

# Imaging Mass Spectrometry of Particulate-Associated Polynuclear Aromatic Hydrocarbons

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Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was employed for the *in situ* investigation of PAHs on individual environmental particulates. TOF-SIMS is a microprobe mass spectrometry technique capable of providing surface elemental and chemical information with lateral spatial resolution  $< 1 \mu\text{m}$ . TOF-SIMS analysis allows for the correlation of microscopic characteristics of different particulate, filter, and sorbent substrates with adsorbed organic species. Silver membrane and glass fiber filters loaded with coal flyash or silica gel were placed in a Method 0010 spiking train and exposed to vapor phase benzo[a]anthracene, benzo[g,h,i] perylene or pyrene. TOF-SIMS allowed surface chemical analysis of single particles on Ag filter media taken directly from the Method 0010 sampling train, without additional sample preparation. Secondary ion images indicated that benzo[a]anthracene is found primarily on the filter media and not on the flyash surfaces, and is of interest with respect to the elucidation of sampling artifacts. Particulate matter was also transferred to silicon wafers where native levels of diesel soot POM were imaged using TOF-SIMS.

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), present in the effluent streams of combustion sources in both the vapor phase and as adsorbed species on particulate matter, are of regulatory interest because many are known or suspected carcinogens. Measured particle-size distributions of PAHs in rural and urban environments reveal that PAHs are most often associated with particles  $< 1.4 \mu\text{m}$ , the size fraction with the greatest retention time in the lung.<sup>1</sup> Furthermore, recent epidemiological studies present consistent evidence that chronic exposure to particulate matter, particularly the respirable fraction with aerodynamic diameter  $< 2.5 \mu\text{m}$ , is responsible for increased morbidity and mortality in populations of susceptible individuals (e.g., those with chronic obstructive pulmonary or cardiovascular diseases) as well as the general populace.<sup>2,3</sup>

Environmental particles are complex mixtures of particle sizes and compositions. Coal combustion plume flyash is a heterogeneous mixture of particles which can be broadly categorized into three major fractions: mineral particles, mainly oxides of Si, Al, Ca and Mg with trace metal impurities; magnetic particles, which are mixtures of various Fe oxides; and carbonaceous particles representing the organic coal fraction. Electrostatic precipitator (ESP) hopper ash is often used as a surrogate for plume or stack flyash in studies of environmental particles. Another common anthropogenic particle, diesel soot, consists of agglomerations of sub-micron, spherical, carbonaceous particles with substantial native levels of nitro-PAH.<sup>4</sup> Studies using model particle surfaces and different coal flyash types have shown that the particle substrate to which the organic molecules are adsorbed can affect the photochemical reactivity of the adsorbed species.<sup>5,6,7</sup>

Currently, studies of PAH adsorption and transformation primarily rely upon bulk analysis schemes whereby large quantities of particles,  $> 100 \text{ mg}$ , are extracted using Soxhlet or supercritical fluid extraction techniques.<sup>8</sup> The extracts are then concentrated and analyzed by HPLC, GC or GC/MS. Bulk extraction methods have a number of disadvantages. Extraction into an organic matrix and subsequent sample work-up can lead to non-quantitative recovery. Irreversible adsorption of some POMs to substrates may also limit the accuracy of extraction-based

techniques.<sup>9,10</sup> In addition, extractions average results over a large number of particles and recover POM not only from the surface but also from within particle pores. Important information regarding organic surface components and their distribution among the various fractions of a heterogeneous particulate matter like flyash is lost. Correlation of the organic species with surface elemental composition, which can differ significantly from the bulk particle composition, is difficult or impossible.<sup>11</sup>

The surface chemistry of organic toxics including photochemical reactions, heterogeneous reactions with gaseous pollutants, and the effects of particle or filter substrates on sorbed organics are not well understood. Photochemical reactions of adsorbed POMs can alter toxicity by creating products of differing mutagenicity than the parent compound.<sup>12</sup> Furthermore, the filter material used in high-volume sampling of ambient airborne particulate matter appears to subtly impact the measured mutagenicity of PAHs on ambient airborne particles.<sup>13</sup> Thus, *in situ* chemical analysis of individual particles is desirable for its ability to detect both precursors and their breakdown products directly in their native, most environmentally relevant, chemical environment.

Microprobe techniques have been employed for the surface elemental analysis of single particles. For example, dynamic secondary ion mass spectrometry (SIMS) and scanning electron microscopy (SEM) coupled with energy dispersive X-ray detection have characterized trace elements on atmospheric particles.<sup>14,15</sup> Neither of these methods, however, are well-suited for the analysis of adsorbed organics. Laser ablation mass spectrometry, which is capable of both organic and inorganic analyses, has been applied to the single particle analysis of coal flyash.<sup>16,17</sup> None of these studies attempted to correlate POM adsorption and reactivity with particle composition.

Time-of-flight secondary ion mass spectrometry, well suited for the surface analysis of organic species, has been shown to provide a method for the *in situ* analysis of organics on single particles. TOF-SIMS was employed for the analysis of organics on polystyrene beads, a commonly used substrate in combinatorial chemistry.<sup>18</sup> Recently, TOF-SIMS was used to determine that the carbonaceous fraction of flyash particles coated with submonolayer coverages of benzo[e]pyrene (BeP) had higher coverages of the adsorbate than did the mineral fraction.<sup>19</sup> That study also demonstrated the ability to monitor the photooxidation of benz[a]anthracene on individual particle surfaces; however, the solution coating scheme employed may swell the particles or alter the levels and distribution of native PAHs. In the present study, the feasibility of TOF-SIMS is evaluated for analysis of toxic organics on coal flyash and diesel soot at either ambient levels or following vapor-phase spiking of PAH. The utility of TOF-SIMS as a tool for investigating artifacts in the Method 0010 sampling train is also demonstrated.

## EXPERIMENTAL METHODS

### Materials

ESP hopper ash was obtained from the CP&L Cape Fear power plant (Moncure, NC). The flyash was size-fractionated according to aerodynamic diameter, and the 3-10  $\mu\text{m}$ -diameter fraction was used in this research. No further separation of the flyash into carbonaceous, mineral or magnetic fractions was made prior to use. The surface area of flyash was 0.85  $\text{m}^2/\text{g}$  using BET nitrogen adsorption. Diesel soot, Standard Reference Material 1650, was obtained from the National Institute of Standards and Technology (NIST). Table 1 lists the certified and non-certified values for organic compound concentrations in the diesel soot. NIST analyses were based upon Soxhlet extraction of 50 to 150 mg samples and either GC/MS or HPLC analyses.<sup>4</sup> Silver membrane filters, 142 mm diameter with an average pore size of 1.2  $\mu\text{m}$ , were obtained from Poretics Corp. (Livermore, CA). Whatman 11.0 cm, GF/A glass microfiber filters were also used. Filters were cleaned by rinsing a minimum of three times with HPLC-grade methylene chloride prior to use. 1,2-Benz[a]anthracene (BaA) and pyrene were purchased at 99% purity from Aldrich Chemical Co. Benzo[g,h,i]perylene (BghiP) was purchased at 99% purity from Radian Corp. (Austin, TX). All compounds were used as received.

### Spiking of Particles

Ambient PAH levels on flyash are estimated to be in the range of  $10^{-4}$  monolayers, thus hindering their direct detection on single particles by TOF-SIMS imaging.<sup>19</sup> Using a Method 0010 sampling train for vapor phase

spiking, particles were coated with higher levels of PAH to facilitate TOF-SIMS technique development. The Method 0010 train consists of a probe and particulate filter, both heated, in series with a condenser, a XAD-2 sorbent module and a train containing knockout, water and silica gel impingers.<sup>20</sup> The train employed to spike particle-loaded filters in this project was a slight modification of the 0010 train: the heated probe and nozzle were replaced by an atmosphere generator manifold and a heated spiking elbow through which a syringe pump introduced a methylene chloride spiking solution. Prior to PAH spiking in the 0010 train, particles were loaded, as received, onto filter media using a Medic-Aid aerosol generator. The temperature of the filters during spiking averaged 55°C.

The total amount of PAH spiked into any Method 0010 sampling train was approximately 200 µg. The PAH spiked onto flyash-loaded filters was determined by extracting the spiked filters in Soxhlet extractors for a minimum of 8 hours in methylene chloride. The extracts were analyzed on a Hewlett-Packard 1050 liquid chromatograph equipped with a Phenomenex Envirosep-PP column (5µm, 125 x 3.2 mm) using water/ acetonitrile gradient elution. The HPLC was equipped with dual UV/programmable fluorescence detection.

### Instrumentation

TOF-SIMS analyses were performed on a Charles Evans & Associates TOF-SIMS system as shown in Figure 1. The mass spectrometer consists of drift sections coupled to three electrostatic analyzers. Ions were detected using a dual microchannel plate followed by a single stop time-to-digital converter (TDC). For these analyses, the ion microprobe mode was utilized to optimize lateral resolution. A Ga<sup>+</sup> beam operating at 25 keV with a beam current of 640 pA was rastered across the surface sputtering off neutrals as well as positive and negative secondary ions characteristic of the near surface composition (top 1-2 nm). The pulse repetition rate of the source was 10 kHz. Pulse widths were varied from 18-2 ns, resulting in corresponding spatial resolutions of 0.2-1.0 µm. Mass resolution, however, improved with decreasing pulse width from 300 (M/ΔM at 28 Da, FWHM) with 18 ns pulse to 1100 with 2 ns pulse. Analysis times typically ranged from 15-35 minutes and were performed at low total primary ion doses (< 10<sup>12</sup> ions/cm<sup>2</sup>), known as the static SIMS domain. This dose corresponds to removal of < 1% of a monolayer of the surface, thereby minimizing beam damage effects on native molecular species.

### Particle Analysis

Samples were prepared initially by cutting pieces approximately 1 cm<sup>2</sup> from the particle-loaded filters and loading them directly into the TOF-SIMS to assess the feasibility of performing single particle chemical analyses directly upon filter media. Particles were also transferred from filter media onto pieces of silicon wafer by first cutting out a small piece of the filter and tapping it above the wafer. Excess particles not adhering to the wafer by electrostatic forces were removed by gently tapping the wafer prior to loading into the TOF-SIMS sample holder. This procedure tended to produce small clumps of a few particles spaced 1-20 µm apart in the case of either silica gel or coal flyash. Diesel soot tended to form agglomerates ranging from less than a micron to greater than 60 µm in length with 1-20 µm spacing between agglomerates. Electron charge compensation was required when imaging soot to prevent loss of signal in the analytical volume due to ion beam-induced electrostatic charging. Analysis areas were typically 60 µm x 60µm or 100 µm x 100 µm.

Instrumental conditions were optimized to improve detection of PAH on the particles. An 8 keV post acceleration potential was used routinely with blanking of low mass secondary ions. Blanking masses below 35 is accomplished by inactivating the TDC for a set time following the primary ion pulse. For samples imaged on silver membrane filters, gating out mid-spectrum masses (e.g., Ag<sup>+</sup> ions) was necessary to prevent detector saturation. Gating is accomplished by deflecting selected mass ions from the detector. The combination of blanking and gating allowed the use of longer primary pulse widths which had the effect of increasing the intensity of higher mass peaks. TOF-SIMS imaging of spiked flyash or native POM levels on diesel soot provided POM intensities of approximately 1 to 3 counts per pixel, for a typical pixel size of 0.055 µm<sup>2</sup>.

Data were typically acquired in the positive ion mode using an 18 ns pulse width and blanking of masses 1-35. Flyash samples were then reanalyzed using an 8 ns pulse width and no low mass blanking to allow sufficient mass

resolution for elemental analysis of particle surfaces. A negative ion mode analysis was performed to allow further characterization of flyash into mineral, magnetic, and carbonaceous particles. Due to their relatively high vapor pressures, PAHs tend to sublime during extended periods of exposure to the instrument's vacuum ( $10^{-9}$  Torr). Thus, total instrumental residence times were limited to roughly 30 minutes.

## RESULTS AND DISCUSSION

### Secondary Ion Spectra of Flyash

One goal of this project is to evaluate the feasibility of using TOF-SIMS to image environmental particles directly on air sampling filter media following vapor phase spiking. In lieu of the standard glass microfiber filter, silver membrane filters were chosen initially because they were anticipated to have a mass spectrum free of overlap with PAHs or flyash and because silver would act as a cationization agent enhancing PAH detection via the formation of (PAH-Ag)<sup>+</sup> adducts. Furthermore, a conductive imaging substrate is required to prevent surface charging from ion bombardment during TOF-SIMS analysis. A silver membrane loaded with 5 mg flyash was spiked with 200  $\mu$ g of BaA. HPLC analysis indicated that 8.6  $\mu$ g of the total BaA spiked into the sampling train was retained on the loaded filter. This suggests that heating of the Method 0010 filter holder tends to favor deposition of vapor phase PAH not on the particulate matter but further downstream in the sorbent module. A more efficient vapor phase spiking system, such as a fluidized bed reactor, needs to be investigated for these experiments.

Figure 2 shows the mass spectrum of this flyash imaged directly on the silver membrane filter media. The spectrum is dominated by signal from the silver membrane, yet strong BaA<sup>+</sup> (228 Da) and (BaA + Ag)<sup>+</sup> adduct (335, 337 Da) signals were observed. The contribution of just the Ag<sup>+</sup> (107, 109 Da), Ag<sub>2</sub><sup>+</sup> (214, 216, 218 Da), Ag<sub>3</sub><sup>+</sup> (321, 323, 325, 327 Da), and Ag<sub>2</sub>Cl<sup>+</sup> (249, 251, 253, 255 Da) mass ions ranged from 24-55% for spiked particle-free, silica gel-loaded, and flyash-loaded membranes. Figure 3 shows (a) the Ag<sub>2</sub>Cl<sup>+</sup> ion image, and (b) the BaA<sup>+</sup> ion image. Dark regions in the Ag<sub>2</sub>Cl<sup>+</sup> image indicate the location of the flyash while the BaA<sup>+</sup> image indicates that the PAH was detected on the membrane and not on the flyash. The signal from the silver overwhelmed the particle signal and prevented optimization of instrumental conditions for detection of PAH on the particles.

### Secondary Ion Spectra of Diesel Soot

Figure 4 shows TOF-SIMS positive ion images for unspiked diesel soot on a silicon wafer support. Image 4(a) is the total ion image followed by subsequent images of the molecular ions (M<sup>+</sup>) for the native PAHs at masses (b) 228, (c) 252, and (d) 276. The mass 228 ion image does not show a high degree of correlation between particle location and the ion counts. The outline of the largest soot agglomeration is discernible in the mass 252 image; whereas the crescent-shaped orientation of all three soot clumps appears more clearly in the mass 276 ion image.

The mass spectrum of the diesel soot is shown in Figure 5. The top spectrum is the total positive ion spectrum for the 55  $\mu$ m x 55  $\mu$ m image field. Note that it closely resembles the region-of-interest (ROI) background spectrum of the silicon wafer. Given the relatively small area of the image field occupied by soot, this is not unexpected. Peaks at 191, 193, 207 and 221 Da are associated with the silicon wafer substrate. These peaks are most likely due to polydimethyl-siloxane (PDMS, [SiO(CH<sub>3</sub>)<sub>2</sub>]<sub>n</sub>) contamination. Both the substrate PDMS contamination and the diesel soot, as discussed below, appear to contribute to a peak at mass 189 Da.

The middle plot in Figure 5 is an ROI spectrum of the soot agglomerate labeled as #1 in Figure 4. In this ROI, a peak at 252 Da (C<sub>20</sub>H<sub>12</sub><sup>+</sup>) corresponds to the molecular ions (M<sup>+</sup>) of benzo[a]pyrene (BaP), BeP, benzo[k]fluoranthene (BkF), and perylene. A peak at 276 Da (C<sub>22</sub>H<sub>12</sub><sup>+</sup>) corresponds to the molecular ions of BghiP and indeno[1,2,3-cd]pyrene. A series of peaks at multiples of 13 Da below the M<sup>+</sup> ion corresponding to the loss of multiple CH groups are typically observed in the TOF-SIMS spectra of surface adsorbed POM [19]. Peaks would be expected at 263 Da (C<sub>21</sub>H<sub>11</sub><sup>+</sup>), 250 Da (C<sub>20</sub>H<sub>10</sub><sup>+</sup>), and 237 Da (C<sub>19</sub>H<sub>9</sub><sup>+</sup>) for the mass 276 PAHs; at 239 Da (C<sub>19</sub>H<sub>11</sub><sup>+</sup>), 226 Da (C<sub>18</sub>H<sub>10</sub><sup>+</sup>), and 213 Da (C<sub>17</sub>H<sub>9</sub><sup>+</sup>) for the mass 252 PAHs; and at 215 Da (C<sub>17</sub>H<sub>11</sub><sup>+</sup>), 202 Da (C<sub>16</sub>H<sub>10</sub><sup>+</sup>), and 189 Da (C<sub>15</sub>H<sub>9</sub><sup>+</sup>) for the mass 228 PAHs. A series of peaks corresponding to the

$[(M-2H)-(CH)_x]^+$  cations are expected as well [19]. Fragments are predicted at masses 226, 213, 200 and 187 Da for the mass 228 PAHs; at 250, 237, 224, and 211 Da for the mass 252 PAHs; and at 274, 261, 248, and 235 Da for the mass 276 PAHs.

Confirmation of these assignments is beyond the scope of the work completed so far. Spiking soot with deuterated compounds could substantiate the fragmentation patterns. Characteristic fragmentation patterns could prove useful in establishing the relative coverages of isomeric PAHs co-adsorbed on a given particle. Ion counts of fragment and molecular ions from soot and the wafer were obtained from high mass resolution spectra and normalized to the respective spectrum integrals. The ratio of soot signal to wafer signal for the first four  $[M-(CH)_x]^+$  ions for each of the isomeric groups and the wafer associated peaks are shown in Table 2. The consistently high ratios confirm the association of PAH signals with the soot particles, and the correlation of suspected fragment ions with the intact parent molecular ions for each PAH series. Images of the 202, 215, and 239 mass ions on unspiked diesel soot are also shown in Figure 6. These suspected fragment ion images correlate well with the location of soot in the total ion image (Figure 4). Since the mass overlaps between the  $[M-(CH)_x]^+$  and the  $[(M-2H)-(CH)_x]^+$  series do not include the 202 or 215 Da peaks, these first two images help support an assignment of these peaks as mass 228 PAHs fragments. A similar lack of overlap suggests that the 239 Da image is likely that of a mass 252 PAH fragment.

## CONCLUSIONS

The feasibility of using TOF-SIMS for the *in situ* surface analysis of organic air toxics on single environmental particles has been demonstrated. Native levels of PAH on diesel soot were imaged with no intervening sample preparation or spiking. Silver membrane filters were not useful as a substrate for TOF-SIMS imaging of environmental particles since the overwhelming secondary ion signal from the membrane prevented optimization of instrumental conditions for PAH detection on the particles. TOF-SIMS was used to detect actifactual deposition of PAH onto filter media when using the Method 0010 sampling train for filter spiking.

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**Table 1. Organic Compound Concentrations in NIST SRM 1650, Diesel Particulate Matter**

Certified Compound	Nominal Mass (Da)	Conc. ( $\mu\text{g/g}$ )	Non-certified Compound	Nominal Mass (Da)	Conc. ( $\mu\text{g/g}$ )
Fluoranthene	202	51 $\pm$ 4	Phenanthrene	178	71
Pyrene	202	48 $\pm$ 4	9-Fluorenone	180	33
Benz[a]anthracene	228	6.5 $\pm$ 1.1	2-Nitrofluorene	211	0.27
1-Nitropyrene	247	19. $\pm$ 2	Chrysene	228	22
Benzo[a]pyrene	252	1.2 $\pm$ 0.3	Benzo[e]pyrene	252	9.6
Benzo[g,h,i]perylene	276	2.4 $\pm$ 0.6	Benzo[k]fluoranthene	252	2.1
			Perylene	252	0.13
			7-Nitrobenz[a]anthracene	273	2.8
			Indeno[1,2,3-cd]pyrene	276	2.3
			6-Nitrobenzo[a]pyrene	297	1.6

**Table 2. Comparison of Relative Intensities for Selected Signals on Diesel Soot and on Silicon Wafer Substrate Normalized to Respective ROI Total Ion Signal Intensities**

228 Series		252 Series		276 Series		Silicon Wafer	
Mass (Da)	Peak ratio (Soot/Si)	Mass (Da)	Peak ratio (Soot/Si)	Mass (Da)	Peak ratio (Soot/Si)	Mass (Da)	Peak ratio (Soot/Si)
189	7.23	213	8.92	237	6.49	191	2.30
202	14.74	226	9.50	250	9.20	207	1.43
215	15.48	239	11.85	263	5.93	221	2.05
228	7.96	252	5.48	276	15.14		

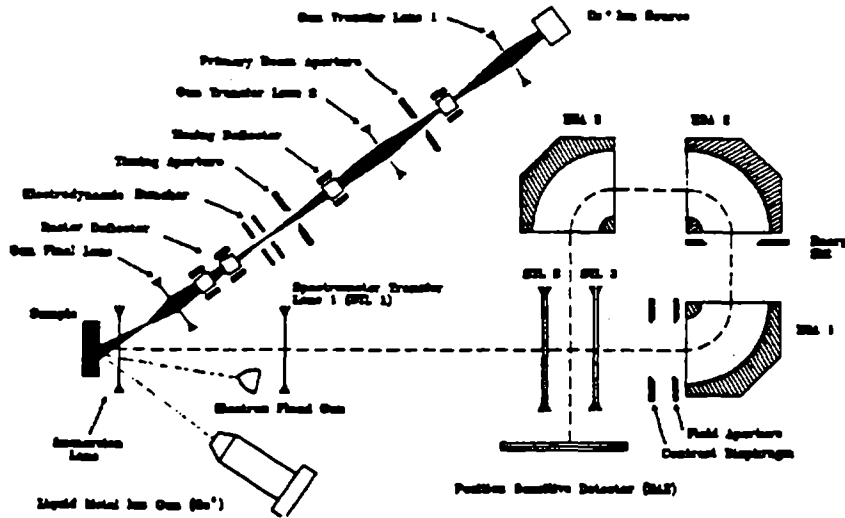


Figure 1. Schematic of Charles Evans & Assoc. Imaging TOF-SIMS. The instrument is operated in microprobe mode using the pulsed Ga<sup>+</sup> source for single particle analysis.

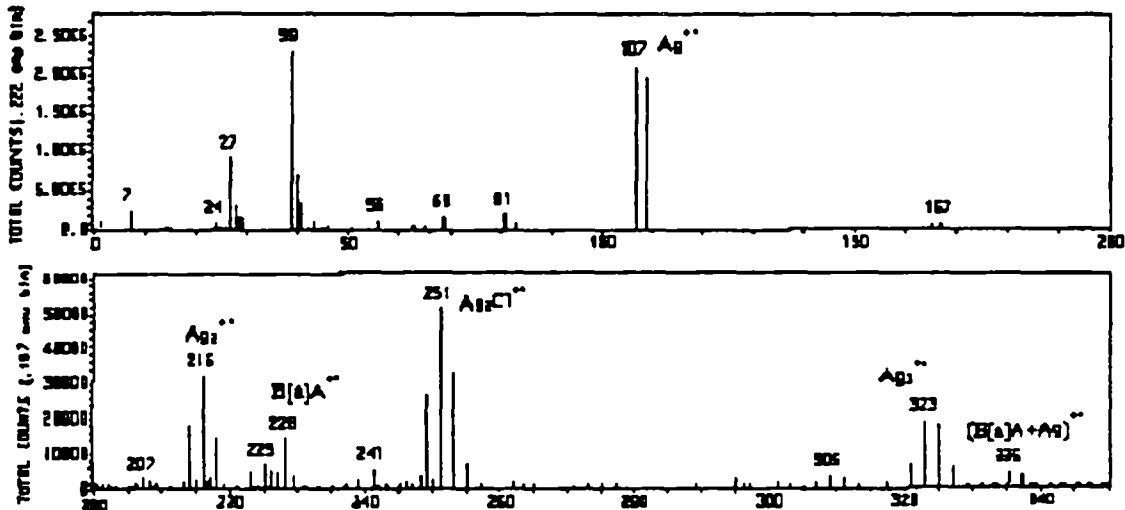


Figure 2. Mass spectrum of BaA-spiked flyash imaged on silver membrane filter.

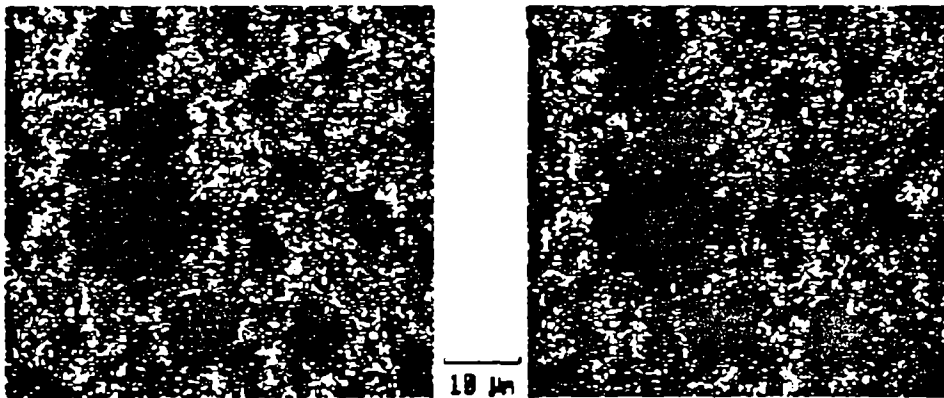


Figure 3. Secondary ion of BaA-spiked flyash on silver membrane. a) Ag<sub>2</sub>Cl<sup>+</sup>, and b) BaA<sup>+</sup>. Dark regions indicate that BaA was not detected images on the flyash.

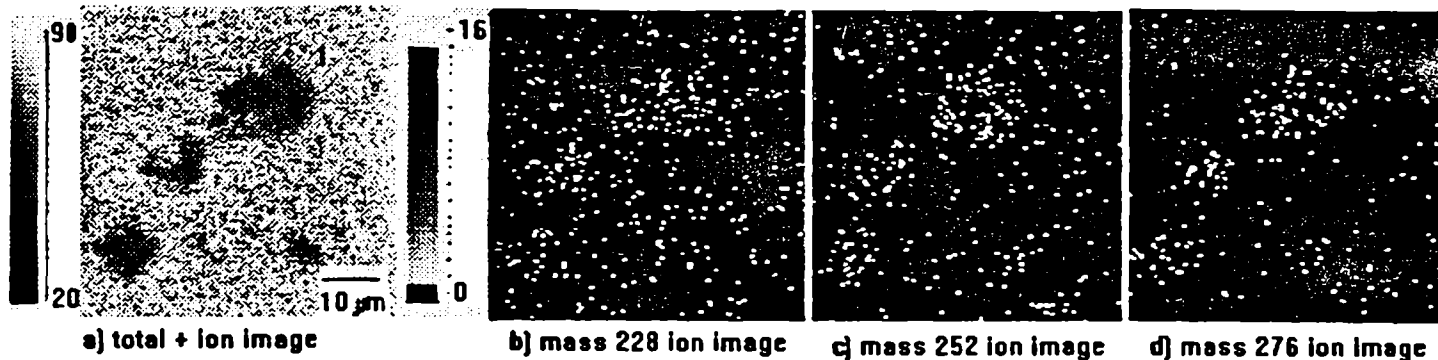


Figure 4. TOF-SIMS images of diesel soot on silicon wafer. The  $M^+$  ions are shown for native PAHs of mass 228 (BaA, chrysene), 252 (BaP, BeP, BkF, perylene), and 276 (BghiP, indeno).

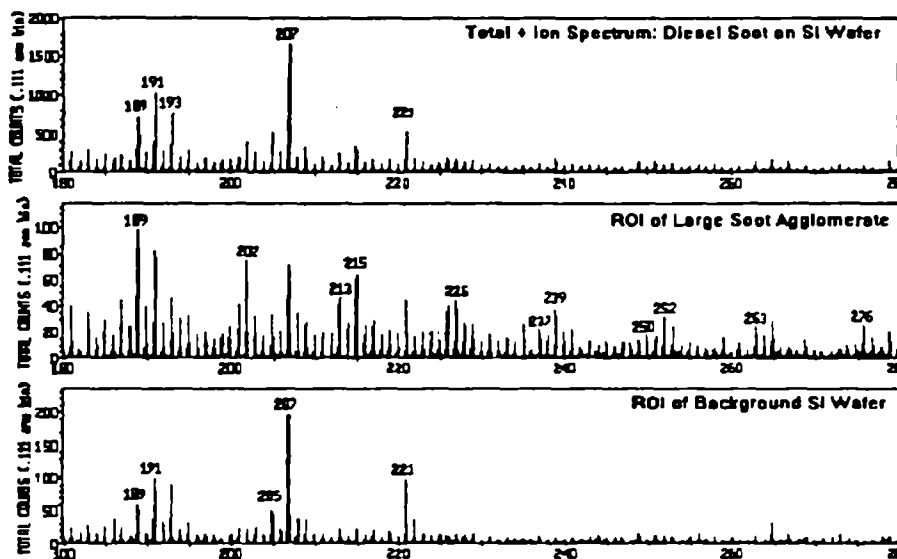


Figure 5. Mass spectrum of unspiked diesel soot on silicon wafer with ROI spectra of soot agglomerate #1 and silicon wafer background.

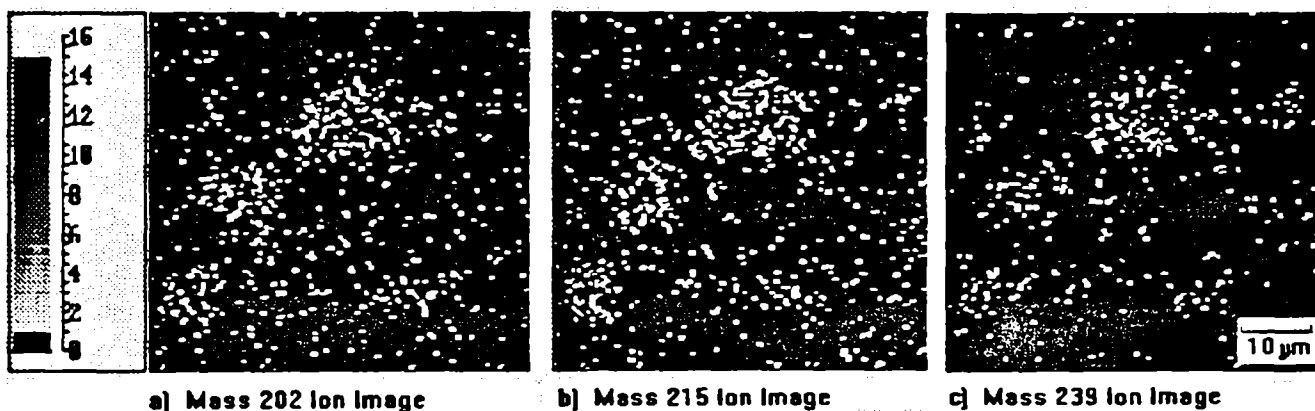


Figure 6. Secondary ion images of PAH fragments: (a) and (b) are fragments of mass 228 PAHs, and (c) is a fragment of the mass 252 PAHs.



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