Determination of Hydrocarbons in Diesel Exhaust

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Abstract

A wide range of sample preparation and analytical methodologies must be employed to fully characterize hydrocarbons in diesel exhaust. Unburnt diesel fuel, diesel oil, particulate-adsorbed combustion products, semi-volatiles, and gaseous combustion products are all organic groupings detectable within an exhaust sample. Each portion has special analytical difficulties that mandate specialized instrumentation to properly identify and quantitate the hydrocarbons.

Hydrocarbons emitted by a diesel engine are measured here with several new techniques. Heavier hydrocarbons are trapped as particulates on a quartz filter and a portion of the filter is directly loaded into a modified injection port on a gas chromatograph (GC). Hydrocarbons are rapidly vaporized in this system and transferred quantitatively to the capillary column and detected by mass spectrometry (MS). Species slightly more volatile than those trapped on the filter are ensnared by a combination of polyurethane foam (PUF) and XAD resin adsorbent, then simply extracted and identified by GC/MS. This direct approach eliminates the extensive use of solvents in the sample preparation and significantly reduces the sample preparation time, while also diminishing the risk of contamination or component loss. Spectral interferences are significantly reduced by employing MS-MS, where only the parent ion is initially trapped and then disassociated to yield very selective daughter ions. By performing this logical "AND" selectivity, background interferences are drastically reduced and target hydrocarbons are readily detected.

Very light hydrocarbon components, which are not usually trapped by the chosen absorbent media, are collected into Tedlar bags and determined with GC and flame ionization/mass spectrometry detection. Special hardware has been developed to improve the detection ability of the flame ionization detector.

Introduction

Chemical characterization of hydrocarbons in diesel exhaust is important both to monitor very toxic compounds released and to assess the combustion chemistry in the engine. As interest shifts toward studies of the particulates generated by diesels, a simple and rapid method would greatly improve the measurement.

Usual approaches for the measurement of semi-volatiles are often based on EPA Method TO13A. This method involves tedious Soxhlet solvent extraction, sample cleanup and concentration steps to prepare the samples for GC/MS analysis. Difficulties with this approach include the long time required for the process, sample contamination during processing, organic solvent disposal, and incomplete recoveries that compound with each additional step of the process.

The technique of direct thermal desorption with on-line gas chromatography has been reported using GC/MS for measuring polycyclic aromatic hydrocarbons in urban dust.[1] The demonstration chromatogram showed some background interferences from paraffins, but as a whole was significantly simpler than equivalent results from diesel exhaust. A second paper demonstrated the ability to measure all particulate-bound hydrocarbons.[2] Chromatograms presented illustrate the difficulty in picking out polycyclic aromatic hydrocarbons in a diesel sample. However, the prospects for analyzing particulates are both simplified and improved by inserting of a portion of the quartz filter directly into the gas chromatograph; all of the cited problems with an extraction process are then resolved. Detecting the aromatics with the very selective technique of MS-MS readily sorts out the important aromatics from all of the interfering paraffins and olefins.

The most volatile components in exhaust, from Ethane to n-Dodecane, can be measured using California Air Resources Board methods (CARB Methods 1002 and 1003), involving the cryofocusing of fixed sample volumes to a set of capillary columns. However, measurement at levels found in diesel exhaust challenges the normal detection limits of these methods (~5 ppbC with 22 ml sample injection). Measuring larger volumes with a mass flow controller, as is done with ambient air studies (for example, CARB Method 032), can introduce significant systematic errors.[3] Exhaust contains major concentrations of carbon dioxide and water vapor. Mass flow controllers are usually calibrated for air and will inaccurately measure a volume of exhaust, due to the variable contributions of carbon dioxide and water. The error is typically twice the percentage of carbon dioxide present and can be as much as 20% too high of a volume. The more accurate approach is to measure a large fixed volume and concentrate into a small volume with double cold trapping prior to on-column injection.

Experimental Methods

Exhaust samples were collected from a dump truck at the heavy-duty dynamometer at the Metropolitan Transit Authority facility in Los Angeles, California, as shown in Figure 1. Details for the vehicle test are given in Table I. Samples included an aliquot of the composite gaseous component after the constant volume dilution apparatus.

Figure 1. Test vehicle mounted on heavy-duty dynamometer.

Vehicle Information	
Engine	Caterpillar 3208
Transmission	Automatic
Test Sequence	FTA Central Business District
Distance	1.986 miles / 3.20 kilometers
Fuel Economy	4.66 mpg
Room Temperature	83.97 ^oF / 28.87 ^oC
Room Relative Humidity	50.1%
Test Volume	24,251 cu. ft. / 686.7 steres
Dilution factor	34.75
Net Total Hydrocarbons from Bench	26.10 ppmC
Particulate Sample Volume	26.5 cu. ft. / 750.2 liters
Minimum Particulate Temperature	84.4 ^oF / 29.1 ^oC
Average Particulate Temperature	86.8 ^oF / 30.4 ^oC
Maximum Particulate Temperature	90.3 ^oF / 32.4 ^oC

Table I. Partial dynamometer test conditions for collection of sample on quartz filter and in PUF/XAD resin cartridge are listed.

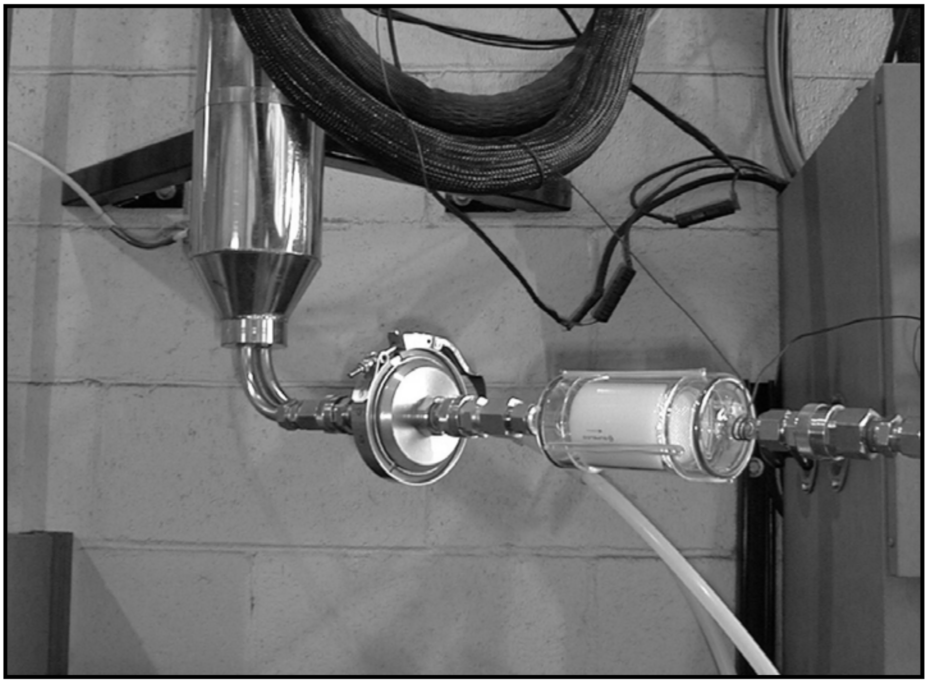

Figure 2. Quartz filter (inside stainless steel filter holder) and polyurethane foam (PUF)/XAD-2 resin cartridge (enclosed in glass) are mounted after the exhaust dilution tunnel of the dynamometer. Typical flow through the filter combination is 750 liters total for the test.

Diesel particulates were collected on a quartz membrane filter (Gelman #7213, Gelman, Ann Arbor, MI). Semi-volatile components were trapped with a commercial PUF/XAD resin cartridge (Supelco # ORBO-2500, Supelco, Bellefonte, PA) and were used as received. The cartridge was mounted inside a special glass apparatus and installed downstream of the filter holder, as shown in Figure 2. Typical volume through the filter/cartridge was 750 liters, as measured by the Horiba mass flow controller (Horiba, Ann Arbor. MI) after the cartridge. The quartz filter was weighed before and after sample collection to determine the total mass of the particulates collected. Before each weighing, the water content of the filter was stabilized by exposing it to a humidity-controlled environment for at least two hours.

The PUF and XAD resin portions in the cartridge were mechanically separated and independently immersed into 30 ml of acetonitrile to extract polycyclic aromatic hydrocarbons from the solid phases. Then 30 microliters of each portion was separately injected into a microvial and inserted into the Varian Chromatoprobe (Varian, Inc., Walnut Creek, CA), mounted in the Varian 1079 Temperature Programmable Capillary Injector. Temperature of the probe was set low, to 88 ^{o}C, to allow very slow evaporation of the acetonitrile without boiling and loss of analytes of interest. Then the probe temperature was rapidly programmed to 300 ^{o}C to volatilize the sample residue into the analytical column of the Varian 3800 Gas Chromatograph, equipped with a Varian Saturn 2000 Ion Trap Mass Spectrometer. Specificity to polycyclic aromatic hydrocarbons was achieved with the MS-MS feature of the Saturn instrument. Separation was performed with a narrow-bore capillary column (Chrompak CP-Sil 5 CB Low Bleed/MS, 50 meters, .25 mm ID, df=0.40, #CP7845, Varian, Inc. Walnut Creek, CA). Calibration was performed with a PAH mix from Supelco (Catalog #47940U, Supelco, Bellafonte, PA) by inserting 1 microliter of the standard into the microvial and processing it as a sample.

Portion of the quartz filter was weighed (2.35 mg net) and carefully inserted into a microvial without any prior treatment (see Figure 3); typically 2% of the filter was analyzed each time. Then it was inserted into the Varian Chromatoprobe, as depicted and analyzed under similar conditions as the PUF and XAD portions.

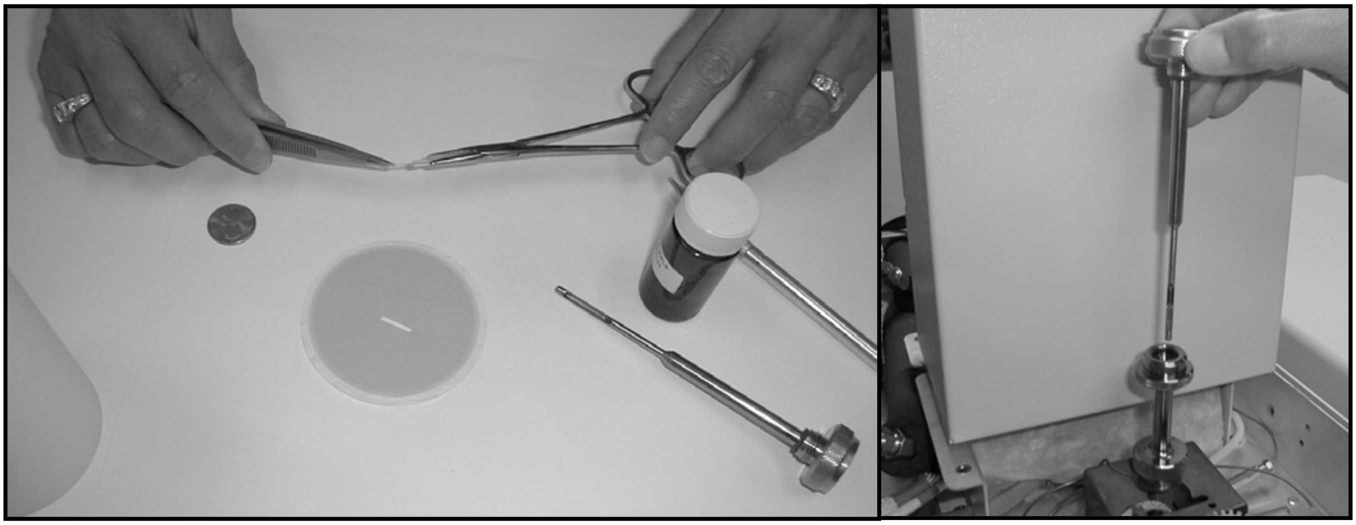

Figure 3. A portion of the quartz filter is cut out and inserted into a microvial suitable for use with the Varian Chromatoprobe. The probe is shown in the lower right corner of the left photograph. The probe is then inserted into the capillary injector port of the gas chromatograph with minimal sample preparations.

The gaseous portion of the diesel exhaust was collected into a Tedlar bag and analyzed for hydrocarbons from Ethane to n-Tridecane. Measurements were made on Micro-Trace Hydrocarbon System (Lotus Consulting, Long Beach, CA), based on two Varian 3800 Gas Chromatographs operating in tandem – one optimized for detection of light-end hydrocarbons (Ethane to n-Octane) and the second designed to measure mid-range hydrocarbons (n-Butane to n-Tridecane). A schematic of the apparatus is shown in Figure 4. Injection volume was 400 ml fixed volume loop for each instrument. Chromatography was performed with a narrow-bore capillary column (Chrompak CP-Sil 5 CB Low Bleed/MS, 50 meters, .25 mm ID, df=0.40, #CP7845, Varian, Inc. Walnut Creek, CA) for the mid-range and with a narrow bore PLOT column (Chrompak Al2O3/Na2SO4 PLOT, 50 meters, 0.25 mm ID, #CP7587, Varian, Inc. Walnut Creek, CA) for the light-end. Detection was achieved with flame ionization detectors, using a flame tip of 0.010” ID and nitrogen make-up gases for enhanced detection of hydrocarbons. The same sample was also measured with the Varian Saturn 2000 Ion Trap Mass Spectrometer as the detector. Calibration was accomplished with NIST primary standards (SRM 1800, NIST, Gaithersburg, MD).

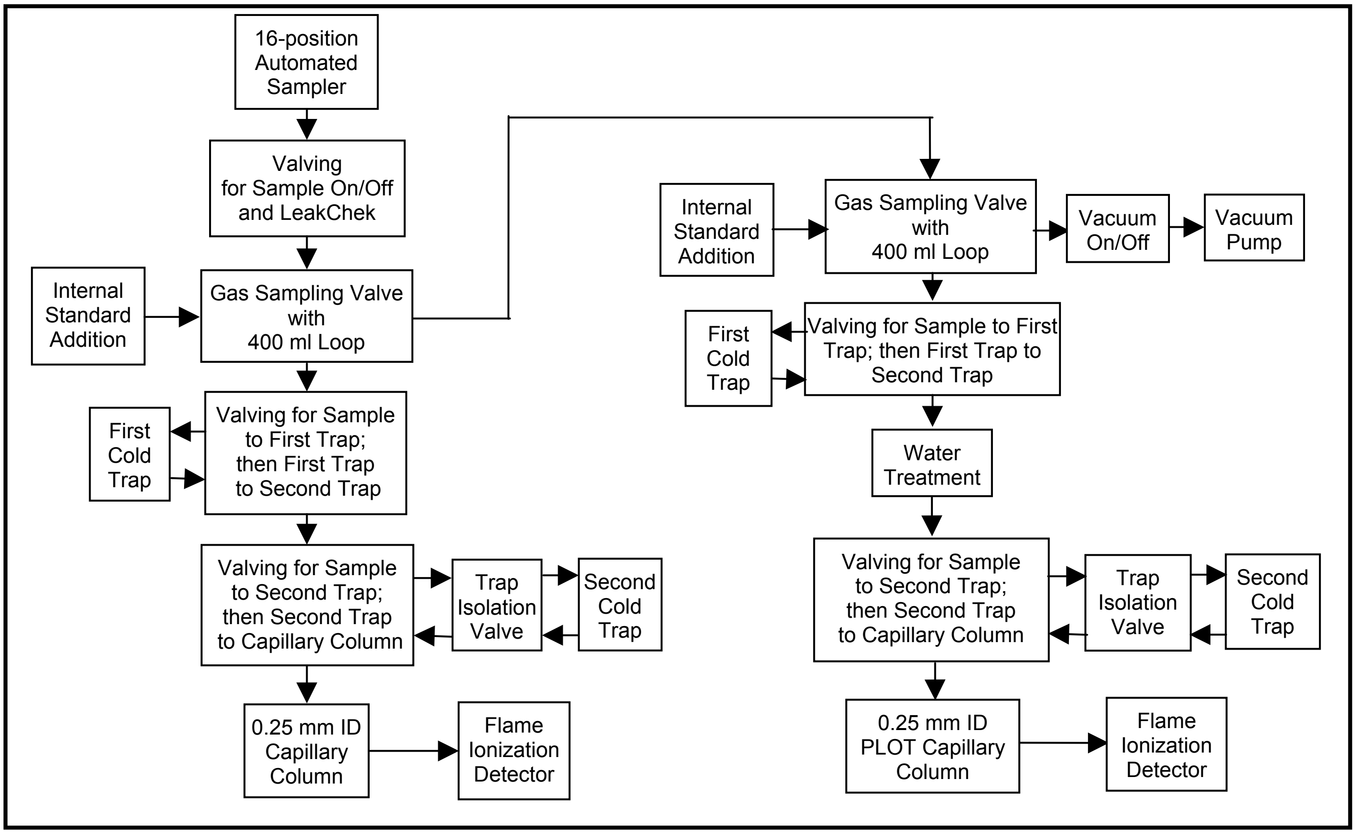

Figure 4. Schematic of Ultra-Trace Hydrocarbon System shows the path for loading a sample into two separate 400 ml sample loops. Both loops are then loaded into separate cold traps to reduce the trace hydrocarbon components to about 1 ml volume. This trap is then heated and directed to transfer the sample to a smaller second cold trap with a volume of 120 microliters. This trap is then rapidly heated to volatilize the hydrocarbons to inject them into appropriate capillary columns. Heavy hydrocarbons (above n-Octane) and water are eliminated from the sample for the light-end measurement by the special water treatment described in the text.

The PLOT column is very sensitive to water and heavy hydrocarbons. These components were kept from the column by using a very polar megabore column (Chrompak CP-Wax 52 CB, 15 meters, 0.53 mm ID, df=1.00, # CP8718, Varian, Inc. Walnut Creek, CA) plumbed after the first cold trap with a valve plumbed in a foreflush/backflush to vent. Timing for the activation was set empirically to just allow Benzene to pass through the stripper column and retain heavies and water. These undesirables were then backflushed to vent.

Results and Discussion

A total ion chromatogram of a portion of the quartz filter shows the difficulty in measuring trace components that are overwhelmed by interfering compounds. In Figure 5, polycyclic aromatic hydrocarbons are severely hidden by paraffins and cannot be detected by this approach. Even using selected ion storage, with the ion storage selected for each region where the aromatic elutes, does not improve the ability to find the elusive aromatics, as shown in Figure 6. Enough interference is generated from the unburnt fuel ensnared in the filter.

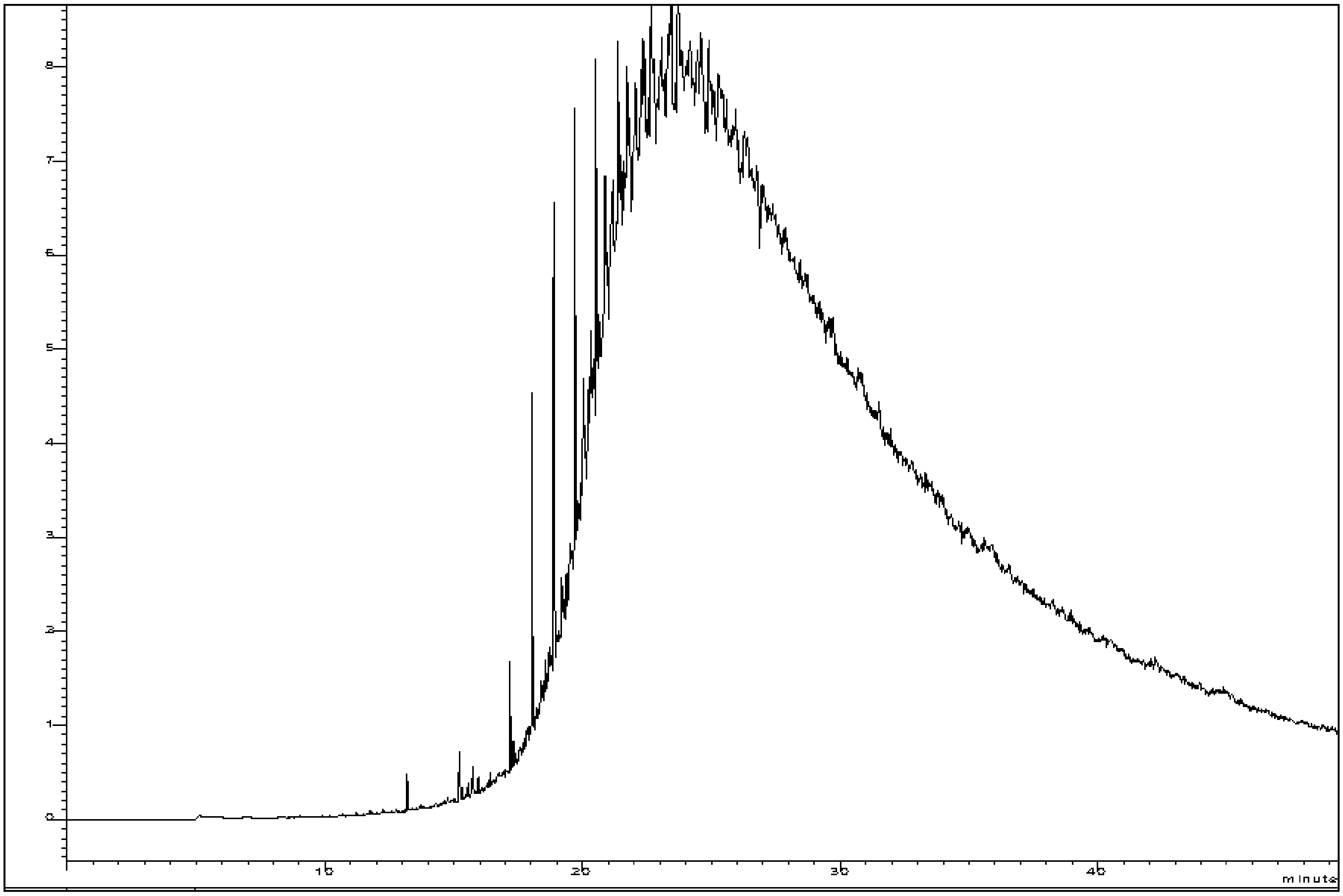

Figure 5. The unburnt diesel fuel that is present in exhaust overwhelms total ion chromatogram (TIC) of a portion of the quartz filter. Polycyclic aromatic hydrocarbons are severely hidden by paraffins and cannot be measured by this approach.

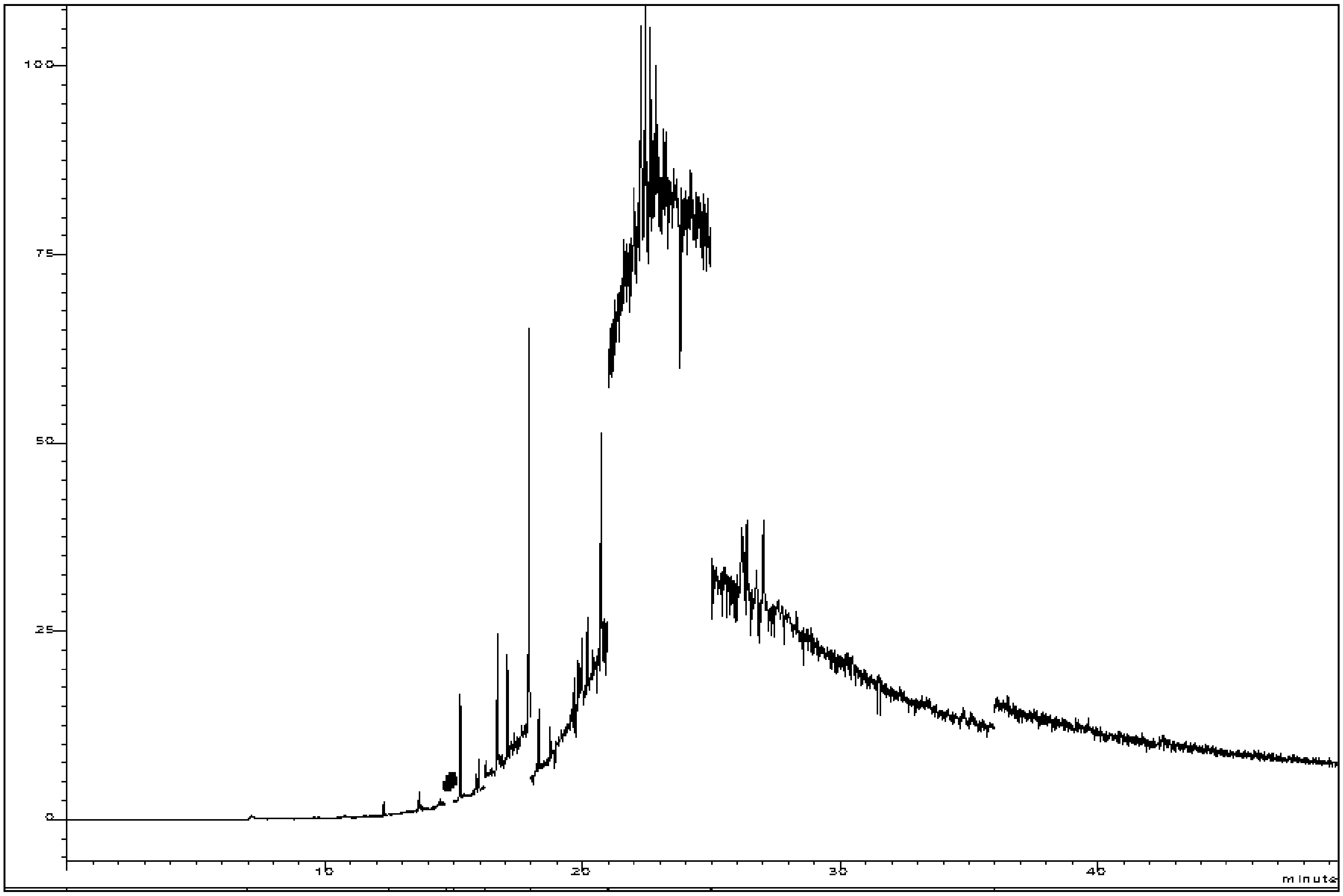

Figure 6. Selected Ion Storage (SIS) improves the background from the unburnt diesel fuel, but is not selective enough to pick out the polycyclic aromatic hydrocarbons with certainty. Disruptions in the chromatogram are generated from the shifts in the ion being monitored in the attempt to locate polycyclic hydrocarbons.

The selectivity of MS-MS permits only the selected parent ions to be retained in the ion trap and all other ions are rejected. Then these parent ions are ionized further into a distinctive pattern of daughter ions. Only molecules that generate the selected parent ions and specific daughter ions are detected. Fortunately, polycyclic aromatics yield very different daughter ion patterns that allow them to stand out in a messy crowd of paraffins. Figure 7 illustrates the conventional mass spectrum for Phenanthrene with no strong pattern for fragment ions. Figure 8 demonstrates the enhancement of the ion pattern with MS-MS with the generation of characteristic daughter ions. The MS-MS chromatogram of a portion of the quartz filter is shown in Figure 9 and quantitative results are listed in Table 2.

Many hydrocarbons that are not trapped on the quartz filter are ensnared in the PUF/XAD resin cartridge. Simple acetonitrile extracts of the foam and resin result in very distinctive MS-MS chromatograms of polycyclic aromatic hydrocarbons. Both Figure 10 and 11 illustrate the excellent sensitivities attainable with MS-MS.

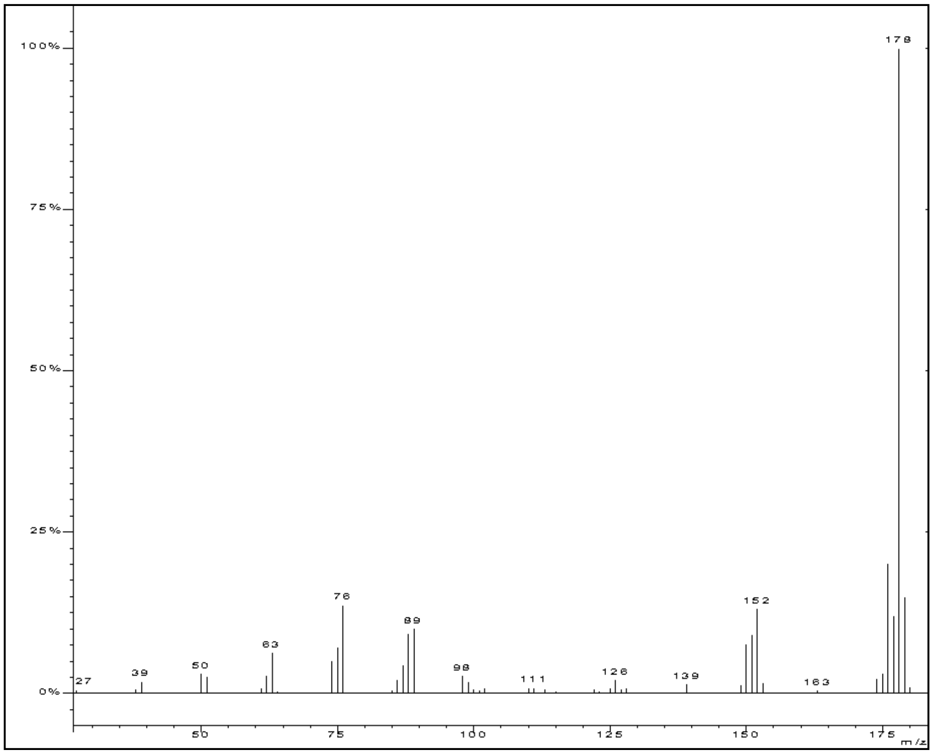

Figure 7. **Conventional mass spectrum for Phenanthrene shows the largest peak by far is the molecular ion at 178 and minor ions scattered from 39 to 152 m/z. The pattern for the fragment ions is not nearly as discerning as with the daughter ion pattern generated from MS-MS.**

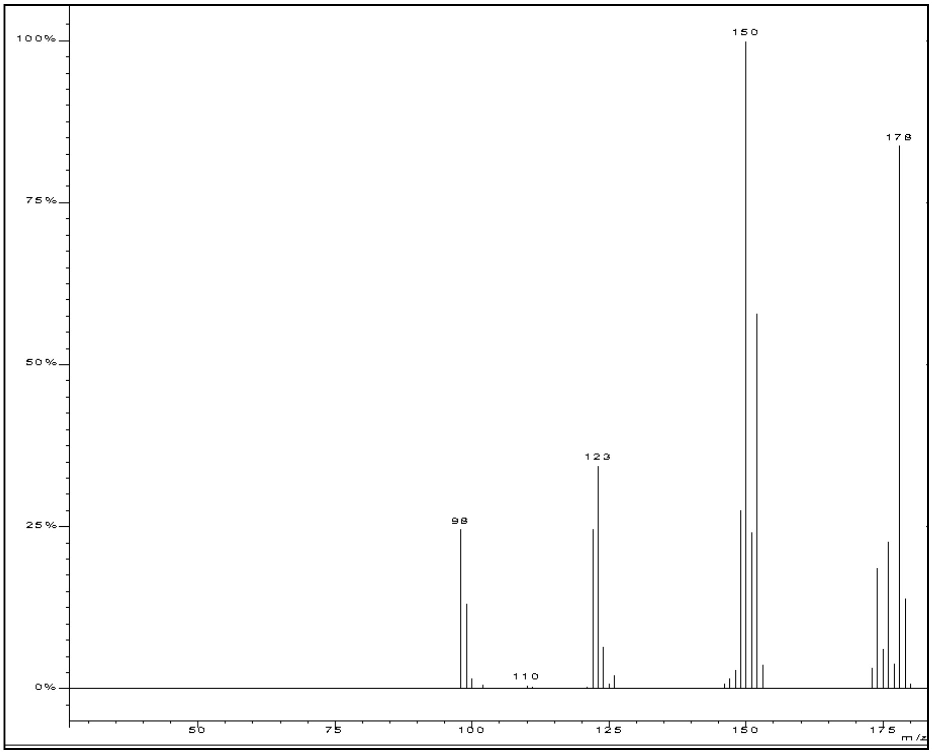

Figure 8. **The MS-MS spectrum for Phenanthrene yields the base peak at 150 m/z and generates a very distinctive peak pattern that becomes a unique identifier for this aromatic. By specifying a parent ion mass of 178 and then labeling the quantitation peak at 150, only the ions that first generate an ion at 178 and subsequently create daughter ions at 150 will be detected and used for quantitation.**

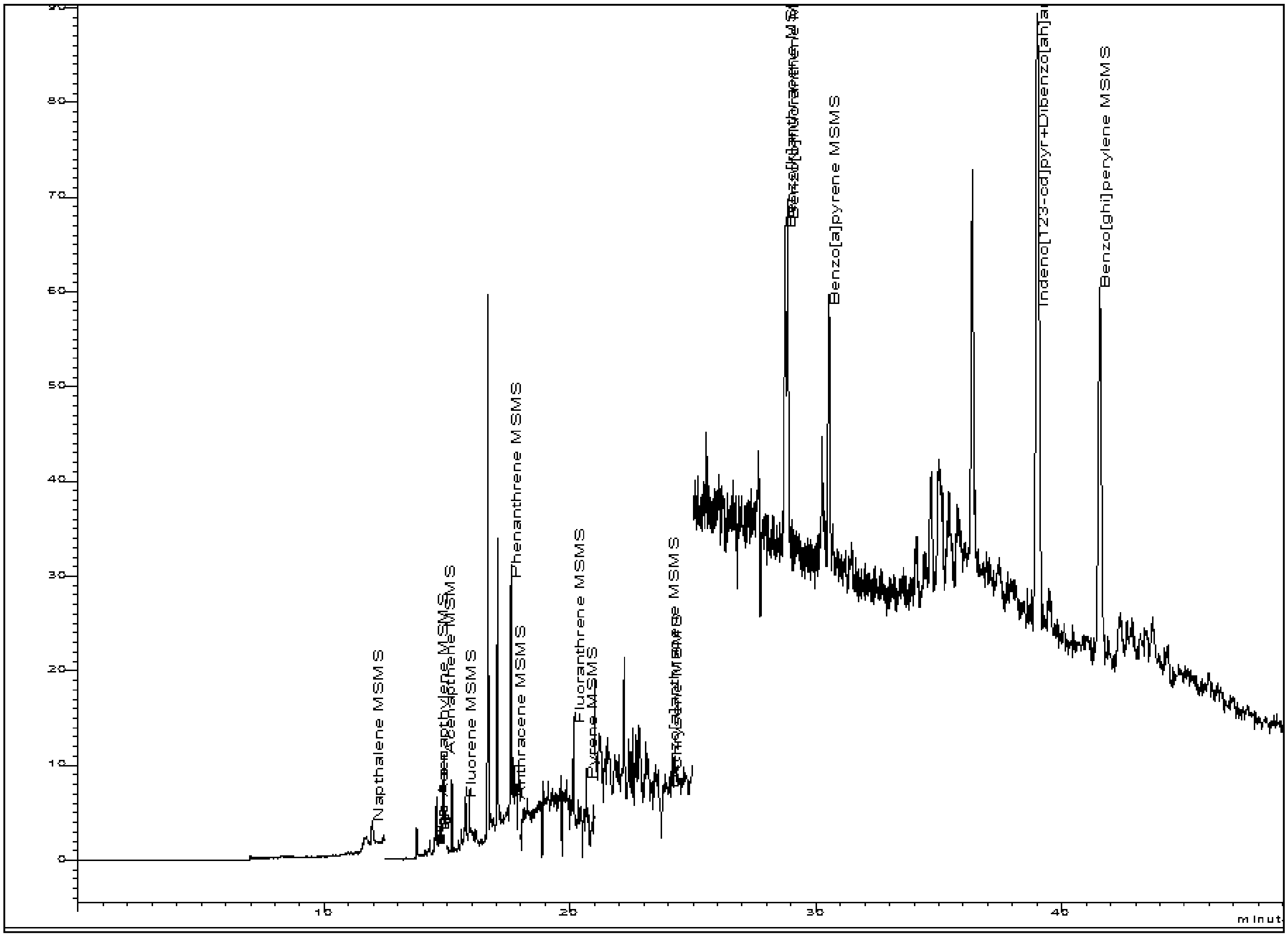

Figure 9. The MS-MS chromatogram of quartz filter sample yields very distinctive peaks for the selected polycyclic aromatic hydrocarbons. Interferences from paraffins are virtually eliminated. Quantitative results are presented in Table 2. The offsets in the chromatogram are due to changes in the MS-MS conditions for particular segments. Indeno[123-cd]pyrene and Dibenzo[ah]anthracene coelute with chromatographic conditions employed; all others are fully resolved.

Compound Name	Quantitation Ion	Concentrations on Quartz Filter (nanograms)	Concentrations in PUF Cartridge (nanograms)	Concentrations in XAD Resin (nanograms)
Naphthalene	126	1,309	122	66
Acenaphthylene	122	459	Not Detected	64
Acenaphthene	122	1,973	Not Detected	176
Fluorene	115	183	18	6
Phenanthrene	150	1,143	187	29
Anthracene	150	Not Detected	Not Detected	Not Detected
Fluoranthrene	174	231	178	14
Pyrene	174	Not Detected	109	10
Benzo[a]anthracene	202	10	460	50
Chrysene	202	15	485	45
Benzo[k]anthracene	226	876	159	30
Benzo[b]fluoranthene	226	1,986	499	58
Benzo[a]pyrene	226	1,359	464	61
Indeno[123-cd]pyrene + Dibenzo[ah]anthracene	248+252	2,519	1,513	124
Benzo[ghi]perylene	248	4,197	1,419	376

Table II. Computed concentrations for 14 polycyclic aromatic hydrocarbons in diesel exhaust detected in a quartz filter, PUF cartridge and XAD resin using the Chromatoprobe with MS-MS.

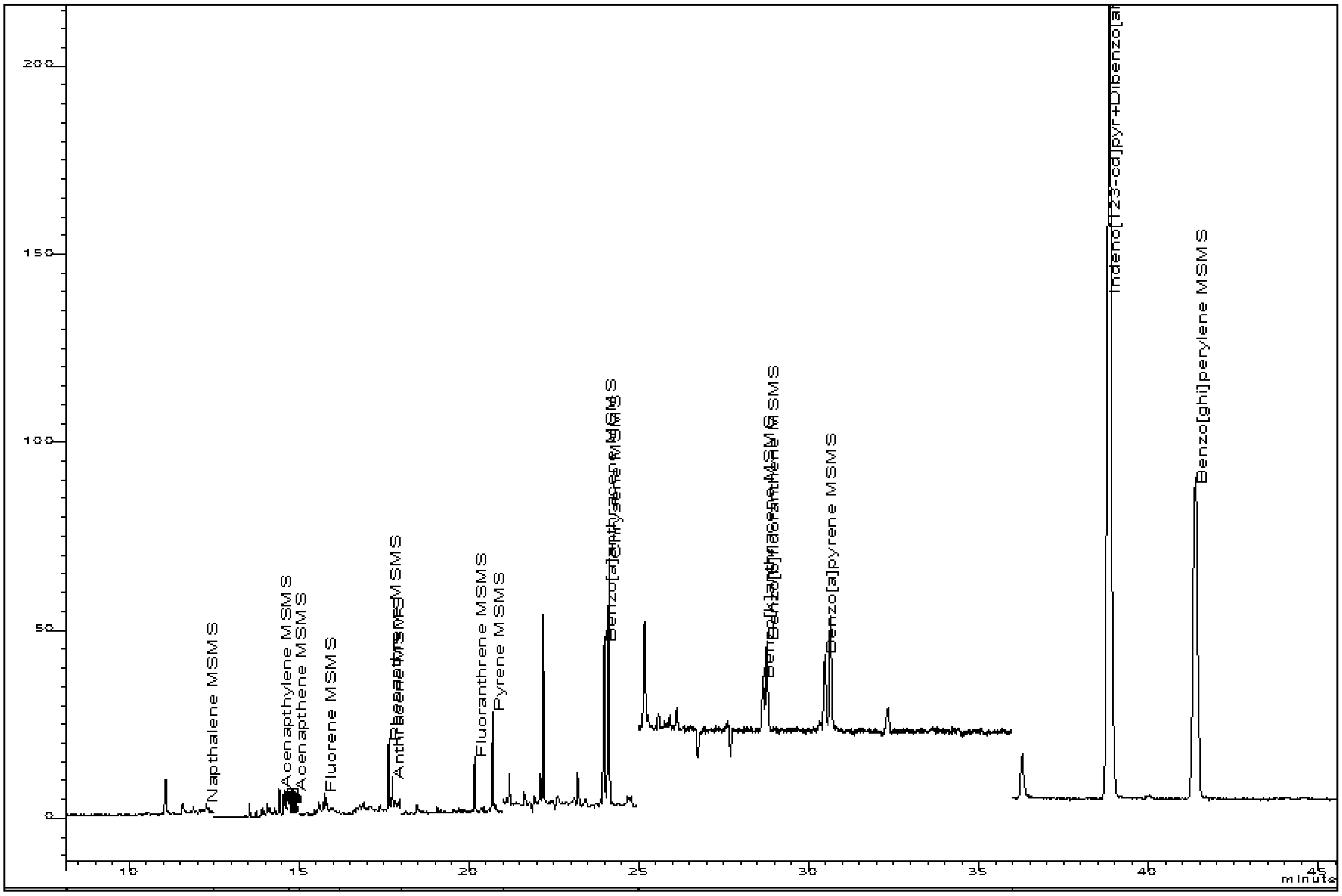

Figure 10. The MS-MS chromatogram for the simple extract from the PUF cartridge illustrates the excellent selectivity and sensitivity available from MS-MS. Quantitative results are listed in Table 2.

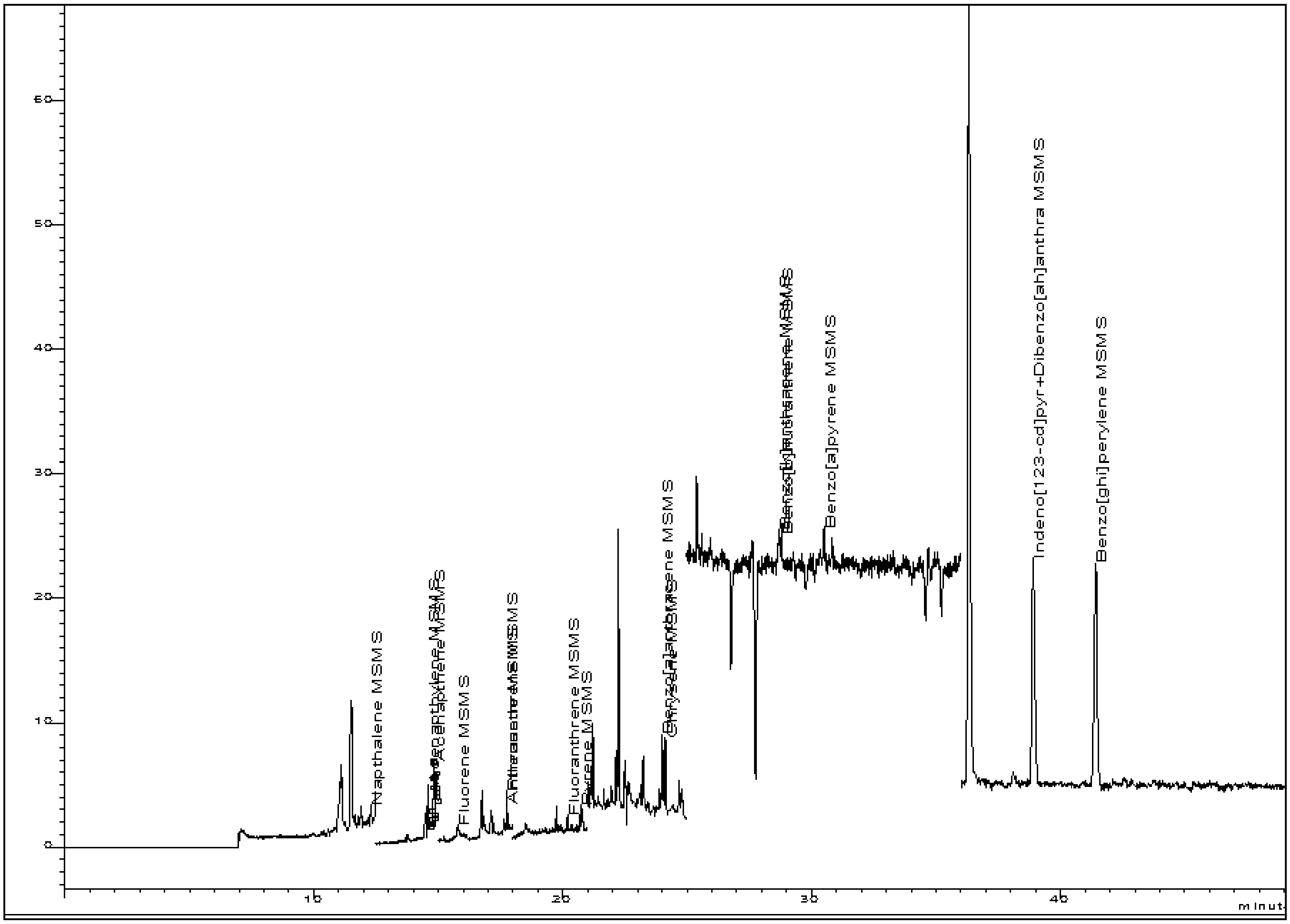

Figure 11. The MS-MS chromatogram for the simple extract from the XAD resin allows proper measurements of concentrations for important polycyclic aromatic hydrocarbons. Quantitative results are listed in Table 2.

Quantitation of volatile hydrocarbons is best performed with detection by flame ionization detection. This detector yields a very even response for all hydrocarbons, including olefins and aromatics. The response for propane is 3608 area counts per ppbC. And small hydrocarbons, including Ethane, Ethene, Ethyne, Propane, Propene and Propyne, are readily monitored with the flame detector. Mass spectrometry offers the some advantage of identifying the hydrocarbons based on their spectra, but too often spectra for similar hydrocarbons are indistinguishable. And since MS picks up every ion, ions below 44 m/z are usually cut off due to the interference of the ubiquitous carbon dioxide. Unfortunately, the very light hydrocarbons all have their parent ions below this cut-off and cannot be detected in exhaust samples. And MS responses for hydrocarbons are not even as many of the ion fragments are also below this cut-off and skew the responses across the range of hydrocarbons. Individual standards for each of the 140 hydrocarbons would be required to generate separate response factors for each with accuracy.

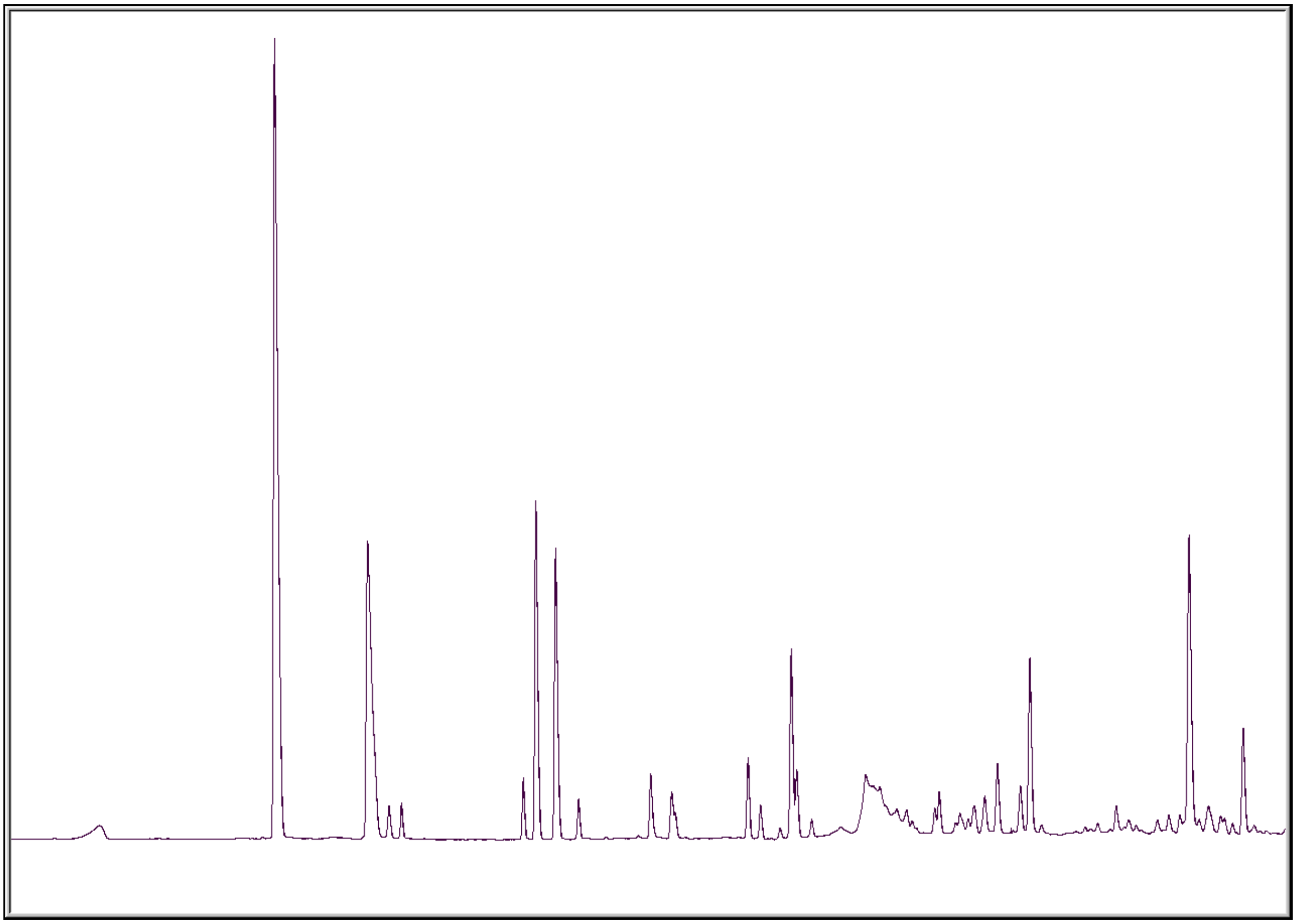

Figure 12. Chromatogram of light-end hydrocarbons illustrates the separation power and detection achievable with injection of 400 ml sample onto a PLOT capillary column. The largest peak is Propene with a concentration of 104 ppbC. Detection is with flame ionization detector.

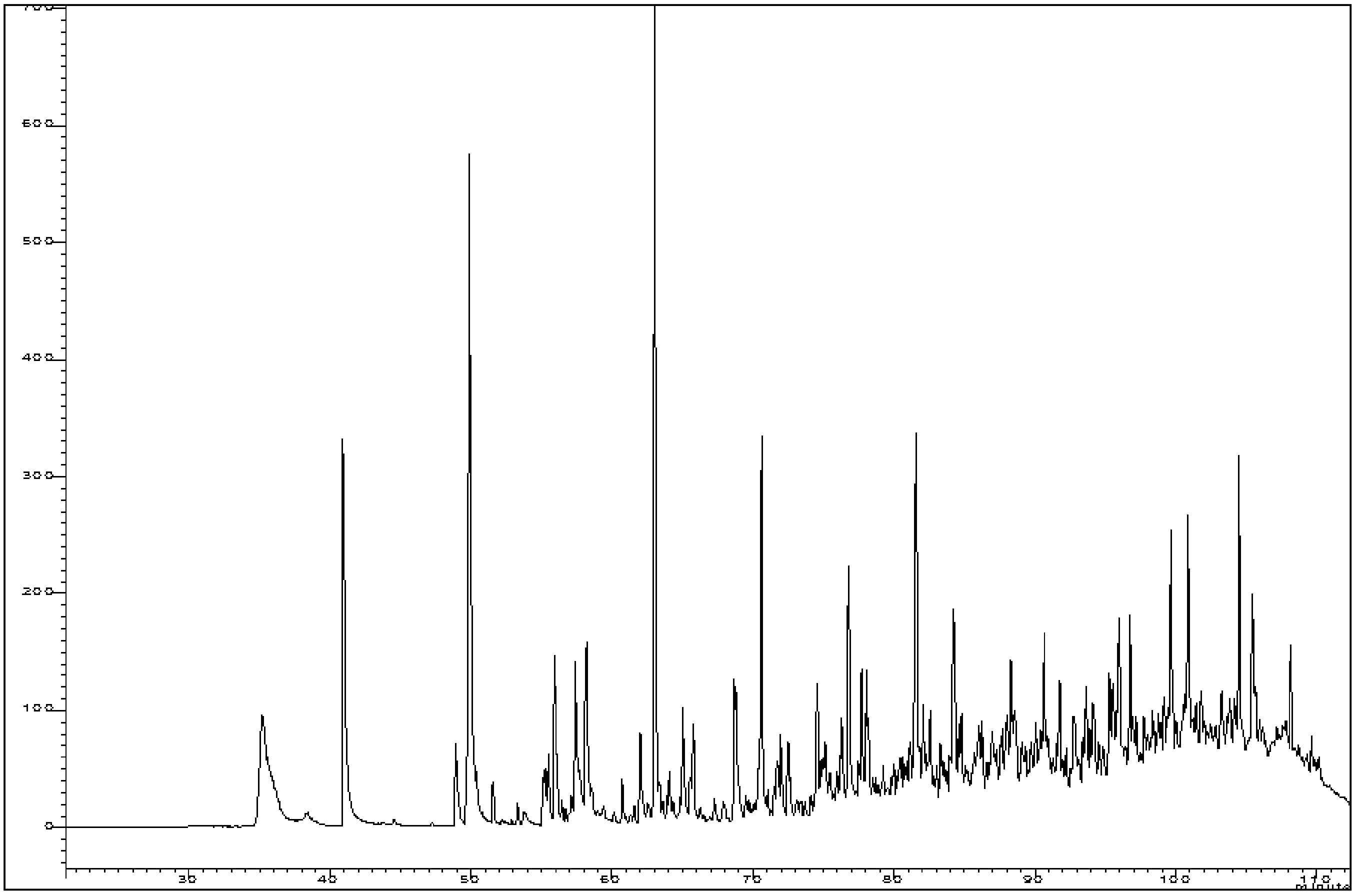

Figure 13. Chromatogram of mid-range hydrocarbons in diesel exhaust with mass spectrometer detection is depicted. Largest peak is toluene with a concentration of 43 ppbC. The last eluting peak is n-Pentadecane. Injection volume is 400 ml fixed volume sample loop. Initial temperature of the second trap is set to 5 °C to exclude CO_2 and water from the measurement; light hydrocarbons below n-Pentane are not detected.

Mass spectrometric measurements of hydrocarbons with the Alumina PLOT capillary column proved to be difficult due to the severe retention and slow release of carbon dioxide throughout the chromatographic run. The carbon dioxide peak at 44 m/z overwhelmed any detection of hydrocarbons. With the mid-range narrow bore column, the carbon dioxide peak was unretained in the column and had no interference with later eluting hydrocarbons.

Conclusion

Combining the direct insertion of a diesel particulate sample on a quartz filter with the selectivity of MS-MS yields a simple, rapid analysis technique for the measurement of polycyclic aromatic hydrocarbons. This approach has advantages over the more conventional solvent extraction and sample clean-up and MS detection:

1) Simple and minimal handling to introduce the sample into the chromatograph.
2) Speed, as lengthy solvent extractions are avoided.
3) Reduced spectral interferences from other, non-target hydrocarbons.

A complication with this new approach is the requirement that all analytes must be anticipated and possess known standards. Only then can MS-MS spectra to be generated by the system employed. Instrumental conditions are set within appropriate regions of the spectrum to only look for very characteristic masses. Virtually all other analytes are not detected.

Measurements of polycyclic aromatic hydrocarbons in the PUF/XAD resin cartridge are very conventional after a simple extraction with acetonitrile. Enhancements are realized with the larger injection volumes possible with the Chromatoprobe and with sensitive detection by MS-MS.

The normally low concentrations of volatile hydrocarbons in diesel exhaust are more readily detected with very large sample injection volumes and use of double cold traps to focus the analytes for direct injection into narrow bore capillary columns. A fixed volume sample loop properly apportions a very repeatable volume, even with varying concentrations of carbon dioxide and water vapor in the sample. Detection down to 0.1 ppbC is realized.

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Keywords

Diesel Exhaust, Polycyclic Aromatic Hydrocarbons, Volatile Hydrocarbons in Diesel Exhaust, Hydrocarbons.

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