

DWPF GC FILTER ASSEMBLY SAMPLING AND ANALYSIS

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K. J. Imrich

November 2009

Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808

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EXECUTIVE SUMMARY

On March 18, 2009 a Defense Waste Processing Facility (DWPF) GC Line Filter Assembly was received at the Savannah River National Laboratory (SRNL). This filter assembly was removed from operation following the completion of Sludge Batch 4 processing in the DWPF. Work on this sample was requested in a Technical Assistance Request.¹ This document reports the pictures, observations, samples collected, and analytical results for the assembly. The assembly arrived at SRNL separated into its three component filters: high efficiency particulate air (HEPA)-1, HEPA-2, and a high efficiency mist evaporator (HEME).

Each stage of the assembly's media was sampled and examined visually and by scanning electron microscopy (SEM). Solids built up in the filter housing following the first stage HEME, were dissolved in dilute nitric acid and analyzed by ICP-AES and the undissolved white solids were analyzed by x-ray diffraction (XRD).

The vast majority of the material in each of the three stages of the DWPF GC Line Filter Assembly appears to be contaminated with a Hg compound that is ~59 wt% Hg on a total solids basis. The Hg species was identified by XRD analysis to contain a mixture of $\text{Hg}_4(\text{OH})(\text{NO}_3)_3$ and $\text{Hg}_{10}(\text{OH})_4(\text{NO}_3)_6$. Only in the core sample of the second stage HEPA, did this material appear to be completely covering portions of the filter media, possibly explaining the pressure drops observed by DWPF. The fact that the material migrates through the HEME filter and both HEPA filters, and that it was seen collecting on the outlet side of the HEME filter, would seem to indicate that these filters are not efficient at removing this material.

Further SRAT off-gas system modeling should help determine the extent of Hg breakthrough past the Mercury Water Wash Tank (MWWT). The SRAT off-gas system has not been modeled since startup of the facility. Improvements to the efficiency of Hg stripping prior to the ammonia scrubber would seem to be the only way to prevent/mitigate the formation of the compounds found in the GC Line Filter Assembly filters and therefore prevent pluggage of this filter assembly.

¹ Wingard, B. R., *GC Filter Assembly Sample and Analysis: Technical Assistance Request*, HLE-DWPF-TAR-2009-002, Savannah River Site, Aiken, SC 29808 (2009).

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LIST OF ACRONYMS/ABBREVIATIONS

AD	Analytical Development
CV-AA	Cold Vapor – Atomic Absorption Spectroscopy
DI	Deionized
DWPF	Defense Waste Processing Facility
EDX	Energy Dispersive X-Ray
FAVC	Formic Acid Vent Condenser
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
HEME	High Efficiency Mist Evaporator
HEPA	High Efficiency Particulate Air
M	Molar
mL	Milliliter
MWWT	Mercury Water Wash Tank
N/A	Not Available
N/D	Not Detected
N/M	Not Measured
PVV	Process Vessel Vent
RSD	Relative Standard Deviation
SB4	Sludge Batch 4
SEM	Scanning Electron Microscopy
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Slurry Receipt Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
Std. Dev.	Standard Deviation
TAR	Technical Assistance Request
TS	Total Solids
Wt %	Weight Percent
XRD	X-Ray Diffraction

1.0 INTRODUCTION AND BACKGROUND

On March 18, 2009 a Defense Waste Processing Facility (DWPF) GC Line Filter Assembly was received at the Savannah River National Laboratory (SRNL). This filter assembly was removed from operation following the completion of Sludge Batch 4 processing in the DWPF. Work on this sample was requested in a Technical Assistance Request.¹ This document reports the pictures, observations, samples collected, and analytical results for the assembly. The assembly arrived at SRNL separated into its three component filters: high efficiency particulate air (HEPA)-1, HEPA-2, and a high efficiency mist evaporator (HEME). The initial intent was to conduct a gamma survey of the assembly to determine if any blockage point could be identified along its length. When the assembly components arrived in SRNL individually bagged, the need for this survey became less clear. Table 1 presents the dose rates reported for the assembly by both DWPF and SRNL.

Table 1. DWPF GC Line Filter Assembly Dose Rates (mrem)

Component	DWPF	SRNL
<i>HEME</i>		
whole body	1	N/D
skin	240	N/M
extremity	3200	1000
<i>HEPA-1</i>		
whole body	1	N/D
skin	75	N/M
extremity	200	200
<i>HEPA-2</i>		
whole body	0.5	N/D
skin	30	N/M
extremity	48	12

N/D = not detected, N/M = not measured

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2.0 APPROACH AND RESULTS

2.1 Filter Assembly Schematic

The DWPF GC Line Filter Assembly is comprised of three component filters: HEME, HEPA-1, and HEPA-2. Shown in Figure 1 is a schematic of the assembly. Note in this diagram, the final HEPA stage is shown at a 90° angle to the first HEPA stage. The current assembly design has all three filters in a linear arrangement.

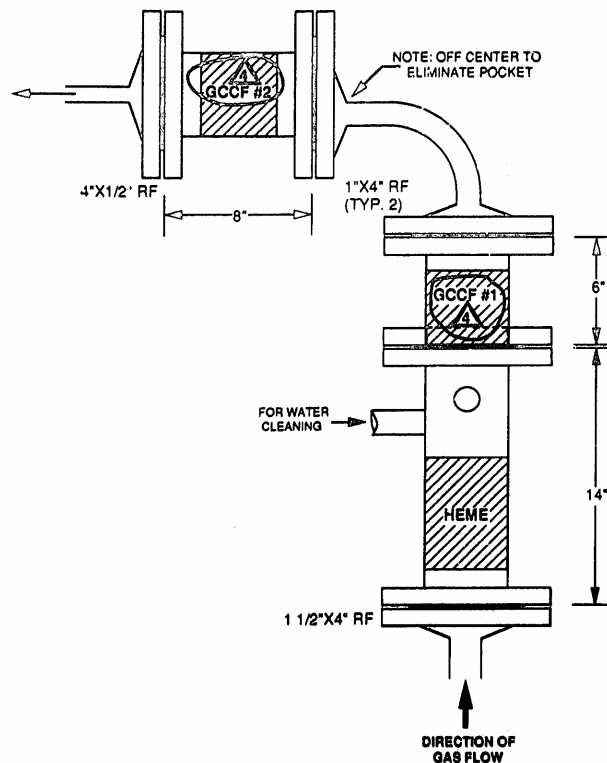


Figure 1. DWPF GC Line Filter Assembly

2.2 Filter Component Sampling

Figure 2 captures the sampling tool developed in SRNL for taking core samples of the filters from the DWPF GC Line Filter Assembly (shown in Figure 1). The tool has a sharp leading edge that cuts the filter media and a hollow core which collects the sample (Figure 3) as the sampler passes through the filter media. The core sample is then removed from the sampler using the polymer rod shown at the bottom of Figure 2. Sampling was done from the outlet side so that the coring tool would move through

the filter media from, what was believed would be, the less contaminated to the more contaminated end of the media.



Figure 2. Core sampling tool developed for the DWPF GC Line Filter Assembly.



Figure 3. Core sampling tool close-up showing relative size and containing a sample of filter media

Figure 4 and Figure 5 show the DWPF GC Line Filter Assembly Stage 1 HEME housing and the outlet side looking into the filter, respectively. White deposits are clearly visible on the inside, outlet end of this filter.

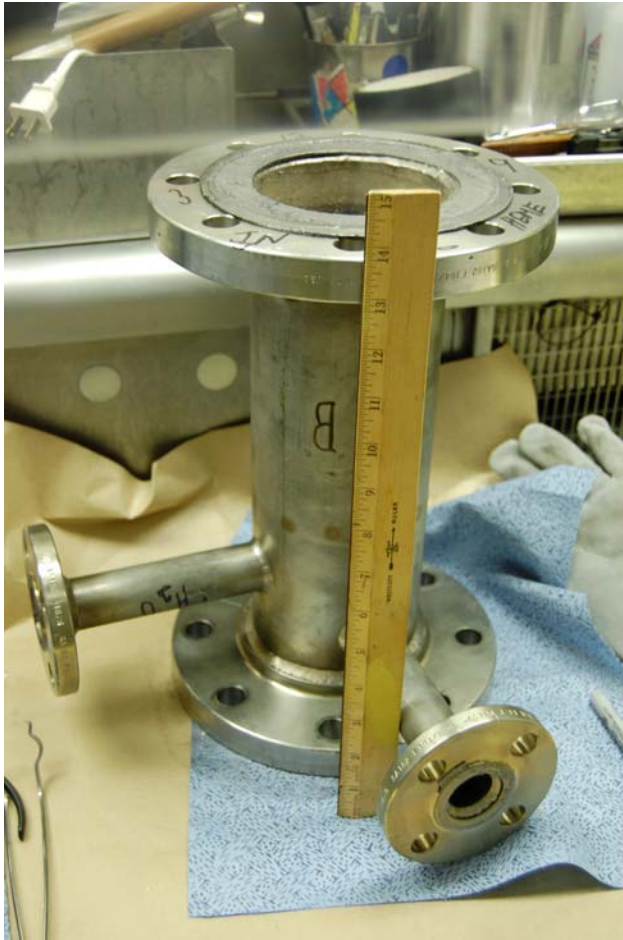


Figure 4. DWPF GC Line Filter Assembly HEME. Orientation has the inlet at the top, so the flow would be from the top down in this image.



Figure 5. DWPF GC Line Filter Assembly HEME, Outlet Side. White solid deposits can be seen on the screen below and on the inside walls of the housing.

The HEME white solids deposits were collected before attempting sampling with the coring tool. It was difficult to cut the media retaining screen on the HEME due to the large rods that protect it. These rods were cut off and removed as shown in Figure 6. The two rods that were elevated above the screen could be cut relatively easily, but two of the rods were flush against the screen and therefore, difficult to grasp in the cutters. This screen may have been welded to the rods in several locations and hence could not be removed completely. The underlying HEME media is packed into the housing like cotton candy. The coring tool was ineffective at cutting through the fiberglass media and tended to rip and/or compact it during sampling (Figure 7). It should be noted that no solids were observed on the HEME's inlet side, neither on the media retaining screen nor on the surrounding housing walls (Figure 8). To get a sufficient sample of the HEME media, it was necessary to pull the media out of the compact bundle. The final sample of HEME media collected is shown in Figure 9.



Figure 6. DWPF GC Line Filter Assembly HEME, Outlet Side after partial removal of retaining rods and mesh screen

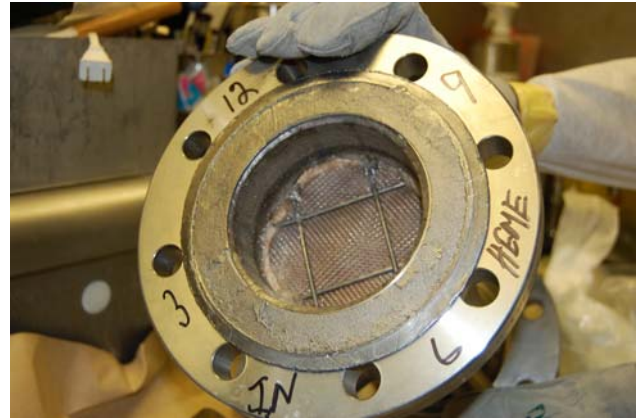


Figure 8. DWPF GC Line Filter Assembly HEME, Inlet Side

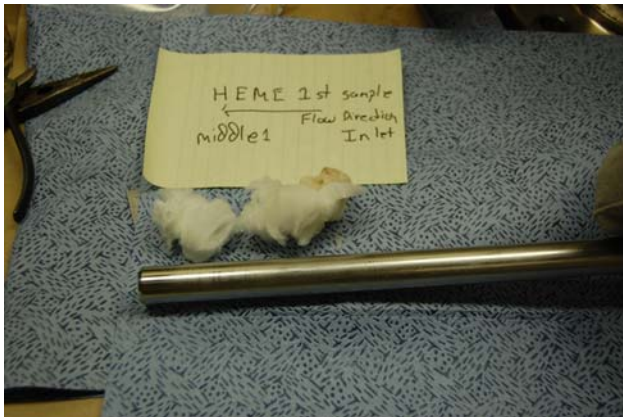


Figure 7. DWPF GC Line Filter Assembly HEME filter media removed with coring tool.



Figure 9. DWPF GC Line Filter Assembly HEME filter media removed from the outlet side.

Figure 10 through Figure 13 show the GC Line Filter Assembly's Stage 2 HEPA-1. Figure 10 and 12 show the inlet and outlet ends of the first HEPA filter. No visible deposits could be seen on the filter housing, screen, or surface of the filter media. A small amount of discoloration (light brown) can be seen at the tip of the core sample (Figure 13), but no loose solids fell from the removed filter media sample. If there had been a large buildup of solids on the media this would have resulted in visible solid residue on the colored towel, but no such solids were observed, hence there was no buildup of solids on the media.



Figure 10. DWPF GC Line Filter Assembly HEPA-1, Inlet Side

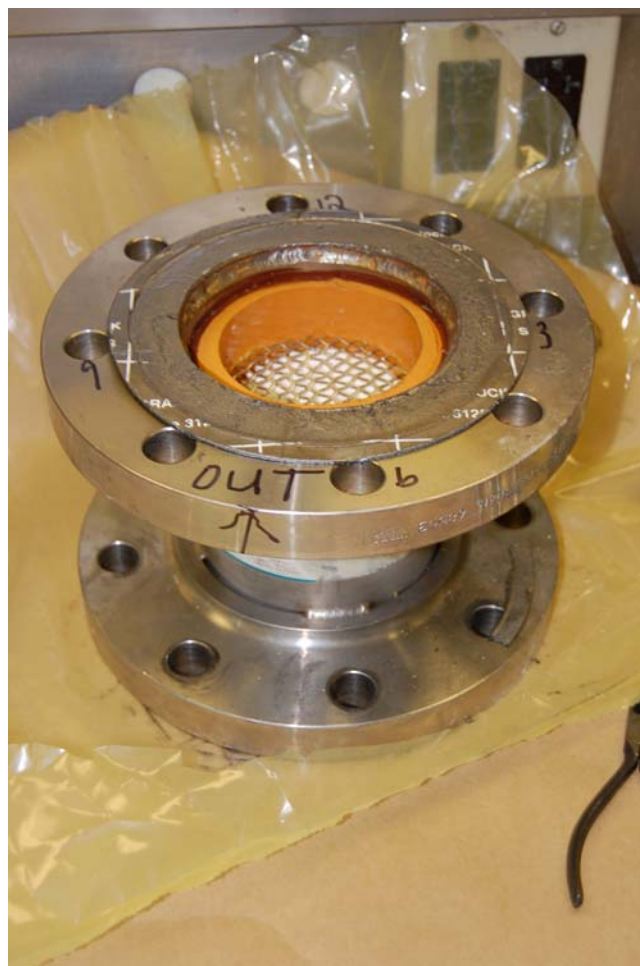


Figure 12. DWPF GC Line Filter Assembly HEPA-1, Outlet Side

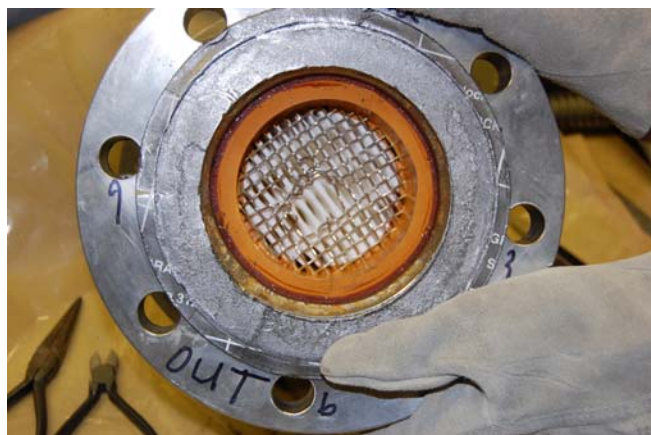


Figure 11. DWPF GC Line Filter Assembly HEPA-1, Outlet Side showing sampling hole in retainer grating.



Figure 13. DWPF GC Line Filter Assembly HEPA-1 filter media sample, showing inlet side on the left.

Figure 14 through Figure 16 show the GC Line Filter Assembly's Stage 3 HEPA-2. Figure 14 and Figure 15 show the inlet and outlet sides of HEPA-2, respectively.

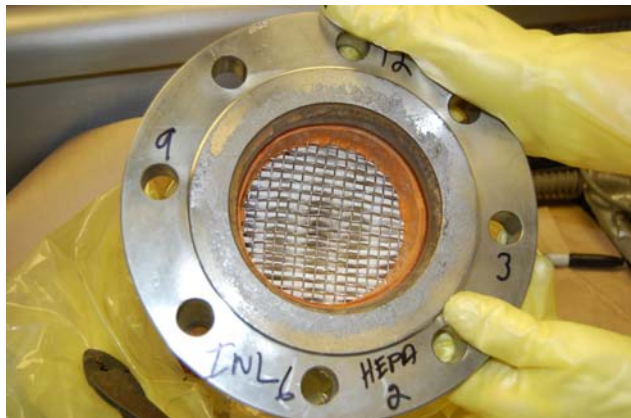


Figure 14. DWPf GC Line Filter Assembly HEPA-2, Inlet Side

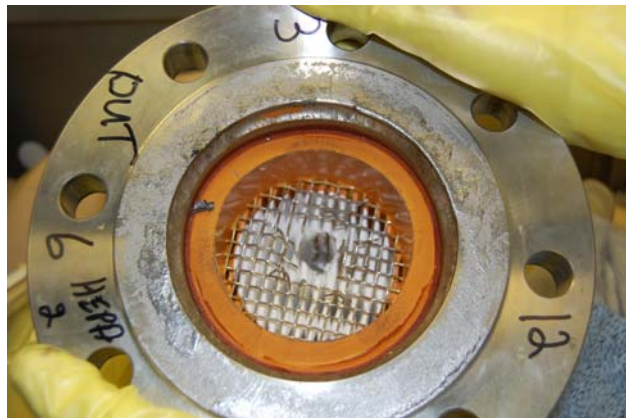


Figure 16. DWPf GC Line Filter Assembly HEPA-2, Outlet Side showing sampling hole in retainer grating

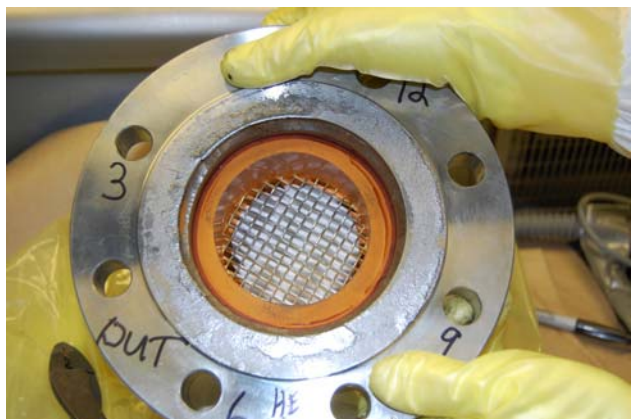


Figure 15. DWPf GC Line Filter Assembly HEPA-2, Outlet Side

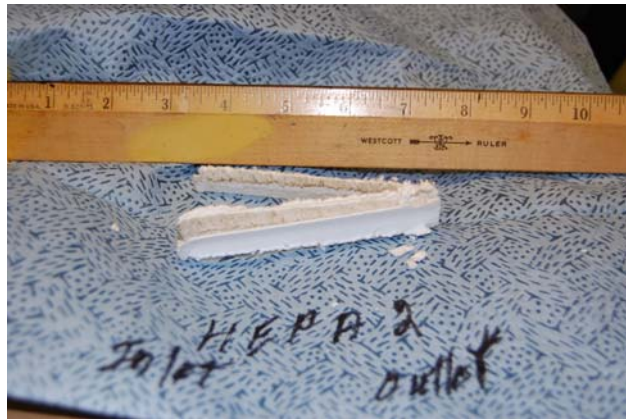


Figure 17. DWPf GC Line Filter Assembly HEPA-2 filter media sample, showing inlet side on the left.

The core sample from HEPA-2, shown in Figure 17, has a visible coating of white solids as can be observed by the smooth surface texture of the filter media. Compare this appearance to the rough texture of the media in Figure 13.

2.2.1 HEME Sample Characterization

A scanning electron microscopy (SEM) raster scans with energy dispersive x-ray (EDX) analysis were requested to get an overall impression of the elemental composition on the filter media. The fibrous nature of the HEME filter media is quite evident in Figure 18. Subtracting out the fiber matrix elemental

composition shown in Figure 22 from that found in Figure 21, indicates the primary and almost exclusive, remaining component is a Hg containing material.

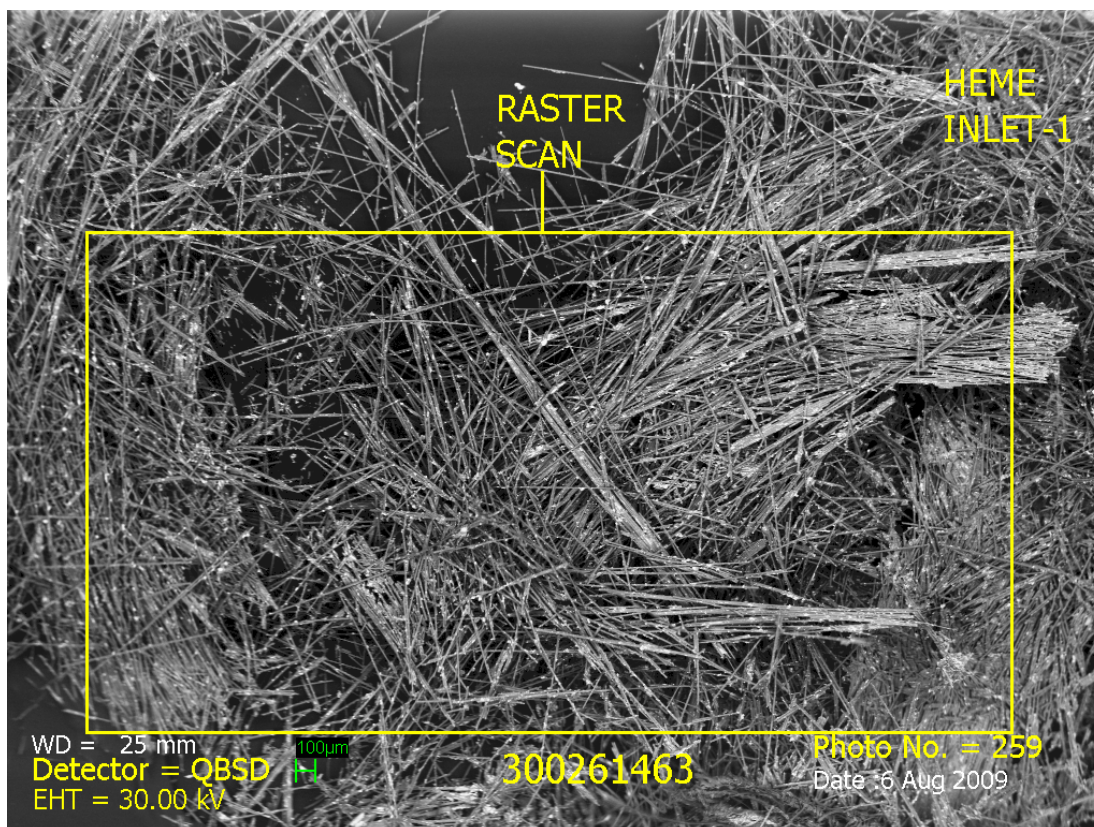


Figure 18. Raster Scan Area of DWPF GC Line Filter Assembly HEME, Inlet Side, Filter Media

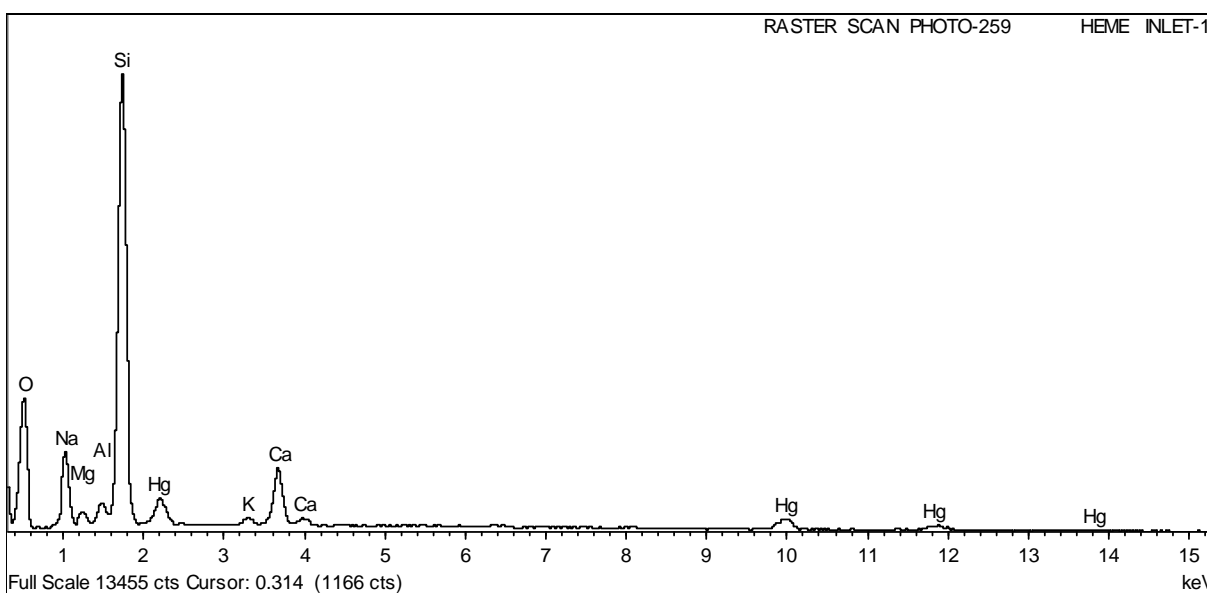


Figure 19. SEM EDX raster scan spectrum of the elements found in the HEME area outlined in Figure 18

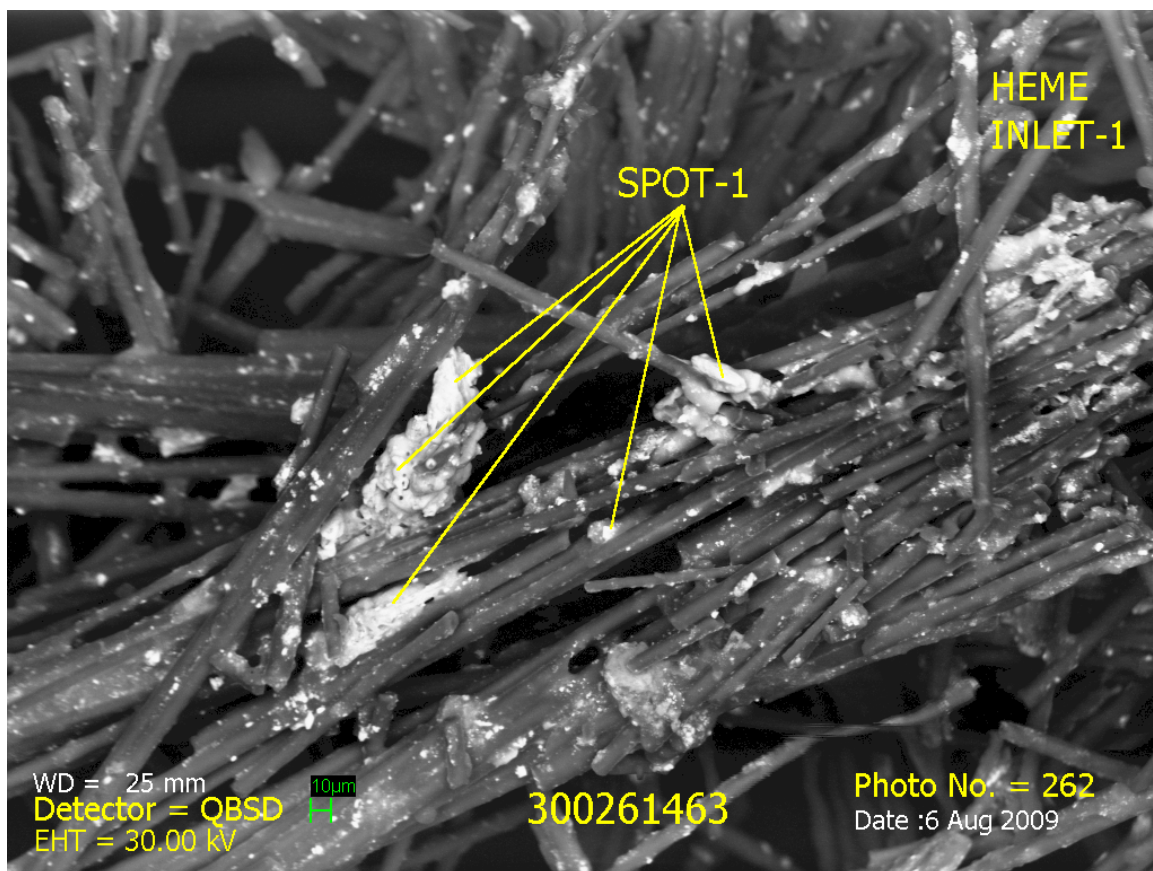


Figure 20. SEM image of DWPF GC Line Filter Assembly HEME, Inlet side, filter media

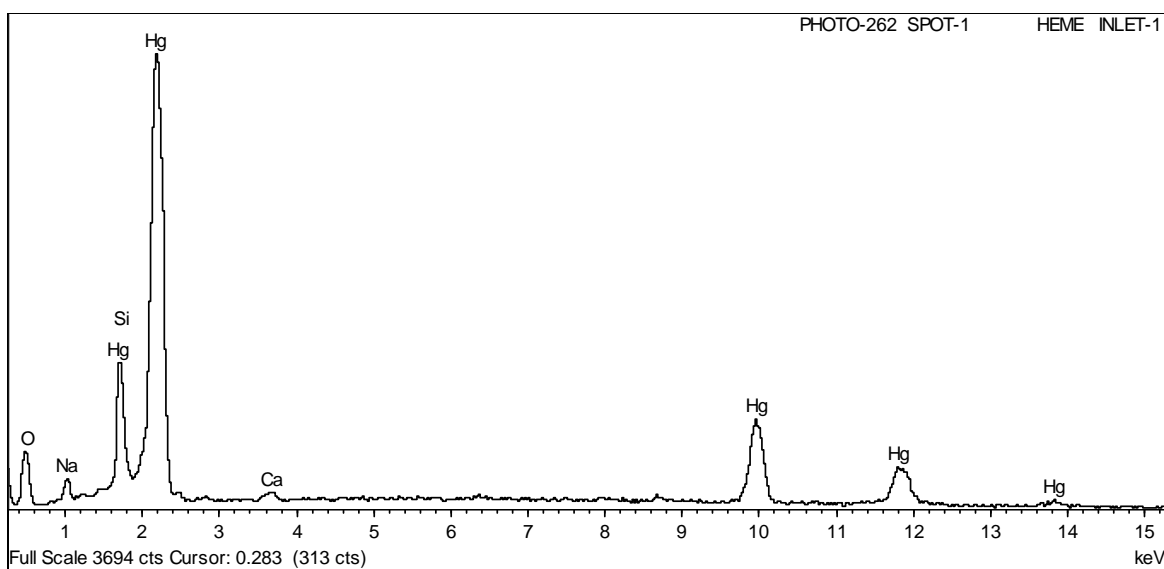


Figure 21. SEM EDX spectrum of the HEME, Spot 1 in Figure 20

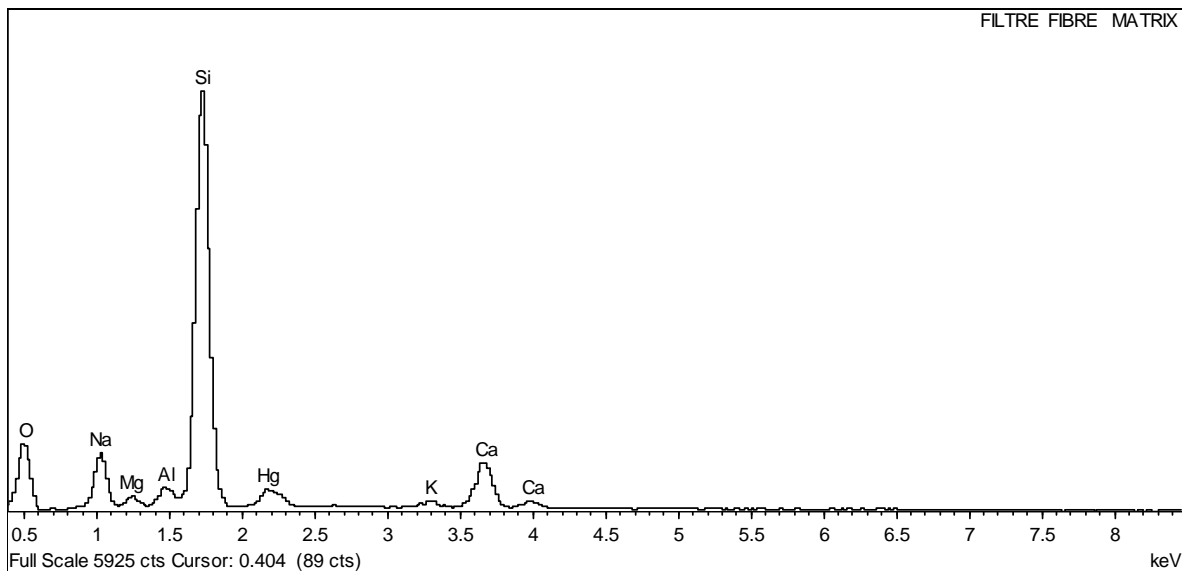


Figure 22. SEM EDX spectrum of the HEME Fiber Matrix in Figure 18

The HEME outlet side raster scan was identical to that obtained for the inlet side. The outlet end of the filter appeared to have even more deposited solids than did the inlet end (refer to Figure 23), which is consistent with the observed solids that were found after the filter media on the outlet side screen and on the surrounding housing walls. There was what appears to be non-Hg containing, trace particulate matter on the filter media, but these did not appear to comprise a significant portion of the deposited solids.

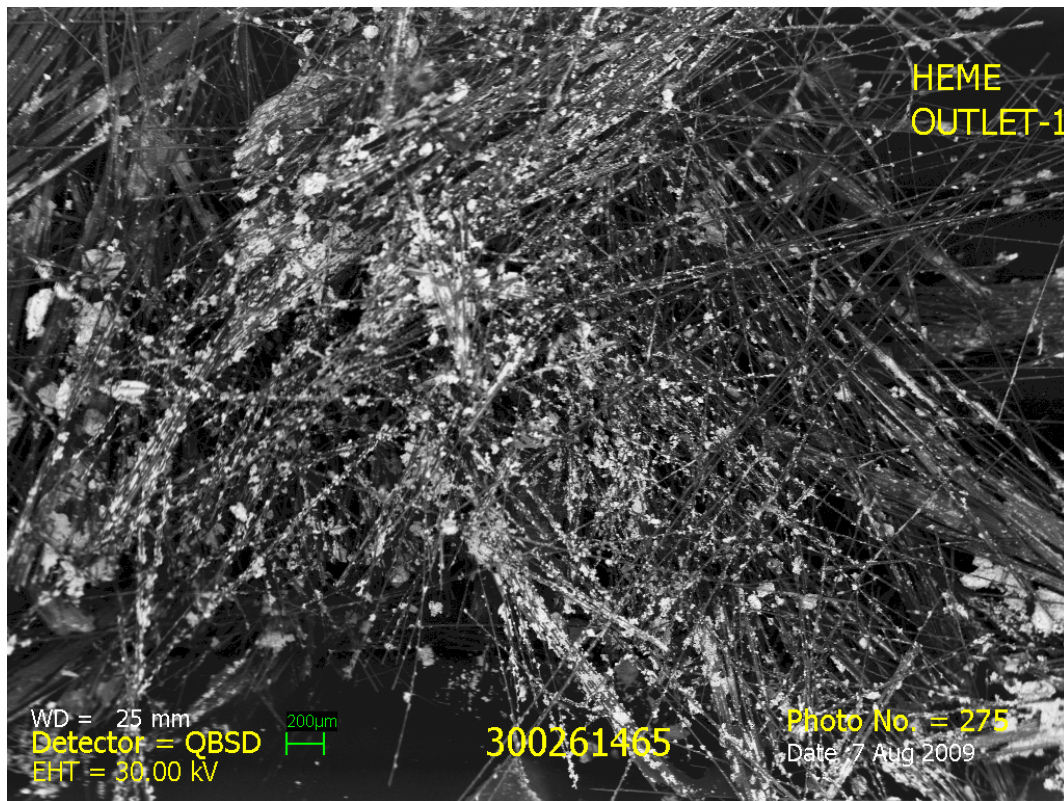


Figure 23. SEM image of DWPF GC Line Filter Assembly HEME, Outlet side, filter media

The deposited solids, shown in Figure 24, removed from the HEME outlet screen and housing walls were found to contain Hg. The SEM EDX spectrum obtained from this material is given in Figure 25. This material when added to deionized (DI) water did not dissolve, but the material dissolved readily in 0.6M HNO_3 to give a colorless solution.

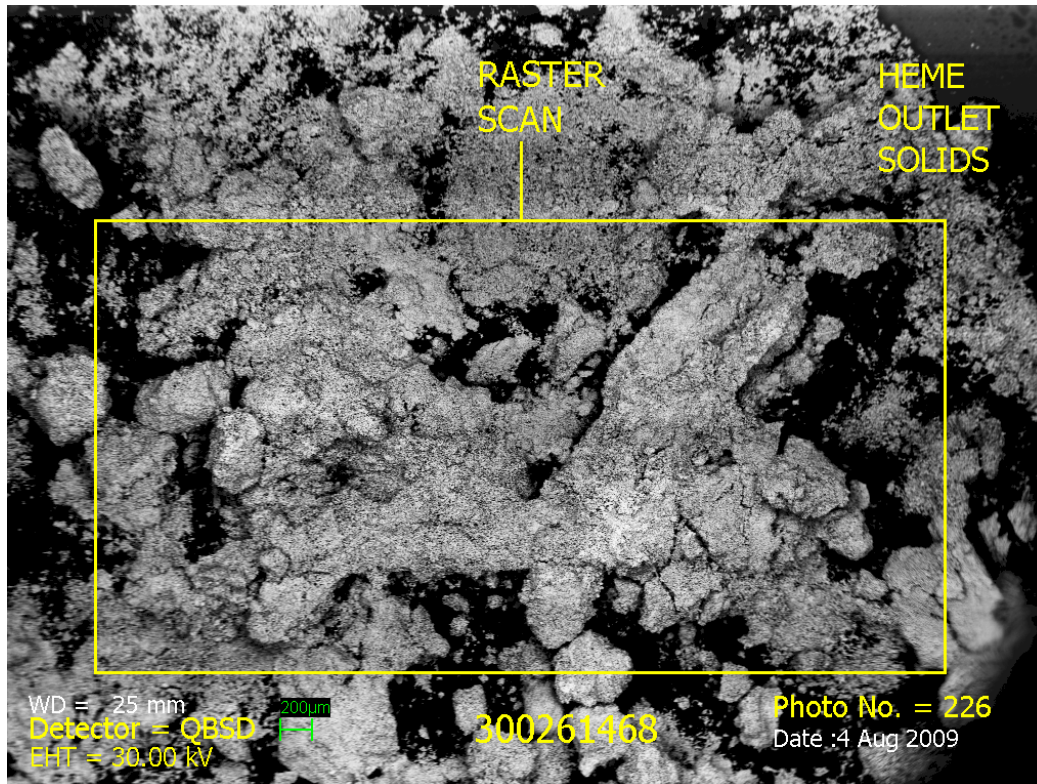


Figure 24. DWPF GC Line Filter Assembly Post-HEME Solids

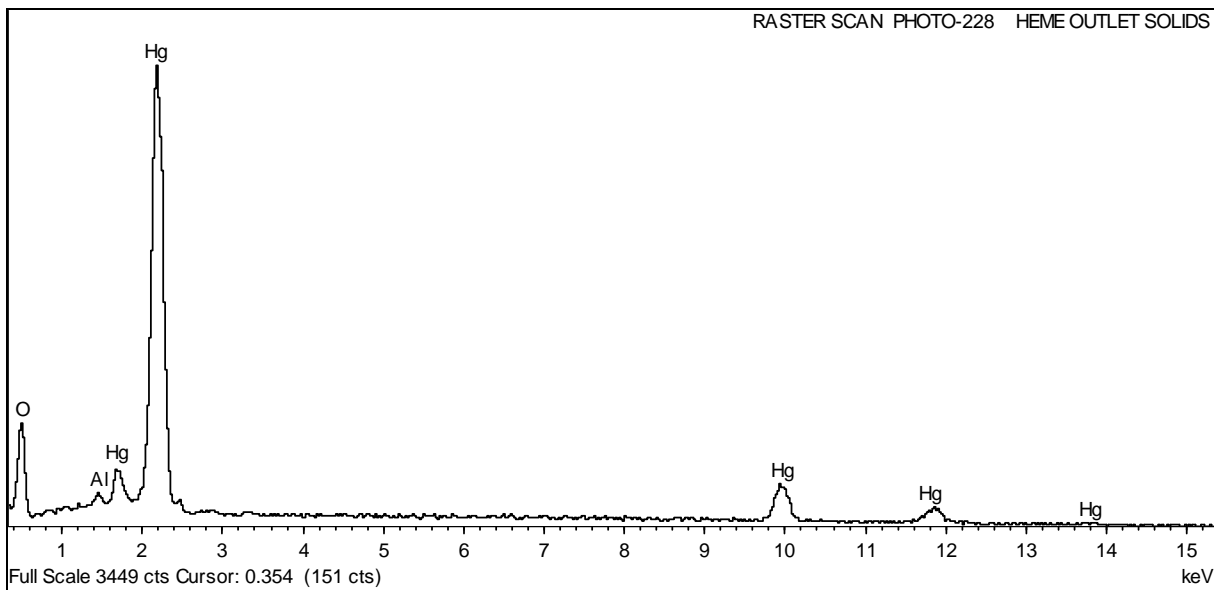


Figure 25. SEM EDX spectrum of the post-HEME solids in Figure 24

2.2.2 HEPA-1 Sample Characterization

The core sample collected from HEPA-1, Figure 26, provides the SEM image for the inlet side HEPA-1 sample with the raster scan area shown in the yellow box.

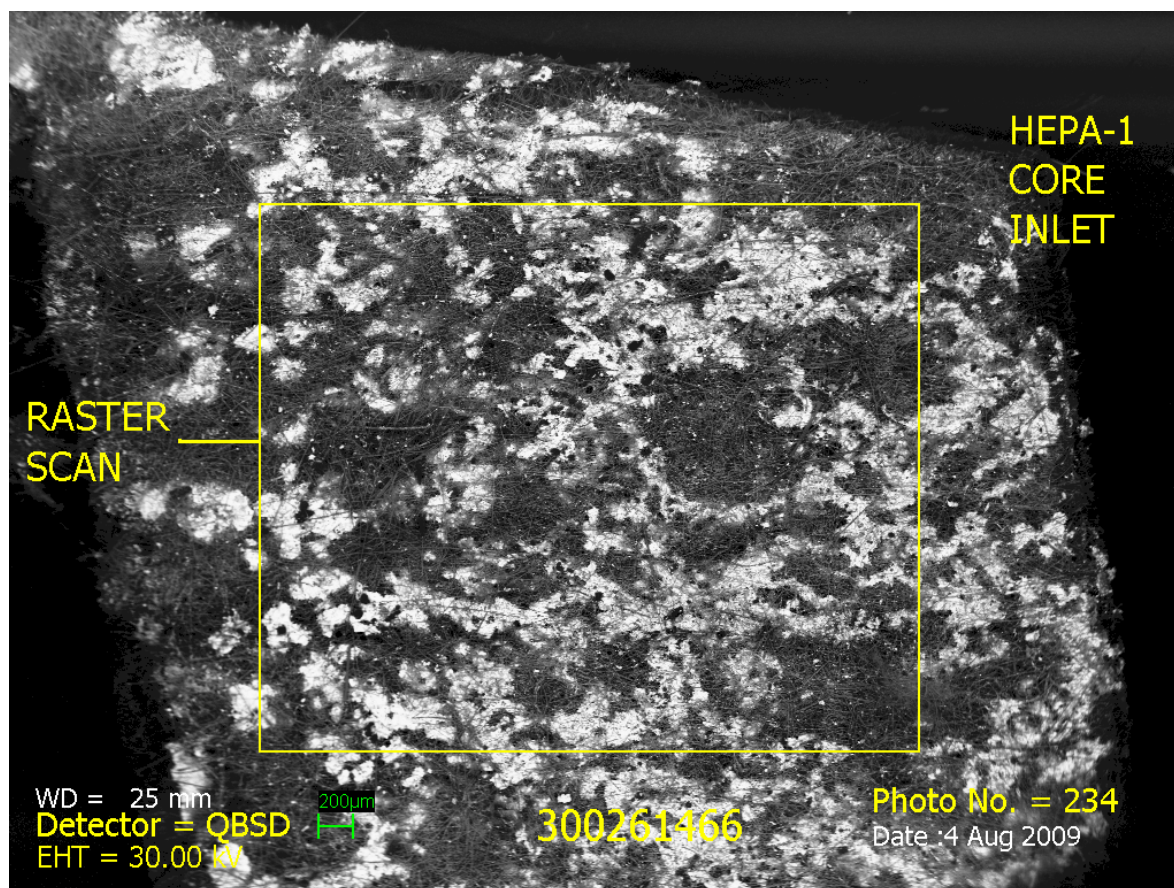


Figure 26. Raster Scan Area of DWPF GC Line Filter Assembly HEPA-1, Inlet Side, Filter Media

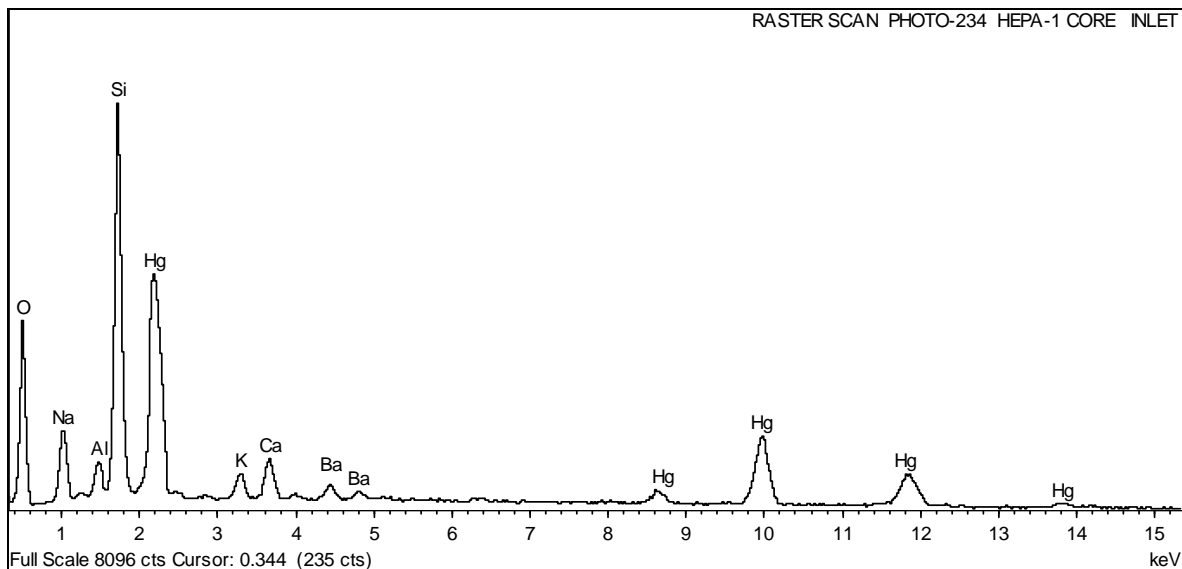


Figure 27. SEM EDX raster scan spectrum of the elements found in the area outlined in Figure 26

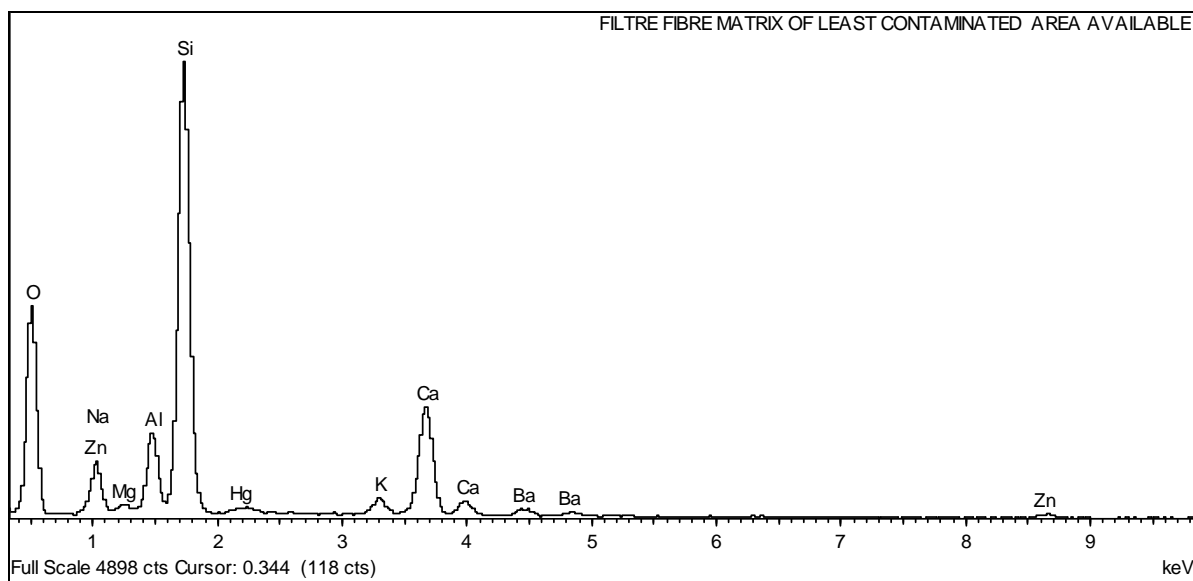


Figure 28. SEM EDX spectrum of the least contaminated area of the filter fiber matrix.

Qualitatively subtracting the spectrum in Figure 28 from that shown in Figure 27, indicates that the primary remaining elements are Hg, Na, and O. SEM EDX spectrums taken of the spots labeled in Figure 29 indicate that those spots marked with a “1” and visible as a white powder in the image are a Hg containing compound (see Figure 30), while the spots marked with a “2” and visible as dark patches in the image is a Na and O containing species. It was not possible to get an exact determination of the Hg species by SEM due to the volatility of Hg compounds in the electron beam.

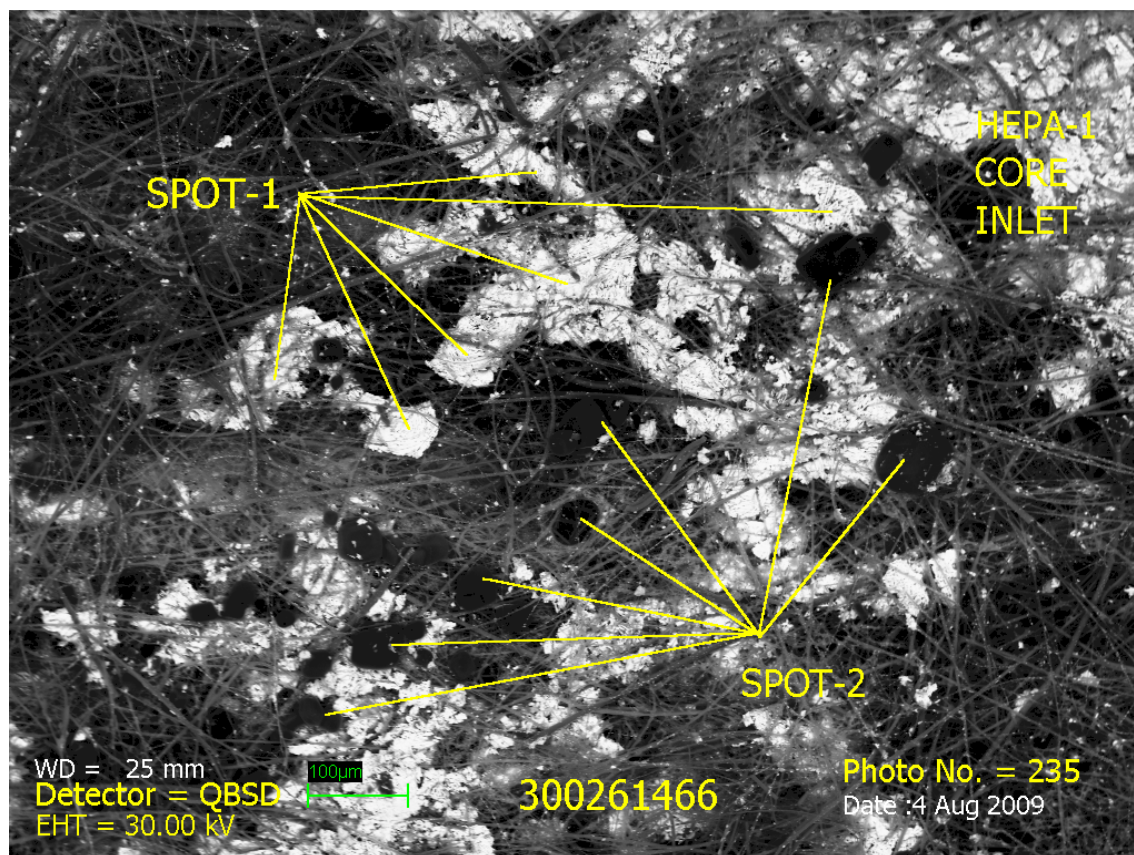


Figure 29. SEM image of DWPF GC Line Filter Assembly HEPA-1, Inlet side, filter media

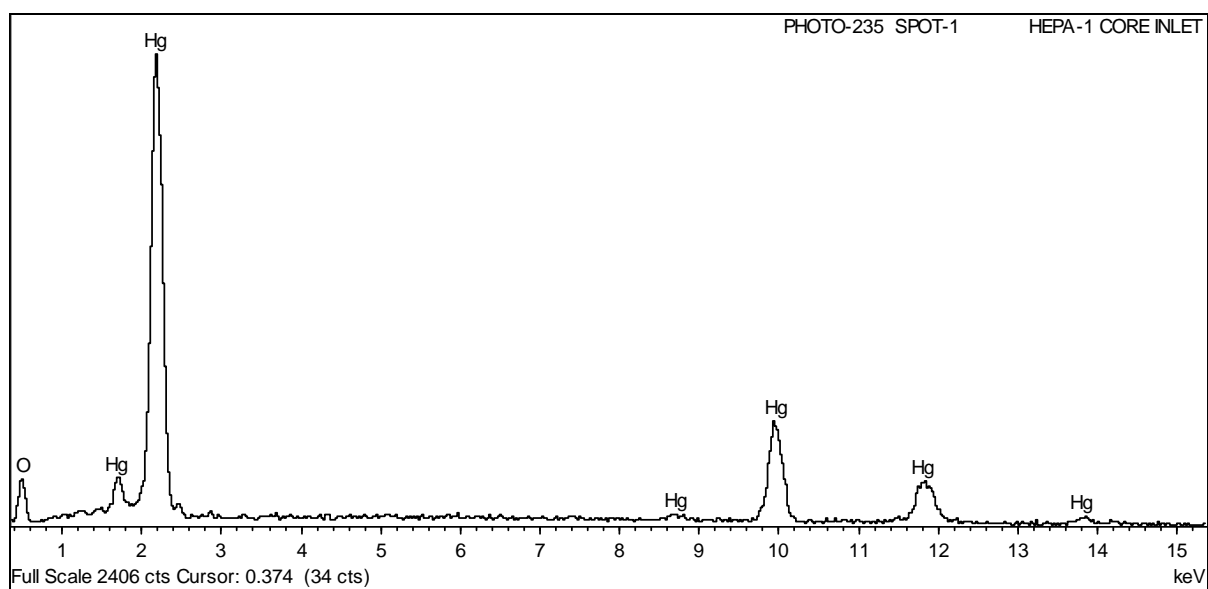


Figure 30. SEM EDX spectrum of HEPA-1, Spot 1 in Figure 29.

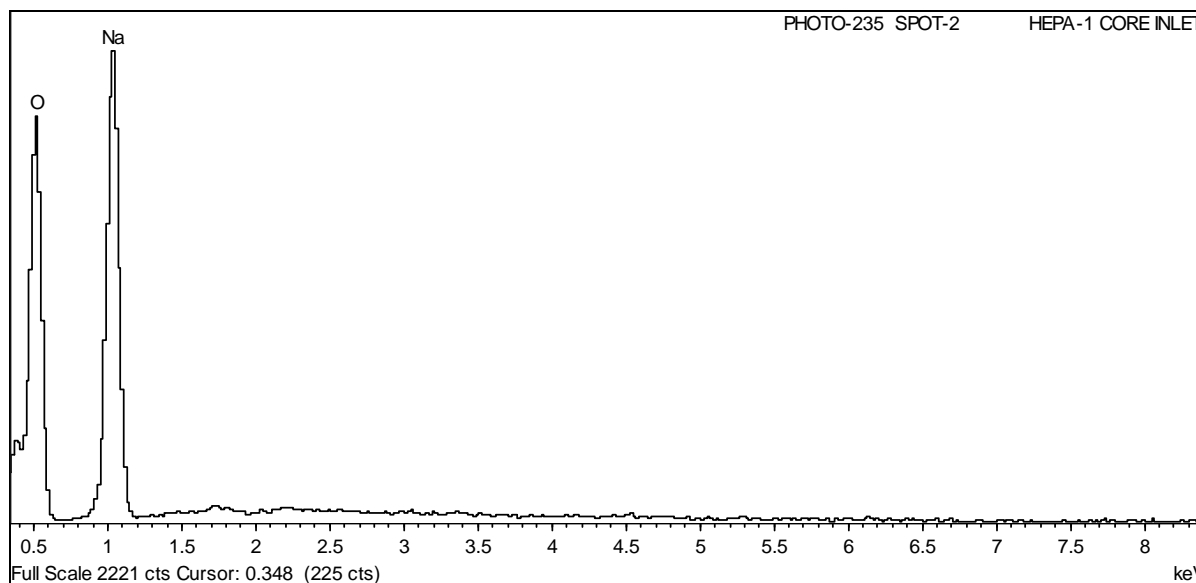


Figure 31. SEM EDX spectrum of HEPA-1, Spot 2 in Figure 29

Similar solids deposits are observed on the HEPA-1 outlet side filter media, though the extent of Hg contamination appears to be lighter as can be observed by comparing Figure 26 with that shown in Figure 32.

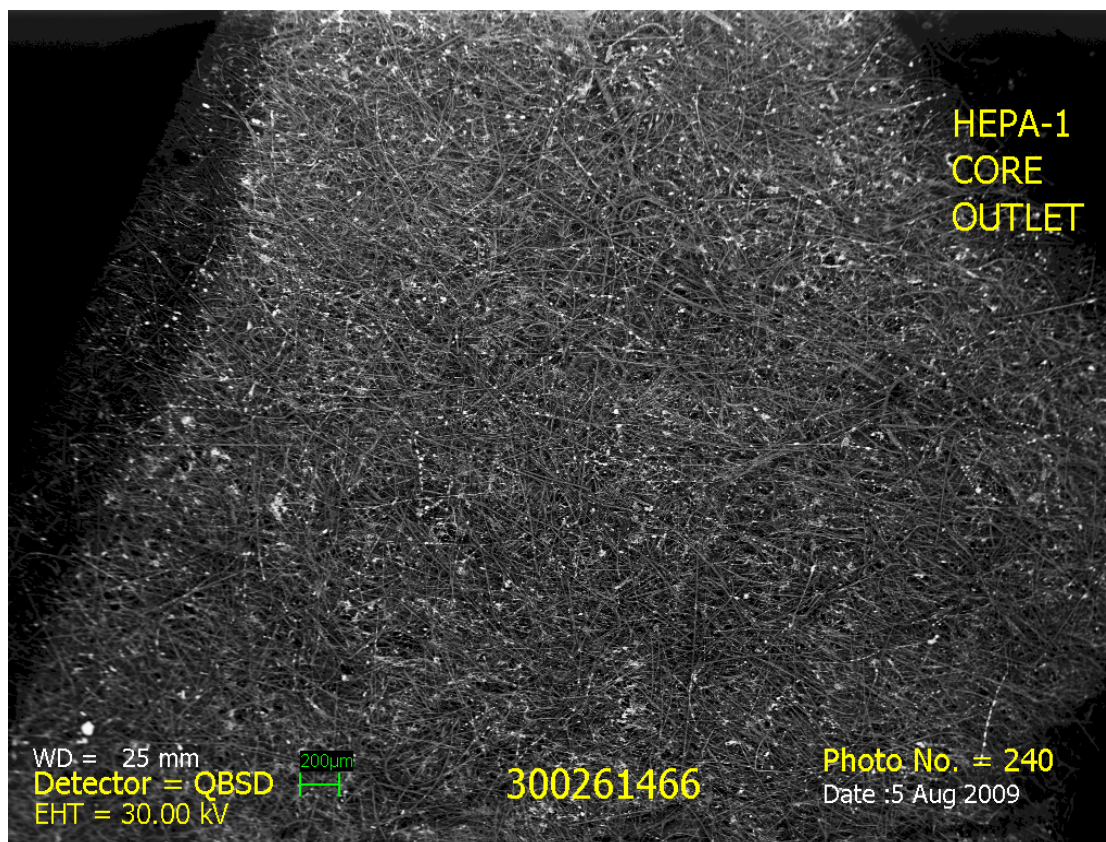


Figure 32. Raster Scan of DWPF GC Line Filter Assembly HEPA-1, Outlet Side, Filter Media

A closer look at the outlet side filter media of HEPA-1, as seen in Figure 33, shows the same Hg species at spot 2 and an additional Mg/Si/O species at spot 1. The SEM EDX spectrum of this material is shown in Figure 34. The SEM EDX spectrum obtained from the raster scan of the outlet side filter media does not show a significant contribution from Mg, so these particles seem to be of limited distribution relative to the Hg species seen across the filter.

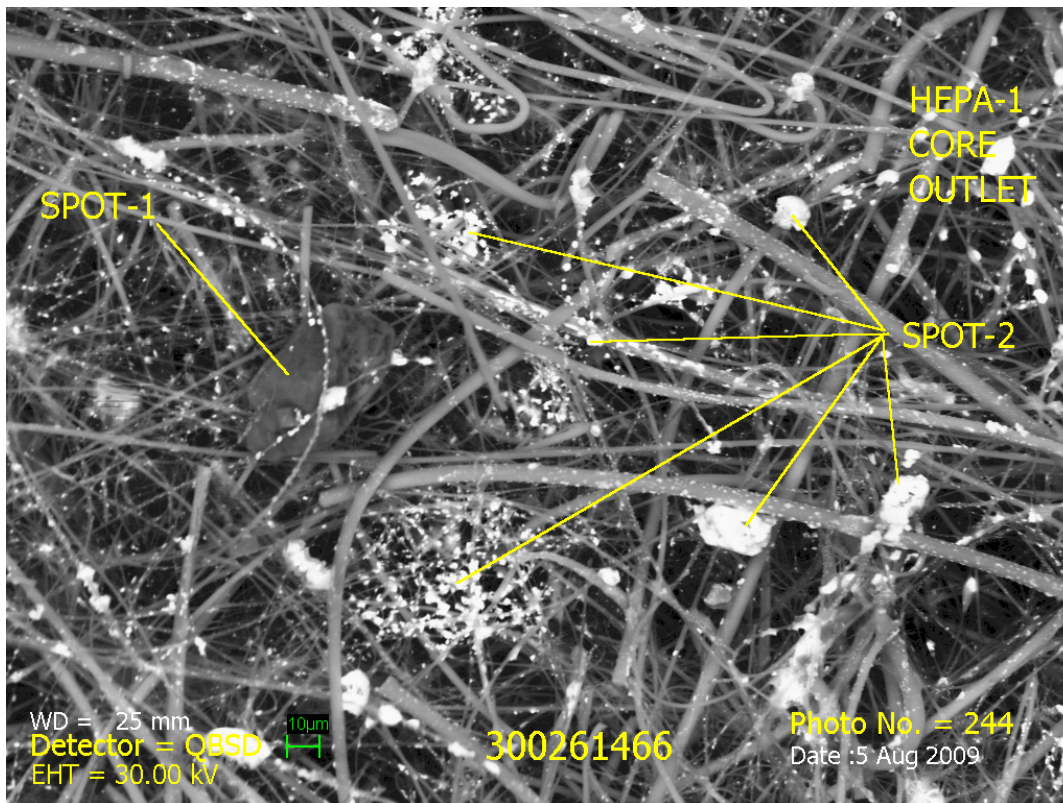


Figure 33. SEM image of DWPF GC Line Filter Assembly HEPA-1, outlet side, filter media

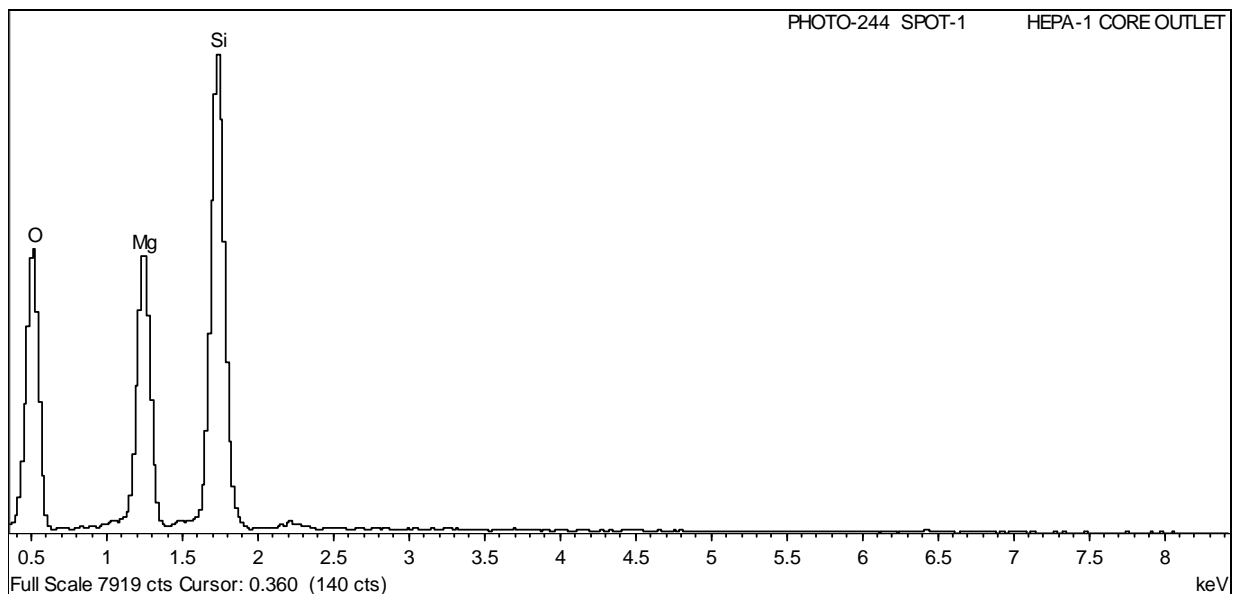


Figure 34. SEM EDX spectrum of HEPA-1, Spot 1 in Figure 33

2.2.3 HEPA-2 Sample Characterization

The deposits observed on the HEPA-2 filter media are more evenly distributed throughout the media and not as concentrated on the inlet side. Figure 35 provides the SEM image for the inlet side HEPA-2 sample with the raster scan area shown in the yellow box. The SEM EDX spectrum obtained for the raster scan is provided in Figure 36

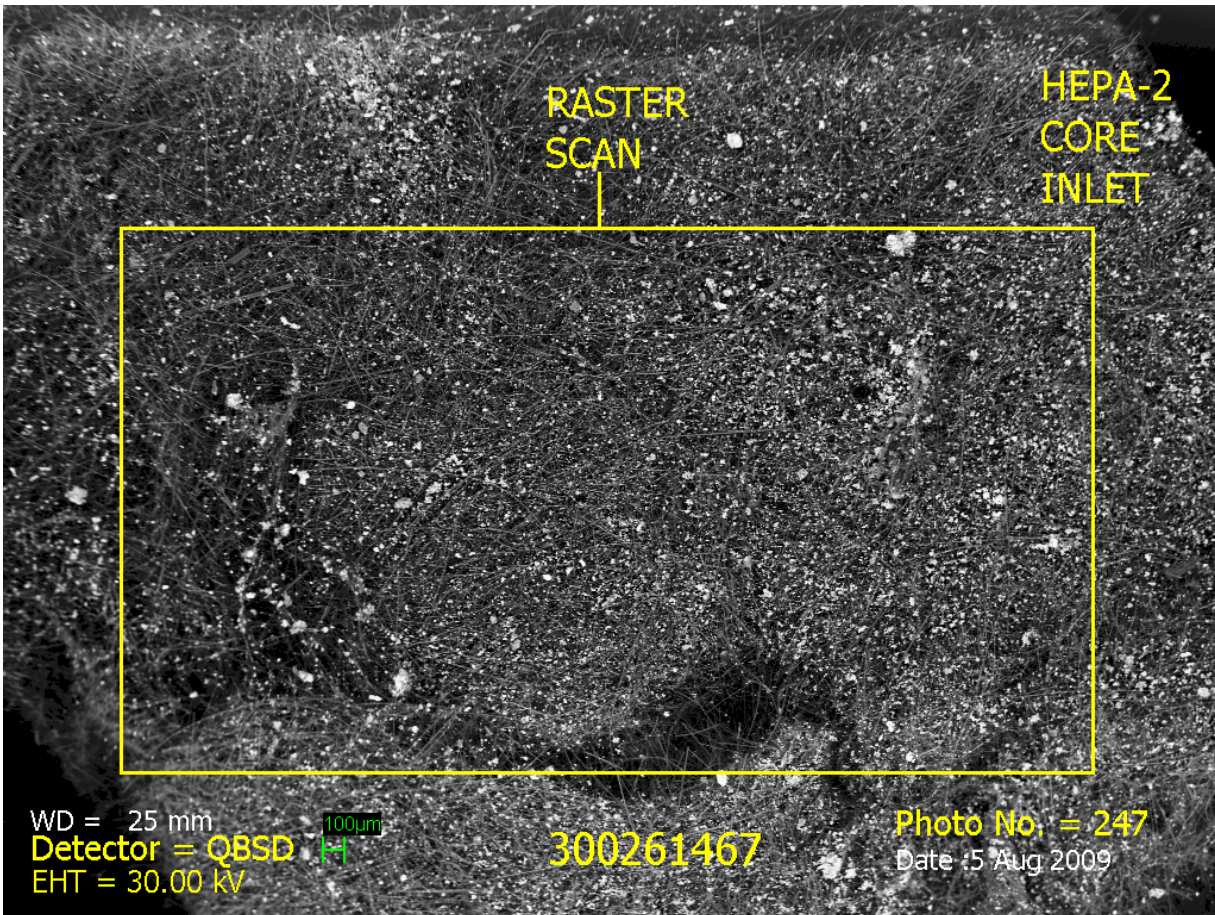


Figure 35. Raster Scan Area of DWPF GC Line Filter Assembly HEPA-2, Inlet Side, Filter Media

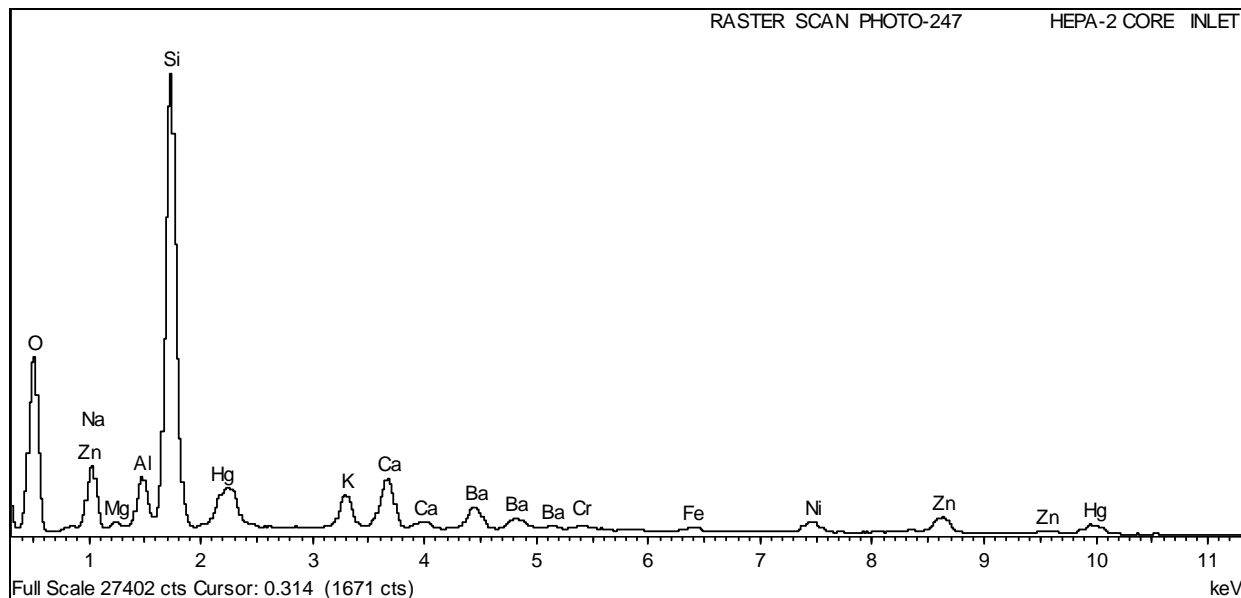


Figure 36. SEM EDX raster scan spectrum of the elements found in the HEPA-2 area outlined in Figure 35

The SEM EDX spectrum shown in Figure 36 is similar to that seen for the HEPA-1 inlet side filter media, but it also shows that several additional first row transition elements, namely Cr, Fe, Ni, Ti, and Zn, are present in the sample. A closer look for these materials provided the spectra and analyses shown in Figure 37 through Figure 44. Some of the particles seem to be aggregate solids indicating they may have solidified on the filter together from the gas stream. Analysis of a number of particles designated as Spot 2 in Figure 37, indicates the Hg containing species (see also Figure 45) is also prevalent in HEPA-2. Spot 1 in Figure 37 indicates the presences of a Ti species while Spot 4 in Figure 41 indicates the presence of a Pb species in addition to the Hg species observed throughout all the samples. It was not possible to determine how common either the Ti or Pb species are in the filter media, but since Ti and Pb did not show up in the raster scan analysis of HEPA-2 as given in Figure 36, it is probably safe to assume that they are minor components.

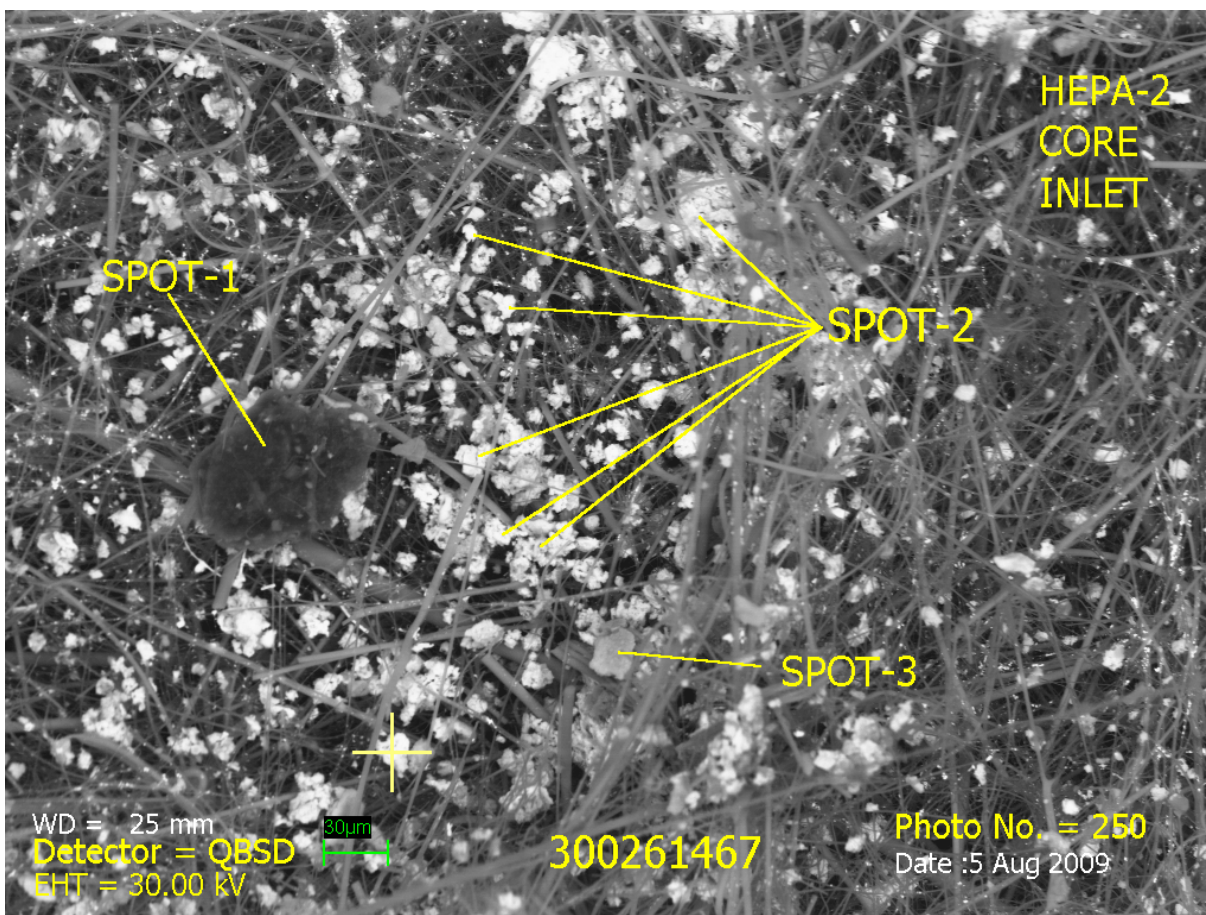


Figure 37. SEM image of DWPF GC Line Filter Assembly HEPA-2, Inlet side, filter media

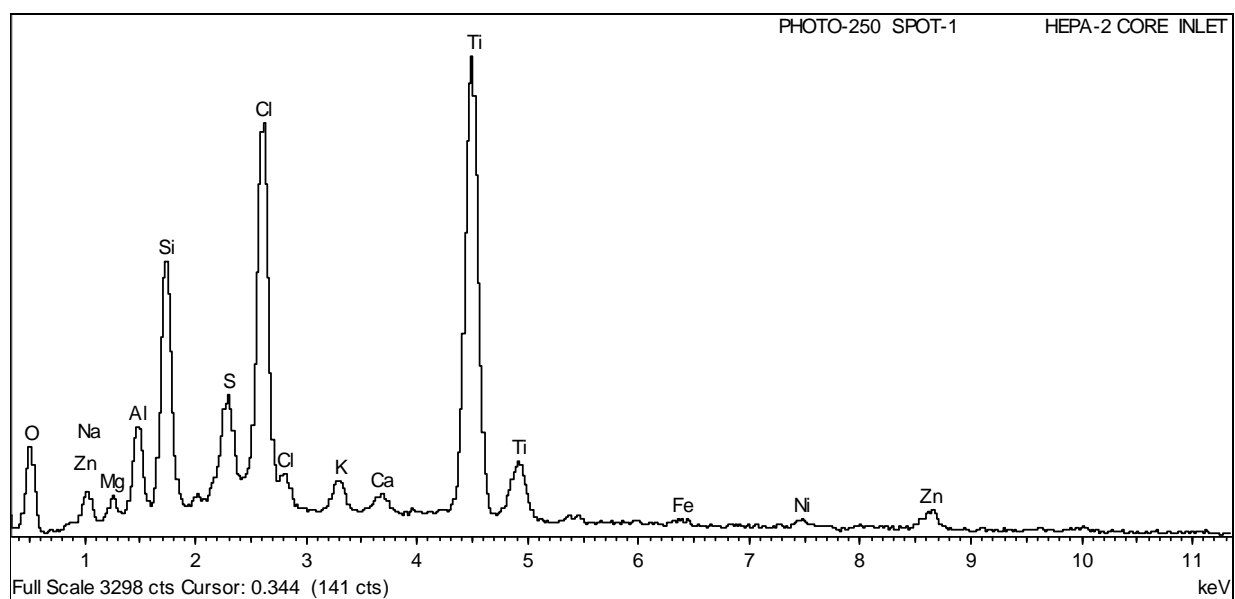


Figure 38. SEM EDX spectrum of HEPA-2, Spot 1 in Figure 37

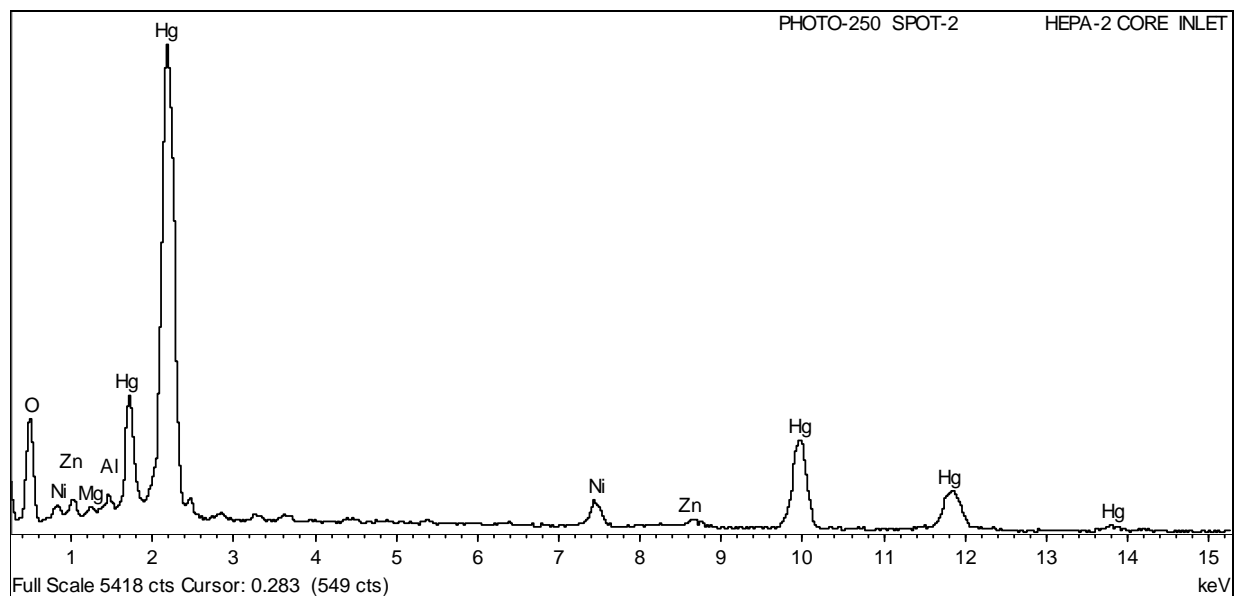


Figure 39. SEM EDX spectrum of HEPA-2, Spot 2 in Figure 37

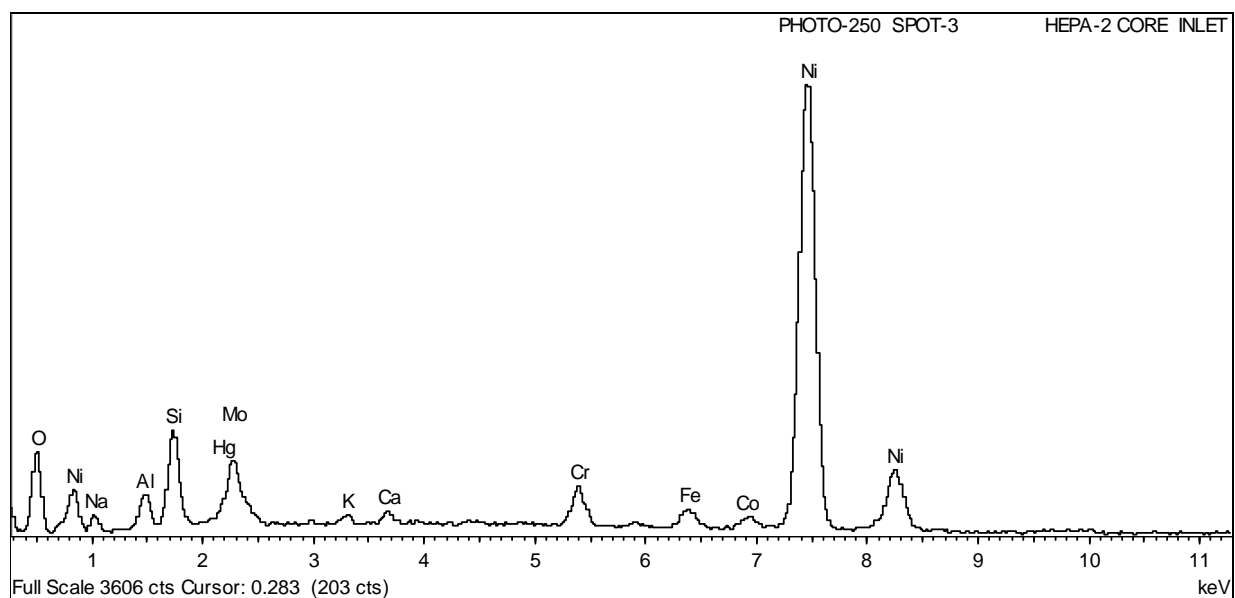


Figure 40. SEM EDX spectrum of HEPA-2, Spot 3 in Figure 37

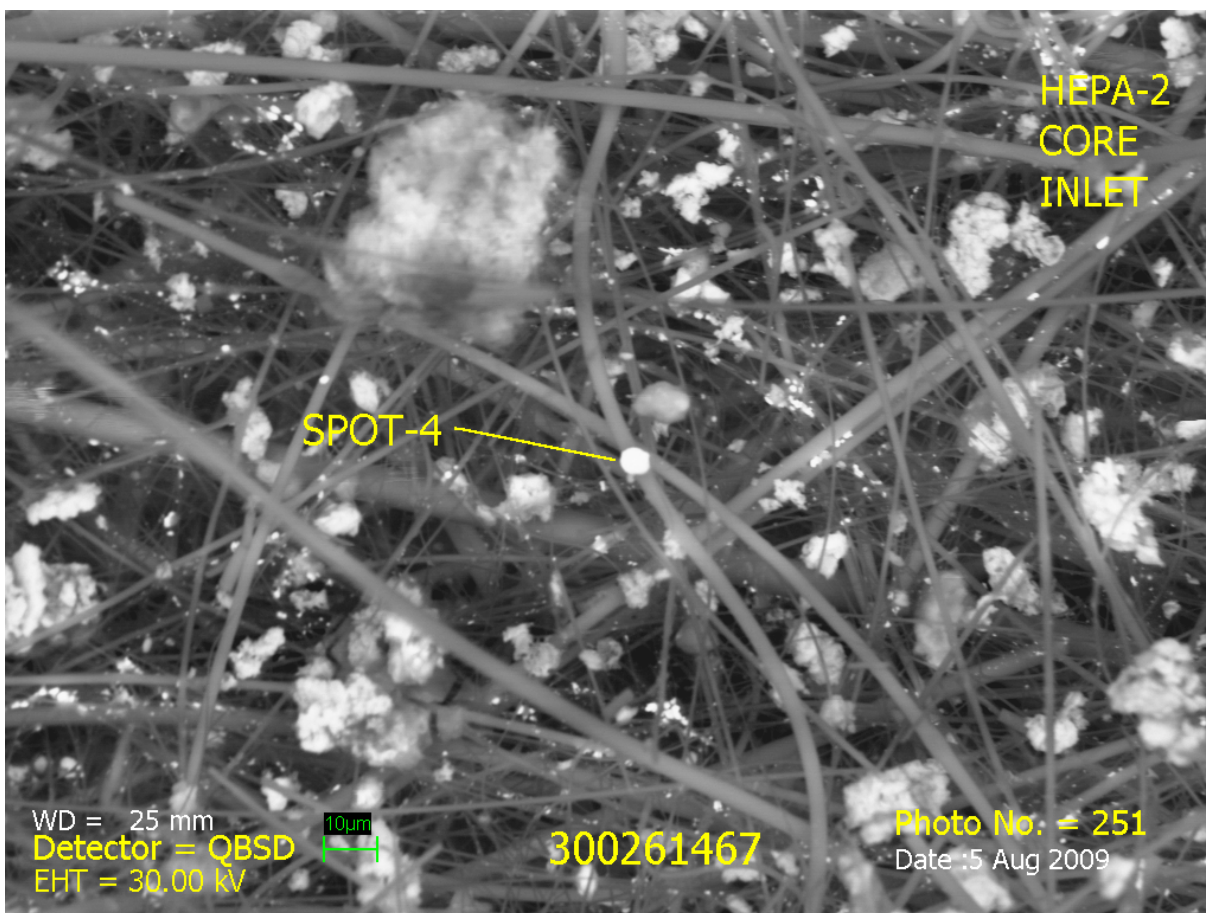


Figure 41. SEM image of DWPF GC Line Filter Assembly HEPA-2, Inlet side, filter media

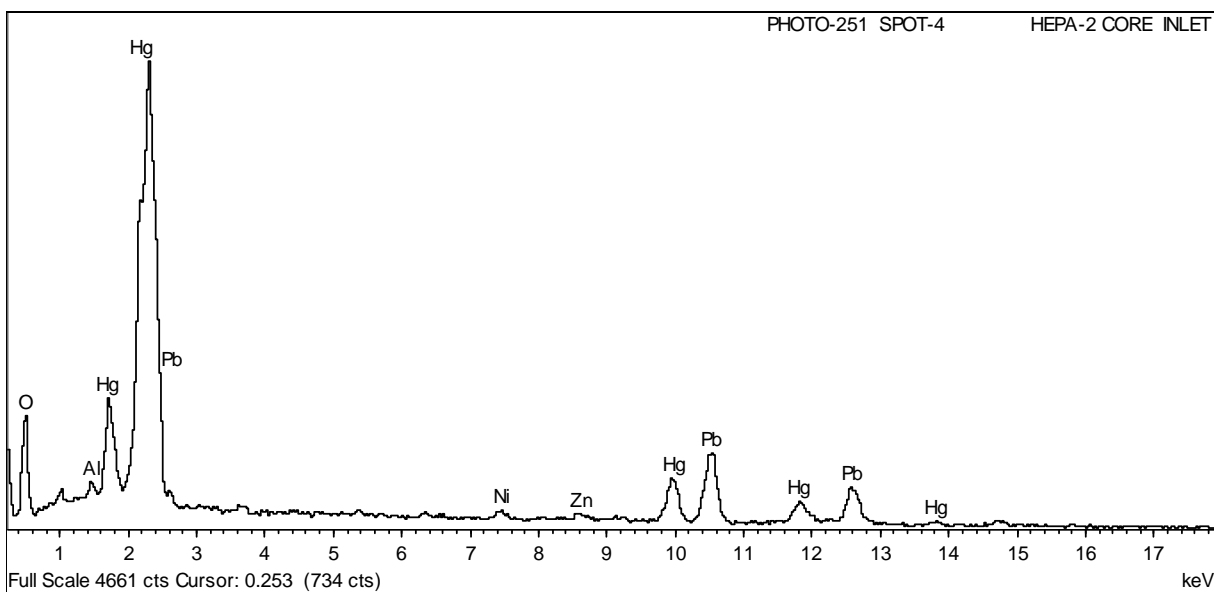


Figure 42. SEM EDX spectrum of HEPA-2, Spot 4 in Figure 41

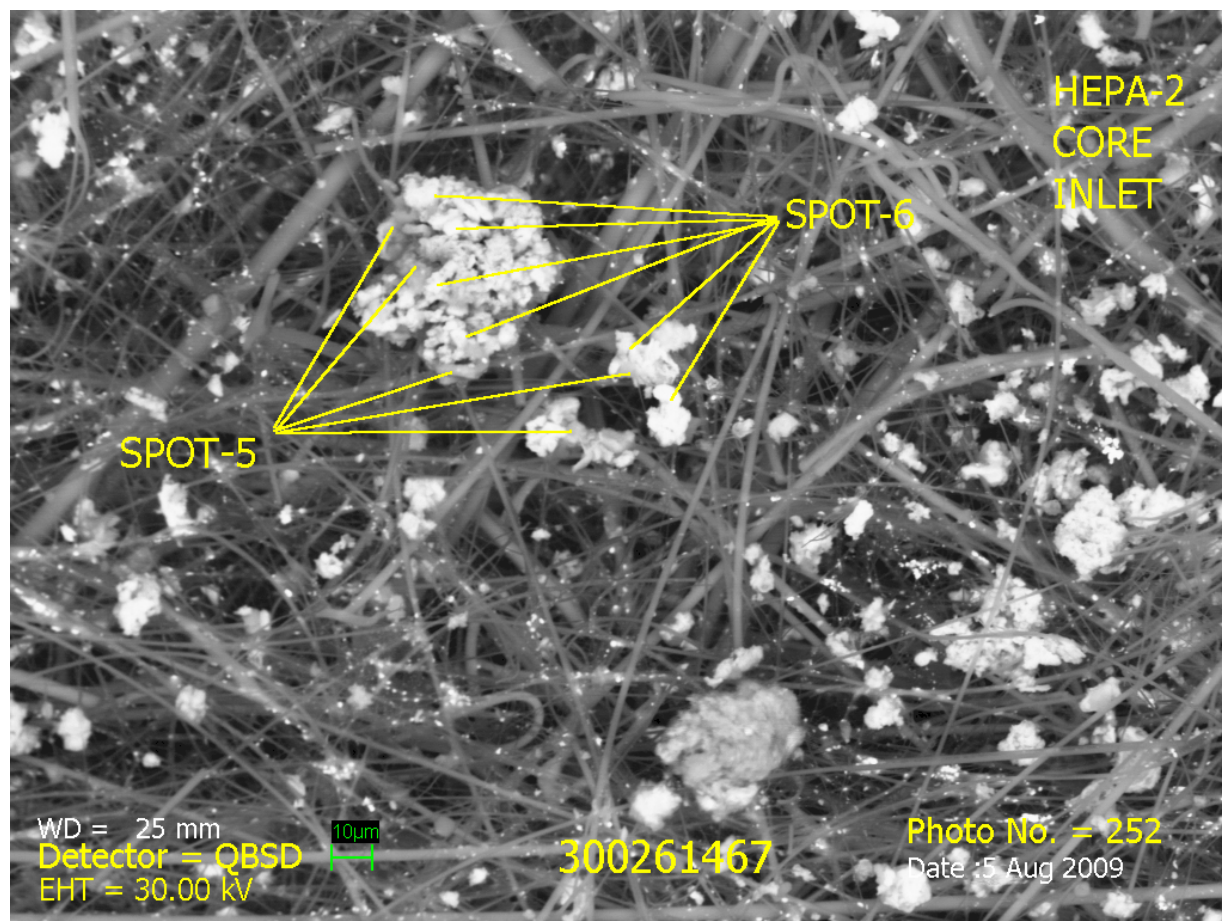


Figure 43. SEM image of DWPF GC Line Filter Assembly HEPA-2, Inlet side, filter media

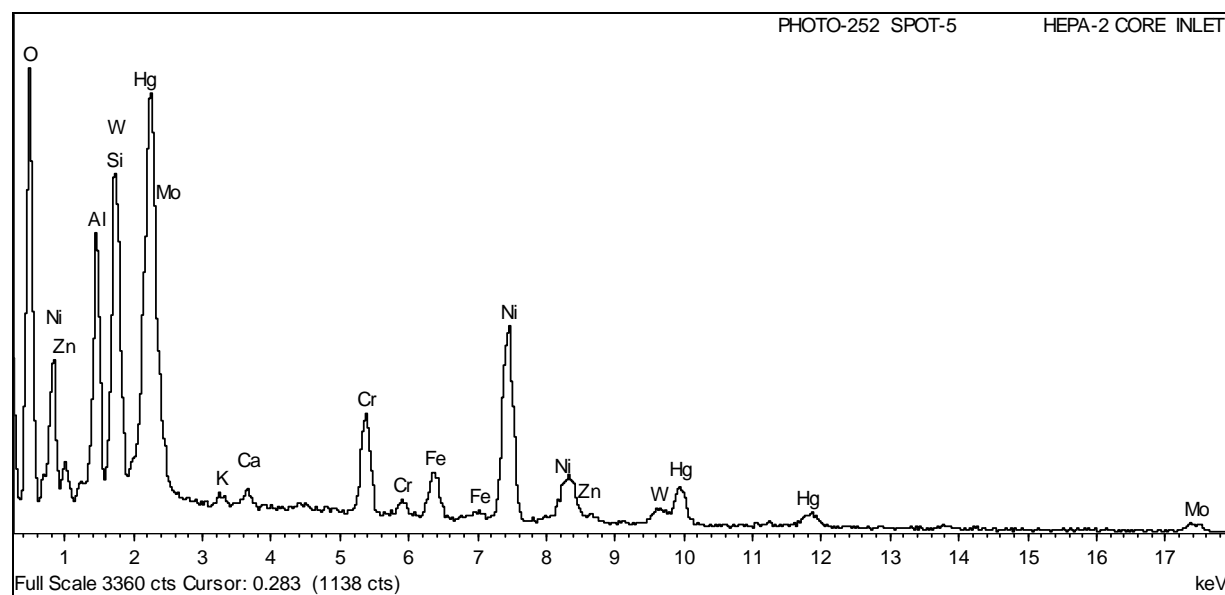


Figure 44. SEM EDX spectrum of HEPA-2, Spot 5 in Figure 43

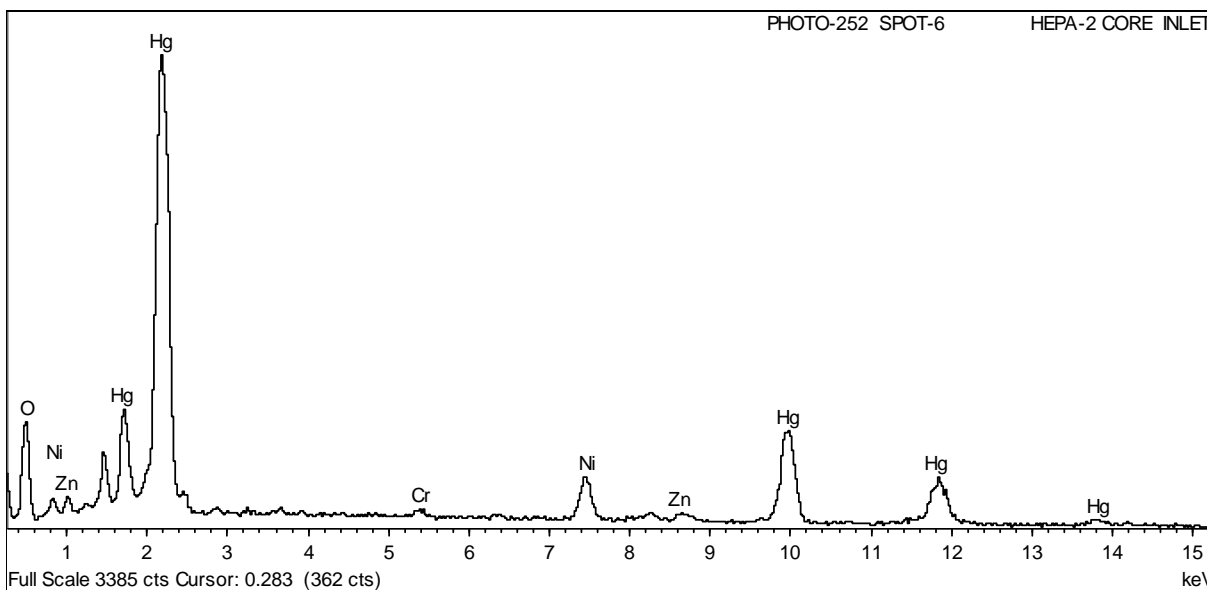


Figure 45. SEM EDX spectrum of HEPA-2, Spot 6 in Figure 43

A raster scan of the outlet end of HEPA-2 is given in Figure 46 and generally reveals the similar list of elements (see Figure 47, Spots 2 – 4) found on the inlet side with the exception of the areas indicated by Spot 1 (Figure 48). This spot revealed a F containing material not previously observed; but again, since F does not show up in the raster scan, it is unlikely that this material contributed significantly to the overall particle contamination in the HEPA-2 component.

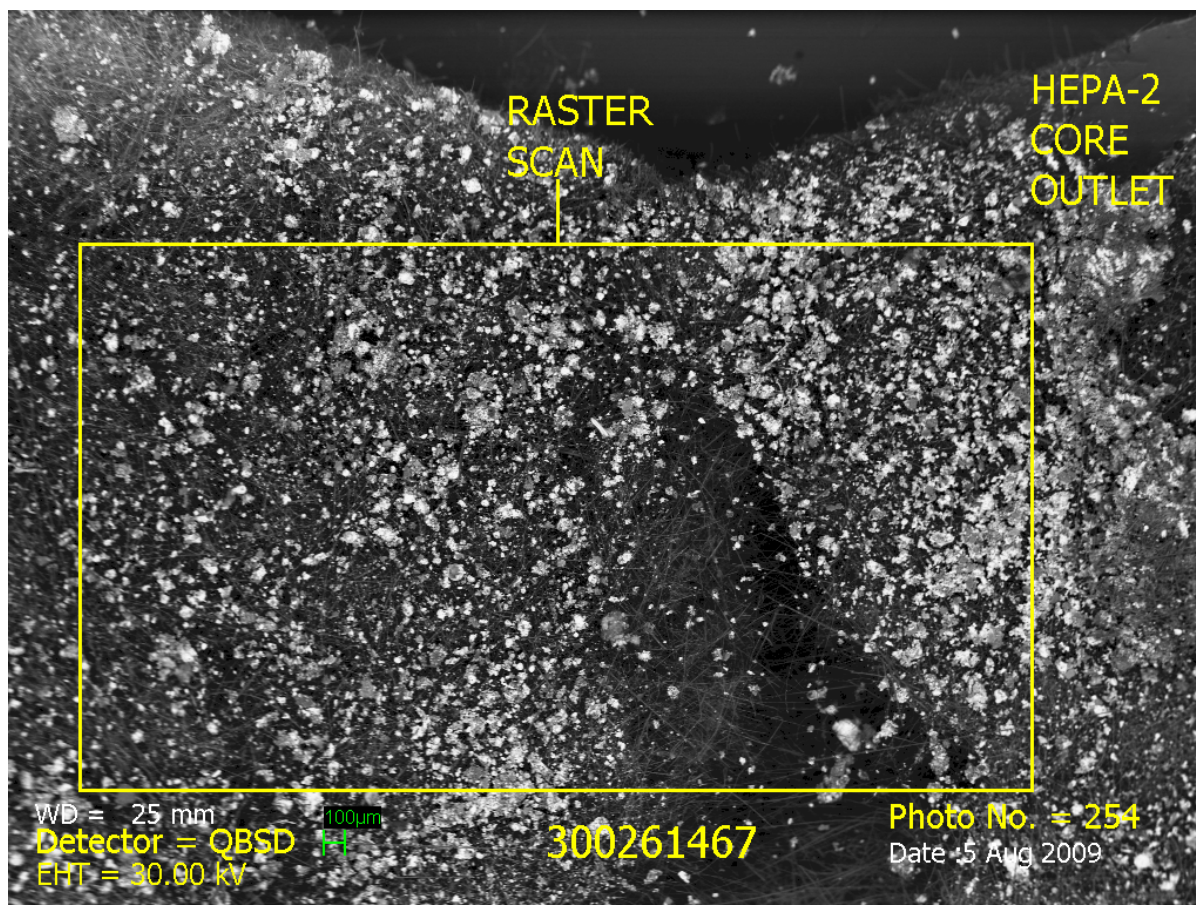


Figure 46. Raster Scan Area of DWPF GC Line Filter Assembly HEPA-2, Outlet Side, Filter Media

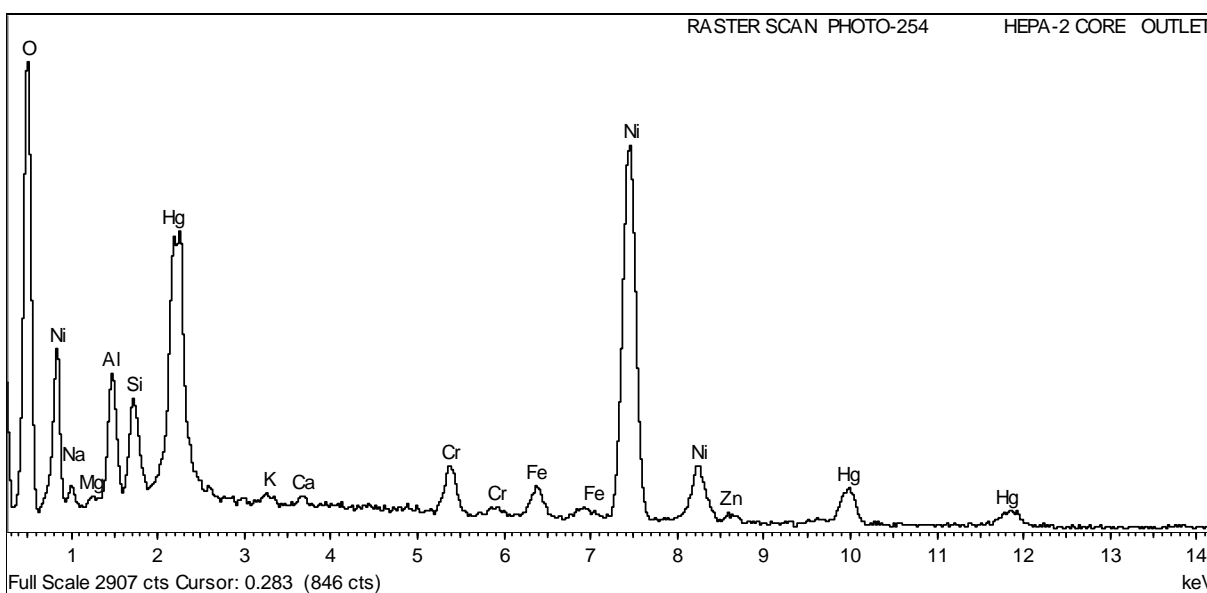


Figure 47. SEM EDX raster scan spectrum of the elements found in the HEPA-2 area outlined in Figure 46

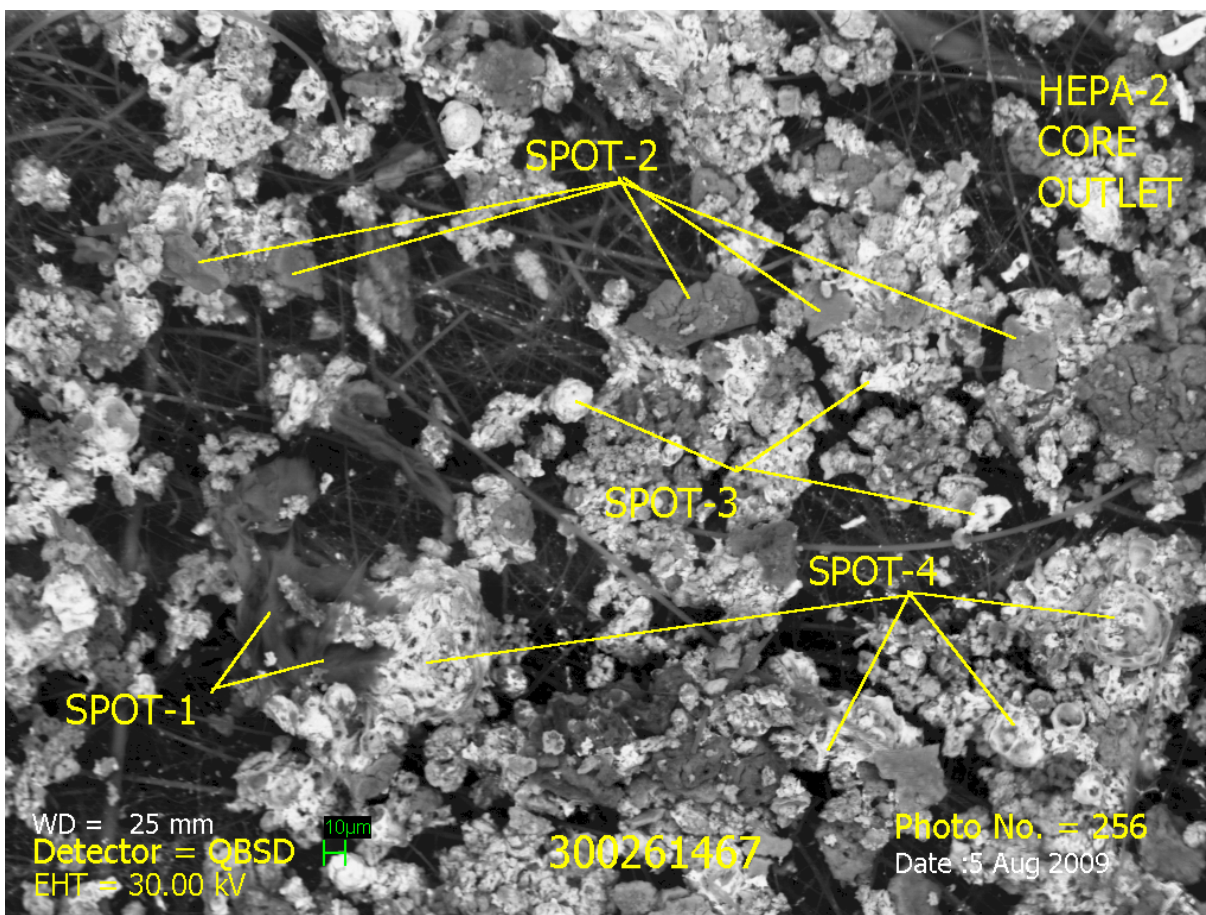


Figure 48. SEM image of DWPF GC Line Filter Assembly HEPA-2, Outlet side, filter media

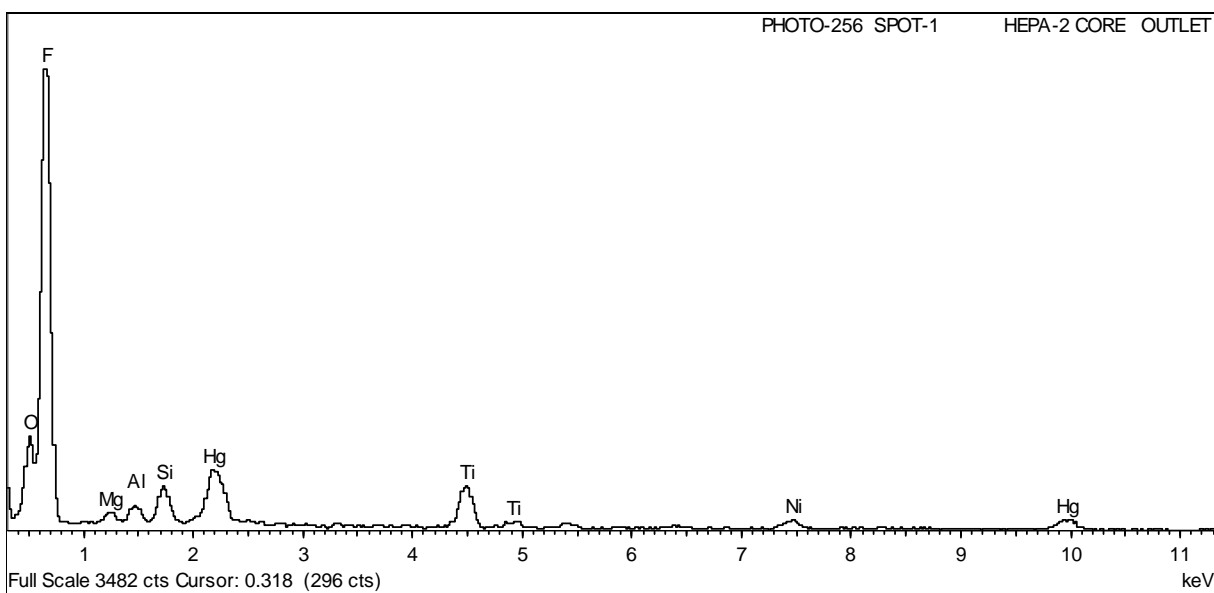


Figure 49. SEM EDX spectrum of HEPA-2, Spot 1 in Figure 48

2.3 Analytical Results

A sample of 0.042g of the solids collected from the outlet side of the HEME were dissolved in approximately 5 mL of 0.06M HNO₃ and submitted for cold vapor atomic absorption spectroscopy (CVAA) analysis for Hg and inductively coupled plasma atomic emission spectroscopy (ICP-AES) for elemental analysis. Since the sample did not dissolve in DI water, it was not submitted for ion chromatography (IC) analysis. The elemental composition of the solids is given in Table 2 and shows that the material is approximately 59 wt% Hg on a total solids basis.

Table 2. Elemental composition of the white solids obtained from the DWPF GC Line Filter Assembly

Element	Wt% of Total Solids	%RSD
Al	0.016	18
B	0.038	0.6
Ca	0.026	1.4
Fe	0.011	3.5
Hg	59	NA
Mg	0.0077	0.2
Mn	0.0015	6.2
Na	0.25	0.9

NA ≡ not available

A sample of these solids was submitted for x-ray diffraction (XRD) and the resulting spectrum obtained is given in Figure 50. The material is a mix of two Hg species, Hg₄(OH)(NO₃)₃ and Hg₁₀(OH)₄(NO₃)₆. The sharp peaks indicate the materials were fairly crystalline. Both compounds are Hg (I) species.

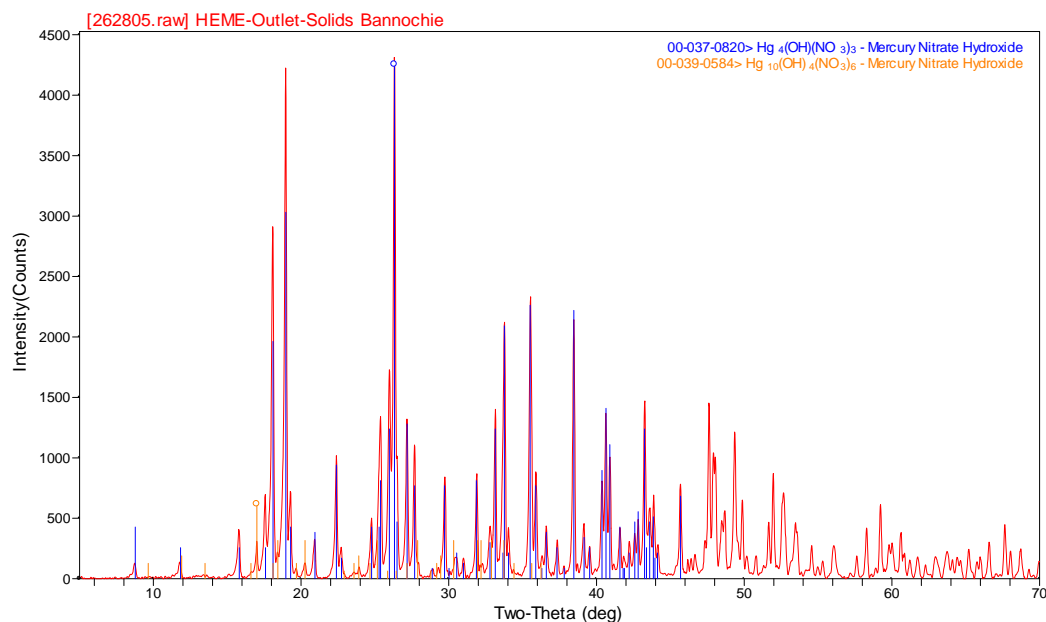


Figure 50. X-ray diffraction spectrum from white solids collected from the HEME outlet of the DWPF GC Line Filter Assembly

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3.0 DISCUSSION

3.1 Filter Deposits

From the observations obtained here, the vast majority of filter deposits are due to the Hg(I) compounds identified in Figure 50. The presence of Hg(I) species is due either to volatilization prior to complete reduction to Hg(0) in the Slurry Receipt Adjustment Tank (SRAT) or re-oxidation in the ammonia scrubber after contact with the Slurry Mix Evaporator Condensate Tank (SMECT) liquid. Since the system is designed to remove Hg and collect it into the Mercury Water Wash Tank (MWWT), this behavior would be considered outside the design criteria.

While the material is found in all three components of the GC Line Filter Assembly (HEME, HEPA-1, and HEPA-2), the first location of significant buildup is on the outlet side of the HEME. Initially, it was thought this may be connected to HEME flushes through the available water inlet that exists after the HEME filter material, but we have since learned that this flush capability is not currently used and was not used when this filter was in service. Why the solids accumulate here in larger quantities is not known, but it is apparent that the mist eliminator is not efficient at trapping these compounds.

The solids that build-up at the inlet side of HEPA-1, as compared with the outlet side, are probably carryover from the solids condensing after the HEME. The fact that solids are more evenly distributed throughout HEPA-2 might indicate that they are not condensing in large degree until this stage of the GC Line Filter Assembly. The even distribution of solids through this final filter stage would indicate that there is likely breakthrough with additional solids condensing after the HEPA-2. Alternatively, the back-flow purges that have been attempted to improve flow through the GC Line may have altered the distribution of solids in the filters and or blown solids back down the line from the outlet to the inlet side of HEPA-2.

Since the GC Line Filter Assembly sample stream is a subset of the gas flow following the ammonia scrubber, it is likely that the SMECT liquid at pH 3, which passes through the ammonia scrubber, is acidifying the gas stream, and the nitrate oxidizing the Hg(0) vapor to Hg(I). This material then begins to condense as it moves through the filters of the GC Line Filter Assembly. The remainder of the gas flow that is not directed to the GC Line would proceed to the Formic Acid Vent Condenser (FAVC) HEME, Process Vessel Vent (PVV) filter, and then on to the sand filters. Since a HEME appears to not effectively trap the two compounds we have identified, those condensing solids in the bulk of the gas stream are probably collecting at the PVV filter or the sand filter.

3.2 Historical Hg Compounds in Offgas Lines

It is not surprising to see Hg in these filters due to the high volatility of Hg compounds. During Integrated DWPF Melter System (IDMS) campaigns with Hg containing simulated sludge at TNX, elemental Hg was detected past the Sludge Receipt and Adjustment Tank (SRAT) condenser.² Hg species were also observed in a SRAT GC instrument sample collected by DWPF in 2007.³ Due to the small sample size received in 2007, it was not possible to make a definitive determination of the species plugging the GC Line at that time. The best fit to the limited XRD data signal was another Hg(I) species, clearcreekite, $\text{Hg}_3\text{CO}_3(\text{OH})\cdot 2\text{H}_2\text{O}$, but much of this sample appeared to be amorphous Hg species.

3.3 Evaluation of Total Hg Present

After the characterization work on the sample was completed and the assembly materials returned to DWPF for disposal, a question arose as to the total quantity of these Hg compounds contained in the components of the GC Line Filter Assembly. This question was not evaluated for the work requested in the TAR. It may be possible to make an educated guess of the upper bound mass of material in the filters, but a more exact estimate is not possible with the information collected here. Since the material is soluble in 0.06M nitric acid, an acid flush of the filter media could remove the vast majority of the Hg from the components should this be necessary prior to disposal.

4.0 CONCLUSIONS

The vast majority of the material in each of the three stages of the DWPF GC Line Filter Assembly appears to be contaminated with a Hg compound that is ~59 wt% Hg on a total solids basis. The Hg species was identified by XRD analysis to contain a mixture of $\text{Hg}_4(\text{OH})(\text{NO}_3)_3$ and $\text{Hg}_{10}(\text{OH})_4(\text{NO}_3)_6$. Only in the core sample of the second stage HEPA, did this material appear to be completely covering portions of the filter media, possibly explaining the pressure drops observed by DWPF. The fact that the material migrates through the HEME filter and both HEPA filters, and that it was seen collecting on the outlet side of the HEME filter, would seem to indicate that these filters are not efficient at removing this material.

Further SRAT off-gas system modeling should help determine the extent of Hg breakthrough past the MWWT. The SRAT off-gas system has not been modeled since startup of the facility. Improvements to the efficiency of Hg stripping prior to the ammonia scrubber would seem to be the only way to prevent/mitigate the formation of the compounds found in the GC Line Filter Assembly filters and therefore prevent pluggage of this filter assembly.

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5.0 REFERENCES

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6.0 ACKNOWLEDGEMENTS

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