Microscopical Studies of World Trade Center Disaster Dust Particles

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Introduction

The terrorist attack and collapse of two towers of the World Trade Center (WTC) in New York City on September 11, 2001 generated tremendous clouds of dust that settled over a wide area. Concern over the potential health effects of breathing this dust made it imperative that the WTC dust be characterized as completely as possible. As part of this characterization, a microscopical examination using several types of microscopes provided key data on the components of the dust. The WTC dust sample that is the primary focus of this report was collected by F.C. Ewing from an outdoor window ledge at 33 Maiden Lane, New York City, NY on October 7, 2001.

Equipment and microscopical methods

The weight of the fibrous fraction (plus attached fine non-fibrous particulate) was determined. The non-fibrous particulate (plus some fiber fragments) was then dry sieved at the following size fractions: >300 μm, 75 - 300 μm, and <75 μm. The sample was dry sieved using standard 4-inch diameter brass sieves (U.S. Standard Sieve Mesh # 50 and 200). The gravimetric determinations were made in triplicate with a SETRA EZ2-500 electronic 3-place balance.

Figure 1. Light microscope image of dust particles on tape from outdoors of 33 Maiden Lane. Glass fibers, cement and plaster are most evident. Bar = 500 μm

Macroscopic examination of the sample was conducted utilizing a Zeiss Stemi 2000 stereomicroscope having a magnification range from 6.5X to 47X. The sample was then analyzed by polarized light microscopy including microchemical tests utilizing an Olympus BH-2 polarized light microscope having a magnification range from 40X to 1000X. Representative portions from the sample were examined and analyzed by scanning electron microscopy (SEM) using a JEOL 6400 coupled with an x-ray energy dispersive spectrometry (EDS) Noran Voyager system. Individual particles from the sample were also analyzed by scanning electron microscopy (SEM) using a JEOL 6500 coupled with an x-ray energy dispersive spectrometry (EDS) Noran Voyager system. The fine (small) fractions of the sample were analyzed with analytical electron microscopy (AEM) using a JEOL 1200, 100 kV scanning transmission electron microscope (STEM), equipped with a Noran EDS x-ray analysis system. A portion of the sample was also analyzed by Fourier transform infrared microspectrophotometry (micro-FTIR) utilizing a Perkin-Elmer Auto Image System coupled to a Series 2000 FTIR.

The SEM analysis used both the secondary and backscattered modes. For the SEM analysis, portions of the sample was transferred to conductive carbon tape and coated with a thin layer of carbon to provide a conductive surface in the electron microscope. The sample was examined at several magnifications in the secondary (SE) mode. Using the backscattered electron (BE) mode, the sample was examined for particles that contained heavy elements. This procedure is useful in locating particles containing toxic metals such as lead and cadmium. X-ray elemental analysis by energy dispersive spectrometry (EDS) was performed on each particle located for further study by either the BE or SE scans.

The fine (small) fraction of the sample was prepared following the ASTM D6602-00 procedure (1). Briefly, this procedure involves suspending the dust in chloroform and placing a drop of the suspension on a carbon-film TEM grid. The grid was analyzed by TEM for soot and to characterize the particles with diameters less than 2.5 μm. Fine particles in the air, those with diameters less than 2.5 μm, are known to be related to long term health effects (2). In 1997 the USEPA set a national ambient air quality standard for fine particulate matter ($PM_{2.5}$) at 15 μg per m^3 as an annual average. For this standard, the samples were collected using samplers that sort the airborne particles based on their aerodynamic characteristics. Larger, heavier particles act differently from small, light particles in an air flow. The measurement is made only by weighing the particulate and no identification of the particles is done. There is interest

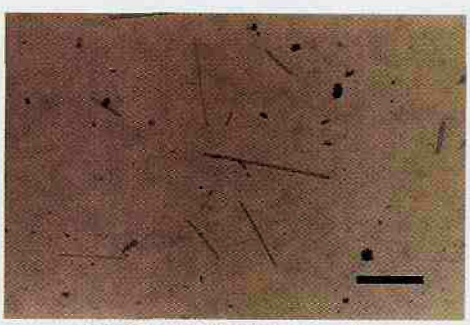


Figure 2. Light microscope image of glass fiber particles and soot aggregates from outdoors of 33 Maiden Lane. The glass (mineral wool) fiber in the center is approximately 1 millimeter long. Bar = 500 μm.

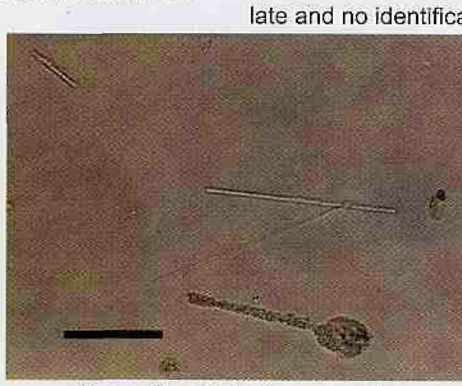


Figure 3. Light microscope image of glass fiber particles and cement from outdoors of 33 Maiden Lane. The glass fiber near the bottom of the micrograph is coated with cement. The glass (mineral wool) fiber in the center is approximately 0.4 millimeter long. Bar = 200 μm.

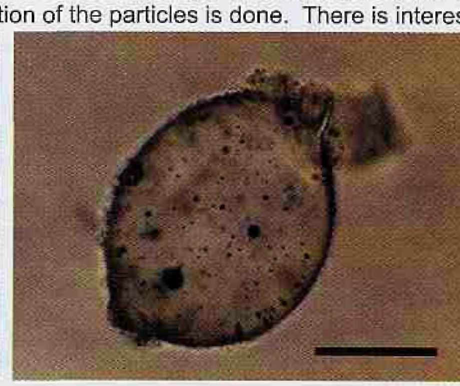
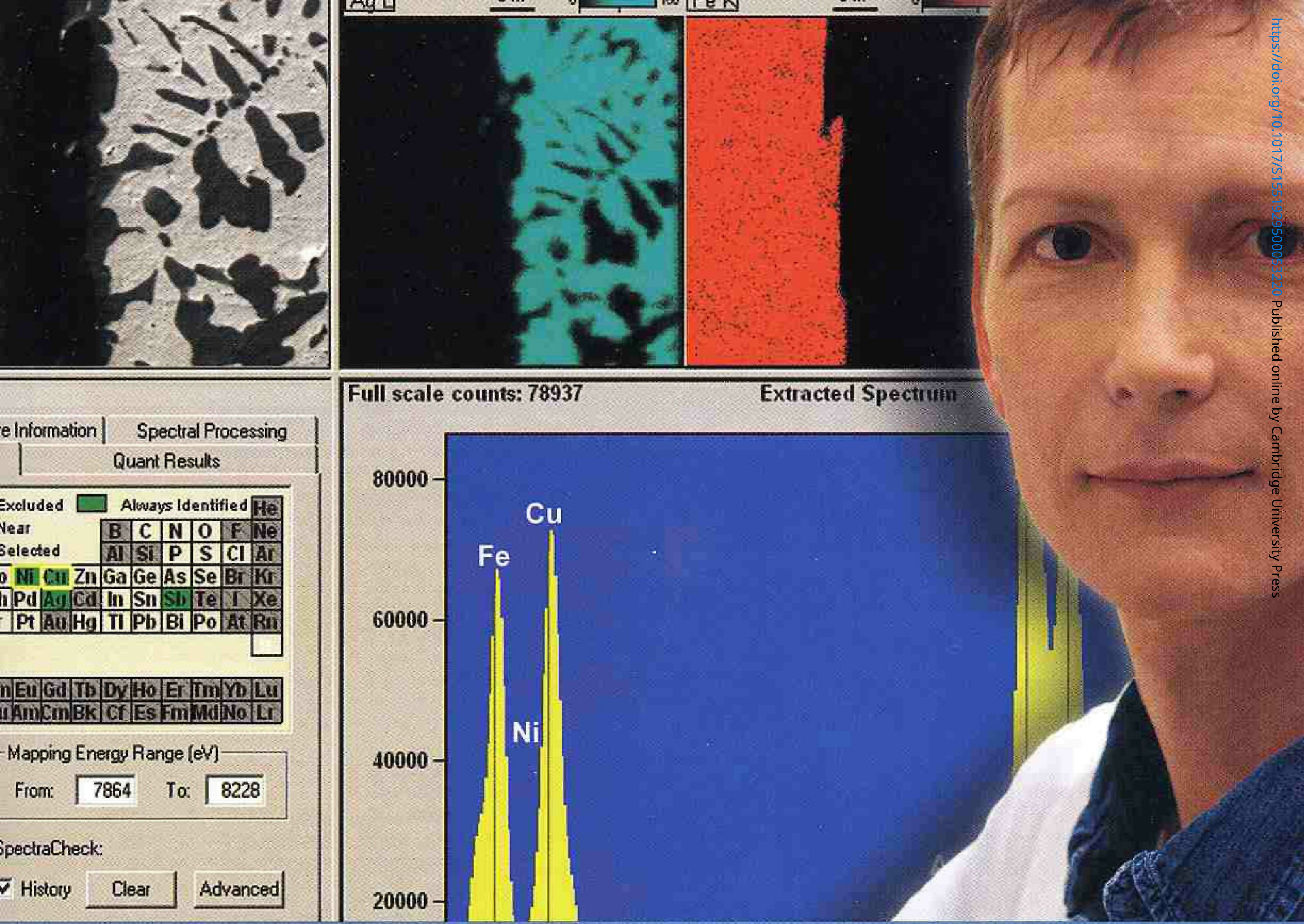


Figure 4. Light microscope image of mineral wool shot from outdoors of 33 Maiden Lane. Diameter of this glass ball is approximately 100 micrometers (0.1 mm). Bar = 50 μm.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Extracted Spectrum
Spectral Processing
Quant Results
Always Identified
Mapping Energy Range (eV)
From: 7864 To: 8228
History
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Advanced
Fe
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80000
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Figure 5. The same mineral wool shot as shown in Figure 4 focused on another plane to show the "tail" of the shot. Diameter of this glass ball is approximately 100 micrometers (0.1 mm). Bar = 50 µm.

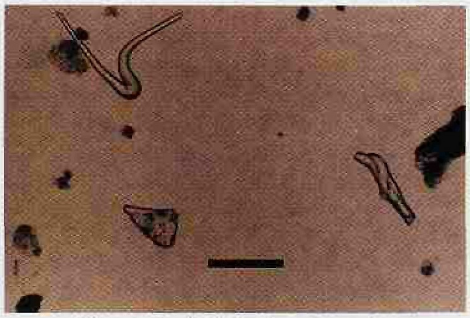

Figure 6. Light microscope image showing two of the more exotic forms of the mineral wool fibers (right and upper left). A triangular glass shard is evident in the lower left area of the micrograph. Bar = 200 µm.

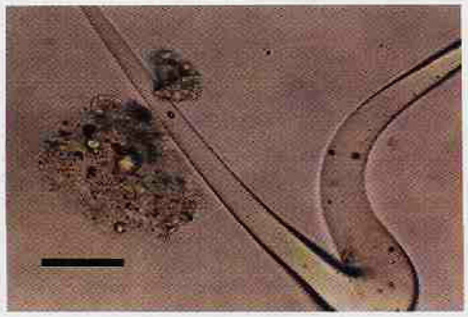

Figure 7. A closer light microscope image of the mineral fiber and cement/ plaster aggregate seen in Figure 6. Bar = 50 µm.

TABLE I

	Comparison of Results of Analyses of the Maiden Lane WTC Sample with Other Analyses of WTC Dusts			
	Column A	**Column B**	**Column C**	**Column D**
Sample	Maiden Ln	Maiden Ln	HP-02,3	L1616
Microscope	Stereo/PLM	TEM	TEM	AutoSEM
Preparation	Bulk	ASTM6602	AHERA	Wet Sieved
Number of Particles	All	400	400	961
Particle Size Range (µm)	All	0.5 - 2.5	0.5 - 2.5	0.5 - 10
Mineral wool fibers/shards	35-40%	0.3%	0.5%	2.6%
Cellulose	5-10%	0.3%	0.0%	NA
Chrysotile asbestos	<1%	7.0%	5.8%	*
Calcium	Present	13.0%	11.5%	7.4%
Plaster / Gypsum	Common	32.5%	41.0%	51.8%
Particles consistent with cement	Common	26.5%	14.5%	12.9%
Particles consistent with cement and gypsum	Common	5.0%	5.2%	5.8%
Combustion products	Common	1.3%	2.5%	NA
Wood fragments	Present	0.3%	0.0%	NA
Fungal/Biological	Present	0.3%	0.0%	NA
Glass shards	Present	0.5%	1.0%	1.4%**
Si-crystalline (quartz)	Present	3.0%	2.3%	1.4%**
Vermiculite/mica sheets	Present	2.0%	3.3%	NA
Perlite	Present	0.3%	0.8%	0.5%
Metal flakes	Present	2.3%	7.5%	1.0%
Paint Particles	Present	0.5%	0.8%	1.1%
Other - Ca-Si-S fibers	***	3.0%	1.8%	****
Mixed/Unclassified	Present	2.3%	1.8%	16.9%
Total		100.0%	100.0%	100.0%

NA - Not included in the analysis

** 0.6% of the particles were in a cluster of particles containing mainly Mg and Si. These could possibly be consistent with talc, chrysotile, or another serpentine mineral. These were included in the unclassified group.*

*** 1.4% of the particles analyzed by SEM-EDS were primarily silicon and could be either glass or quartz.*

**** Not detected by PLM*

***** Included in the particles consistent with cement and gypsum cluster*

in characterizing the composition of the $PM_{2.5}$ and therefore, a preparation of the fine particles was examined by microscopy. The relationship between the less than 2.5 µm particles analyzed by microscopy and the particulate matter less than 2.5 aerodynamic diameter ($PM_{2.5}$) has not been fully researched. However, it has been reported that, "except for very dense materials and clusters, the aerodynamic diameter is very similar to the geometric diameter as might be measured with an electron microscope"(3).

Results

The fibrous portion of the sample was approximately 10% by weight. Gravimetric measurements of the sieved sample fractions showed that 18% of the Maiden Lane WTC dust was >300 µm, 45% was between 75 and 300 µm, and 37% was less than 75 µm.

The results of a typical PLM bulk analysis showed that the Maiden Lane WTC dust contained approximately 35 - 40% mineral wool, 5-10% cellulose, and less than 1% chrysotile asbestos (Figures 1-9). The mineral wool composition is shown in Figure 10. The remainder, non-fibrous components as analyzed by PLM, SEM and micro-FTIR, was composed chiefly of plaster, cement particles and combustion products. Some glass shards, charred wood fragments (Figure 11), soil minerals, metal flakes, vermiculite sheets and perlite were present.

Table I shows a comparison of the TEM particle data from the Maiden Lane sample, two other TEM analyses of small WTC dust particles and the Maiden Lane sample PLM bulk analysis. Column A is the bulk analysis of the Maiden Lane sample performed using stereomicroscopy, PLM and microchemical testing. Column B is the TEM analysis from the Maiden Lane sample of 400 particles in the range of 0.5 - 2.5 µm prepared using the procedure described in ASTM method D6602. Column C is the result of a TEM analysis of 400 particles in the range of 0.5 - 2.5 µm prepared from an air sample of WTC dust using

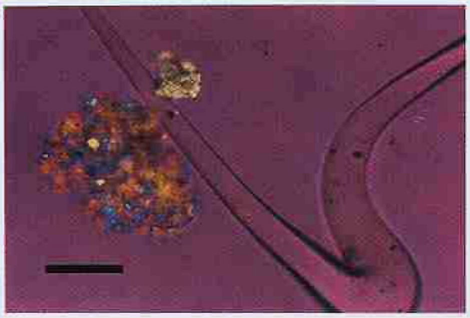

Figure 8. Light microscope image of the same area as seen in Figure 7. Polarized light with a red plate filter to show the mixture of materials in the aggregate associated with the fiber. Bar = 50 µm.

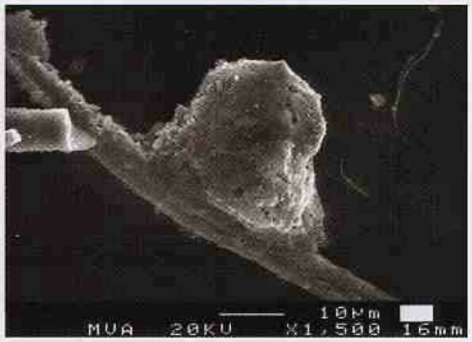

Figure 9. Scanning electron microscope image of cement on mineral wool from outdoors of 33 Maiden Lane. Chrysotile asbestos fibers are evident on the right. Bar = 10 µm.

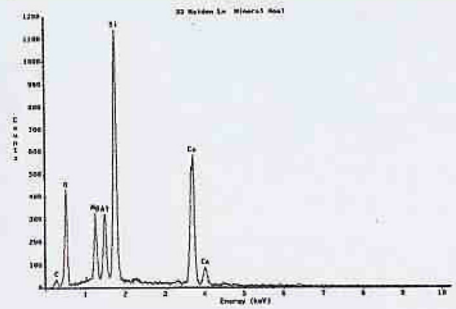

Figure 10. X-ray spectrum obtained by SEM-EDS from an uncoated mineral wool fiber.

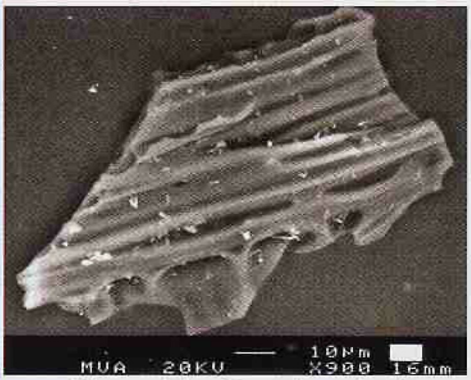

Figure 11. Scanning electron microscope image of a charred wood fragment. Bar = 10 µm.

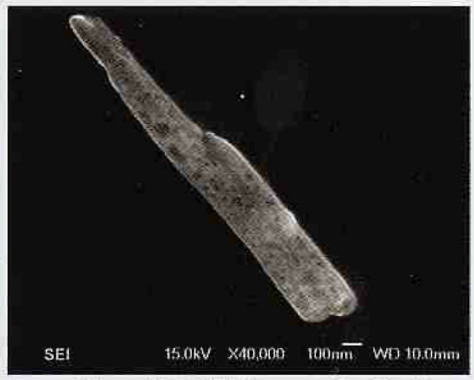

Figure12. SEM image of a Ca-Si-S fiber in the Maiden Lane Sample. (Micrograph by T.B. VanderWood)

Figure 13. TEM image of a Ca-Si-S fiber in the Maiden Lane Sample.

the direct AHERA preparation procedure (4). The air sample was created by resuspending a sample of WTC dust and collecting the airborne particulate on a 0.4 polycarbonate filter. Column D is the result of an automated SEM-EDS analysis using a dispersion of less than 10 µm particles prepared by wet sieving a sample of WTC dust in alcohol through a 10 µm pore sized sieve. The particles were dispersed on a polished carbon stub.

The data suggest that the population of WTC particles in the small size range is composed primarily of gypsum particles and cement fragments. Particles of the mineral wool (fibers and fragments) which make up a high percentage of the WTC dust are present only at a trace level (<1%) in the range of 0.5 - 2.5 µm and slightly higher in the range of 0.5 - 10 µm range. The automated SEM data is less descriptive than the TEM data because it relied only on the elemental compositions of the particles. Cluster analysis was used to determine the classes of particles found. The TEM analysis provided more information because the operator could distinguish different particle classifications based on morphology and diffraction patterns as well as elemental composition. For example, plates of vermiculite, particles of crystalline silica, and fibers

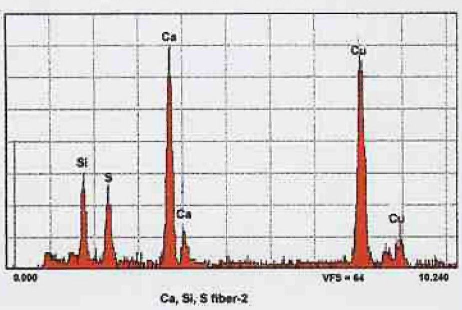

Figure 14. X-ray Spectrum of a Ca-Si-S fiber shown in Figure 13. The copper peaks are from the copper TEM grid.

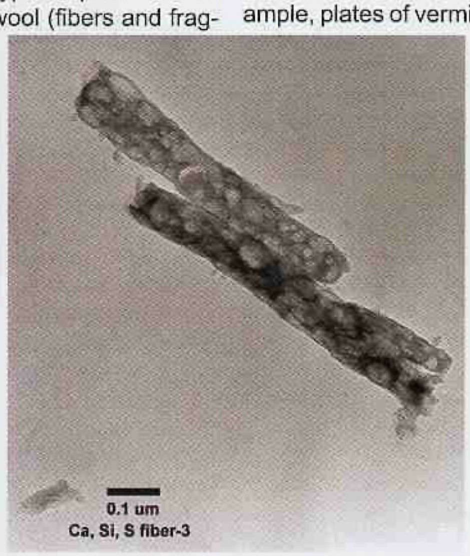

Figure 15. TEM image of a Ca-Si-S fiber in the Maiden Lane Sample.

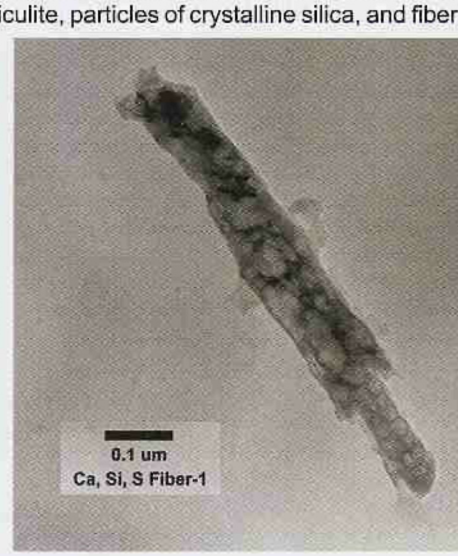

Figure 16. TEM image of a Ca-Si-S fiber in the Maiden Lane Sample.

of chrysotile were distinguished from other classes of particles with similar chemistries.

In the less than 2.5 µm population of particles from the WTC dust samples, one particle type was identified that had not been seen in other dust samples. These were elongated particles composed mainly of calcium, sulfur and silicon with occasionally some aluminum (Figures 12-16). These particles had diameters in the range of 0.1 µm. With aspect ratios greater than 5:1, these particles are considered fibers under the AHERA counting rules. The Ca-Si-S fibers had a distinct morphology; appearing mottled in the TEM image and with a "blistered" image as viewed by the SEM. The particles did not show any evidence of an electron diffraction pattern. The elemental composition of calcium, silicon, and sulfur with occasionally some aluminum was quite different from that of the mineral wool fibers that exhibited an x-ray spectrum of magnesium, aluminum, silicon and calcium.

Discussion

Although it was collected nearly a month after the tragedy, the WTC Maiden Lane dust was found to be very similar to samples of WTC dust collected earlier and examined by the authors and others (5). With the exception of the Ca-Si-S fibers, the constituents of the dust appear to be particles that have been found previously in indoor dust samples. Research is continuing to determine the identity and source of the Ca-Si-S fibers. More of the WTC dust is in the small size range than is seen in other dusts. The percentage of particles less than 75 µm in diameter has generally been less than 20% of the household or office dusts by weight (6). In this WTC dust sample (Maiden Lane) the percentage of particles less than 75 µm is 37%. The particles less than 2.5 µm are dominated by gypsum and cement fragments. Many of these fragments have small amounts of other elements or materials attached or associated with them.

Acknowledgements

The authors would like to acknowledge the automated SEM analysis work of Richard Brown. Valeriy Shapiro performed the data cluster analysis. Ron Schott of DCM Science produced the wet sieved fine particle fraction of sample L1616. Lastly, the authors would like to thank William M. Ewing for providing this interesting sample.

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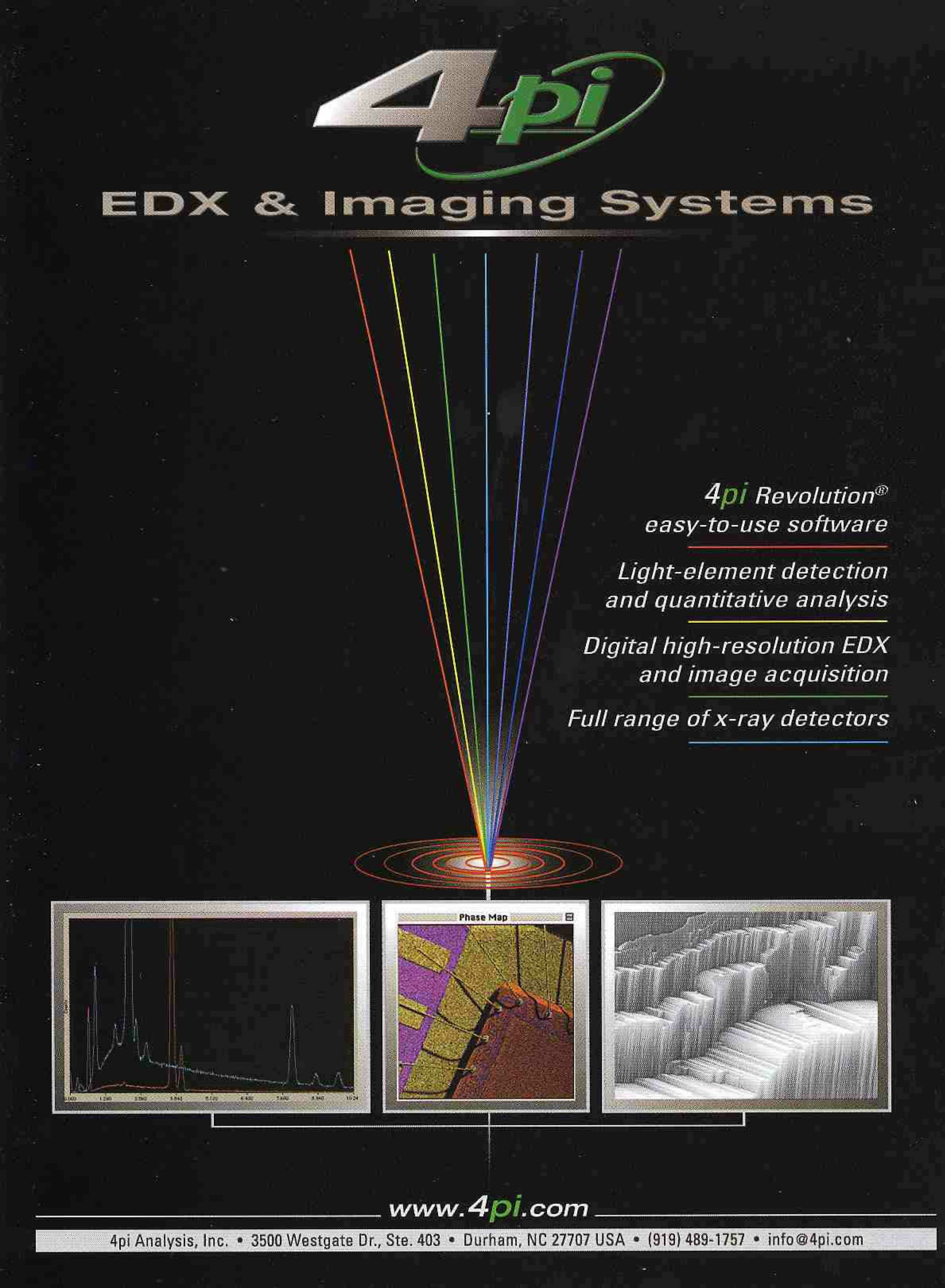
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