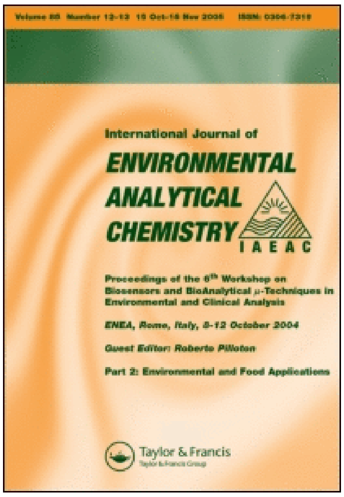

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Gardella Jr., Joseph A. and Hercules, David M.(1979) 'Surface Spectroscopic Examination of Diesel Particulates—A Preliminary Study', International Journal of Environmental Analytical Chemistry, 7: 2, 121 — 136
To link to this Article: DOI: 10.1080/03067317908071483
URL: http://dx.doi.org/10.1080/03067317908071483

Intern. J. Environ. Anal. Chem., 1979, Vol. 7, pp. 121 136
0306-7319/79/0702-0121 $4.50/0

Printed in Great Britain

Surface Spectroscopic Examination of Diesel Particulates— A Preliminary Study

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(Received June 28, 1979)

Preliminary studies on the use of combined surface analytical techniques such as X-ray Photoelectron Spectroscopy (XPS or ESCA), Auger Electron Spectroscopy (AES), Secondary Ion Mass Spectrometry (SIMS) and Ion Scattering Spectrometry (ISS) to probe the surfaces of diesel particulates are presented. Studies of two different particulate systems are reported.

Results of the first study show common chemical forms associated with the surface of particulate emission. Oxygen, sulfur and nitrogen in various chemical states are seen on the surface of a carbonaceous-graphitic (pyrolytic) center. These elements are postulated as organically bound surface segregated species. Observation of particles extracted for routine adsorbed organic analysis by gas chromatography show that nitrogen and sulfur compounds are left behind, along with residual organics. Trace metals were not seen on any sample.

The second study involves samples collected under different running speed conditions of a diesel engine. Typical analytical procedures for surface examination by the above techniques were used to monitor the forms and amounts of elements present.

Data are shown to support the applicability of these techniques to a study of source particulate emission, and the unique results obtainable.

KEY WORDS: Diesel particulates, surface analysis, ESCA/Auger/SIMS, source particulates, particulate analysis.

I. INTRODUCTION

Interest has grown recently in the development and application of surface analytical methods to the examination of environmental particulates. Techniques like X-Ray Photoelectron Spectroscopy (XPS or ESCA),

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Presented at the 9th Annual Symposium on the Analytical Chemistry of Pollutants, May 7–9, 1979, Jekyll Island, Georgia, U.S.A.

Auger Electron Spectroscopy (AES), Secondary Ion Mass Spectroscopy (SIMS) and Ion Scattering Spectroscopy (ISS) provide unique information about the structure, composition and reactivity of surfaces.[1] In this study we describe the techniques and preliminary results from our examination of the surfaces of diesel particulates.

The problem of analyzing airborne particulates is central to understanding the nature of air pollution. Particulates cause such environmental problems as acid rain and reduced visibility. Health problems can be related to the deposition of respirible particulates in the lungs. Previously, airborne ambient particulates on filters have been examined by ESCA in conjunction with other spectroscopic techniques.[2,3] Findings note the chemical states indentifiable on ambient filters, and semi-quantitative results were compared with more classical wet chemical analyses. Secondary Ion Mass Spectrometry (SIMS) as an Ion Microprobe has been used together with Auger Spectroscopy (AES) in the microprobe mode to depth profile coal fly ash from coal-powered generator plants.[4] These results are part of a larger study aimed at characterizing surface deposition mechanisms and particle size concentration dependencies of environmental particulates.[5,6] SIMS and Ion Scattering (ISS) have also been used to examine particulates suspended in filters.[7] All of these surface studies have been limited by various aspects of each of the techniques used. Each surface analysis method has its own limitation, which can be complemented by the multi-technique approach. Our work has stressed this multi-technique approach to analyzing particulate surfaces.

The system chosen for analysis is relevant for several reasons. The characterization of source generated particulates has several advantages over ambient particulate analysis. The generation system is known and can be controlled for modeling analysis. This means laboratory studies are more easily accomplished. Collection techniques, a significant variable in analysis, can be varied to minimize spurious effects. Thus, source particulates, illustrated by diesel particulate emission in this study, are an interesting alternative to ambient particulates in solving analytical problems in the description of air pollution. Secondly, diesel particulates themselves are relevant because of the intent to use small diesel engines to meet EPA fuel standards for the 1980's; engines must also meet the EPA requirements for gaseous and particulate emission. Diesel engines emit large amounts of particulates, most of which are smaller than 1 μm average aerodynamic diameter; they fall in the respirable range. We feel that controlled studies of diesel particulate surfaces may lead to the formulation of a formation mechanism, through study of the nature of the particulate surface, surface segregation, and comparison of routine analytical techniques to surface analysis.

II. DESCRIPTION OF TECHNIQUES

A. ESCA

The underlying principle of ESCA is the photoelectric effect. In ESCA, soft-X-rays of a known energy (usually MgKα or AlKα) are used to ionize core level electrons, from a solid sample (see Fig. 1). These electrons are energy analyzed and their kinetic energy can be related to the binding energy of the electron by the equation shown in Figure 1, where hν is the energy of the X-ray. The binding energy is characteristic of the element being analyzed, and its intensity can be related to the concentration of the element. Another unique feature of the ESCA spectrum is the chemical shift effect, which can be related to chemical state and environment of the atoms. These shifts in the core level photoemission lines are small (1–4 eV) relative to the shifts between lines of different elements, making the selectivity of ESCA very good.

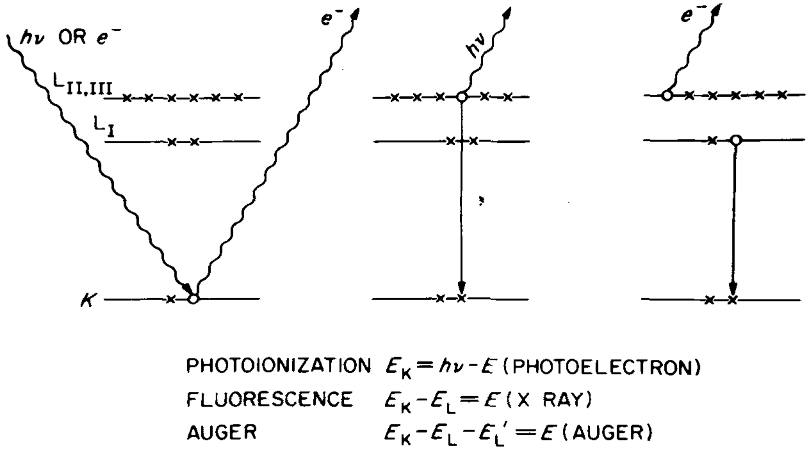

FIGURE 1 Schematic of the ESCA, X-Ray Fluorescence, and Auger processes. ESCA shows photoemission of core level electron and the energy relationship T_e—kinetic energy and E_B—the binding energy of the ejected 1s electron. X-Ray Fluorescence and Auger are competing secondary relaxation processes.

The mechanics of ESCA measurements are described by the schematic in Figure 2. The sample is mounted on a probe in line with an X-ray source. The photoejected electrons are passed through a hemispherical analyzer. The voltages on the hemispheres are varied, which allows the spectrum of kinetic energies to be scanned. The electrons are detected by an electron multiplier and counted by suitable counting electronics.

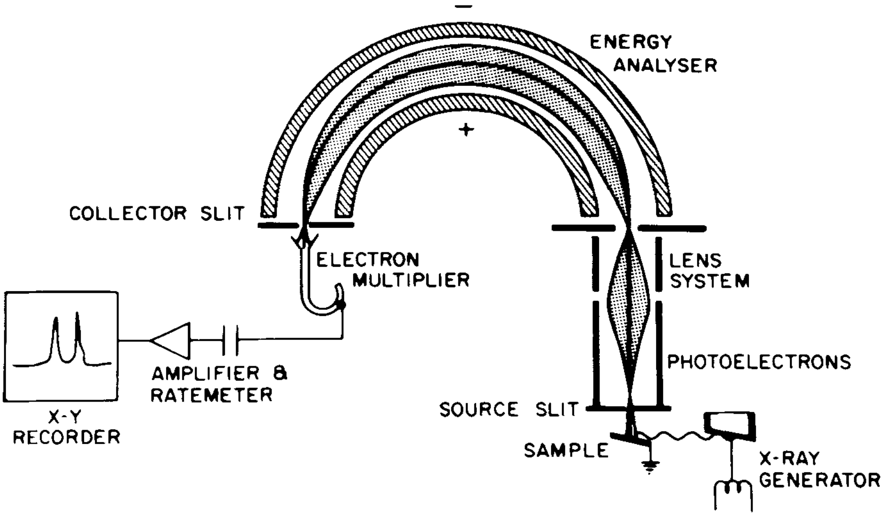

FIGURE 2 Schematic of ESCA instrumentation. Sample in line with X-Ray source photoejects electrons which are analyzed by passing through hemispheres with a variable potential across them. This scans the allowable kinetic energies of the electrons which are detected, counted and displayed.

B. Auger Electron Spectroscopy

In Auger Electron Spectroscopy an electron or X-ray beam ionizes a core electron; subsequently a higher energy electron falls to fill the hole. This leads to both the secondary processes of X-ray Fluorescence and Auger Electron emission, which are competing phenomena (Figure 1). The kinetic energy of the secondary electron ejected in the Auger Process is characteristic of the element, and is independent of the primary ionizing source energy. Thus, to increase signal intensity, high energy electrons are used as the primary beam; this gives a high background level of scattered electrons from the sample. To differentiate between signal and background, Auger Spectra are usually displayed in the derivative mode.

ESCA and Auger are surface sensitive because the electrons measured are attenuated by the solid sample and thus originate from approximately the first 50 Å of the sample or less.

C. SIMS

The basis of SIMS is the sputtering of secondary ions by a primary ion beam incident on a surface (Figure 3). These secondary ions are mass analyzed by a mass spectrometer; the mass fragments are characteristic of the surface structure. An important facet of SIMS analysis is the ability to "tune" sampling depth by changing primary ion beam energy and current. This allows the range of sampling depths to extend from monolayer surface sensitivity (so-called static SIMS) to the microprobe range where sputtering rates are on the order of 100 atomic layers/second (dynamic SIMS). Most SIMS work previously described[4,5,6] on particulates has employed the ion microprobe. The advantage of the microprobe is that the beam diameter is small so the area analyzed can be well described, allowing *x*-*y* resolution. However, in comparison with other surface techniques the ion microprobe mode of SIMS is not really "surface" sensitive. Static SIMS, employed in this study uses a much larger beam diameter (100 μm) but has higher surface sensitivity. Sputter rates in static SIMS are usually ca. 10^{-3} atomic layers/second. Static SIMS does not have the elemental sensitivity of the microprobe, but is more useful for describing interesting surface structure and bonding by analysis of mass fragmentation patterns. Quantitation is only possible on well defined systems, but depth profiling is provided by measuring signal intensity variations with time.

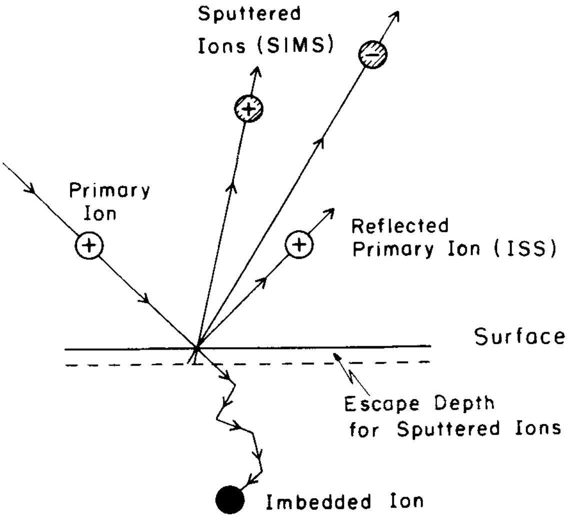

FIGURE 3 Schematic of the Ion Beam Techniques, SIMS and ISS. Primary ions can induce secondary sputtered ions which are mass analyzed for SIMS, or the primary beam can reflect and the subsequent energy loss can be measured for ISS.

D. ISS

Ion Scattering Spectroscopy is based on the reflection of primary ions (Figure 3) and the energy loss associated with classical conservation of momentum during the scattering process. ISS energy loss is characteristic, for a known primary ion mass and energy, of the mass of the surface atom involved in scattering. The equation describing the energetics is given below:

$$\frac{E_1}{E_0}=\frac{M_1^2}{(M_1+M_2)^2}\left[\cos\theta_1+\left(\frac{M_2^2}{M_1^2}-\sin^2\theta_1\right)^{1/2}\right]^2 \tag{1}$$

where θ_1 is the scattering angle, M_1 and M_2 the primary ion and target atom masses and E_0 and E_1 primary and scattered ion energies. For the case of 90° scattering the equation reduces to the simple form shown below:

$$\frac{E_1}{E_0}=\frac{M_2-M_1}{M_2+M_1} \tag{2}$$

This process, at low primary ion energies, is sensitive to the first atomic layer, and thus gives unique elemental descriptions of samples. Depth profiles are obtainable along with semiquantitative information about the elemental composition of this surface layer; however no chemical information is derived from ISS.

A diagram of a combined SIMS/ISS system is given in Figure 4. The primary ion gun is coaxial with the ion energy analyzer for ISS. The acceptance angle for scattered ions is fixed and the voltages on the cylindrical mirrors can be varied to scan over the range of kinetic energies. The ions are detected by an electron multiplier and counted by suitable electronics. Alternatively, secondary ions from the SIMS process are analyzed by a quadrupole mass spectrometer, detected by a suitable multiplier and counted by the same electronics. The surface sensitivity of both SIMS and ISS is derived from attenuation of the ejected ions emerging from below the first few layers, similar to the ejected electrons in ESCA and AES. The particles analyzed by the four techniques necessitate a vacuum high enough to allow them to reach the detector without being scattered. High vacuum imparts an important perturbation on the sample, which can seriously affect environmental samples. This effect has been examined,[2] but not in a systematic manner. It is presently under study in our laboratory.

III. EXPERIMENTAL

Table I describes the physical characteristics of the three samples exam-

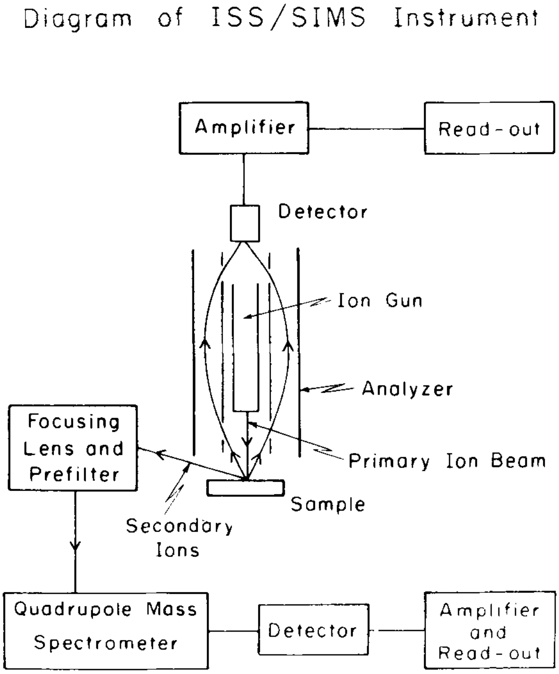

FIGURE 4 Diagram of SIMS/ISS combined instrumentation. Ion gun for primary ion beam is coaxial with Cylindrical Mirror Analyzer which energy analyzes reflected primary ions for detection and counting in ISS mode. Alternatively, secondary ions for SIMS analysis are filtered and mass analyzed by a quadrupole mass spectrometer, detected and counted.

TABLE I
Physical characteristics of samples

Sample name	Diesel engine types	Extraction conditions	Observations
DDA	Detroit Diesel Allison	CH_2Cl_2	Dry black powder
PEUG	Peugeot	none	Fluffy black powder
DES	Oldsmobile	CH_2Cl_2	Dry black powder

ined in the first part of this study. These samples were mounted as agglomerates for analysis by pressing into Indium foil for Auger and ISS/SIMS or supporting them on double sided sticky tape for ESCA. The samples themselves have an average aerodynamic diameter of 0.3 μm, yet these particles can be shown to be composed of smaller particles in the range of 50 to 100 Å. These results are similar to those obtained by laser Raman analyses of the phonon vibrational modes of crystalline graphite in an analysis of diesel particulates.[8] These particles were collected by electrostatic precipitation at 100°C.

ESCA analyses were performed using an AEI ES200A spectrometer with AlKα excitation. Results were charged referenced to the carbon 1s line set at 284.0 ± 0.1 eV by vacuum deposited gold referenced to the Au $4f_{7/2}$ line at 83.8 eV.

Auger analyses were done on a Physical Electronics Model 545 Scanning Auger Microprobe. The base pressures in both of these instruments were in the low 10^{-9} torr range for these analyses. SIMS was performed on a 3M model 610 SIMS interfaced with a model 525 ISS instrument. The base pressure in this instrument was in the high 10^{-9} torr range, typically 8.0×10^{-9} torr with cryopanel operation. The instrument was backfilled with ^{20}Ne gas for the primary ion beam to 2×10^{-5} torr.

IV. RESULTS AND DISCUSSION

A. Study I—Surface studies

1. ESCA Studies Figure 5 shows a typical wide scan ESCA spectrum of the DES-Oldsmobile sample with major constituents labeled. Figure 6 shows high resolution spectra for each of the peaks; these spectra were used for binding energy calculations and quantitation. Table II summarizes the binding energies for all three samples along with selected standards for comparison. For the standards, Cls at 284.8 eV was used for charge referencing, the carbon originating from hydrocarbon contamination. The results show that small amounts of oxidized sulfur (probably sulfate) and reduced nitrogen (probably amino) along with adsorbed NO_x or organic nitro nitrogen are found on the unextracted particles. Also found was reduced or elemental sulfur. Other peaks identified were the oxygen peak and the low binding energy carbon peak, probably graphitic or carbidic in nature. The nature of the carbon was investigated more extensively by Auger analysis.

Several interesting conclusions can be drawn from the ESCA data. First, it is noted that extraction methods fail to extract all heteroatom compounds. Since, typically on ambient particles, N and S containing compounds were assigned to $(NH_4)_2SO_4$ and/or NH_4HSO_4 one possibility is that these species are present on diesel particulates. Since no other

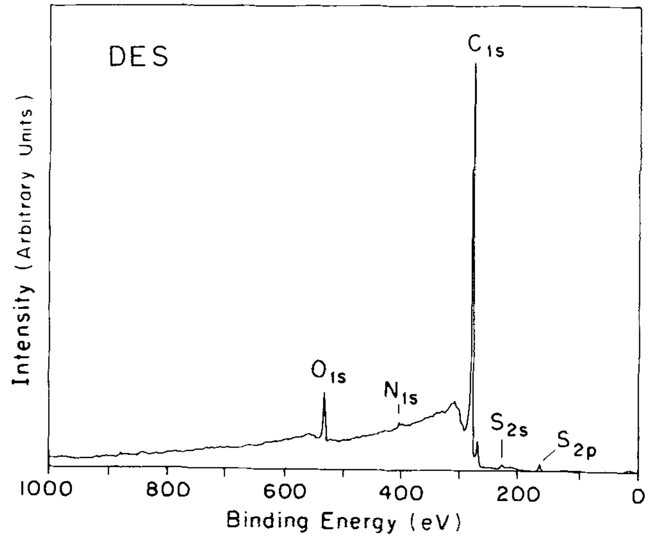

FIGURE 5 ESCA wide scan for sample DES: 0–1000 eV binding energy. AlKα excitation; Base pressure $< 5 \times 10^{-9}$ torr.

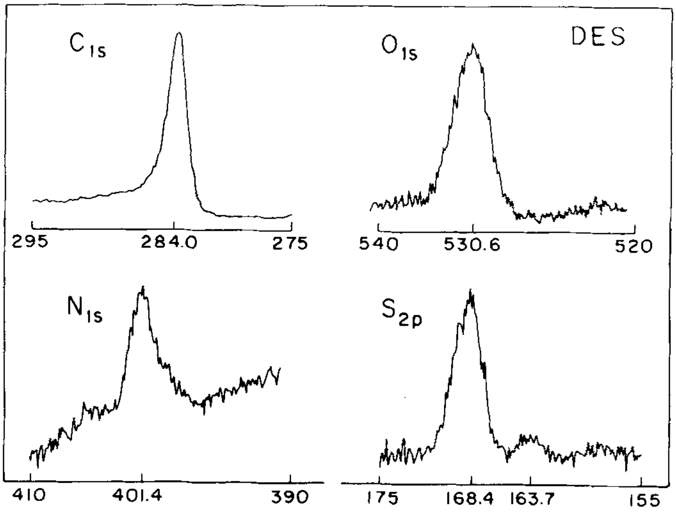

FIGURE 6 ESCA narrow scans for core level binding energy calculation. Carbon 1s, oxygen 1s, nitrogen 1s and sulfur 2p regions, shown with charge corrected binding energies given. Two chemical states of sulfur shown, with two corresponding binding energies. Intensity scales not normalized.

TABLE II

Binding energies (eV) of diesel particulate surfaces

Sample	C_{1s}(eV)	O_{1s}(eV)	N_{1s}(eV)	S_{2p}(eV)
DDA	284.0±0.1	531.0±0.1	400.5±0.5	168.5±0.1
PEUG	284.0±0.1	531.6±0.2	399.7±0.2 405.1±0.3	168.3±0.3
DES	284.0±0.1	531.6±0.2	401.4±0.2	163.5±0.3 168.4±0.3
$(NH_4)_2SO_4$	284.8	532.0	401.8	168.6
$NaNO_3$	284.8	532.0	406.7	–
Na_2S	284.8	—	—	161.4
PbS	284.8	—	—	160.3

inorganic ion is present at these levels, the only remaining possibility is that of unextracted heteroatom organics. Since the carbon peak is so intense, from the graphitic type substrate, carbon shifts for organic species are not conclusive in identifying residual organic species. This was investigated further by SIMS.

Quantitative results used to support the above ideas were calculated by the following equation:

$$\frac{n_x}{n_c}=\frac{I_x\sigma_c\lambda_c(\varepsilon_c)}{I_c\sigma_x\lambda_c(\varepsilon_x)} \tag{3}$$

where $\frac{n_x}{n_c}$ is the atomic ratio of species x of interest to carbon,
I_x and I_c are the integrated ESCA core level intensities,
σ_x and σ_c are the free atom care level cross-sections,[10]
$\lambda_c(\varepsilon_c)$ and $\lambda_c(\varepsilon_x)$ are the mean free paths for electrons at energies, ε_c and ε_x respectively, in a graphitic carbon host medium.[11]

Quantitative results are given in Table III in the form of corrected atomic ratios. The fact that the N/C ratio is one order of magnitude lower than the sulfate S/C ratio supports our conclusion that some of the nitrogen and sulfur may be unextracted organics. These results show that nitrogen, sulfur and oxygen constitute approximately 10% atomic of each sample surface.

ESCA's unique surface sensitivity is exploited in the following analysis. Surface segregation of chemically toxic species is a phenomenon associated

TABLE III

ESCA quantitation results

Sample	Atomic Ratios[a] O/C	N/C	S/C
DDA	0.18 ± 0.02	0.0055 ± 0.0005	0.036 ± 0.002
PEUG	0.12 ± 0.02	0.0014 ± 0.0003[b] 0.004 ± 0.001	0.012 ± 0.002
DES	0.078 ± 0.005	0.0064 ± 0.0005	0.0117 ± 0.0003[b] 0.0008 ± 0.0002

[a] Calculated and corrected, see text.

[b] First value listed for higher binding energy component.
Second value listed for lower binding energy component.

with more complex source particulates.[4] For particles in the respirible range, this phenomenon will be especially important, since surface concentrations would not be the same as bulk concentrations measured by more classical techniques.[6]

SIMS and AES have been used to confirm the surface segregation effect on various particulate types[4,6] especially coal flyash. Conclusions drawn about the presence of toxic species preferentially on the surface supported a deposition mechanism which includes high temperature volitilization of the toxic species followed by their surface deposition during particle formation. This accounts for such surface segregation.[5] These studies present no results from respirable particulates because of analysis problems in focusing beams, the analyses typically used agglomerates of large particles.[4,5]

We wished to explore a parallel mechanism in the formation of diesel particulates. As stated above, the average aerodynamic diameter is ca. 0.3 μm. These, in turn, are made up of smaller crystallites of 50–100 Å diameter. Two possibilities exist for chemical volitilization and deposition on the particles, if it occurs. If deposition occurs on the smaller particles (50 100 Å), ESCA results should be on the order of bulk results, since the ESCA sampling depth is on the order of 20–50 Å. If, however, deposition occurs after aggregation to 0.3 μm then the ESCA would give a representative analysis of 10% volume of a 0.3 μm particle; and the ESCA results should show significantly different atomic concentrations, relative to bulk analyses.

A preliminary comparison is given in Table IV. Results were corrected for the fact that hydrogen is a significant percentage of the bulk combustion results, yet is undetectable by ESCA. The results of Table IV

TABLE IV

Comparison of ESCA and bulk (from combustion) results before extraction PEUG sample

	(Weight percent)			
	%C	%O	%N	%S
Bulk[a]	67.9	27.3	2.9	2.0
ESCA	84.1	12.7	0.4	2.7

[a] Corrected for lack of detectability of hydrogen.

show ESCA analyses to be on the order of bulk results, which would lead to a preliminary conclusion that deposition occurs before aggregation. Further work involving the combined use of ISS atomic ratios in comparison with ESCA ratios to elucidate surface segregation[9] is in progress.

2. *Auger Studies* Because of the low binding energy of the Cls line in all three samples, we wished to elucidate further the structure of the carbon substrate. Other work[8] has shown the form of the carbonaceous component of diesel particulates to be that of pyrolytic graphite. The low binding energy of the Cls line also indicated the possibility of carbide. Auger Electron Spectroscopy provides unique information about the carbon chemical state through analysis of the C LMM Auger Lineshape. Figure 7 shows a comparison of standards and a sample. Spectrum (a) is a carbide standard showing characteristic peaks at 252, 260 and 272 eV kinetic energy.[12] Spectrum (b) is that of sample DES, which shows the same features of spectrum (c), that of the graphite standard. Thus, it was concluded that the carbon component is pyrolytic graphite, also supported by the laser Raman work cited above.[8]

3. *SIMS Studies* Sims was used to substantiate the claim that unextracted organics still remain after extraction. Static SIMS, because of its unique sensitivity to the surface and to electropositive elements should be useful for trace analysis of these constituents. Figure 8 shows a SIMS spectrum of an extracted sample, DES. Organic fingerprint mass clusters

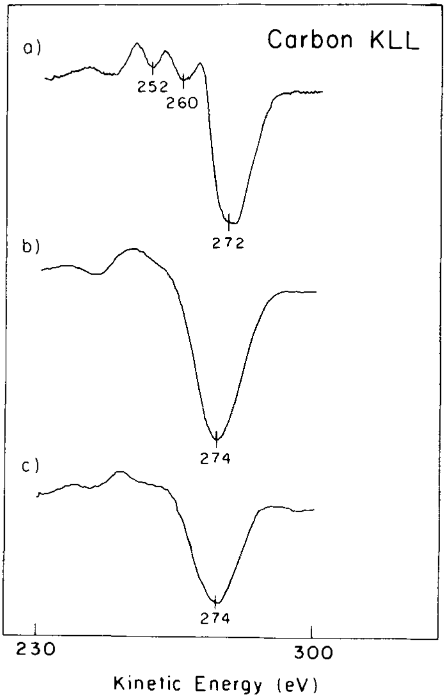

FIGURE 7 Carbon KLL Auger spectra for (a) carbide carbon standard, (b) sample DES, (c) pyrolytic graphite standard. Spectra run at 5 kV, 0.11 μA primary beam energy scanned over 70 eV kinetic energy range. Base pressure $<1 \times 10^{-8}$ torr.

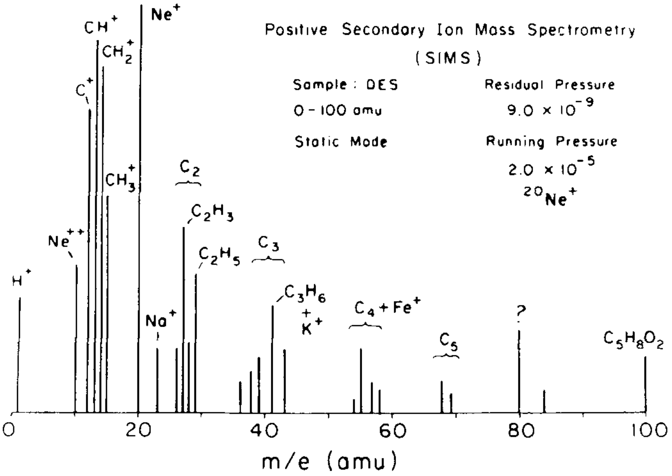

FIGURE 8 Positive SIMS spectrum of sample DES (extracted). 0 100 amu. Base pressure $<1 \times 10^{-8}$ torr, back filled to 2×10^{-5} torr ^{20}Ne for primary ion beam.

are labeled which indicate the presence of unextracted residual organics. Aluminium, silicon, sodium and potassium are also indicated but in relatively small amounts, not enough to be counterions for S and N compounds (these elements could not be detected by ESCA).

B. Study II—Running speed variations

Samples for this study are described in Table V. They were all unextracted and were collected by electrostatic precipitation. The samples were examined for variations in surface concentrations with running speed. Analysis of major surface constituents was by ESCA; similar results were obtained for binding energies of carbon, oxygen, sulfur and nitrogen, as in Study I. Both forms (SO_4^{2-} and reduced S or elemental S) of sulfur were observed on all samples as were both nitrogen forms (NH^+ and NO_x).

TABLE V

Physical description of running speed samples

Sample	Engine	Running speed	Comments
2.1.3	Olds 350-D	32 km/hr	Collected at 100°C
2.1.1	Olds 350-D	65 km/hr	Collected at 100°C
2.2.1	Olds 350-D	65 km/hr	Collected at 100°C different electrostatic precipitator
2.1.4	Olds 350-D	90 km/hr	Collected at 100°C

TABLE VI

Major constituents and trace elements found by ESCA and D.C. arc emission

ESCA	D.C. arc emission
Carbon (graphitic/pyrolytic)	Magnesium
Nitrogen (two forms)	Boron
Sulfur (two forms)	Silicon
Oxygen	Aluminum
	Calcium
	Manganese
	Copper

Bulk trace analysis by D. C. Arc Emission using an ARL emission spectrograph is shown in Table VI along with the ESCA results. Results from the D. C. Arc emission were not quantified but the elements identified were at trace levels.

Variations in surface concentrations for different running speeds in this narrow range are given in Figure 9. The only significant variation seen over this range is in SO_x concentration. If this is SO_4^{2-} which is the product of SO_2 oxidation and deposition catalyzed by the carbonaceous particle surface,[13] then one would expect the oxidation to vary inversely with temperature. At higher running speeds, there is an increase in running temperature and thus less SO_2 oxidation and adsorption.

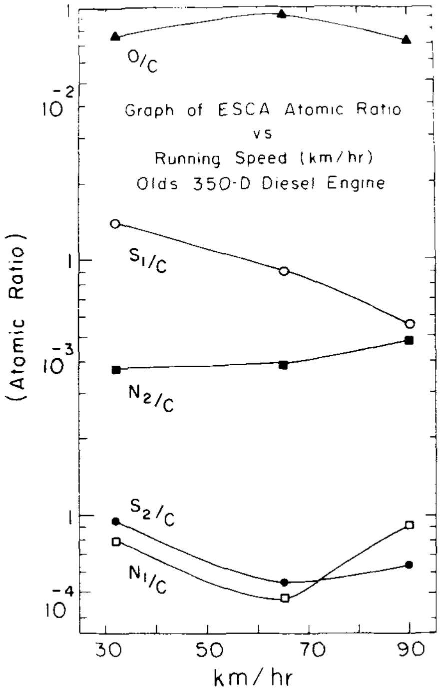

FIGURE 9 Plot of ESCA atomic ratio vs. running speed for surface constituents. O/C—oxygen/carbon, S_1/C—high binding energy (SO_x) sulfur carbon, N_2/C = low binding energy (NH^+) nitrogen/carbon, S_2/C = low binding energy (SH or S) sulfur/carbon, N_1/C = high binding energy (NO_x) nitrogen/carbon.

V. CONCLUSIONS

This study has used the synergistic approach to surface analysis by combining results from various methods with bulk methods to elucidate the structure and reactivity of the surface of diesel particulates. We have identified pyrolytic graphitic carbon, oxygen, sulfur as both SO_x and a reduced form and nitrogen as both NO_x and NH^+ as surface species. Sulfur and nitrogen constitute approximately 1% atomic of the surface, yet cannot be accounted for solely as counter ions; some heteroatom organic species may be present. Particles extracted for routine G.C. analysis show residual N and S species from ESCA and residual organic species from SIMS. Auger confirmed previous laser Raman work on the chemical form of the carbonaceous component as that of pyrolytic graphite as opposed to carbide.

Variations in running speed over a narrow range show only a significant change in the SO_x concentration. Assuming the mechanism of deposition to be soot catalyzed oxidation of SO_2, the higher running speeds (and therefore temperatures) could account for the decrease in adsorption. The multitechnique approach used here has given unique surface information about this system's chemical composition and shows how the limitations of each technique can be overcome by their synergistic use.

Acknowledgement

This work was supported by the National Science Foundation under Grant CHE 78–00876.

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