen as the normalization reference, since this compound was considered to be relatively stable and was known to be restricted to the particle phase under atmospheric conditions. Although Daisey et.al. also reported ratios for diesel exhaust derived from tunnel measurements, only the ratios reported for direct measurements of diesel exhaust at dilution ratios greater than four were considered

here:

The ratios calculated by Daisey et.al., from the data reported by Spindt (1974, 1977) for diluted heavy-duty diesel engine exhaust, are compared with results for the 500 kW generator field test in Table 11-8. Since CERL did not analyze for BeP, only analytical results reported by CARB (Alta Analytical) for both the RADS and MM5 samplers were used to calculate the ratios. In general, the ratios for the RADS are larger than those for MM5 and exhibit less run-to-run variation as evidenced by the substantially smaller coefficient of variation. This is notable since the 500 kW diesel exhaust stack conditions were quite constant over all three of the sampling trial runs. Stack temperature 200°C (392°F) and velocity 10.5 m/s (34.0 ft/s) varied by less than 1%, while stack gas concentrations (O_2@17%, CO_2@2.5%, CO@317ppm, NO_x@208ppm, and SO_2@34ppm) were unchanged within 3% to 5%. Under those conditions little variation in the PAH/BeP ratio might be expected between sampling trials. For the RADS samples, the coefficient of variation for this ratio was between 2% and 5% (8% for Pyrene) and for MM5 the variation was between 12% and 33%. By far, the largest coefficient of variation (103%) was seen for the acenaphthylene collected by MM5. Acenaphthylene, collected in the MM5 resin bed, is known to be susceptible to degradation and has been shown to undergo-oxidation on an XAD-2 resin substrate under the milder conditions of atmospheric sampling (Chuang, Hannan and Silvon, 1987).

Unlike acenaphthylene, BaP is much less susceptible to oxidative degradation, but is in a high reactivity class for electrophilic substitution (Nielsen, 1984). The proportion of BaP, relative to the much less reactive BeP, was significantly smaller for the MM5 collected samples and exhibited a coefficient of variation near 28%, compared to 2% for the RADS samples. Interestingly, the only parameter which displayed large run-to-run differences was the

Table 11-8. Selected PAH to BeP Ratios for the Field Trial Samples Collected by the MM5 and the RADS Methods.

PAH Species	MM5 ($\bar{R}$ ± c.v.[α])	RADS ($\bar{R}$ ± c.v.)	Heavy Duty Diesel Exhaust Dilution[β] (Daisey et.al., 1986)
Acenaphthylene	18.4 ± 103%	23.4 ± 6%	-
Phenanthrene	60.0 ± 20%	204. 0 ± 4%	1082
Fluoranthene	5.2 ± 14%	6.9 ± 5%	63
Pyrene	8.0 ± 13%	11.6 ± 8%	87
Benz(a)anthracene	1.2 ± 33%	2.2 ± 4%	5-25
Chrysene	1.8 ± 12%	2.3 ± 2%	1.2
Benz(e)pyrene	1.0	1.0	1.0
Benzo(a)pyrene	0.7 ± 28%	1.2 ± 2%	1.5-10
Benzo(ghi)perylene	1.7 ± 16%	0.9 ± 2%	0.5-1.2

α $\bar{R}$, Mean Ratio ± c.v., coefficient of variation for the three sampling trials.

β Ratios reported by Daisey et al. (1986) as calculated from the data of Spindt (1974, 1978) for dilution factors greater than four.

exhaust gas moisture content with a coefficient of variation near 24%. Water in conjunction with reactive gases (e.g. NO_2, SO_3) maybe important in producing acidic conditions which could promote the formation of artifacts due to degradation and electrophilic substitution.

Another indicator is the Nielsen PAH reactivity scale (Nielsen, 1984) for electrophilic substitution. This ranking scale, provides a convenient starting place to examine the potential for chemical artifact formation for different PAH species. However, the Nielsen scale is a qualitative ranking system and is difficult to utilize in a quantitative evaluation scheme. Accordingly, rather than taking ratios of relatively reactive to non-reactive PAH, the Nielsen scale can be used to rank the expected reactivity of each PAH within a carbon number class. Using the plotting format of Figure 11-8, this technique has been applied to all three sampling runs as shown for the third sampling trial in Figure 11-9. The Nielsen reactivity classes are indicated by Roman numerals with the first class (I) being the most reactive. Arrows are used to indicate a significant increase in the enhancement factor associated with an increase in the Nielsen reactivity for PAH in a carbon number class.

For example, the enhanced collection of BaP (reactivity class II) by the RADS is two fold greater than the enhanced collection for the benzofluoranthenes (reactivity class V). In all three field trials, a consistent correlation between greater enhancement factors (CERL/M429) and more reactive Nielsen rankings was observed for the highest carbon number classes (carbon numbers 20 and 22). These classes were expected to be completely in the particle phase and collected by filtration. Increases in enhancement factor accompanying greater Nielsen reactivity were noted for all carbon classes in the first and third field trials, with the largest increases occurring in the latter trial as shown in Figure 11-9.

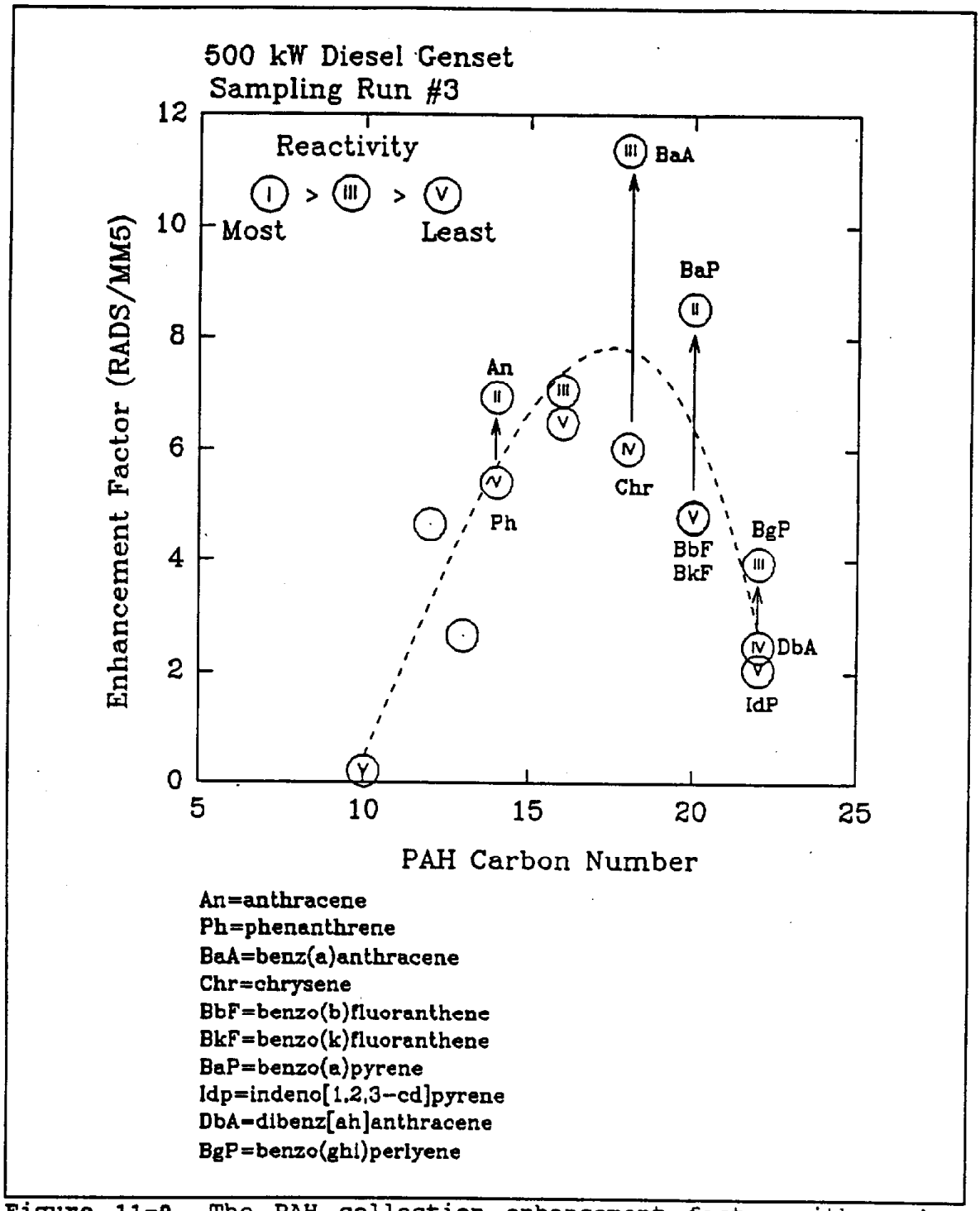


Figure 11-9. The PAH collection enhancement factor with carbon number showing the chemical reactivity of individual compounds. Arrows indicate an increase in enhanced collection by the RADS associated with increased reactivity.

The first and third field trials had substantially more moisture (60% and 40% more respectively) than the second trial. Except for the two highest carbon classes, enhancement factors for the second trial were not correlated with increases in Nielsen reactivity.

12.0 DISCUSSION

The dilution tunnel portion of the Reduced Artifact Dilution Sampler (RADS) was assembled and tested in the laboratory. A new lightweight dual blower system was devised to control both the dilution ratio and stack probe sampling rate by controlling the AC voltage supply to the blowers. Using this control technique, the inlet sampling velocity of the stack probe can be continuously matched with the stack free stream velocity to maintain isokinetic sampling.

A fixed portion 2 L/s (4 CFM) to 2.5 L/s (5 CFM) of the combustion products from the dilution tunnel are collected by up to four Reduced Artifact Sampler (RAS) trains designed to operate at 30 L/min. A new dual-channel pump system has been shown to automatically maintain the required constant flowrate of 30 L/min ±10% to each train, which is independent of filter pressure drop (from particulate loading) up to 330 mm (13 in) Hg.

A monolithic polyurethane foam (PUF) plug, has been adapted for use in the RADS system to replace the XAD-2 resin currently used to collect vapor phase PAH in Modified Method Five (MM5). A new Simple Compression Rinsing (SCR) procedure, developed to clean as many as four PUF plugs in only two hours, was found to be as effective as cleaning by Soxhlet extraction for 22 hours with methyl alcohol (MeOH), DCM and then hexane.

The compression procedure was also adapted as a post-sampling PAH extraction procedure, termed Simple Compression Extraction (SCE). In general, the recoveries for internal standards extracted from pre-cleaned PUF plugs by SCE at the 2000 ng/sample level (see Table 10-5) were significantly higher (factor of 2) than the recoveries routinely reported for pre-cleaned XAD-2 by the Soxhlet extraction technique of CARB Method #429 (CARB Source Test Report #C-87-001, 1989).

The new analytical method for the determination of PAH in combustion source particulate matter was successfully applied to diesel particulate matter. In general, PAH recovery efficiencies were similar to those reported for a 24 hour Soxhlet extraction of SRM #1650 using the same cyclohexane/DCM (4:1) solvent (Zajc et al., 1991). Recovery of 1-nitropyrene by the three minute Pulsed Control Ultrasonic (PCU) extraction was significantly higher (93%) than for the 24 hour Soxhlet technique (46%). The nearly complete recovery obtained for 1-nitropyrene, without an internal standard correction, is consistent with low losses of nitro-PAH compounds in the micro-column clean-up procedure.

A brief preliminary evaluation of supercritical fluid extraction (SFE) as a combined PAH extraction and clean-up technique was also conducted using Standard Reference Materials (SRM) from NIST. The mechanical problems previously experienced with the commercially available SFE instrument (ISCO model #1200) were solved by redesigning the capillary restrictor. In general, SFE extractions for 60 minutes using carbon dioxide with 5% methanol recovered significantly less PAH than a three minute extraction with the Pulse Ultrasonic Extraction (PUE) technique.

Initial attempts were made to utilize SFE as a single step extraction and clean-up technique by collecting a series of extract fractions at increasing SFE pressures. Although the solubility of PAH increases with supercritical fluid extraction pressure, a pressure fraction could not be identified which gave a sufficiently selective extraction of PAH to avoid the necessity of sample clean-up before analysis. Accordingly, SFE was not considered a viable alternative to PCU for combustion derived PAH particles.

A simple combustion source was constructed in the laboratory which consists of a modified catalytic kerosene combustion source, dilution system and a glass emissions stack. The laboratory combustion source provides freshly generated particle and vapor

phase PAH compounds to be used to evaluate the collection efficiency of the Reduced Artifact Dilution Sampler (RADS) train, the recovery efficiency of the new PAH analytical method, and the potential for calibrating the PAS for particle phase BaP.

Side-by-side comparisons of the RADS, PAS, and the MM5 sampling technique, currently used by CARB as part of the PAH Method #429, were conducted on the 500 kW diesel emergency generator at the California Department of Health Services in Berkeley. The intent was to perform a source test under field sampling conditions which would provide a realistic setting for a preliminary comparison of the two methods. Preliminary field evaluation results suggest that the new integrated stack sampling method incorporating the RADS and PAS offers significant advantages over the conventional methods employing Modified Method Five (MM5) manual sampling.

Utilizing the PAS as a source survey tool, CERL successfully determined that the optimum time for sampling was on the order of 10 minutes due to the high levels of PAH containing particulate matter in the generator exhaust. Forced to base sampling time estimates on previous experience with other diesel generator emission sources, ELB elected to sample for unnecessarily long periods. Accordingly, MM5 samples had to be diluted by up to a factor of 100 before analysis. This example illustrates the value of the PAS as a source survey tool. The response of the real-time PAS for diesel combustion derived PAH aerosol was sufficiently consistent with calibrations conducted on other combustion source types to be useful as a loading monitor during sample collection.

A source specific calibration was required to predict when the RADS had collected sufficient sample for chemical analysis of specific PAH compounds. The Micro-capillary combustor (MCC) has been operated to produce a source signature similar to that for the diesel generator and a fluidized bed combustor. A similar PAS response was observed for stack emissions from the diesel generator

and Micro-capillary Combustor (MCC) operating in diesel signature mode, as well as, the fluidized bed incinerator and the MCC operating in fluidized bed combustor mode. The MCC offers a promising approach to source signature specific calibrations which would allow the concentration of individual PAH to be estimated.

In these first field trials, the RADS system successfully maintained isokinetic and isothermal sampling conditions for diesel exhaust stack velocities near 11 m/s (36 f/s) at STPC and temperatures exceeding 200°C (392°F). A dilution factor of 35:1 was automatically maintained to reach near ambient temperature conditions for sample collection. Dilution to ambient air temperature conditions was a necessary operating condition, so that chemical reactions between condensing constituents occur under physical and chemical conditions similar to those at the stack exit. Sampling losses in the five meter stack probe represented less than 15 percent of the filter deposit for most PAH aerosol including BaP. PAH losses to the probe liner are of concern for artifact formation since they do not undergo the dilution and cooling which occurs at the stack exit. Although thorough cleaning was achieved with the new RADS interior surface extraction methods, liner replacement would be recommended before sampling a new emission source. Vapor phase PAH was collected in the first 5 cm of the 7.5 cm thick PUF plug indicating sufficient capacity to prevent breakthrough losses for up to an hour of sampling, except for naphthalene.

The analytical results of the side-by-side comparison indicate that the CERL method using the RADS reported substantially higher PAH levels than found with Method #429 using the MM5 sampler. For example, over six times more BaP was determined by the CERL method than reported for Method #429. The CERL method levels were higher by up to a factor of 10 for all 16 priority PAH compounds except naphthalene. Naphthalene is expected to be primarily in the vapor

phase and to deposit in the polyurethane (PUF) foam plugs behind the Teflon filter in the RADS. Unlike the filter, the PUF plugs were not changed during a sampling run and may have suffered break through for the highest vapor pressure PAH, naphthalene. This was in agreement with the theoretical calculations suggesting that the PUF plug collection efficiency was nearly 100% for all vapor phase PAH, except for acenaphthylene (70-90%) and naphthalene (<10%). In future the PUF plug will always be changed along with the Teflon filter to avoid this problem.

Chemical analysis for the field trial RADS samples was conducted using the new CERL analytical method for combustion source PAH. The Pulsed Ultrasonic Extraction (PUE) and a micro-column clean-up procedure proved to be a simplified and rapid analytical approach for the determination of PAH in the complex diesel combustion particle matrix. Simple Compression Extraction (SCE) of the PUF plugs and the same simplified single step clean-up technique provided efficient extraction of vapor phase PAH without interference from other substances co-extracted from the collection matrix. As agreed in the original protocol for the field tests, the CARB contract laboratory (Alta Analytical) analyzed the RADS composite samples previously analyzed by CERL to verify the results. CERL had also agreed to verify Alta's results for the MM5 samples; however, these samples were not stored at low temperature after analysis and suffered significant loss of volume. No CERL analysis was performed since the integrity of these samples was uncertain.

The sampling system was designed to collect PAH from the dilution system without significant artifact formation from acidic combustion gases or volatility loses from the particulate matter collected on the filter. Dilution volume sampling was utilized so that chemical reactions between the condensing constituents occurred under physical and chemical conditions similar to those at the stack exit. For this field study, the RADS was utilized in the

simplified Volume Dilution System (VDS) sampler configuration without particle size segregation. Intended for routine monitoring applications, this configuration was the most suitable choice for the intermethod comparison with MM5. A correlation between enhanced PAH collection by the RADS and carbon number suggests that sampling artifacts which act to reduce the PAH collected in MM5 occur in both the XAD-2 resin bed and on the heated filter. These results are consistent with the artifact arguments made in the original research proposal which prompted the development of the RADS system.

Together the PAS and RADS provide a promising integrated approach to determining the PAH emissions from stationary combustion sources. Although the PAS cannot be considered to be specific for individual PAH compounds, calibration with combustion aerosol has demonstrated the usefulness of the PAS as a total PAH aerosol monitor. Field screening of emission sources using the real-time PAH sensor provides an efficient approach to identifying sources with sufficiently high levels to warrant a more extensive chemical characterization. Depending on the level of PAH present, the RADS can be used as a high volume dilution sampler without particle size segregation or as a low volume reduced artifact sampler for respirable PAH. In either configuration, the PAS can be used as a RADS loading monitor to ensure sufficient sample is collected for the level of detailed chemical analysis required at a particular source. With a proper source specific calibration, the PAS real-time sensor may be useful as a continuous PAH source monitor for regulatory purposes.

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14.0 GLOSSARY OF TERMS

AIHL	Air and Industrial Hygiene Laboratory (now EHLB)
BaP	benzo(a)pyrene
BeP	benzo(e)pyrene
CARB	California Air Resources Board
CERL	Combustion Emissions Research Laboratory (EHLB)
CH	cyclohexane
DCM	dichloromethane
EHLB	Environmental Health Laboratory Branch
ELB	Engineering and Laboratory Evaluation Branch
GC/MS	gas chromatography/mass spectroscopy
^1H	undeuterated native compound
^2H	deuterium labeled compound
HTVS	High Temperature Velocity Sensor
LCS	laboratory control sample
MCC	Micro-capillary Combustor
MLD	Monitoring Laboratory Division
MID	Multiple Ion Detection
MM5	Modified Method Five
NIST	National Institute of Standards and Technology
PAH	polycyclic aromatic hydrocarbons
PA^2H	deuterated PAH
PAS	Photoelectric Aerosol Sensor
PCU	Pulsed Control Ultrasonic (instrument)
PDVF	polyvinylidene fluoride
POM	polycyclic organic matter
Pt-RTD	Platinum Resistance Thermometer Detector
PDVF	polyvinylidene fluoride
PTFE	polytetrafluoroethylene
PUE	Pulsed Ultrasonic Extraction
PUF	polyurethane foam
PVS	Photoelectric Vapor Sensor
RADS	Reduced Artifact Dilution Sampler

RAS	Reduced Artifact Sampler (low volume)
SCE	Simple Compression Extraction
SCR	Simple Compression Rinsing
SRM	Standard Reference Material
SSR	solid state relay
STPC	Standard Temperature and Pressure Conditions (20°C, 760 mmHg)
USEPA	United States Environmental Protection Agency
VDS	Volume Dilution System (high volume)

APPENDIX A

Development of an Improved Source Sampling Method For Polycyclic Aromatic Hydrocarbons, and Other Semi-volatile Organic Species, by Stephen Wall, reprint from J. Aerosol Sci., Vol. 21 (1990).

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DEVELOPMENT OF AN IMPROVED SOURCE SAMPLING METHOD FOR POLYCYCLIC AROMATIC HYDROCARBONS, AND OTHER SEMI-VOLATILE ORGANIC SPECIES

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INTRODUCTION

Benzo(a)pyrene (BaP) and other polycyclic aromatic hydrocarbons (PAH) are currently being considered for classification as toxic air contaminants in California. The EPA Modified Method 5 (MM5) sampling procedure is used in the United States to monitor sixteen EPA priority PAH compounds from combustion sources. MM5 is known to produce an underestimate of the PAH originally present due to artifacts produced by irreversible chemical reactions. In order to make assessments of combustion sources that emit PAH, a more accurate reduced artifact dilution sampling (RADS) system is under development which employs established and well characterized atmospheric sampling techniques.

CURRENT PAH SAMPLING METHOD

In Modified Method 5, combustion products sampled from the stack are passed through a heated filter to collect particles and the vapor phase components are collected by a resin trap placed downstream of the particulate filter. Artifacts are known to occur under the artificial environment created by the sampling conditions of MM5 (Griest et al., 1980; Gorse et al., 1983; Korfmacher et al., 1981). The effect of these chemical artifacts is to produce an underestimate of the amount of priority PAH pollutants present.

The atmospheric fate and potential adverse health effects are determined by the form in which these toxic organic materials are emitted after the initial atmospheric dilution at the stack exit. MM5 is designed to determine only the total concentration of PAH present in the hot combustion products in the stack. Although particles and gases are collected separately, the partition between particle and gas phase cannot be expected to reflect the partition that exists either in the stack or after emission into the atmosphere. This is due to the large differences which exist between the conditions in the stack, at the stack exit and in the MM5 sampling train.

PARTITION COEFFICIENT

PAH compounds are expected to occur in both the gas and particle phase, with the ratio of particle to gas phase concentration (partition coefficient, K_p) decreasing with increasing temperature as $K_p = C \exp(-\Delta H_a/RT)$ and increasing with decreasing vapor pressure (i.e. increasing with molecular weight within a homologous series). Here C is constant, T is temperature (°K), ΔH_a is the adsorption energy and R is the gas constant.

In Table 1, the excess energy of adsorption ($-\Delta H_p = \Delta H_a - \Delta H_v$) above the heat of vaporization (ΔH_v) for several PAH is compared for incinerator fly ash adsorption studies, fly ash sampled by MM5 and atmospheric aerosol collected by a PUF sampler. The excess adsorption energy is significantly greater and more variable for particulate samples taken with MM5. This suggests that PAH is bound much more strongly under conditions of MM5 collection than PAH on atmospheric aerosol or direct laboratory adsorption measurements on fly ash. This is consistent with a potential for MM5 adsorption sampling artifact.

Table 1. Excess Heat of Adsorption
(calculated from temperature dependence of the PAH partition coefficient)

Source:	Coal-Fired Power Plant	Municipal Incinerator	Tire Incinerator	Atmospheric
System:	Fly ash adsorption†		MM5 Sampler	Aerosol Sampler‡
PAH	Excess Heat of Adsorption, ΔH_a (Kcal/mole)			
Naphthalene	1.3	-1.1	2.8	---
Fluorene	4.6	2.6	8.5	---
Phenanthrene	0.0	2.2	18.5	1.6
Pyrene	0.1	-1.8	1.4	1.0

†Eiceman et al. (1983)
‡Yamasaki et al. (1982)

In Figure 1, a good correlation between the K_p and vapor pressure (at fixed temperature) for incinerator fly ash and for atmospheric aerosol sampling is consistent with simple reversible PAH condensation. Nearly linear slopes (slope ~ 1)

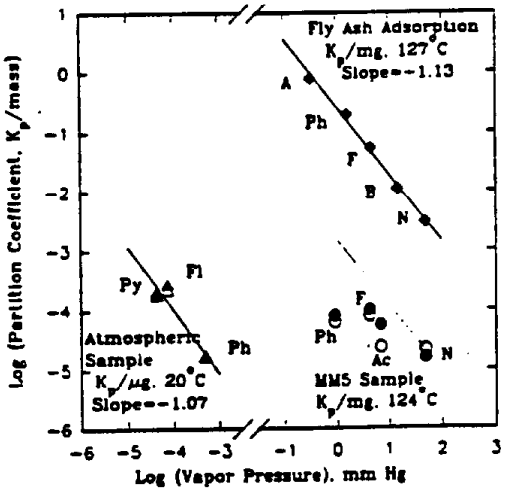

Figure 1. Relationship between the partition coefficient and the vapor pressure at fixed temperatures for different types of combustion aerosol samples. N=naphthalene; B=biphenyl; Ac=acenaphthalene; F=fluorene; Ph=phenanthrene; A=anthracene; Fl=fluoranthene; Py=pyrene.

were observed except for the striking deviation for higher molecular weight PAH compounds collected by MM5. The apparent undersampling of these adsorbed PAH by MM5 is consistent with a chemical conversion artifact, which interferes with the simple reversible condensation equilibrium for MM5 samples.

DILUTION SAMPLING

An improved sampling approach would include dilution of the combustion products to inhibit chemical artifacts, but in a manner that reflects the actual conditions of emission into the ambient atmosphere. In dilution volume sampling, the sampling conditions are designed to reflect those at the stack exit to the atmosphere. The undiluted combustion products are maintained at the stack temperature in the sampling inlet until emission into the dilution tunnel where the temperature, particulate and vapor levels decrease rapidly with the addition of large volumes of dilution air. In contrast to MM5, condensation of PAH vapors, reactive gases and water occur together on the surface of airborne combustion particles at near ambient temperature. Chemical reactions between the condensing constituents occur under physical and chemical conditions similar to those at the stack exit rather than under the artificial environment of MM5.

Despite recent advances, the currently available dilution sampling systems do not incorporate all the necessary design features to sample PAH and other semi-volatile organics in a manner which is representative of the physical or chemical form in which these compounds are emitted into the atmosphere.

REDUCED ARTIFACT DILUTION SAMPLER

A schematic diagram of the reduced artifact dilution sampling (RADS) system is shown in Figure 2. The dilution volume segment consists of a heated stack probe for iso-kinetically sampling the combustion products, a dilution tunnel in which the combustion products are mixed with large volumes of clean dilution air, and a residence chamber in which the diluted combustion products are given sufficient time (>1 minute) for condensation of vapor phase material onto the pre-existing combustion particles. The reduced artifact PAH collection segment consists of up to six samplers which collect the PAH particles and vapor phase components from the residence chamber.

The samplers consist of: a cyclone to remove particles greater than 2.1 μm in diameter, followed by an aluminum denuder to remove acidic gases (Wall et al., 1988), a Teflon filter to collect particulate matter, and a backup sorbent to trap PAH volatile loss from the filter catch. The aluminum denuder can also be followed by a PAH denuder to collect vapor phase PAH compounds ahead of the Teflon filter. This is to avoid chemical reactions which are known to occur with the surfaces of fly ash and other carbonaceous particles in the filter deposit. The PAH denuder collects the vapor phase PAH component, and combined extracts of the filter and PUF backup provide an accurate measure of the particulate phase PAH present during sampling.

CONCLUSION

A reduced artifact dilution sampling (RADS) system is under development which consists of an automated dilution system and reduced artifact PAH sampling system. The primary advantage of dilution volume sampling is that chemical reactions between the condensing constituents occur under physical and chemical conditions similar to those at the stack exit.

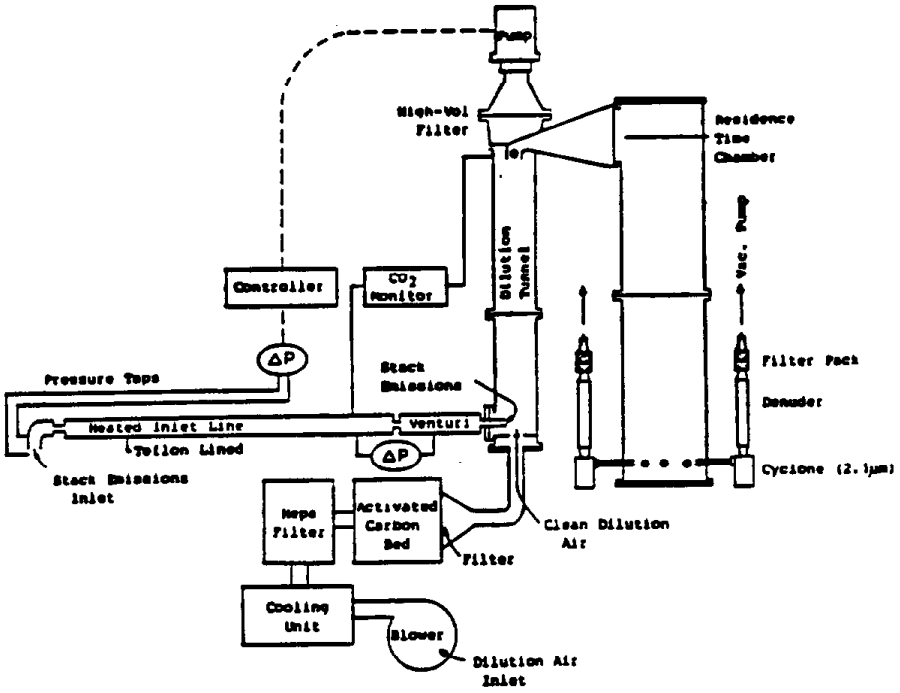

Figure 2. Improved Reduced Artifact Dilution Sampler for combustion source PAH collection.

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APPENDIX B

New Sample Preparation Methods for PAH Analysis by MID-GC/MS.

PULSED ULTRASONIC EXTRACTION (PUE):

1. Place the particulate filter sample to be extracted in precleaned 40 ml glass vials with Teflon-lined screw caps (see page B-6 for glass cleaning procedure). Add 35 ml of 4:1 (v/v) cyclohexane/dichloromethane (CH/DCM) and spike with 1000 ng (5 μL x 200 ng) of the deuterium labeled forms for the sixteen priority PAH compounds to be analyzed.

2. Cap the vial and ultrasonicate for six minutes, using a NEY proSONIK 360 watt ultrasonic unit (model #40-PRO-0506N) with the following control settings:

cf	band	sweep	train	degas	burst	quiet
5	5	10	10	8	5	5
(40 MHz)	(1 MHz)	(2 MHz)	(1 s)	(0.8 s)	(1.2 ms)	(1.2 ms)

Twelve samples can be extracted simultaneously.

3. The samples are then transferred to a 40 mL reservoir (30 mL graduated disposable syringe with the plunger removed) attached to a 25mm diameter 0.45 μm pore size Acropore(R) Teflon cartridge filter. The reservoir/filter combination has been previously mounted on a multi-port vacuum filtration chamber and rinsed with 15 mL of 4:1 (v/v) CH/DCM solution added to the reservoir. A valve on the port controls the flow of solution into a receiver vial in the chamber and prevents the filter cartridge from going to dryness during rinsing.

4. The extraction vial is rinsed with an additional 5 mL of the 4:1 CH/DCM solution, the cap replaced, and the vial vigorously shaken before addition to the reservoir.

5. The vial is then rinsed three times with the 4:1 solution to remove insoluble particulate matter which is discarded. The rinsed vial is then placed in the vacuum chamber and is used to catch the

filtrate.

6. The sample is filtered under a slight vacuum, < 100 mm (4 in) Hg below atmospheric pressure, to avoid loss of the more volatile PAH. If the filter is allowed to go to dryness during the rinsing step, the chamber vacuum must be increased temporarily, > 100 mm (4 in) Hg below atmospheric pressure to rewet the filter cartridge and initiate filtration. A 12 port vacuum chamber will allow 12 extracted samples to be filtered simultaneously.

7. After filtration is complete, the 12 reservoir/filter combinations are replaced with a manifold which allows a metered stream of nitrogen to pass through each chamber port above the sample filtrate collection vials. Under a slight vacuum, < 100 mm (4 in) Hg below atmospheric pressure, the sample volumes are reduced to approximately 1 mL under the constant nitrogen stream.

8. After volume reduction, the residual 1 mL is transferred to a calibrated 2 mL graduated vial. The 40 mL vial is rinsed with an additional 1 mL of the 4:1 CH/DCM solution, which is also added to the 2 mL graduated vial. The sample is returned to the nitrogen stream process until the volume is reduced to 500 μL mark on the vial. The graduated vials must be calibrated in advance, since the manufacturers 500 μL mark was found to be inaccurate by as much as 30%.

SAMPLE CLEAN-UP: MICRO-COLUMN TECHNIQUE

Micro-column Preparation:

(columns only prepared just before use)

1. Use a small amount of clean glass wool to plug the inner neck of a disposable glass Pasteur pipet to form the bottom of the column.

2. Silica gel 60 (70-230 mesh) is wetted with an sufficient amount of n-hexane to make a slurry in a 50 mL beaker. The slurry is swirled to prevent settling and pored into the plugged pipet until a height of 7.5 cm is reached after solvent evaporation. A vacuum is applied to remove the solvent and tightly pack the column to remove voids. Up to 12 columns can be processed by inserting the pipet tips into the ports of the vacuum chamber.

3. A moisture barrier is then applied to the top of the column using Silica gel 60 (230 mesh). The finer mesh Silica gel is wetted with an appropriate amount of n-hexane to make a slurry in a 50 ml beaker and added to the top of the column to from a 0.5 cm layer.

4. Another small amount of glass wool is packed on top of the column to act as an end plug.

Micro-column Sample Clean-up:

1. A thin wall Teflon tube is pushed onto the top of the Pasteur pipet column to form a convenient solvent reservoir. The tip of each column is inserted into a port of the vacuum chamber and up to 12 columns are rinsed with 10 mL of n-hexane delivered into the solvent reservoir under a slight vacuum, < 100 mm (4 in) Hg below atmospheric pressure.

2. A 200 µL aliquot of the total 500 µL sample extract obtained after volume reduction is added to the glass wool plug at the top of the column.

3. Addition of 2 mL of n-hexane is made to the top of the column

and the first fraction is collected under a slight vacuum in a 4 mL amber vial placed under the column inside the vacuum chamber. This fraction can be discarded.

3. Addition of 3.5 mL of n-hexane is made to the top of the column and the second fraction containing polychlorinated biphenyl (PCB) is collected under a slight vacuum in a clean 4 mL amber vial. The vial is sealed with a Teflon lined screw cap and stored at -17°C.

4. Addition of 3.5 mL of 4:1 (v/v) n-hexane/DCM is made to the top of the column and the third fraction containing PAH is collected under a slight vacuum in a clean 4 mL amber vial. The vial is sealed with a Teflon lined screw cap and stored at -17°C.

5. Addition of 5.5 mL of 2:1 (v/v) n-hexane/DCM is made to the top of the column and the fourth fraction containing nitro-PAH is collected under a slight vacuum in a clean 8 mL amber vial. The vial is sealed with a Teflon lined screw cap and stored at -17°C.

6. After fractionation is complete, the twelve Pastuer pipet columns are replaced with a manifold which allows a metered stream of nitrogen to pass through each chamber port above the sample fraction collection vials. Under a slight vacuum, < 100 mm (4 in) Hg below atmospheric pressure, and with a constant stream of nitrogen the sample volumes are reduced for each fraction in turn to yield approximately 1 mL.

7. The residual 1 mL is transferred to a calibrated 2 mL graduated vial. The 4 mL amber vial is rinsed with an additional 1 mL of the solvent corresponding to that fraction (e.g. 4:1 hexane/DCM for the third fraction extract containing PAH) and is added to the 2 mL graduated vial. The sample is returned to the nitrogen stream process until the volume is reduced to 500 μL mark on the vial.

8. The remaining 500 μL is transferred to a 1.8 mL amber autosampler vial. An additional 500 μL rinse of the graduated vial is added to the autosampler vial which is then capped with a Teflon lined septa and stored at -17°C until analysis by GC/MS.

Volumetric Vial Clean-up Procedure:
Since the calibrated volumetric vials must be reused, a cleaning procedure was used to remove all traces of organic compounds from previous samples.

1. Acetone is used to wash off any extract identification markings from previous samples (the volumetric vials are identified by numbers permanently engraved on the underside of each vial during the gravimetric 500 μL calibration process).

2. The vials are washed with a surfactant soap, rinsed with deionized water, and allowed to soak in a dichromate acid cleaning solution overnight.

3. After removal from the bath, the vials were thoroughly rinsed with deionized water to remove the acid. The vial are then rinsed with acetone to remove the residual water and then n-hexane.

4. The vials are wrapped in n-hexane rinsed aluminum foil and stored in a vacuum oven at 250°C and 720 mm (28 in) Hg below atmospheric pressure until required.

SIMPLE COMPRESSION EXTRACTION (SCE)

PUF Collected PAH Vapor:

1. A 2.5 cm (1 in) x 15 cm (6 in) diameter PUF plug is extracted in loaded into a 4.8 cm ID Pyrex glass columns and a Teflon plunger is inserted to compress the plug. Extraction of PAH proceeds by successive compressions of the PUF plug in several solvents. The compressions can be accomplished manually; however, an automatic compression device has been designed to conduct the extraction unattended, using timed application of pressure and vacuum to move the plunger.

2. The extraction column is closed and 520 mmHg (10 psi) above atmospheric pressure is applied to the plunger to compress the PUF plug.

3. Each PUF plug is extracted in 35-40 mL of CH/DCM (4:1) which is contained in a clean 40 mL glass vial below the extraction column. Application of vacuum, 100 mm (4 in) Hg below atmospheric pressure, lifts the plunger drawing the extraction solution into the PUF plug.

4. The successive cycles of pressure and vacuum compress the plug to extract the sorbed PAH from the PUF. Extraction continues for 35 one-minute cycles and ends with a last compression stroke at 1550 mmHg (30 psi) above atmospheric pressure to squeeze most of the extraction solvent from the PUF plug.

5. The extraction solution is then concentrated to 500 μL using the same procedure as for the filtered particulate extracts.

6. The residual 500 μL is transferred to a 1.8 mL autosampler vial. An additional 500 μL rinse of the graduated vial is also added to the autosampler vial which is capped with a Teflon capped septa and stored at -17°C until analysis by GC/MS.

SIMPLE COMPRESSION RINSING (SCR)

Pre-sampling Clean-up:

1. PUF plugs are loaded into 4.8 cm diameter Pyrex columns in the same manner as with SCE. The same compression technique used to extract the collected sample is also used to pre-extract the PUF to remove residuals from the PUF which are a by-product of the manufacturing process. This pre-cleaning is termed Simple Compression Rinsing (SCR).

2. Steps #2 through #4 of page B-8 are repeated four times. The first time using toluene as the solvent, the second using acetone and finally twice with CH/DCM (4:1). Each time the SCR solvent containing the extracted impurities is discarded.

3. After the final compression in CH/DCM (4:1), the plunger is removed, the extraction column is capped and evacuated to 720 mmHg (28 in) below atmospheric pressure to remove the residual solvent.

4. When the PUF is dry, the plug is transferred to a glass storage jar, which is filled with argon, capped, and stored in the dark.

APPENDIX C

Typical Chromatograms for MID-GC/MS of Sixteen Priority PAH at the Lowest Calibration Level (5 pg/μL).

During the development of the CERL analytical method for PAH analysis, the gas chromatograph operating conditions recommended by CARB in method #429 were modified to improve peak shape and height for maximum sensitivity. The optimum operating conditions used by CERL for all PAH analysis for this study are included in Table C-1.

Noteworthy are the use of a Special Programmable Injector (SPI) and an extended length of guard column at the head of the analytical column. This combination allowed low temperature (50°C) injection of large extract volumes (2 μL sample plus 1 μL solvent wash), followed by rapid injector heating, to recondense and concentrate the PAH ahead of the analytical column. Use of a low-bleed rate DB-5MS column allowed the feasibility of ramping to a higher temperature for better resolution of the higher boiling point compounds without a marked increase in the background signal.

The following stacked chromatograms are examples of the retention time windows utilized to identify and quantitate the 16 priority PAH compounds at the 5 pg/μL level. In each chromatogram, the ion current for the target PAH compound mass (as a function of retention time) is shown as the upper trace and the ion current for the corresponding deutrated internal standard mass is shown as the lower trace. Mass numbers for identification are shown to the left of each chromatogram, with the exact mass for each compound shown on the right-side. The numbers above each peak indicate the retention time scan number, peak height and peak area, reading from top to bottom. For identification purposes, the mass numbers and retention time scan numbers of each of the 16 priority PAH are listed in Table C-2.

Table C-1. Gas Chromatograph Operating Conditions for PAH Analysis.

GC/MS Component	Operational Parameter	Standard Setting
Autosampler:	Type	Varian 8100
	Injection Volume (μL)	2
	Solvent Plug (μL)[α]	1
Injector :	Type	Varian SPI[β]
	Mode	Splitless
Injector Program:	Temperature (^{0}C)	
	Initial	50
	Final	320
	Rate (^{0}C/min)	175
Carrier Gas:	Type	He (99.9999%)
	Velocity (cm/s)[η]	32
Guard Column:	Type	deactivated
	Length (m)	2-3
	ID (mm)	0.52
Column:	Type	DB-5MS
	Length (m)	30
	ID (mm)	0.25
	Film Thickness (μm)	0.25
Column Program:	Temperature (^{0}C)	
	Initial	70
	Final	320
	Rate (^{0}C/min)	10
	Hold Time (min)	
	Initial	8
	Final[κ]	13

α Hexane solvent plug separated from the sample by an air gap and used to wash any residual sample left in the syringe.

β Special Programable Injector (SPI) which allows cold injection followed by rapid heating.

η Linear velocity determined by direct retention time measurement.

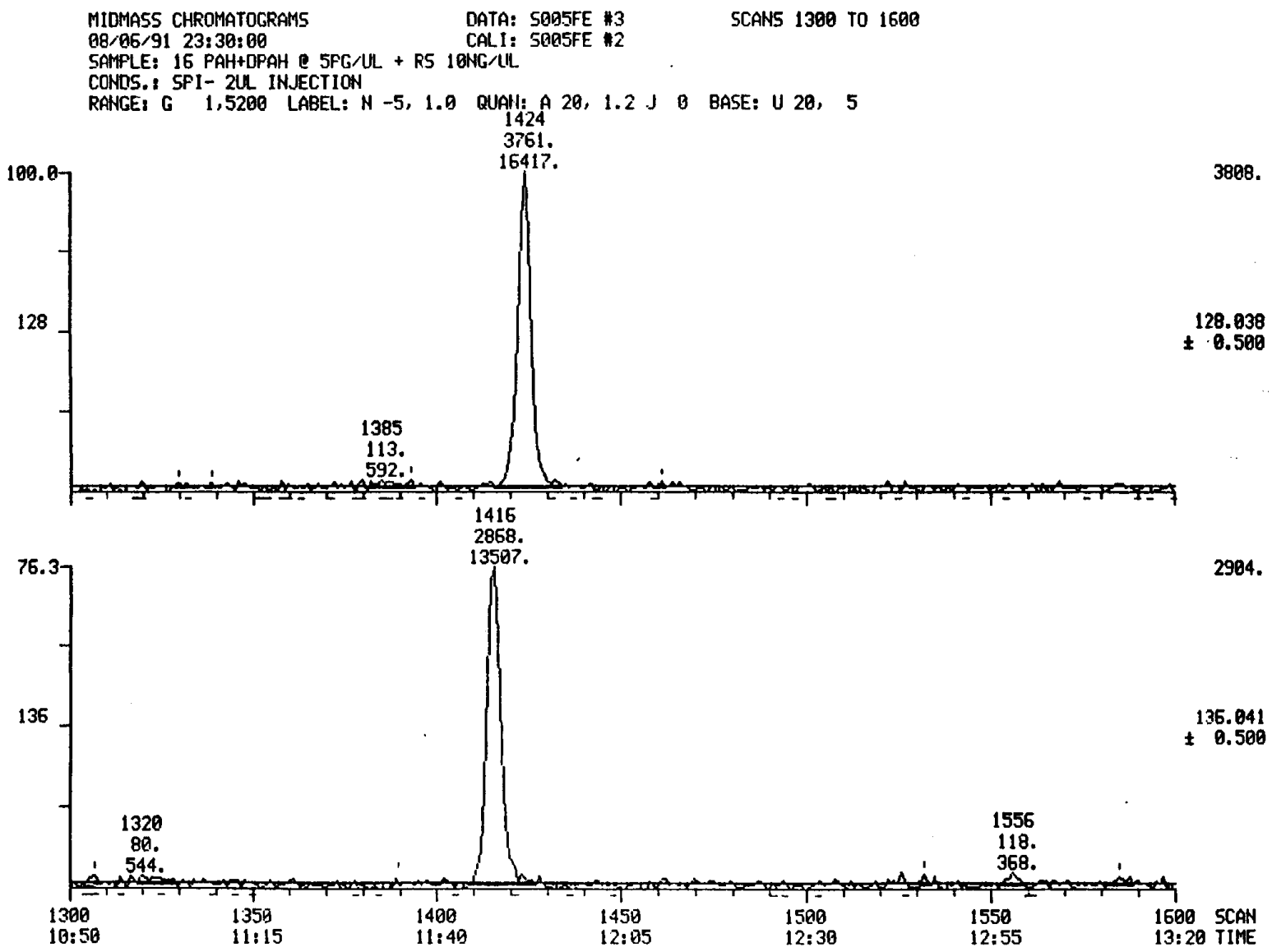
κ Final temperature held constant well past last eluting PAH compound to remove higher boiling compounds from the column.

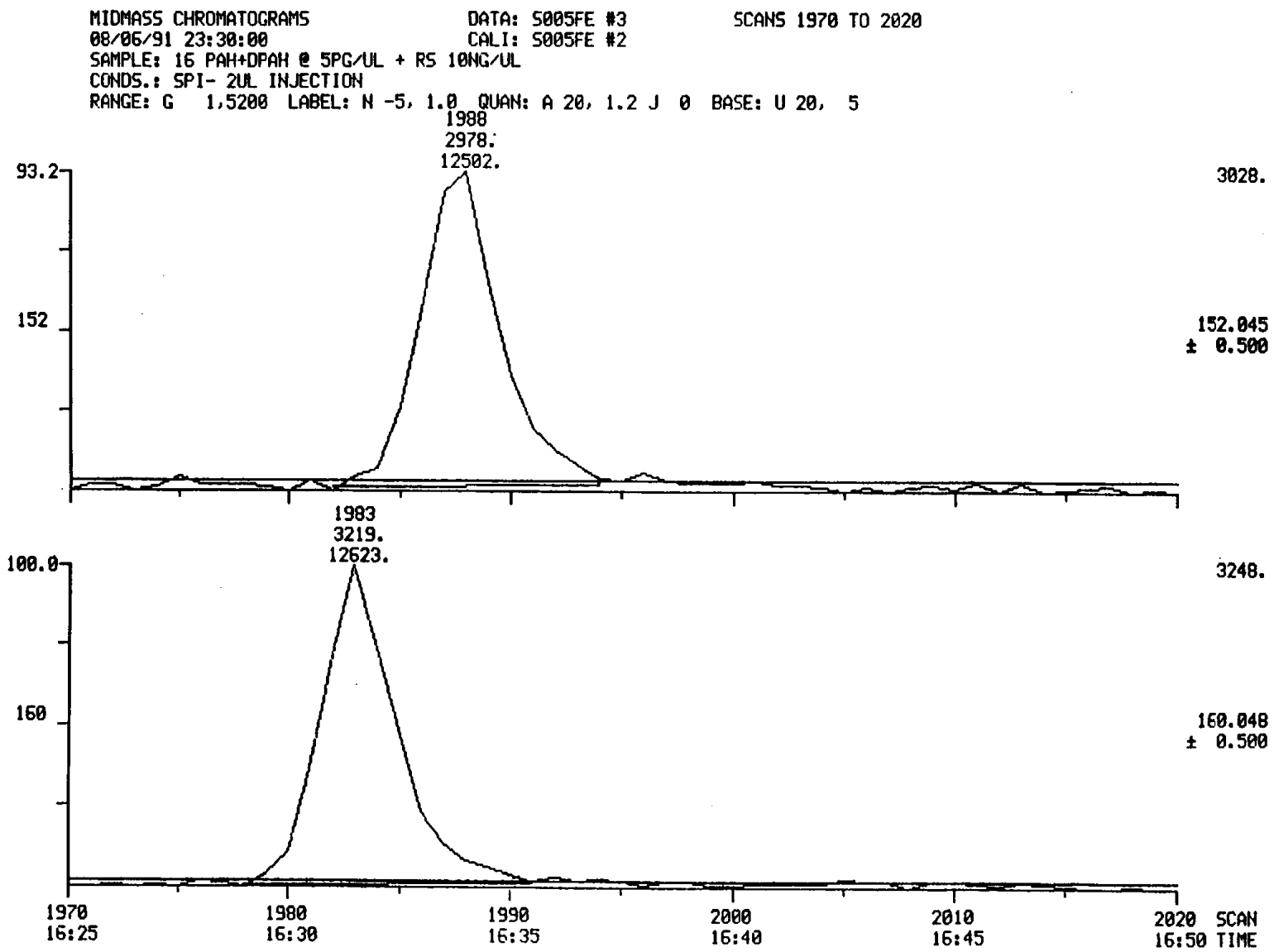
Table C-2. Mass Numbers and Peak Scan Numbers for Identification of PAH Compounds on Sample Chromatograms.

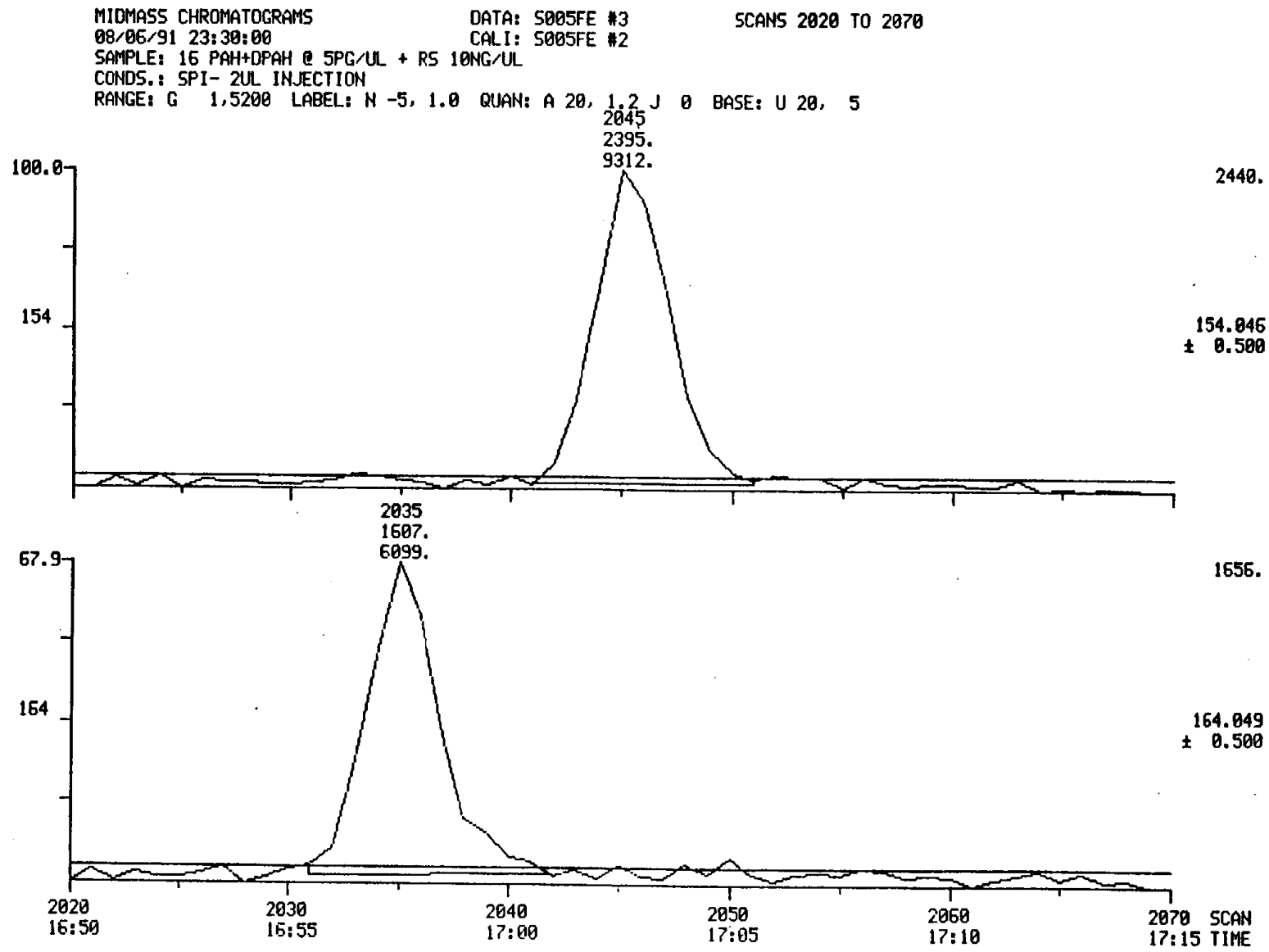
PAH Species	PAH Target Compound		PA^{2}H Internal Standard	
	Mass Number[α]	Scan Number[β]	Mass Number	Scan Number
Naphthalene	128	1424	132	1416
Acenaphthylene	152	1988	160	1983
Acenaphthene	154	2045	164	2035
Fluorene	166	2210	176	2201
Phenanthrene	178	2499	188	2492
Anthracene	178	2515	188	2509
Fluoranthene	202	2853	212	2847
Pyrene	202	2919	212	2913
Benz(a)anthracene	228	3288	240	3281
Chrysene	228	3298	240	3290
Benzo(b)fluoranthene	252	3693	264	3681
Benzo(k)fluoranthene	252	3705	264	3695
Benzo(a)pyrene	252	3851	264	3837
Indeno[1,2,3-cd]pyrene	276	4620	288	4600
Dibenz[ah]anthracene	278	4671	292	4646
Benzo(ghi)perylene	276	4848	288	4822

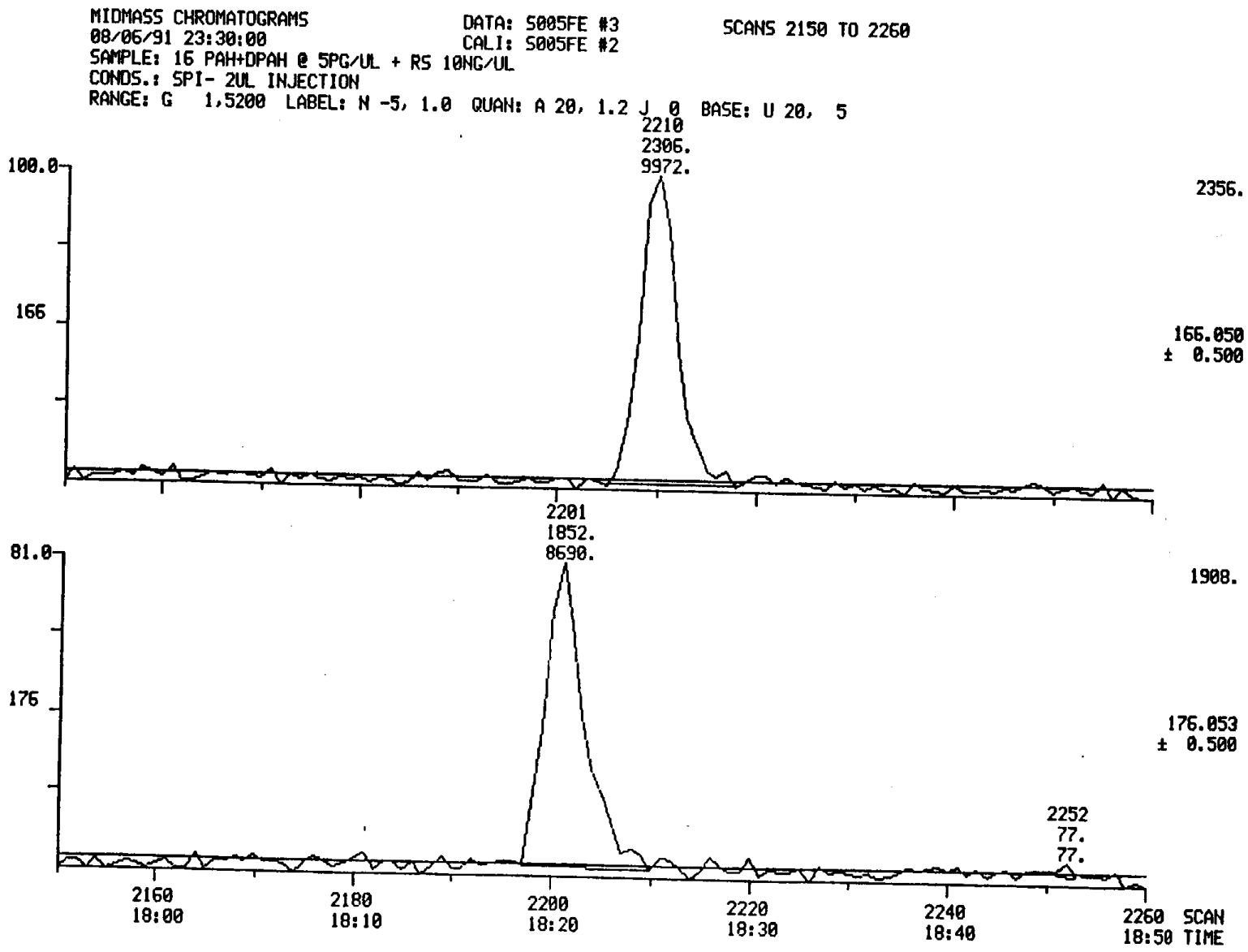
α Nominal masses used to label the PAH compounds on the GC/MS chromatograms.

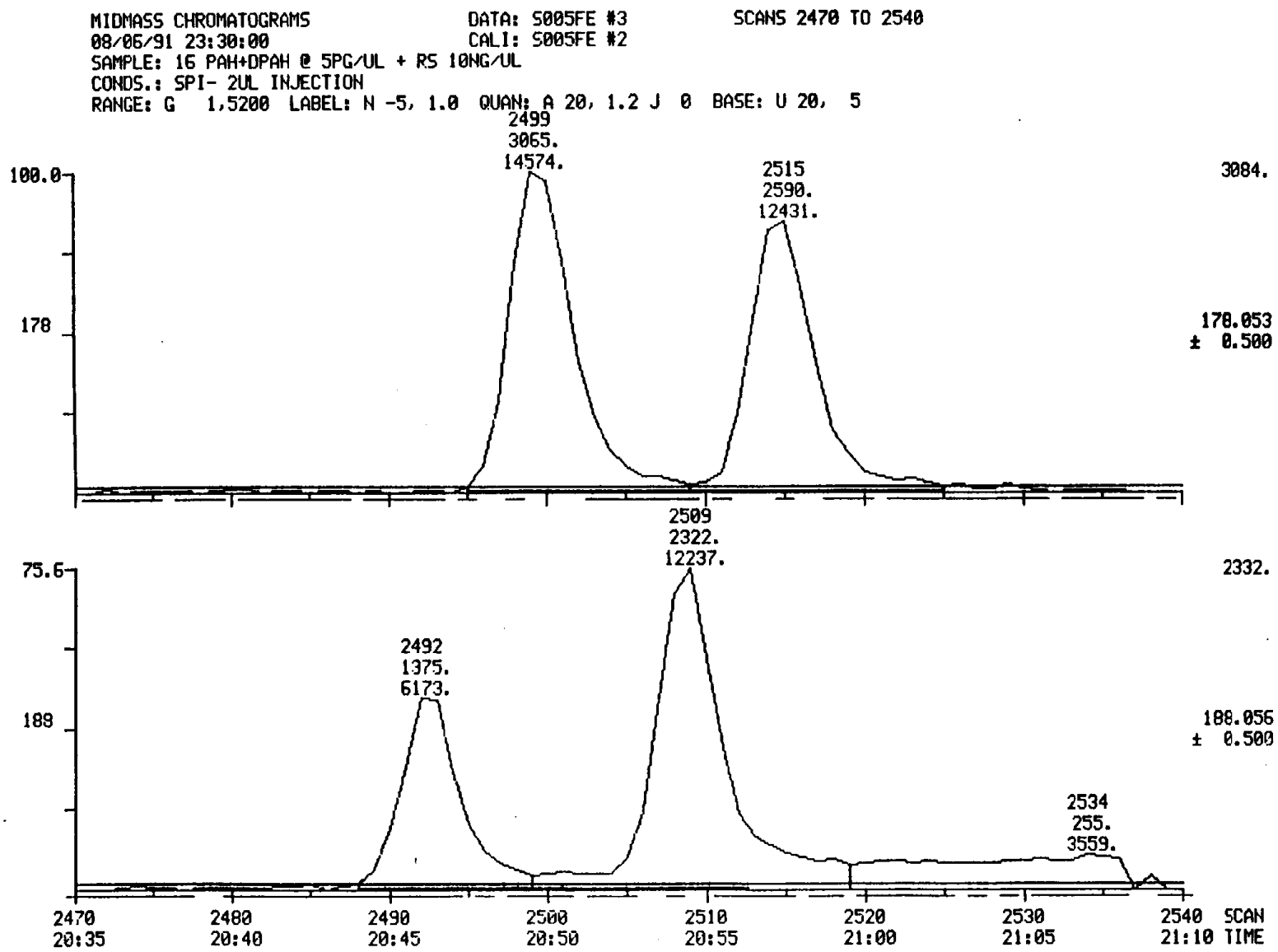
β Nominal retention time scan numbers used to identify the PAH compounds on the GC/MS chromatograms.


MIDMASS CHROMATOGRAMS
08/06/91 23:30:00
DATA: S005FE #3
CALI: S005FE #2
SCANS 1300 TO 1600
SAMPLE: 16 PAH+DPAH @ 5PG/UL + RS 10NG/UL
CONDS.: SPI- 2UL INJECTION
RANGE: G 1,5200 LABEL: N -5, 1.0 QUAN: A 20, 1.2 J 0 BASE: U 20, 5
1424
3761.
16417.
100.0
3808.
128
128.038
± 0.500
1385
113.
592.
1416
2868.
13507.
76.3
2904.
136
136.041
± 0.500
1320
80.
544.
1556
118.
368.
1300
10:50
1350
11:15
1400
11:40
1450
12:05
1500
12:30
1550
12:55
1600
13:20
SCAN
TIME


MIDMASS CHROMATOGRAMS
08/06/91 23:30:00
DATA: S005FE #3
CALI: S005FE #2
SCANS 1970 TO 2020
SAMPLE: 16 PAH+DPAH @ 5PG/UL + RS 10NG/UL
CONDS.: SPI- 2UL INJECTION
RANGE: G 1.5200 LABEL: N -5, 1.0 QUAN: A 20, 1.2 J 0 BASE: U 20, 5
1988
2978.
12502.
93.2
3028.
152
152.045
± 0.500
1983
3219.
12623.
100.0
3248.
160
160.048
± 0.500
1970
16:25
1980
16:30
1990
16:35
2000
16:40
2010
16:45
2020 SCAN
16:50 TIME


MIDMASS CHROMATOGRAMS
08/06/91 23:30:00
SAMPLE: 16 PAH+DPAH @ 5PG/UL + RS 10NG/UL
CONDS.: SPI- 2UL INJECTION
RANGE: G 1,5200 LABEL: N -5, 1.0 QUAN: A 20, 1.2 J 0 BASE: U 20, 5
DATA: S005FE #3
CALI: S005FE #2
SCANS 2020 TO 2070
2045
2395.
9312.
100.0
154
2440.
154.046
± 0.500
2035
1607.
6099.
67.9
164
1656.
164.049
± 0.500
2020
16:50
2030
16:55
2040
17:00
2050
17:05
2060
17:10
2070
17:15
SCAN
TIME


MIDMASS CHROMATOGRAMS
08/06/91 23:30:00
SAMPLE: 16 PAH+DPAH @ 5PG/UL + RS 10NG/UL
CONDS.: SPI- 2UL INJECTION
RANGE: G 1,5200 LABEL: N -5, 1.0 QUAN: A 20, 1.2 J 0 BASE: U 20, 5
DATA: S005FE #3
CALI: S005FE #2
SCANS 2150 TO 2260
2210
2306.
9972.
100.0
166
2356.
166.050
± 0.500
2201
1852.
8690.
81.0
176
1908.
176.053
± 0.500
2252
77.
77.
2160
18:00
2180
18:10
2200
18:20
2220
18:30
2240
18:40
2260 SCAN
18:50 TIME


MIDMASS CHROMATOGRAMS
08/06/91 23:30:00
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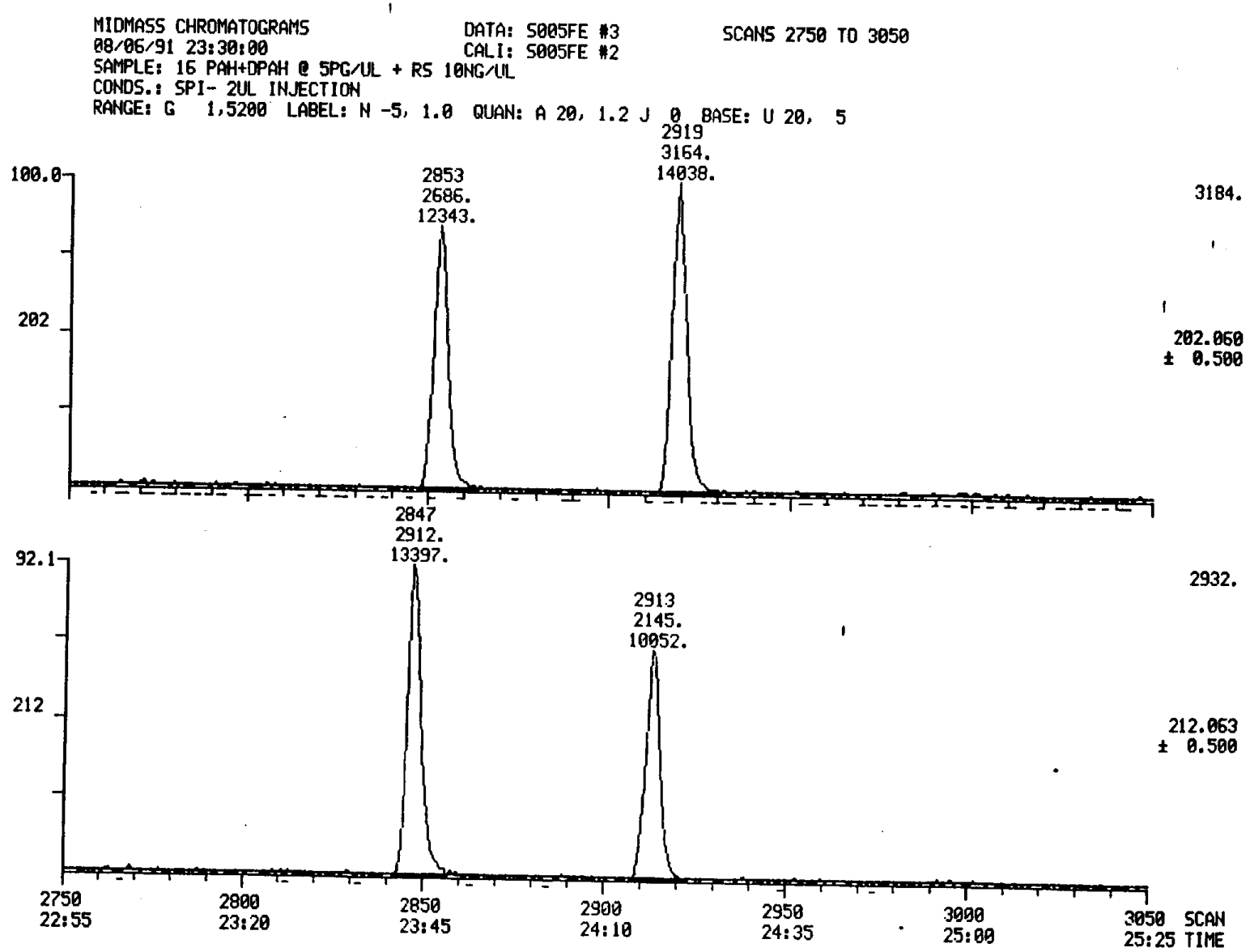
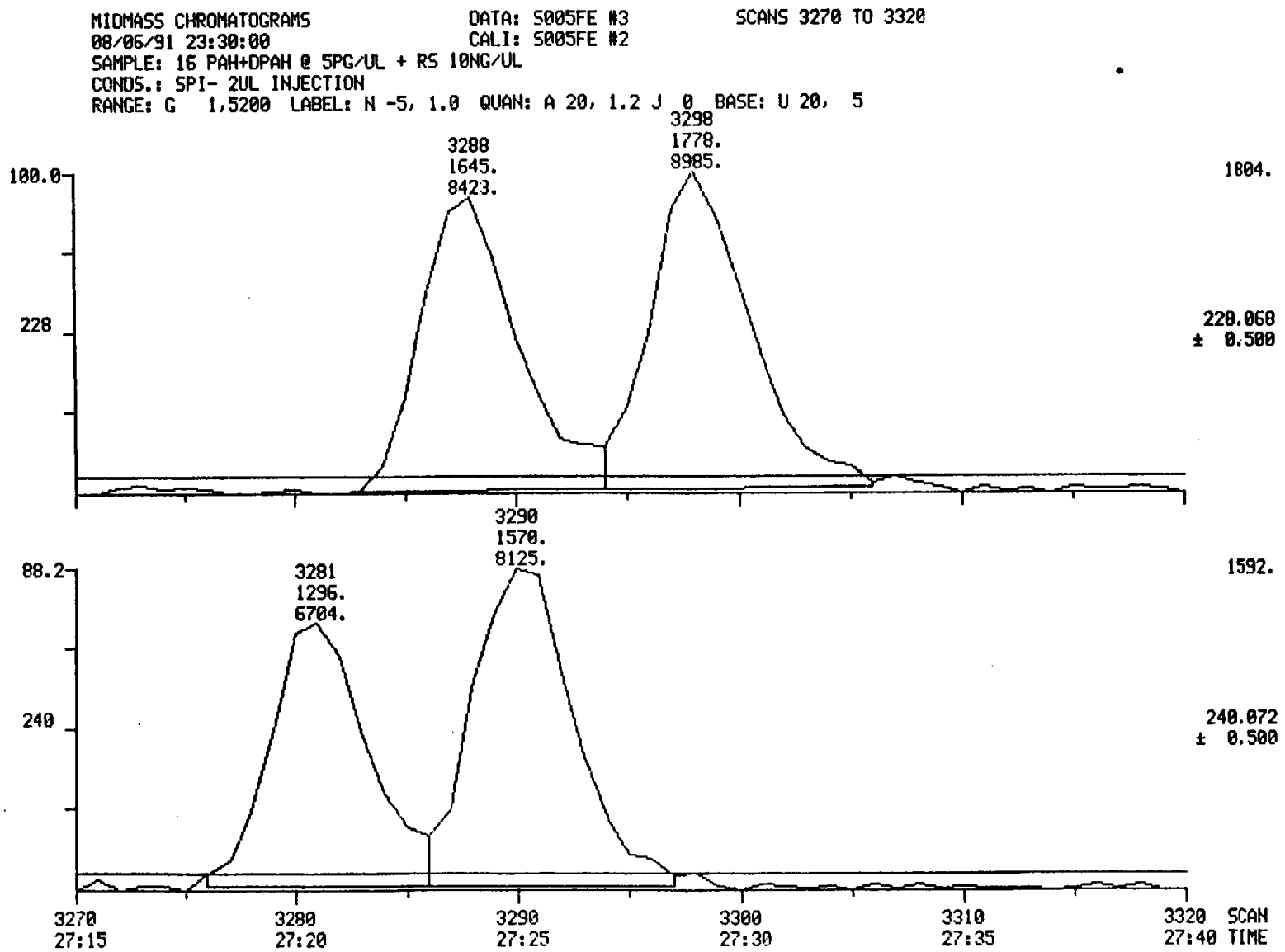
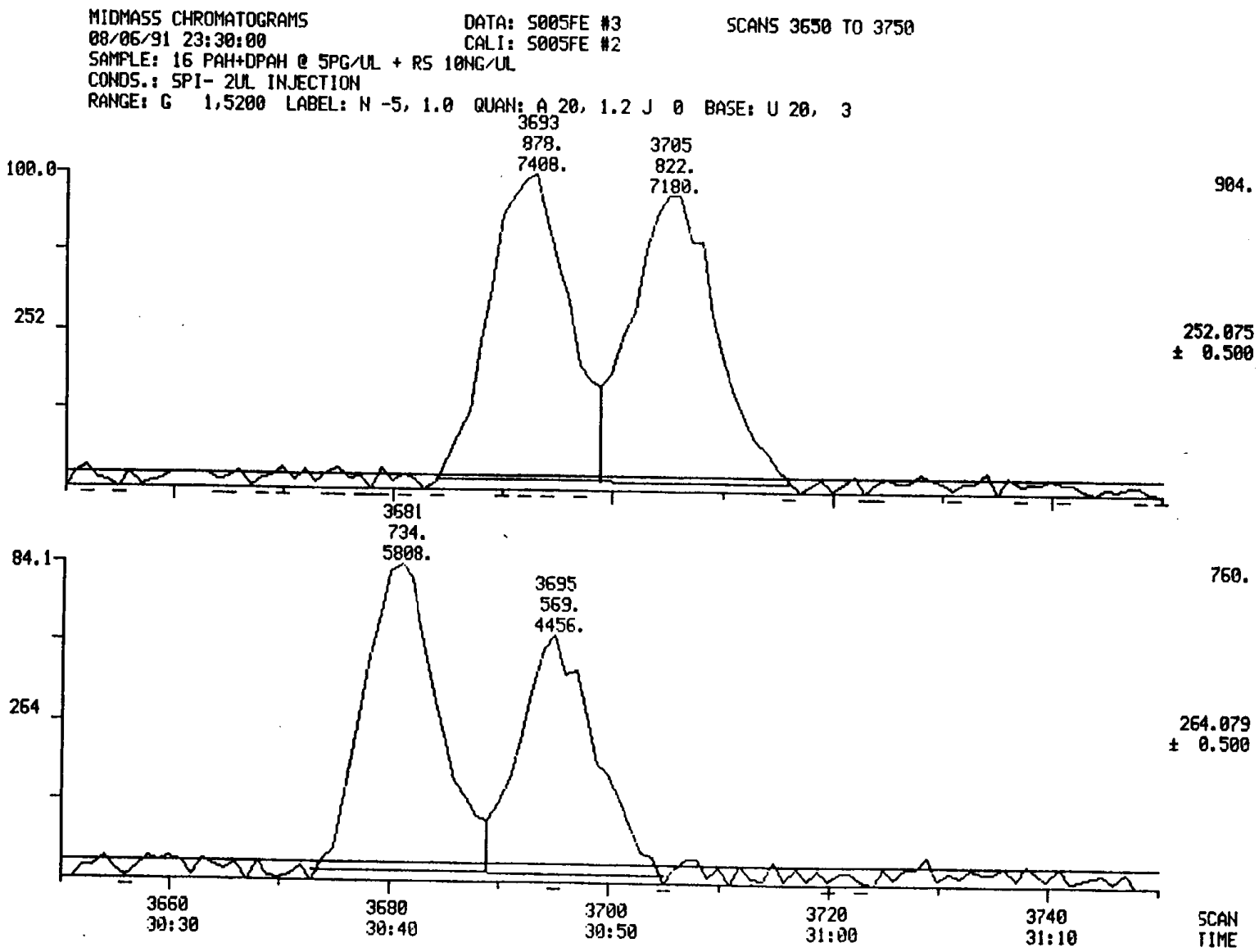
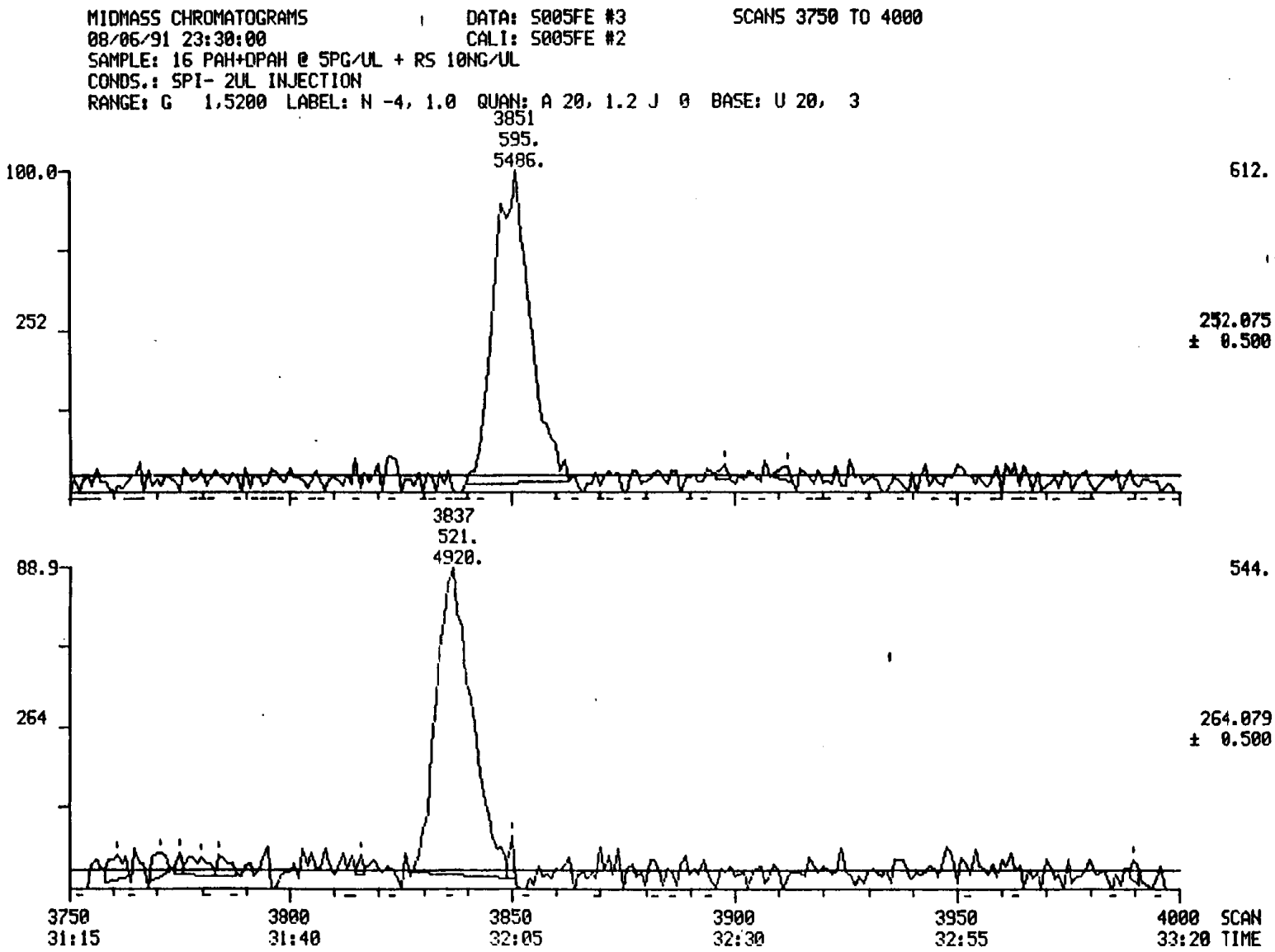
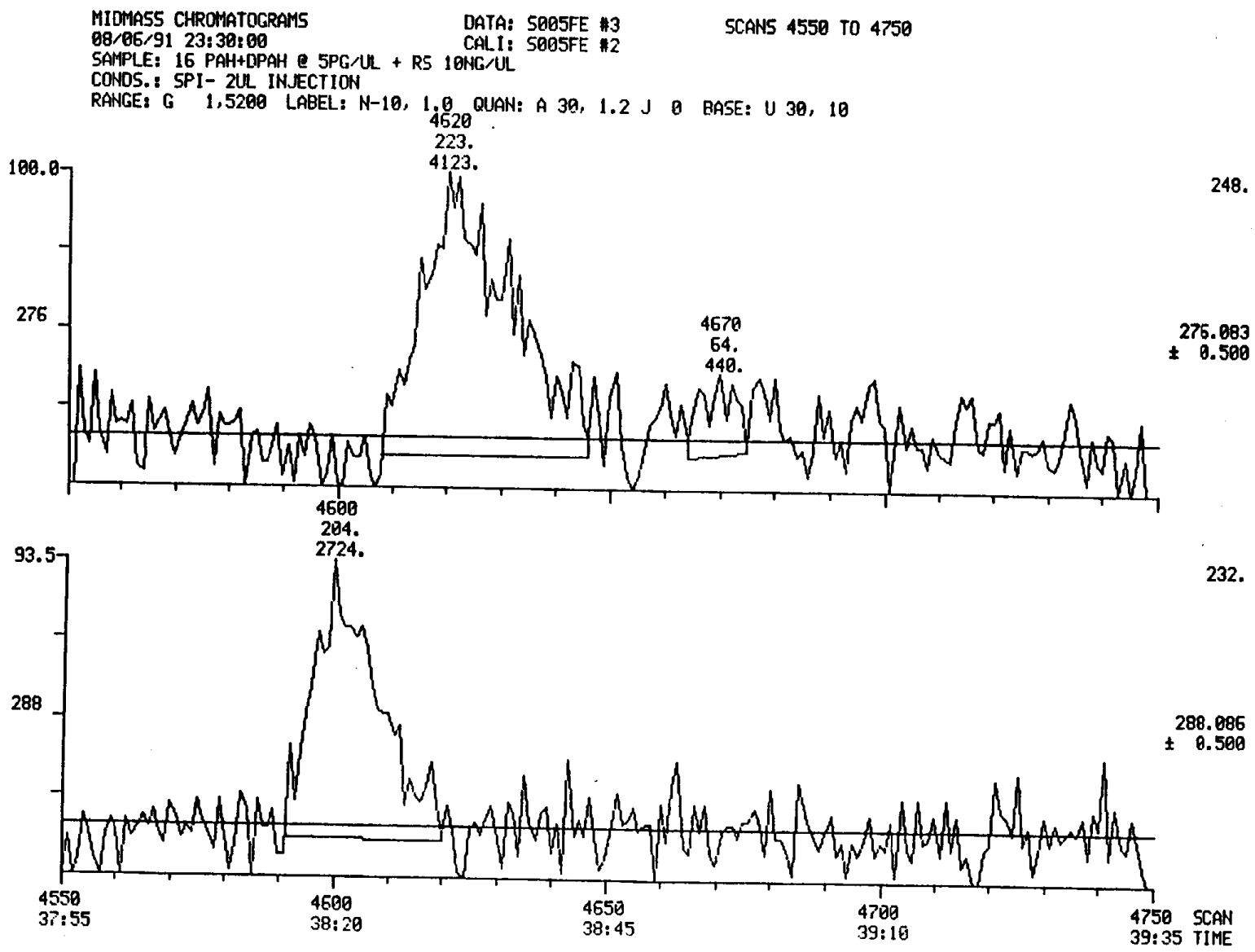
CALI: S005FE #2
SCANS 2470 TO 2540
SAMPLE: 16 PAH+DPAH @ 5PG/UL + RS 10NG/UL
CONDS.: SPI- 2UL INJECTION
RANGE: G 1,5200 LABEL: N -5, 1.0 QUAN: A 20, 1.2 J 0 BASE: U 20, 5
2499
3065.
14574.
2515
2590.
12431.
3084.
100.0
178
178.053
± 0.500
2509
2322.
12237.
2332.
75.6
2492
1375.
6173.
188
188.056
± 0.500
2534
255.
3559.
2470
20:35
2480
20:40
2490
20:45
2500
20:50
2510
20:55
2520
21:00
2530
21:05
2540 SCAN
21:10 TIME

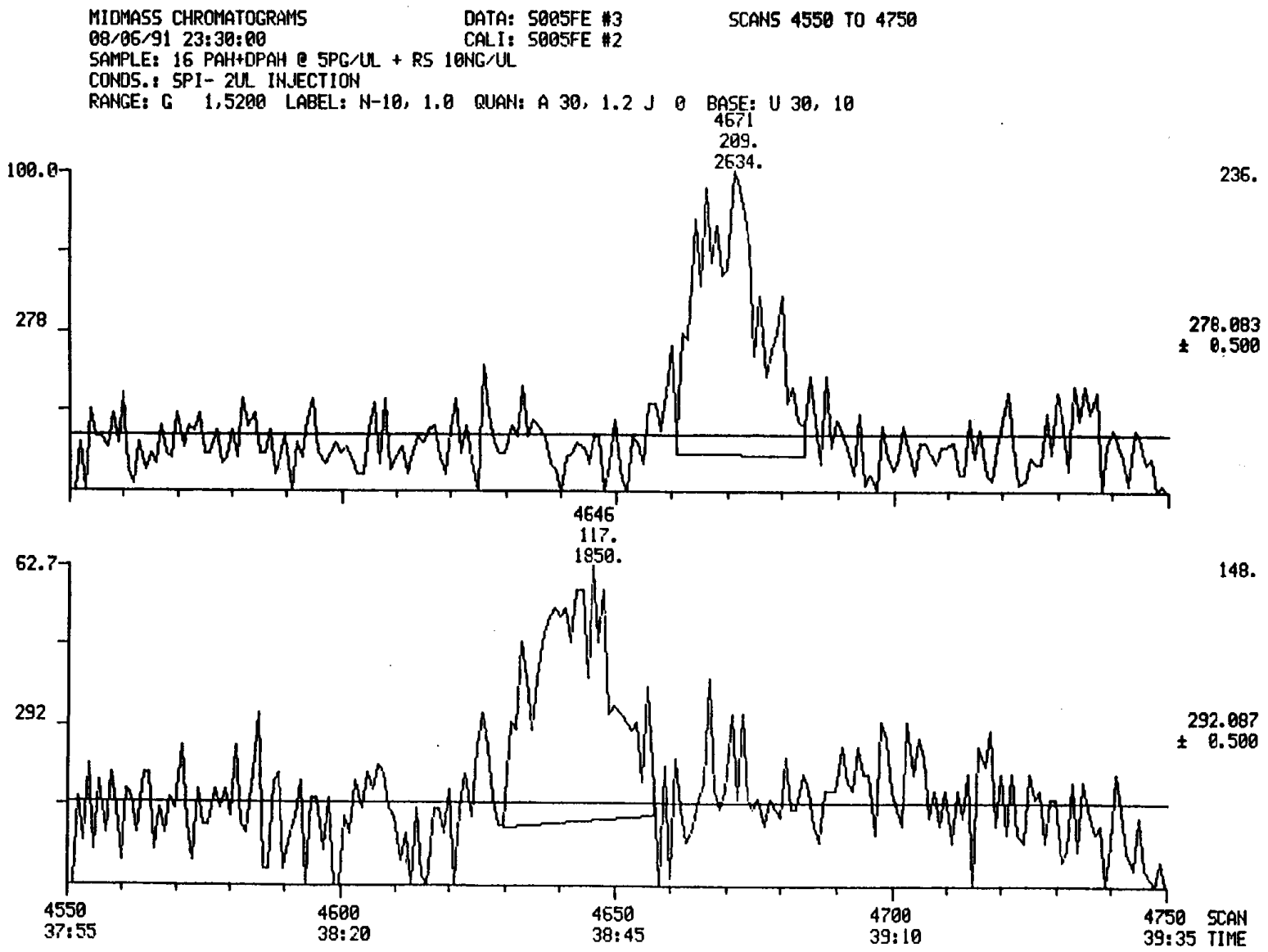

MIDMASS CHROMATOGRAMS
08/06/91 23:30:00
DATA: S005FE #3
CALI: S005FE #2
SCANS 2750 TO 3050
SAMPLE: 16 PAH+DPAH @ 5PG/UL + RS 10NG/UL
CONDS.: SPI- 2UL INJECTION
RANGE: G 1,5200 LABEL: N -5, 1.0 QUAN: A 20, 1.2 J 0 BASE: U 20, 5
100.0
202
2853
2686.
12343.
2919
3164.
14038.
3184.
202.060
± 0.500
92.1
212
2847
2912.
13397.
2913
2145.
10052.
2932.
212.063
± 0.500
2750
22:55
2800
23:20
2850
23:45
2900
24:10
2950
24:35
3000
25:00
3050 SCAN
25:25 TIME

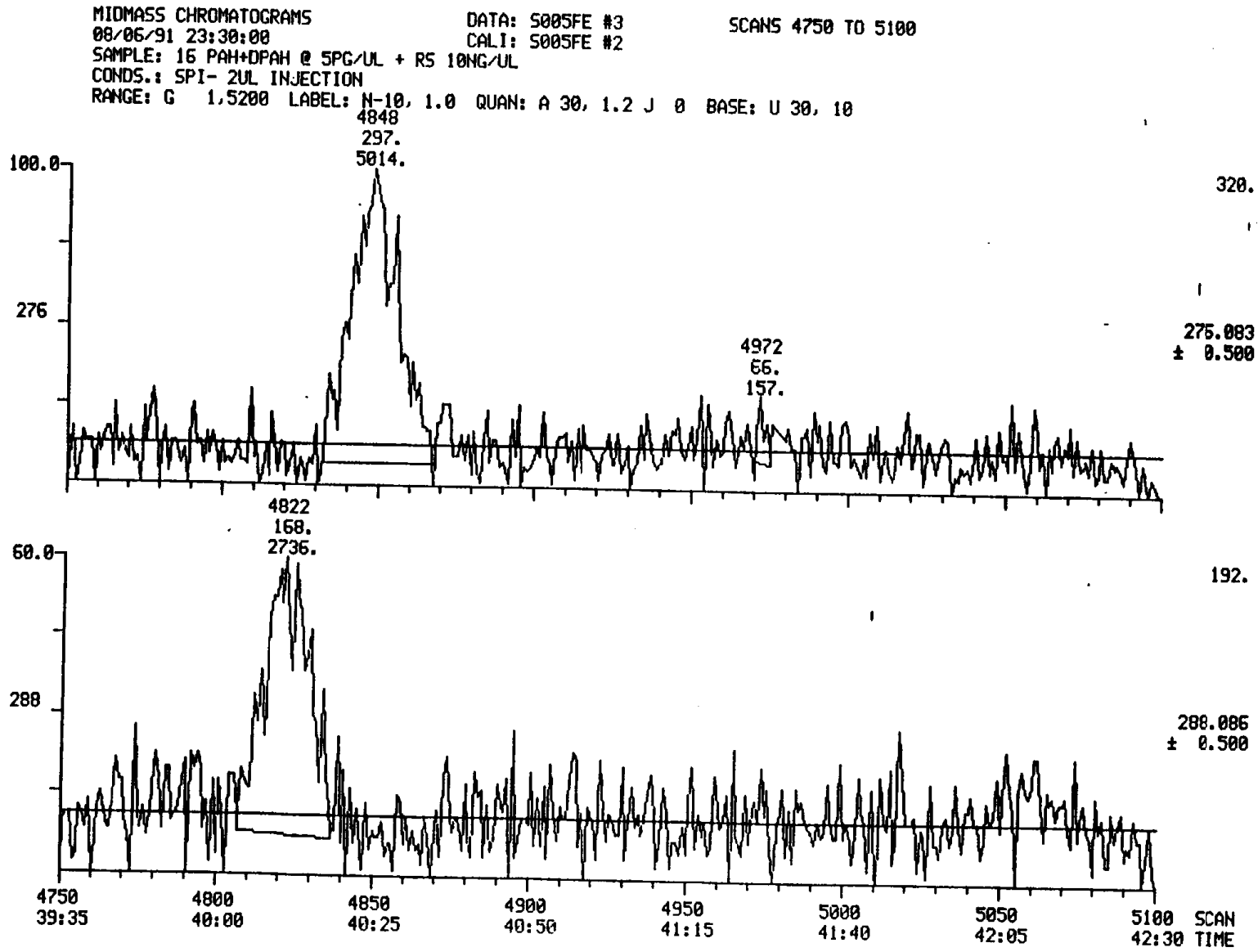

MIDMASS CHROMATOGRAMS
08/06/91 23:30:00
DATA: S005FE #3
CALI: S005FE #2
SCANS 3270 TO 3320
SAMPLE: 16 PAH+DPAH @ 5PG/UL + RS 10NG/UL
CONDS.: SPI- 2UL INJECTION
RANGE: G 1,5200 LABEL: N -5, 1.0 QUAN: A 20, 1.2 J 0 BASE: U 20, 5
3288
1645.
8423.
3298
1778.
9985.
1804.
100.0
228
228.068
± 0.500
3290
1570.
8125.
3281
1296.
6704.
1592.
88.2
240
240.072
± 0.500
3270
27:15
3280
27:20
3290
27:25
3300
27:30
3310
27:35
3320
27:40
SCAN
TIME


MIDMASS CHROMATOGRAMS
08/06/91 23:30:00
SAMPLE: 16 PAH+DPAH @ 5PG/UL + RS 10NG/UL
CONDS.: SPI- 2UL INJECTION
RANGE: G 1,5200 LABEL: N -5, 1.0 QUAN: A 20, 1.2 J 0 BASE: U 20, 3
DATA: S005FE #3
CALI: S005FE #2
SCANS 3650 TO 3750
3693
878.
7408.
3705
822.
7180.
100.0
252
904.
252.075
± 0.500
3681
734.
5808.
3695
569.
4456.
84.1
264
760.
264.079
± 0.500
3660
30:30
3680
30:40
3700
30:50
3720
31:00
3740
31:10
SCAN
TIME


MIDMASS CHROMATOGRAMS
08/06/91 23:30:00
DATA: S005FE #3
CALI: S005FE #2
SCANS 3750 TO 4000
SAMPLE: 16 PAH+DPAH @ 5PG/UL + RS 10NG/UL
CONDS.: SPI- 2UL INJECTION
RANGE: G 1,5200 LABEL: N -4, 1.0 QUAN: A 20, 1.2 J 0 BASE: U 20, 3
3851
595.
5486.
100.0
612.
252
252.075
± 0.500
3837
521.
4920.
88.9
544.
264
264.079
± 0.500
3750
31:15
3800
31:40
3850
32:05
3900
32:30
3950
32:55
4000 SCAN
33:20 TIME


MIDMASS CHROMATOGRAMS
08/06/91 23:30:00
DATA: S005FE #3
CALI: S005FE #2
SCANS 4550 TO 4750
SAMPLE: 16 PAH+DPAH @ 5PG/UL + RS 10NG/UL
CONDS.: SPI- 2UL INJECTION
RANGE: G 1,5200 LABEL: N-10, 1.0 QUAN: A 30, 1.2 J 0 BASE: U 30, 10
4620
223.
4123.
100.0
248.
276
4670
64.
440.
276.083
± 0.500
4600
204.
2724.
93.5
232.
288
288.086
± 0.500
4550
37:55
4600
38:20
4650
38:45
4700
39:10
4750 SCAN
39:35 TIME


MIDMASS CHROMATOGRAMS
08/06/91 23:30:00
DATA: S005FE #3
CALI: S005FE #2
SCANS 4550 TO 4750
SAMPLE: 16 PAH+DPAH @ 5PG/UL + RS 10NG/UL
CONDS.: SPI- 2UL INJECTION
RANGE: G 1,5200 LABEL: N-10, 1.0 QUAN: A 30, 1.2 J 0 BASE: U 30, 10
4671
209.
2634.
100.0
278
236.
278.083
± 0.500
4646
117.
1850.
62.7
292
148.
292.087
± 0.500
4550
37:55
4600
38:20
4650
38:45
4700
39:10
4750 SCAN
39:35 TIME


MIDMASS CHROMATOGRAMS
08/06/91 23:30:00
DATA: S005FE #3
CALI: S005FE #2
SCANS 4750 TO 5100
SAMPLE: 16 PAH+DPAH @ 5PG/UL + RS 10NG/UL
CONDS.: SPI- 2UL INJECTION
RANGE: G 1.5200 LABEL: N-10, 1.0 QUAN: A 30, 1.2 J 0 BASE: U 30, 10
4848
297.
5014.
100.0
320.
276
275.083
± 0.500
4972
66.
157.
4822
168.
2736.
60.0
192.
288
288.086
± 0.500
4750
39:35
4800
40:00
4850
40:25
4900
40:50
4950
41:15
5000
41:40
5050
42:05
5100 SCAN
42:30 TIME

APPENDIX D

Field Study Quality Assurance Methods

Method blanks for both the Teflon coated filter and the polyurethane foam (PUF) plugs were analyzed for the 16 priority PAH compounds along with the composite samples for the three field sampling trials. The Teflon filter method blank was taken from the same batch of Teflon coated glass fiber filters used in the RADS for field sampling. A PUF plug method blank was die cut from the same batch of foam sheets used to produce the plugs used in the RADS as a backup adsorbent for the Teflon coated filter. Both the PUF method blank and the PUF plugs used for field sampling, were pre-cleaned in the same batch using the solvent compression rinsing (SCR) procedure detailed in Appendix B.

Method blank levels for both the Teflon coated filter and the PUF plug are listed in Table D-1. For all 16 priority PAH, the blank levels were less than the method detection limit (MDL) for both substrates and are reported as $\leq$ MDL. The MDL listed for each PAH extracted from the Teflon and PUF substrates was calculated based on the guidelines included in the most recent version of CARB method #429 (Appendix A, 1995). The standard deviation of repeat analysis for 80 ng/sample spikes of all sixteen PAH was used to determine the MDL for each sampling media. In general, the MDL was much less than 1% of the lowest level PAH measured in the composite samples from all three field trials.

PERFORMANCE EVALUATION SAMPLES

Standard Reference Materials (SRM), from the National Institute of Standards and Technology (NIST), have been used as performance evaluation samples for the development of new analytical techniques for PAH as described in section 10.4. Currently SRM #1649 (Urban Dust/Organic Particulate Matter) and SRM #1650 (Diesel Particulate Matter) are the only aerosol derived materials certified for PAH content by NIST. SRM #1649 was chosen for routine performance evaluations of the CERL analytical method due to the larger variety

Table D-1. Method Blank Levels for RADS Teflon Coated Glass Fiber and PUF Plug Media used in the Field Study.

PAH Species	Teflon Filter[α] (ng/sample)	PUF Plug[β] (ng/sample)
Naphthalene	≤ 16[η]	≤ 21
Acenaphthylene	≤ 27	≤ 66
Acenaphthene	≤ 60	≤ 79
Fluorene	≤ 53	≤ 100
Phenanthrene	≤ 67	≤ 91
Anthracene	≤ 40	≤ 96
Fluoranthene	≤ 23	≤ 92
Pyrene	≤ 33	≤ 90
Benz(a)anthracene	≤ 47	≤ 92
Chrysene	≤ 27	≤ 84
Benzo(b)fluoranthene	≤ 35	≤ 85
Benzo(k)fluoranthene	≤ 19	≤ 67
Benzo(a)pyrene	≤ 46	≤ 81
Indeno[1.2.3-cd]pyrene	≤ 71	≤ 93
Dibenz[ah]anthracene	≤ 101	≤ 70
Benzo(ghi)perylene	≤ 78	≤ 96

α Filter taken from same batch as used in field sampling

β PUF plug cut from same sheet as the plugs used for field sampling. Same SCR pre-cleaning procedure used for the blank and the field samples.

η Values reported as ≤ represent the Method Detection Limit (MDL).

of certified priority-PAH compounds in this material when compared to the SRM #1650.

Triennial analysis of the SRM #1649 serves as an indicator of the performance of the CERL analytical method. These samples undergo the same extraction, cleanup, and GC/MS analysis as the field samples for the RADS. Results for the most recent performance evaluation samples analyzed by CERL are shown in Table D-2. For each PAH species, the results are expressed as a percent of the published NIST values, and include the relative standard deviation for replicate analysis. Although no strict criteria has yet been developed by CARB to evaluate analytical performance, CERL has established general guidelines which are utilized to trigger corrective action. For most of the PAH species, no action is considered necessary for analytical results which are in the range between 90-110% of the NIST values, and have a relative standard deviation less than 15%. For a few PAH, which include phenanthrene, pyrene, indeno[1,2,3-cd]pyrene, and benzo(ghi)perylene the analytical results must be between 60 and 80% of the NIST value, and have a relative standard deviation of less than 10%. These guidelines are based on a limited set of historical data for the analysis of SRM #1649 by the CERL Method.

LABORATORY CONTROL SAMPLES

Two laboratory control samples (LCS) were analyzed along with the samples collected in the 500 kW diesel generator sampling trial. These control samples were prepared by spiking polyurethane foam plugs with a cocktail of the 16 priority PAH. The LCS plugs were cut from the same batch of foam sheet used to die cut the plugs for the RADS field trials. Before spiking, the laboratory control plugs were pre-cleaned using the CERL Simple Compression Rinsing (SCR) method as detailed in Appendix B. Directly after spiking, the laboratory control samples were included in the same analysis batch as the field samples and underwent the same extraction, clean-up and analysis procedures.

Table D-2. Performance Evaluation Samples of NIST SRM #1649 for the Field Study.

PAH Species	NIST Value (ng/sample)	Pulsed Ultrasonic[β] (% recovered)
Phenanthrene	1125 ± 75	69 ± 1
Fluoranthene[α]	1775 ± 125	95 ± 7
Pyrene	1575 ± 100	77 ± 6
Benz(a)anthracene[α]	650 ± 75	100 ± 10
Chrysene	875 ± 25	105 ± 10
Benzo(b)fluoranthene[α]	1550 ± 75	97 ± 10
Benzo(k)fluoranthene	500 ± 25	95 ± 10
Benzo(a)pyrene[α]	725 ± 125	109 ± 9
Indeno[1,2,3-cd]pyrene[α]	825 ± 125	63 ± 7
Benzo(ghi)perylene[α]	1125 ± 275	72 ± 7

α Value certified by NIST for this species.
β Pulsed ultrasonic extraction for 6 minutes using cyclohexane/DCM (4:1).

$$V_s = \sum_{i=1}^{n} q_i t_i. \qquad \text{(E-4)}$$

Accordingly, the total time per sampling period ,T_s, was calculated from the number of time internals, n, and the time per internal, t_i = 6 seconds, using the simple summation expression:

$$T_s = \sum_{i=1}^{n} t_i. \qquad \text{(E-5)}$$

Sampling period duration, T_s, and total air volume for each sampling period, V_s, are also included for all three field trials in Tables E-1, E-2, and E-3. Each field trial was comprised of a number of consecutive RADS sampling periods. Composites of the sample extracts for these periods (see Figure 11-5) were used for comparison with single sample collected by MM5 for each field trial. Total air volumes sampled by the RADS were simply calculated by summing air volumes for the sampling periods in each of the field trials. Stack concentrations for all 16 priority PAH were calculated from the analytical results of the RADS sample extract composites using these total air volumes.

Periodic spot checks were made during each sampling period to ensure accurate data collection by the RADS on-board data logger. Means calculated for flowrates recorded manually every three minutes agreed with the means calculated from the datalogger within 3%.

Table E-1. RADS Control System Performance During Sampling Trial Number 1.

Sampling Period	Period[α] Duration (seconds)	Performance Index[β] Isokinetic Sampling (%)	Performance Index[β] Dilution Ratio 35:1 (%)	Air Volume Sampled[η] (m^3)
1	528	99.4 ± 1.6	100.4 ± 0.3	0.191
2	528	99.9 ± 1.0	100.5 ± 0.8	0.191
3	528	98.7 ± 1.3	100.4 ± 0.6	0.180
4	528	97.0 ± 6.4	99.8 ± 0.4	0.180
5	528	99.4 ± 1.1	99.6 ± 0.9	0.190
6	528	99.6 ± 0.5	100.2 ± 0.9	0.192
7	576	98.6 ± 1.9	100.3 ± 0.6	0.206
8	528	99.6 ± 0.9	100.0 ± 1.3	0.189
9	552	98.4 ± 1.0	99.8 ± 1.0	0.199

α Determined from the RADS on-board data logger clock.

β Calculated from the data logger record using equation E-2 to assess isokinetic sampling and equation E-3 to assess the dilution ratio performance.

η Calculated from the data logger record using equation E-4.

APPENDIX E

RADS Stack Operation Assessment

The RADS system utilized solid-state sensors to control the stack sampling and dilution air flows. These flows were continuously adjusted by the RADS microprocessor control system to maintain isokinetic stack sampling at a fixed dilution ratio as described in section 5.0. During operation, the signals from these High Temperature Velocity Sensors (HTVS) were digitized, recorded and graphically displayed by the on-board data logging system. The HTVS installed in the sampling probe and the HTVS installed in the dilution tunnel (see Figure 5-2) were calibrated in-place to operate as mass flowmeters. An example of the graphical display of flowrate control performance has already been given in Figure 11-2.

In-place calibration of the sampling probe HTVS was accomplished with a precision mass flowmeter which was temporarily installed between the flexible probe section and the dilution tunnel. The HTVS in the dilution tunnel was calibrated in-place using a precision laminar flow element temporarily installed at the dilution air intake. As received, all three RADS HTVS were factory calibrated (NIST traceable) to measure air velocity referenced to the standard temperature and pressure conditions (STPC) of 20°C and 760 mmHg. In-place calibrations (NIST traceable) were necessary to verify the factory calibration, and to provide a direct reading of volumetric flowrates (at STPC) for subsequent data reduction.

From the start of sampling, the RADS data logger recorded and displayed the isokinetic probe flowrate, q_i, and the dilution tunnel flowrate , Q_i, at time intervals, t_i, of six-seconds. Isokinetic sampling was maintained by matching the free-stream velocity ,s_i, measured by the stack HTVS, and the probe nozzle velocity ,v_i, calculated as:

$$v_i = \frac{q_i}{a}, \qquad \text{(E-1)}$$

where a is the area of the probe nozzle. For these 500 kW diesel exhaust sampling trials, the stack flowrate was almost 11 m/s (36 fps) and required the use of a 0.645cm (0.25 in) diameter probe nozzle to reach isokinetic conditions. The ratio of the free-stream and stack probe velocity was computed for each six-second interval to yield the performance index for isokinetic sampling as follows:

$$\phi_i = \frac{v_i}{s_i}. \qquad \text{(E-2)}$$

In a similar manner, the performance index for the RADS dilution ratio (R_d = 35) was computed at six-second internals as:

$$\varphi_i = \frac{Q_i}{q_i R_d}. \qquad \text{(E-3)}$$

Performance index values (%) for the multiple sampling periods, which comprise each of the three field trial runs, are given in Tables E-1, E-2 and E-3. Values are expressed as the mean and standard deviation of the performance measurements, for every six-second interval throughout the sampling period. Typically, the flow control system was capable of maintaining isokinetic and iso-dilution conditions within a few percent with a standard deviation of less than 2%.

At the completion of a field trial, the total air volume for each sampling period, V_s, was calculated from the probe flowrate values, q_i, which were downloaded from the RADS data logger to a personal computer. The graphical display trace for the performance indexes was examined to determine the first, $q_{i=1}$, and last, $q_{i=n}$, six-second flow measurement interval. Total air volume for a sampling period was then calculated for the n intervals as:

Results for the laboratory control samples (LCS) including the spike levels for each PAH are shown in Table D-3. Spike levels were different for each PAH since the special spiking solution was prepared gravimetrically from the solid form of these compounds for highest accuracy. In accordance with the CARB guidelines (Method #429), the mean recovery and the relative recovery difference between recoveries for the two LCS samples were calculated. The acceptance criteria adopted by CARB requires that the LCS recovery is between 50% and 150% and the relative recovery difference is 50% or less. As shown in Table D-3, the results for all 16 priority PAH compounds were well within the required acceptance criteria.

Table D-3. Laboratory Control Samples for the Field Study.

PAH Species	PUF Plug Spike PAH[α] (ng/sample)	Mean PAH Recovery[β] (%)	Relative Recovery Difference[η] (Δ%)
Naphthalene	1928	133	3
Acenaphthylene	2006	89	5
Acenaphthene	1909	83	4
Fluorene	1986	102	7
Phenanthrene	1870	94	1
Anthracene	1928	96	1
Fluoranthene	2473	94	5
Pyrene	2006	94	5
Benz(a)anthracene	1947	123	1
Chrysene	1986	93	5
Benzo(b)fluoranthene	1889	95	4
Benzo(k)fluoranthene	1441	112	11
Benzo(a)pyrene	2025	88	15
Indeno[1,2,3-cd]pyrene	2264	88	13
Dibenz[ah]anthracene	2606	95	11
Benzo(ghi)perylene	1519	96	26

α Spiking solution was prepared gravimetrically from the solid compounds.
β Recoveries are for spot-spikes delivered to the interior of the PUF plug and are not corrected for extraction losses.
η Difference between duplicate samples relative to the calculated mean expressed as a percentage.

breakthrough volumes for specific PAH compounds. As might be expected, the collection efficiency decreases with increases in the ratio of sampling volume to retention volume. The rate of decrease in efficiency is slow for sampling volumes less than half the retention volume and quite rapid for sampling volumes greater than the retention volume. You and Bidleman measured PAH breakthrough volumes which were equivalent to the retention volume definition used by Senum to predict collection efficiency.

Chromatographic theory predicts a linear relationship between log breakthrough volume and log vapor pressure. Breakthrough volume measurements for fluorene, phenanthrene, anthracene and pyrene were found by You and Bidleman to be more closely correlated with the subcooled-liquid vapor pressure for these compounds, than the vapor pressure for the solid. As outlined by You and Bidleman for the above PAH compounds, subcooled-liquid vapor pressures were estimated (after McKay et al., 1982) for naphthalene, acenaphthylene, and acenaphthlene from the vapor pressures of the corresponding solids taken from Sonnefield, Zoller and May (1983). Both the solid and subcooled vapor pressures for all of these compounds, which were expected to be collected by the PUF plugs of the RADS, are listed in Table F-1.

Breakthrough volumes for naphthalene, acenaphthalene and acenāphthlene were then determined from the corresponding subcooled vapor pressure estimates by extrapolating the data of You and Bidleman (1984). This assumes that the linear relationship between breakthrough volume and vapor pressure on a log-log plot is preserved for the lowest molecular weight PAH. The breakthrough volumes shown in Table F-1 for the RADS PUF plugs were derived by applying a factor of 3.8 to the breakthrough volumes extrapolated from the data of You and Bidleman. This scaling factor was required to take into account the larger flow cross-section provided by the 15 cm (6 in) diameter PUF plugs, used in the RADS, relative to the 7.8 cm plugs used for the direct measurement of breakthrough volume. The thickness of the PUF plugs was similar, with the RADS

Table F-1. Vapor Pressure Data and the Corresponding PUF Breakthrough Volume Calculated for Selected PAH Expected to be in the Vapor Phase.

PAH Species	Vapor Pressure @ 20°C Solid Compound[α] (torr)	Subcooled Liquid[β] (torr)	RADS PUF Plug Breakthrough Volume[η] (m^3)
Naphthalene	4.56×10^{-2}	1.84×10^{-1}	4[κ]
Acenaphthylene	3.98×10^{-3}	2.14×10^{-2}	44[κ]
Acenaphthene	1.16×10^{-3}	6.81×10^{-3}	157[κ]
Fluorene	3.20×10^{-4}	2.97×10^{-3}	458
Phenanthrene	6.20×10^{-5}	4.06×10^{-4}	3054
Anthracene	3.2×10^{-6}	3.02×10^{-4}	4199
Pyrene	2.4×10^{-6}	5.64×10^{-5}	38175

α Values from measurements by Sonnefield, Zoller and May (1983).
β Calculated from the solid vapor pressure after MacKay et al. (1982).
η Estimated from the subcooled liquid vapor pressure using the breakthrough volume relation of You and Bidleman (1984) scaled to the RADS PUF plug dimensions.
κ Estimated by extrapolating the relation of You and Bidleman (1984) to higher vapor pressures.

APPENDIX F

PUF Plug Collection Efficiency Estimation

The capacity of the PUF plugs, used to collect the more volatile PAH in the Reduced Artifact Dilution Sampler (RADS), has been examined using the available models for calculating adsorbent collection efficiency. Collection efficiencies of PUF for PAH vapor have been extensively studied by You and Bidleman (1984) utilizing the earlier theoretical work by Senum, G.L. (1981). You and Bidleman conducted measurements to determine breakthrough volumes for fluorene and higher molecular weight PAH, using the relations of Senum to yield the associated PUF plug collection efficiency. We have extended this theoretical analysis to include naphthalene, acenaphthtylene, and acenaphthene based on a general solution to the differential equations presented by Senum.

The analysis of Senum was directed toward developing a model for the collection efficiency of adsorbent samplers based on the application of chromatographic response theory. The model utilized the chromatographic response treatment of Reilley et.al. (1962), which was rewritten in terms of the number of theoretical plates and the adsorbent retention volume. Senum considers the number of theoretical chromatographic plates to be solely a function of the adsorbent and to be independent of the adsorbate and sampler temperature. An integral equation was provided which can be numerically solved to determine the collection efficiency as a function of the ratio of sampling volume to retention volume. For this analysis, the equation of Senum has been rewritten in the form shown in Figure F-1, which was more easily treated to obtain a general numerical solution.

The solution for collection efficiency as a function of the ratio of sampling volume to the adsorbate retention volume is shown graphically in Figure F-1 for the case of 7.5 theoretical plates. This specific number of theoretical plates was chosen to match the experimental conditions used by You and Bidleman to measure PUF

$$G(Vb) := \int_0^{Vb} 1 - \mathrm{erf}\left[\left(\frac{N}{2}\right)^{\frac{1}{2}} \cdot \left(1 - \frac{V}{Vg}\right)\right] dV$$

$$F(Vb) := \int_0^{Vb} 1 - \mathrm{erf}\left[\left(\frac{N}{2}\right)^{\frac{1}{2}} \cdot \left(1 + \frac{V}{Vg}\right)\right] dV$$

$$f(Vb) := \left(2 \cdot \frac{Vb}{G(Vb) + F(Vb)} - 1\right)^{-1}$$

$$E(Vb) := 100 \cdot (1 - f(Vb))$$

Where:
N = number of theoretical plates (7.5)
Vb = volume sampled when f(Vb) is lost
Vg = chromatographic retention volume
f(Vb) = fraction uncollected at volume Vb
erf(X) = error (distribution) function of X
E(Vb) = collection efficiency after Vb sampled

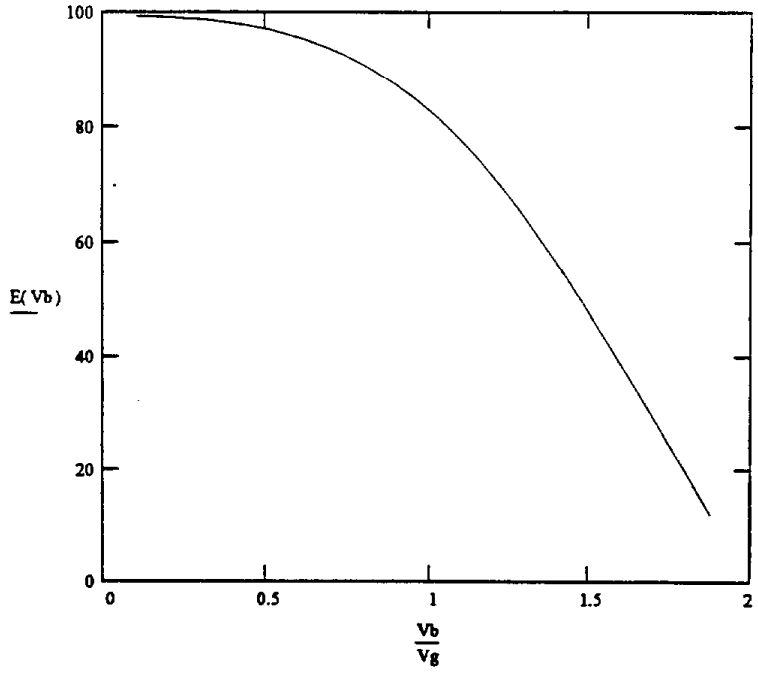


Figure F-1. Theoretical prediction of PUF collection efficiency as a function of the sampling volume to breakthrough volume ratio.

Table E-2. RADS Control System Performance During Sampling Trial Number 2.

Sampling Period	Period[α] Duration (seconds)	Performance Index[β] Isokinetic Sampling	Performance Index[β] Dilution Ratio	Air Volume[η] Sampled (m^3)
1	576	98.5 ± 1.8	100.0 ± 0.8	0.206
2	576	99.1 ± 1.2	100.0 ± 1.1	0.207
3	576	99.2 ± 1.3	100.2 ± 0.9	0.206
4	480	98.4 ± 2.5	100.6 ± 0.9	0.173
5	672	98.8 ± 1.9	100.0 ± 0.6	0.230

α Determined from the RADS on-board data logger clock.
β Calculated from the data logger record using equation E-2 to assess isokinetic sampling and equation E-3 to assess the dilution ratio performance.
η Calculated from the data logger record using equation E-4.

Table E-3. RADS Control System Performance During Sampling Trial Number 3.

Sampling Period	Period[α] Duration (seconds)	Performance Index[β] Isokinetic Sampling	Dilution Ratio	Air Volume[η] Sampled (m^3)
1	480	99.9 ± 0.6	100.4 ± 0.7	0.171
2	384	99.5 ± 0.8	100.5 ± 1.5	0.137
3	480	98.9 ± 2.3	100.2 ± 0.3	0.171
4	480	99.2 ± 0.8	100.0 ± 0.9	0.173
5	480	98.4 ± 3.7	100.9 ± 0.8	0.170
6	432	98.4 ± 0.3	101.0 ± 1.2	0.151
7	480	99.1 ± 2.0	100.0 ± 0.8	0.172
8	480	99.2 ± 0.9	100.6 ± 0.8	0.173
9	480	99.3 ± 0.7	100.3 ± 1.4	0.171

α Determined from the RADS on-board data logger clock.
β Calculated from the data logger record using equation E-2 to assess isokinetic sampling and equation E-3 to assess the dilution ratio performance.
η Calculated from the data logger record using equation E-4.

plugs measuring 7.6 cm (3 in) compared to 7.5 cm for the plugs used by You and Bidleman for breakthrough measurements. PUF used for the RADS field trials and the direct measurements of breakthrough volume were obtained from the same manufacturer (Olympic Products Corporation).

Using the relation of Figure F-1 and the breakthrough volumes estimates of Table F-1, PUF plug collection efficiencies were calculated for the RADS sampling volumes in each of the three field trials, as shown in Table F-2. In all cases, the collection efficiency was estimated to be greater than 98%, except for naphthalene and acenaphthylene. For naphthalene, the sampling volume was over twice the breakthrough volume producing a collection efficiency estimate of less than 10%. The predicted collection efficiency for acenaphthylene was always greater than 70%, but varied considerably since the sampling volumes for the field trials were close to the breakthrough volume.

These estimates of collection efficiency were consistent with the results of this side-by-side field study, in which the RADS using PUF collected substantially higher levels of all the sixteen priority PAH, except for naphthalene. Unfortunately, PUF plugs were not changed with the Teflon filter samples every ten minutes but were used for up to 7 ten minute sampling internals due to a shortage of cleaned plugs. Only four sets of PUF plugs were prepared; since, based on the PAS measurements, only three ten minute runs were expected to be necessary to collect sufficient sample for GC/MS analysis.

Even in this worst case scenario, only the plug breakthrough volumes for naphthalene and acenaphthylene were exceeded. In future, the PUF must be changed with the filter sample to avoid significant breakthrough and loss of PUF plug efficiency. Additional laboratory research is also required to verify the theoretical prediction of the PUF collection efficiency.

Table F-2. Calculated PUF Collection Efficiency for RADS Samples Collected for the Field Sampling Trials.

PAH Species	Sampling Trial Number			
	1A[α]	1B[α]	2	3
	Sampling Air Volume (m^3)			
	13.4	47.9	36.6	53.1
	PUF Collection Efficiency (%)[β]			
Naphthalene	< 10	< 10	< 10	< 10
Acenaphthylene	98.7	78.4	89.8	71.0
Acenaphthene	99.3	98.7	99.0	98.5
Fluorene	99.4	99.3	99.3	99.3
Phenanthrene	99.4	99.4	99.4	99.4
Anthracene	99.4	99.4	99.4	99.4
Pyrene	99.4	99.4	99.4	99.4

α PUF plug changed once during this sampling trial. Estimated collection efficiency for the entire trial is the weighted average of trials 1A and 1B.

β Estimated from the sampling to breakthrough volume ratio using the relation of Figure F-1.