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Disclaimer:

Analysis of an MCU HEPA Filter

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EXECUTIVE SUMMARY

A series of direct analyses on three portions (inlet, center, and outlet) of the High Efficiency Particulate Air (HEPA) filter material from the Modular Caustic-Side Solvent Extraction Unit (MCU) have been performed; this includes x-ray methods such as X-Ray Diffraction (XRD), Contained Scanning Electron Microscopy (CSEM) and X-Ray Fluorescence (XRF), as well as Fourier Transform InfraRed spectroscopy (FTIR). Additionally, two leaching studies (one with water, one with dichloromethane) have been performed on three portions (inlet, center, and outlet) of the HEPA filter material, with the leachates being analyzed by Inductively-coupled plasma emission spectroscopy (ICPES), Semi-Volatile Organic Analysis (SVOA) and gammascan.

From the results of the analyses, SRNL feels that cesium-depleted solvent is being introduced into the HEPA filter. The most likely avenue for this is mechanical aerosolization of solvent, where the aerosol is then carried along an airstream into the HEPA filter. Once introduced into the HEPA filter media, the solvent wicks throughout the material, and migrates towards the outlet end. Once on the outlet end, continual drying could cause particulate flakes to exit the filter and travel farther down the airstream path.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AD	Analytical Development
CSEM	Contained Scanning Electron Microscopy
DEHP	Diethylhexylphthalate
DI	Deionized
FTIR	Fourier Transform InfraRed spectroscopy
HEPA	High Efficiency Particulate Air
HPLC	High Performance Liquid Chromatography
ICPES	Inductively-coupled plasma emission spectroscopy
MCU	Modular Caustic-Side Solvent Extraction Unit
NGS	Next Generation Solvent
SE	Strip Effluent
SEM	Scanning Electron Microscopy
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SVOA	Semi-Volatile Organic Analysis
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

1.0 Introduction

A HEPA filter is used at MCU ventilation system to ensure that contamination from MCU operations does not travel outside of containment. The HEPA filter requires periodical change-out due to high dose rates from accumulation of radioactive contaminants.

In January 2016, MCU started to process the higher cesium feed of Salt Batch 8B. Since that time, the HEPA filter has required a higher frequency of change-outs. Furthermore, on several occasions, the downstream MCU stack filter paper has shown signs of radioactive contamination. The mechanism by which radio-contamination migrates to and passes through the HEPA filter is not known. It is necessary to understand the nature of the problem before a proper solution can be proposed.

Savannah River Remediation (SRR) sent the Savannah River National Laboratory (SRNL) a sample from a HEPA filter removed from service on 2/5/2016, and delivered to SRNL on 7/16/2016. The sample was a 6" diameter core bored out of the HEPA, through the axis of filtration. SRNL examined the filter material and has attempted to determine the method of contamination passage through the filter media.

This scope was requested through Technical Task Request X-TTR-H-00062.[i] Details of SRNL's activities were identified in Task Technical and Quality Assurance Plan SRNL-RP-2016-00480.[ii]

2.0 Experimental Procedure

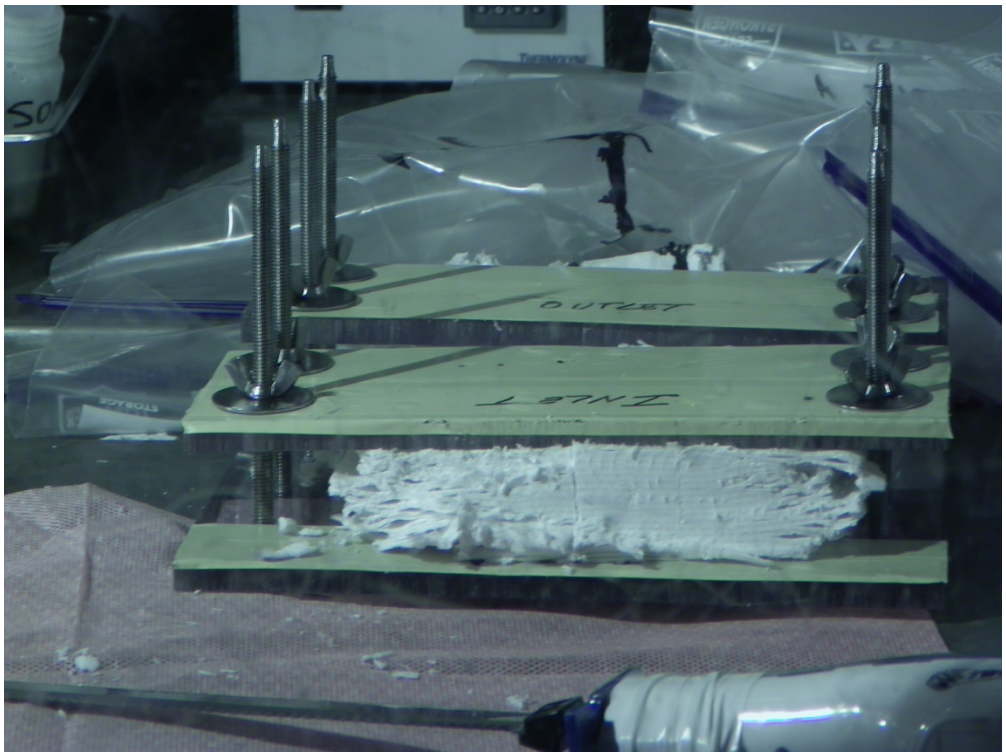
SRR Maintenance personnel used a custom built tool (Figure 1) to core a 6" diameter center portion cylinder of the filter element (~12" long) and this sample was delivered to SRNL. SRR noted the direction of air flow on the filter sample and the shipping container.

Figure 1. Coring Tool Used to Sample the HEPA Filter

Once received, the direction of flow on the packaging material was carefully noted and the filter material inspected for obvious signs of fouling. The filter was observed to be visually clean, with no discoloration or other obvious signs of issues.

SRNL devised a tool by which sections could be cut from the HEPA sample. Using a Plexiglas frame, the filter media was compressed into a roughly flat sheet, with three sections exposed for cutting. See Figure 2.

Figure 2. Cutting Frame for HEPA Filter



The orientation of the filter was noted (Inlet, Center, and Outlet). Using a small reciprocating saw, the cells technicians were able to cut 1" wide sections from the Inlet, Center and Outlet sides. With the material under compression, the cuts were fairly clean, and easily made. The long, 1" wide sections were then cut in half , leaving six sets of samples, Inlet-A, Inlet-B, Center-A, Center-B, Outlet-A, and Outlet-B.

Inlet-A, Center-A and Outlet-A were first analyzed by optical microscopy and Raman Infrared spectroscopy. Optical microscopy was used to first identify possible locations on the filter media of interest, and then the samples were sent to Analytical Development (AD) for analysis by Scanning Electron Microscopy (SEM), XRF, and XRD.

Inlet-B, Center-B and Outlet-B were each cut into two further pieces (Inlet-B1, Inlet-B2, Center-B1, Center-B2, Outlet-B1, and Outlet-B2). The B1 pieces were leached in 300 mL of deionized

(DI) water solution for ~24 hours and the leachate was analyzed by gammascan and ICPES. The B2 pieces were leached in dichloromethane for ~24 hours and the leachate analyzed by SVOA, high performance liquid chromatography (HPLC) and by gammascan.

2.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. For SRNL documents, the extent and type of review using the SRNL Technical Report Design Checklist is outlined in WSRC-IM-2002-00011, Rev. 2.[iii] Records for this work are contained in an electronic notebook ELN-A4571-00084-26.

3.0 Results and Discussion

3.1 Composition of the HEPA Filter

The HEPA filter is from Flanders Corporation. According to product documentation, the filter material is a boron silicate microfiber which contains a waterproofing binder. No further product details have been found. The sheets of filter material appear to be folded such that when sections are cut, the material separates into individual strips of material.

3.2 Leaching Tests

Samples Inlet-B1, Center-B1, and Outlet-B1 were each soaked in 300 mL of DI water for a period of 24 hours. The samples did not appear to wet appreciably and mostly floated on top of the water solution. When the samples were first introduced into the water, vigorous mixing was used to ensure all the pieces had thoroughly contacted the water. The water solutions did not discolor to any notable extent. See Figure 3.

Samples Inlet-B2, Center-B2, and Outlet-B2 were each soaked in 300 mL of dichloromethane for a period of 24 hours. The samples did wet, and sank to the bottom, indicating thorough contact with the solution. The Outlet-B2 pieces discolored the darkened solution slightly, while the Inlet and Center pieces did not. See Figure 4. The reason for the color of the Outlet-B2 leachate solution is not known and none of the later analytical results provide a reason.

Figure 3. Water Leaching

Figure 4. Dichloromethane Leaching

After 24 hours of leaching, samples of each of the six solutions were sent forward for analysis. The water leaching samples were analyzed by gammascan and ICPES (Table 1). The one-sigma analytical uncertainty is 5.0% for ^{137}Cs and 10% for ICPES.

Table 1. Gammascan and ICPES Data of Water Leachates

Sample	Cs-137 (dpm/mL)	Na (mg/L)
Inlet-B1	6.08E+04	13.8
Center-B1	7.69E+04	17.4
Outlet-B1	1.90E+05	25.6

A clear increase in analyte concentrations is noted from inlet to outlet, although the actual concentrations are low. Sodium is the only ICPES analyte in meaningful concentration (trace levels of Al, B, Ba, Ca, Mg, Mn, Sr and Zn were noted) in the samples, and the low levels would suggest that aqueous salt solution uptake into the HEPA filter is not occurring. SRNL cannot discount the possibility that the water leach could act as a stripping solution on any solvent material that was present in the HEPA, and therefore, the cesium and sodium values may simply be from organic entrainment.

For the dichloromethane samples, moderate levels of ^{137}Cs were noted as well as appreciable concentrations of Modifier, a component of the MCU solvent (Table 2). In addition, an SVOA scan was used to identify other organic compounds.[∇]

Table 2. Gammascan and ICPES Data of Dichloromethane Leachates

Sample	Cs-137 (dpm/mL)	Modifier (HPLC, mg/L)	^{137}Cs:Modifier ratio	Diisooctylphthalate (SVOA, mg/L)
Inlet-B2	8.53E+04	64000	1.33	2.4
Center-B2	2.64E+05	312000	0.846	39
Outlet-B2	4.41E+05	218000	2.02	37

The one-sigma analytical uncertainty is 5.0% for ^{137}Cs, 10% for Modifier and 20% for Diisooctylphthalate.

As with the water leaches, there seems to be a general increase in analyte concentrations from inlet to outlet, although the HPLC data for Modifier declines from center to outlet. The substantial concentrations of Modifier would seem to indicate that a volatilized whole solvent uptake into the HEPA is occurring. Furthermore, the ^{137}Cs to Modifier ratio is suggestive of a depleted solvent (such as from the solvent hold tank where the ^{137}Cs:Modifier ratio would be ~1.05), and not highly cesium loaded solvent material from the extraction or scrub contactors (^{137}Cs:Modifier ratio of ~2500). Diisooctylphthalate (a commonly used plasticizer) was found in

[∇] In the inlet sample (only), the SVOA scan found a few other compounds at low concentrations. For example, 2,3-dichloro-2-methylbutanoic acid was identified at 2 mg/L concentration. The unusual chlorinated nature of these chemicals combined with the low concentrations leads SRNL to believe that these identifications are a result of high uncertainty analytical instrument peak matching.

all three samples, although at varying levels. It is possible that this material is part of the HEPA filter material construction.

3.3 Optical Microscopy and Raman FTIR Results

Optical microscopy was used to locate spots of potential interest on the sample pieces. Once located, Raman FTIR was to examine the points to determine composition. There were no obvious visual indications of contamination. Figure 5 shows the results of analysis of three points on an unused portion (a clean, different HEPA filter of the same type) of HEPA filter. The spot corresponding to the red trace showed evidence of disiloxane compounds. The spot corresponding to the purple trace showed evidence of diethylhexylphthalate (DEHP - a plasticizer) and some sort of an amine compound. The spot corresponding to the blue trace shows strong evidence of DEHP. Given that the sample was a clean, unused piece, we take these three compounds as background signals.

Figure 6 shows the results of analysis of two points on a piece from the inlet portion of the HEPA filter. The spot corresponding to the blue trace showed evidence of sec-butylphenol (a decomposition product of the modifier) and DEHP. The spot corresponding to the red trace showed evidence of modifier and DEHP.

Figure 7 shows the results of analysis of two points on a piece from the center portion of the HEPA filter. The spot corresponding to the blue trace showed evidence of aluminosilicates. The spot corresponding to the red trace showed evidence of modifier and DEHP.

Figure 8 shows the results of analysis of three points on a piece from the inlet portion of the HEPA filter. The spot corresponding to the red trace showed evidence of DEHP. The spot corresponding to the blue trace showed evidence of modifier and DEHP. The spot corresponding to the purple trace showed evidence of ethyl acrylate and DEHP.

Figure 9 shows an examination of DEHP and modifier at various spots, and shows that the modifier:DEHP concentration ratio changes from the inlet to the other pieces, corroborating the leaching results in Table 2.

The disiloxane compound, the amine and the DEHP noted in the unused piece are attributed to inherent characteristics of the HEPA filter. The disiloxane and amine compounds are probably in low initial concentrations that are washed away during use and no longer seen. The DEHP is probably instead actually diisooctylphthalate which was noted in the SVOA results; it is difficult to distinguish between the two compounds with FTIR. The aluminosilicate compound is likely some small quantity of aerosolized material from the MCU process. The ethyl acrylate is a total unknown and there is no reason for it to be there. This may be a spurious result. Modifier is the only organic compound found in each used section and this corroborates the leaching results.

Figure 5. FTIR scan of an Unused Piece

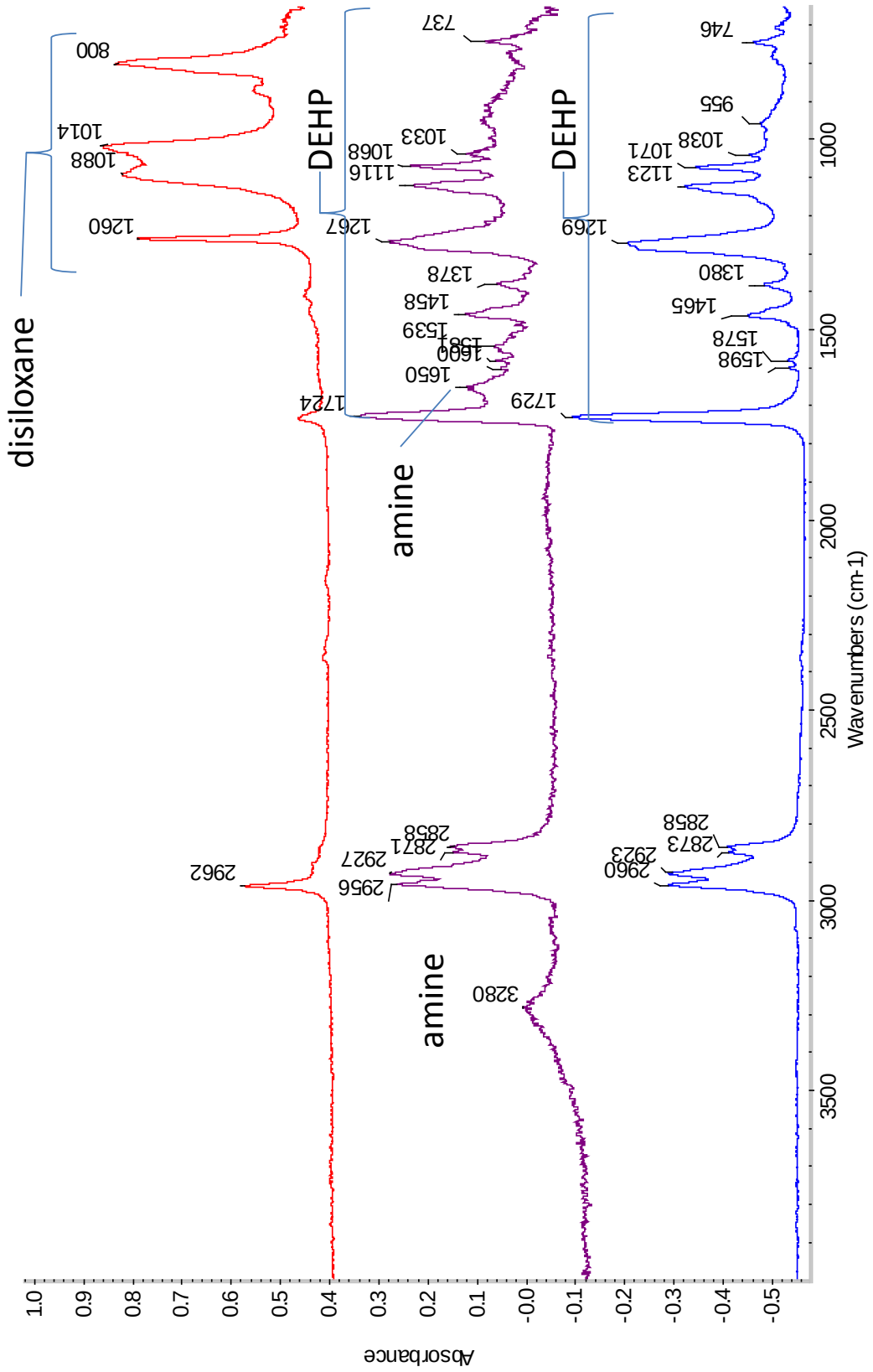


Figure 6. FTIR Scan of an Inlet Piece

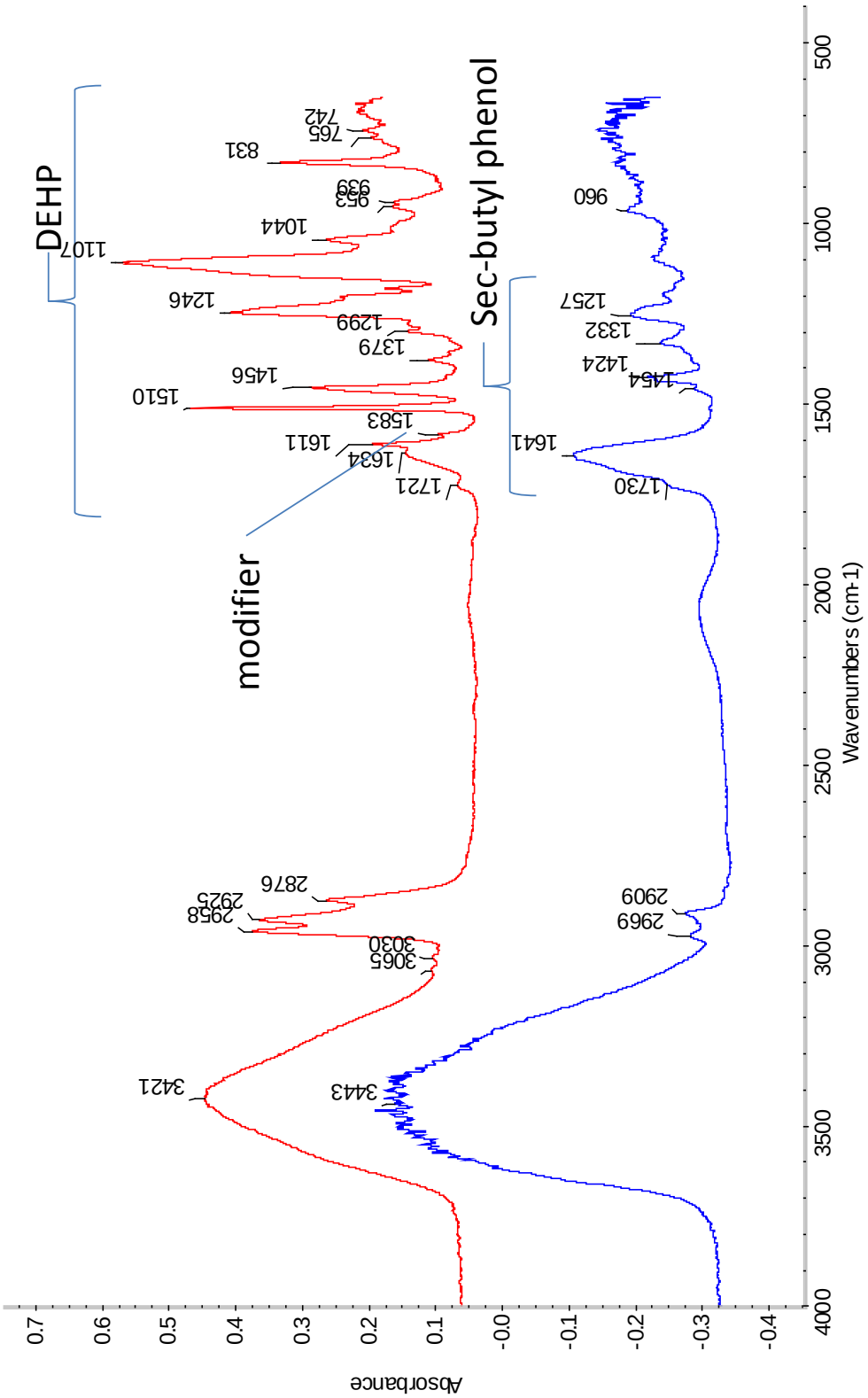


Figure 7. FTIR Scan of a Center Piece

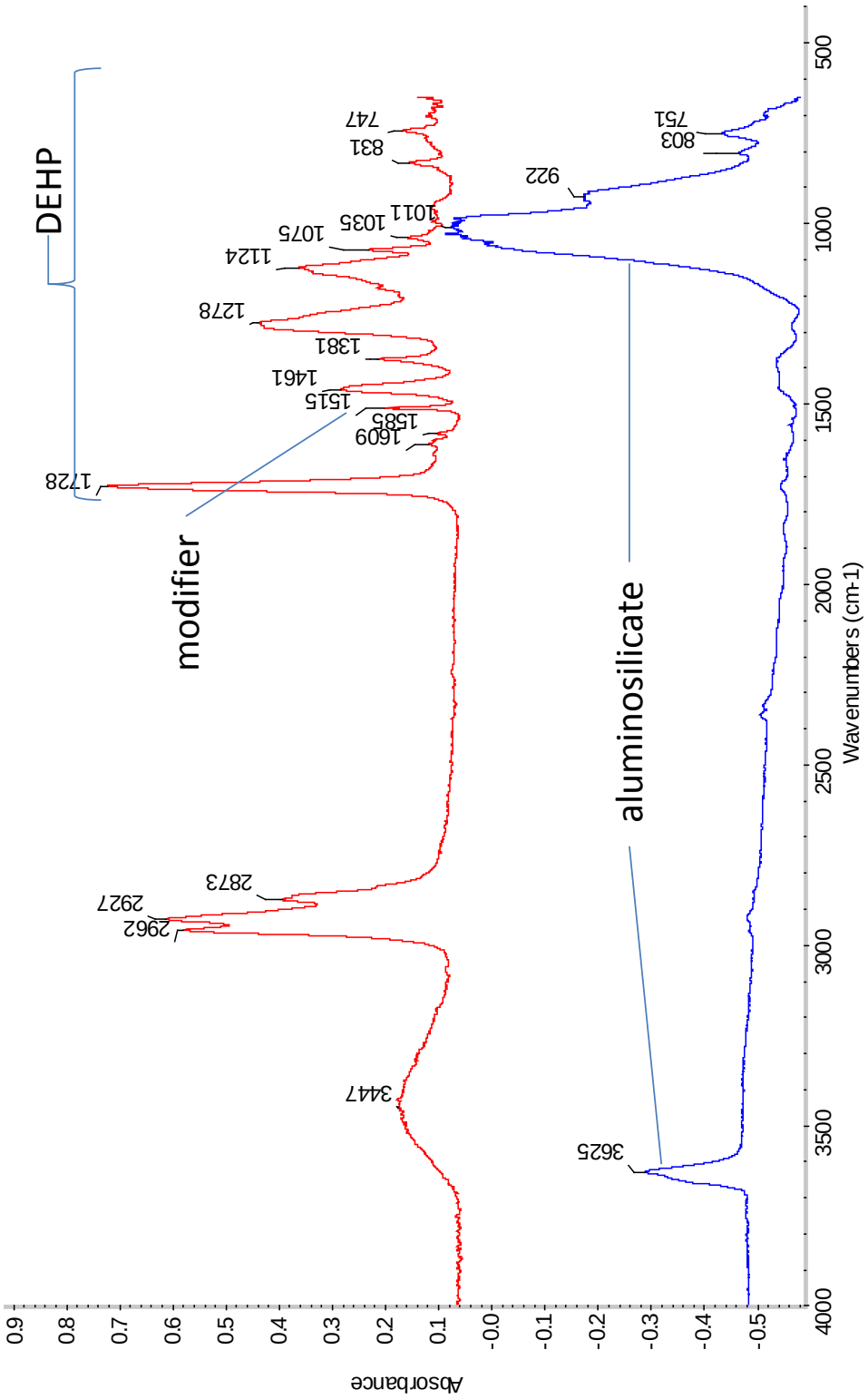


Figure 8. FTIR Scan of an Outlet Piece

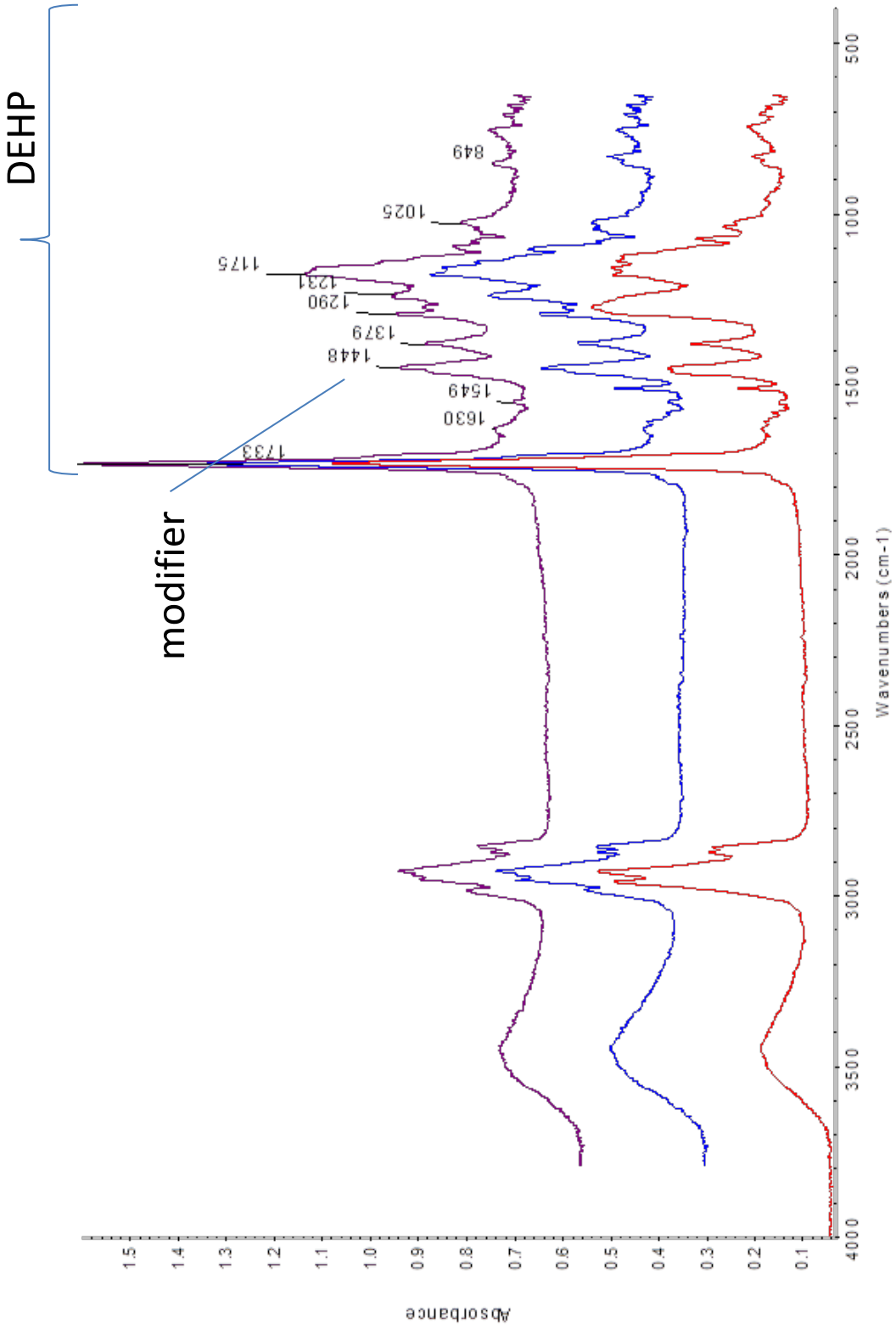
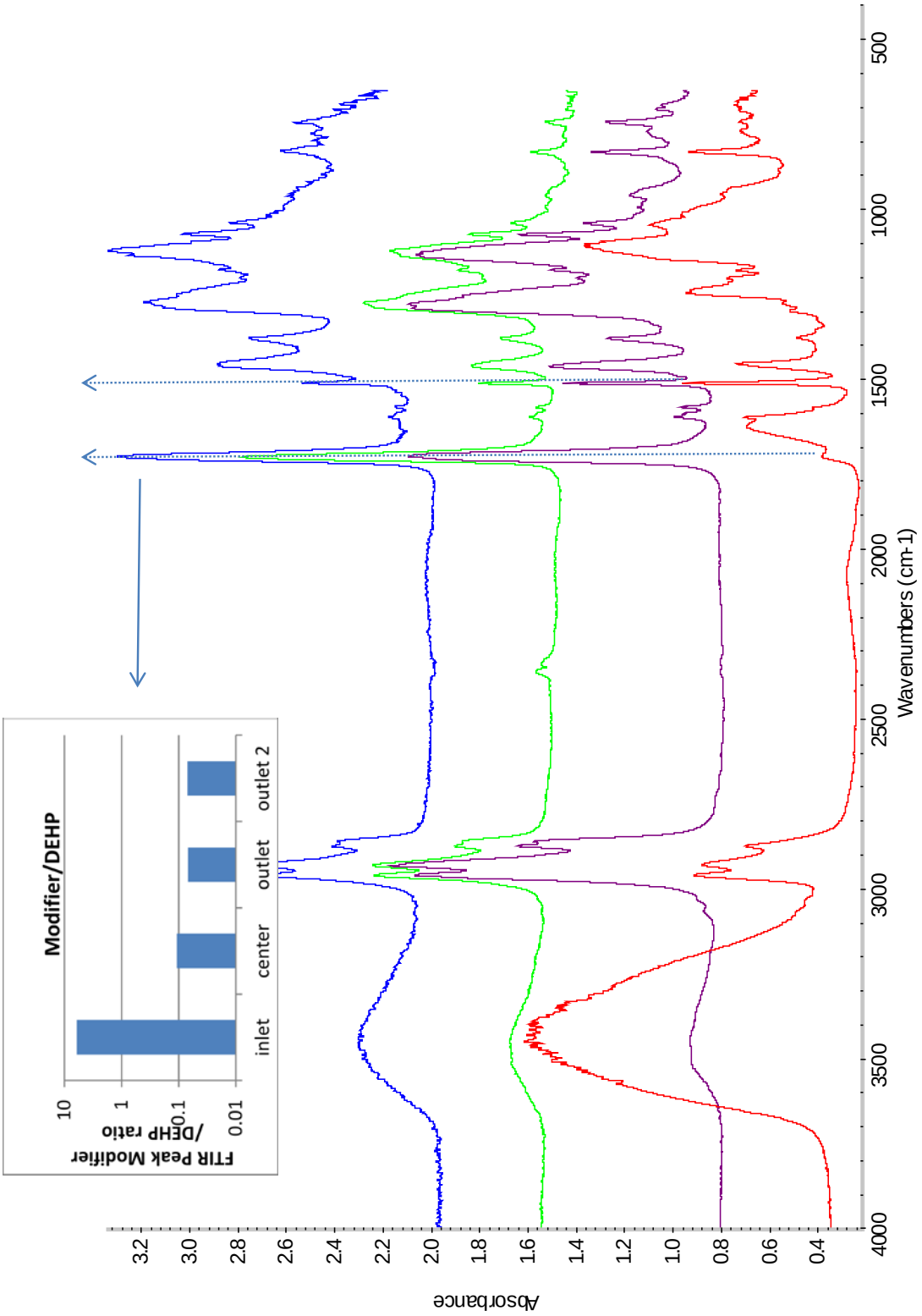


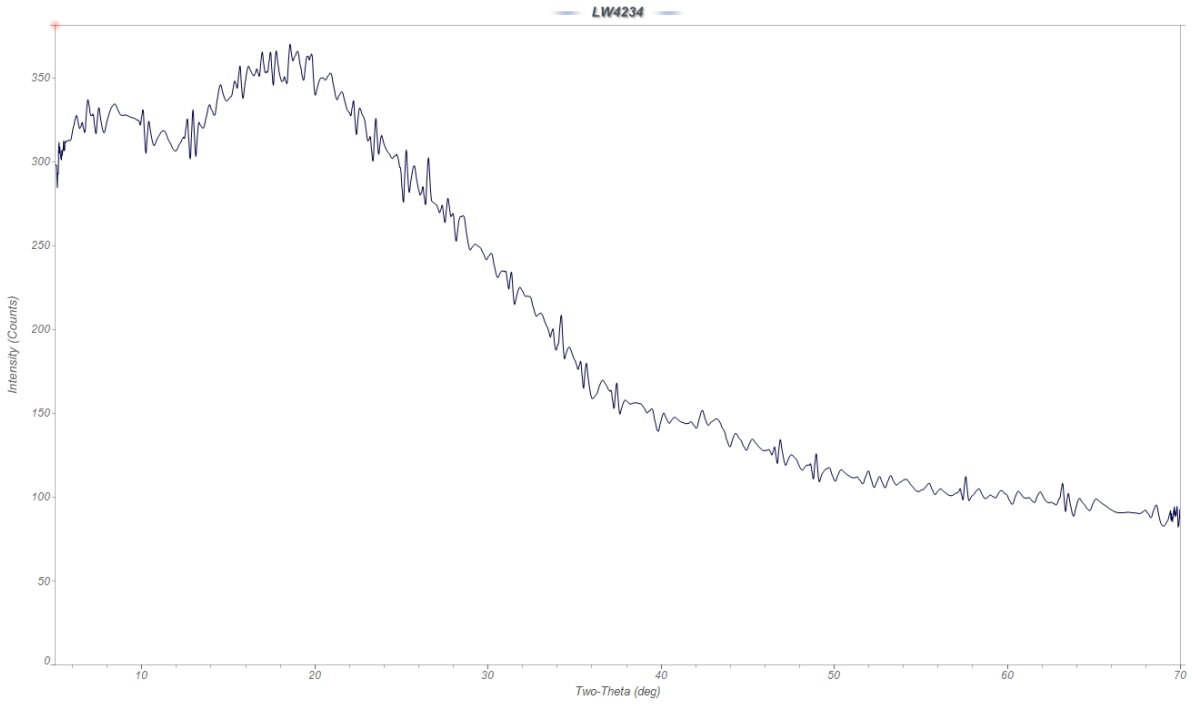
Figure 9. Modifier vs. DEHP Concentrations



3.4 XRD and XRF Results

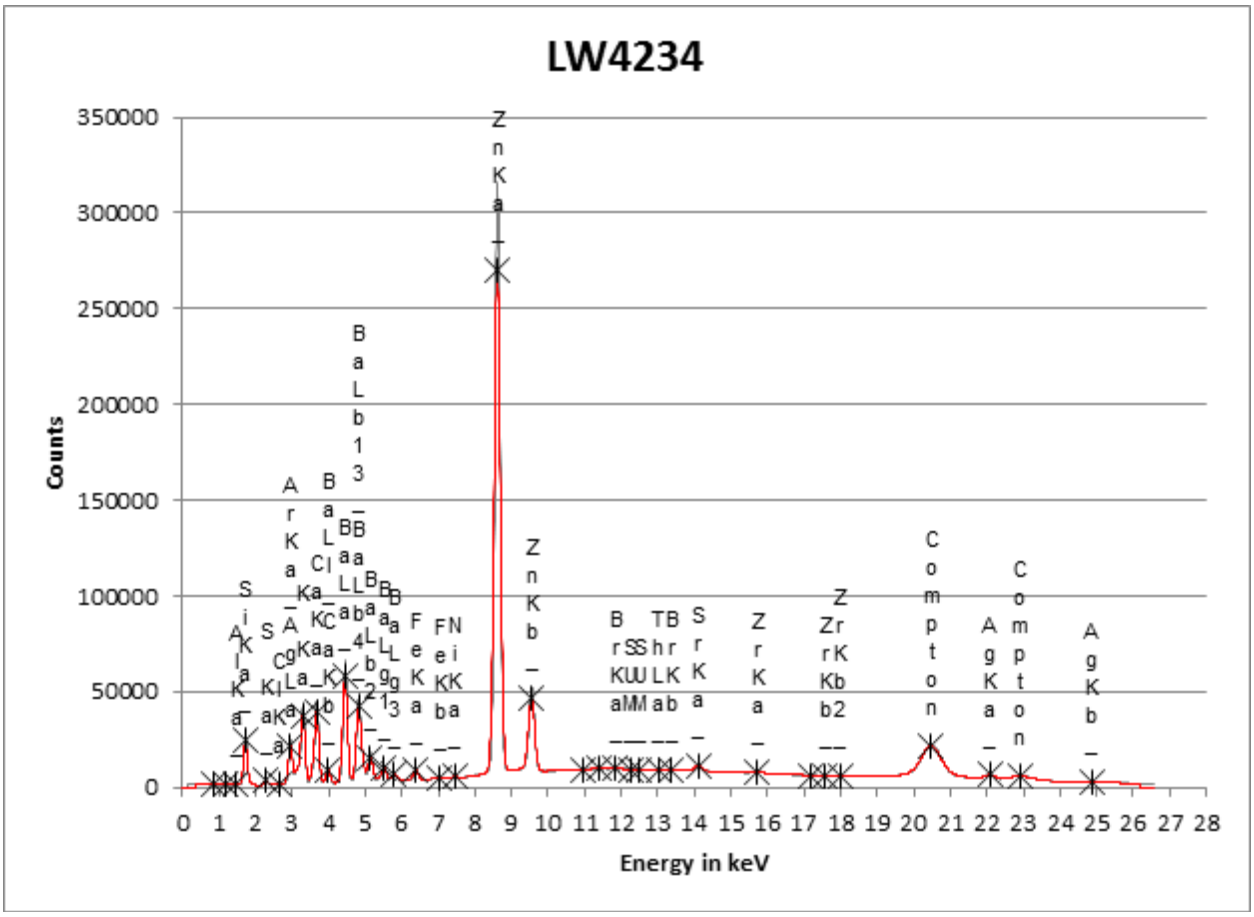
Both XRD and XRF methods are suitable for crystalline material, which is usually exhibited by inorganic salts. Both methods were used to scan spots on the filter material and compared to a blank, clean sample. In all cases, the samples gave results that appeared as the blank samples – no apparent crystalline materials were present (Figures 10 and 11).

Figure 10. Typical Result from XRD



The XRD result of a broad, featureless spectrum indicates a lack of crystalline signals.

Figure 11. Typical Result from XRF



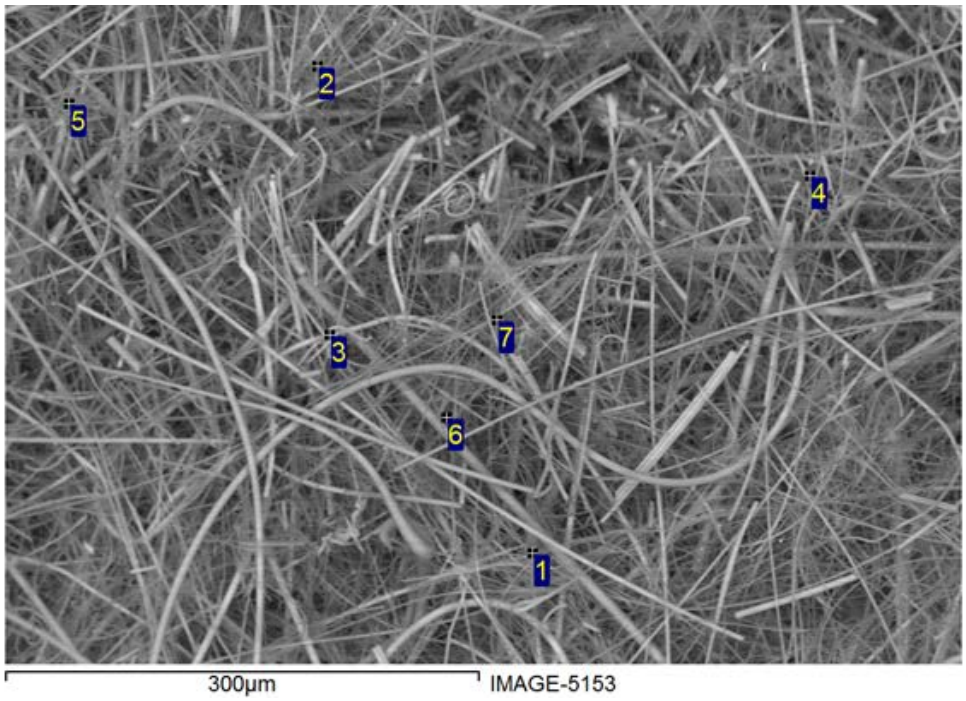
The XRF result indicates the major analyte is zinc, suggestive of some sort of zinc coating on the filter material.

Overall, the XRD and XRF results lead SRNL to believe that salt solution, which would normally contain many analytes that would show up in these methods – is not likely to have saturated the filter media.

3.5 CSEM Results

CSEM is a microscopy method that can examine selected points on a sample for elemental composition. See Figure 12 for a typical example.

Figure 12. Example of CSEM Sample



In this example, the scale is approximately 100 µm per inch; the analyst located 7 spots of possible interest. Each post is then subjected to an electron beam which generates a spectrum of elemental signals. The spectrum is semi-quantitative and as such the areas of the peaks may, but do not necessarily correspond to analyte concentrations.

Figure 13 is an example spectrum of a clean, unused sample. This spectrum shows the expected silicon and oxygen (from the glass matrix) as well as zinc, barium and a few other peaks (the prevalence of the zinc and barium suggest some sort of coating as part of the substrate). Figure 14 is a spectrum from point #1 in Figure 12. While it shows the expected background peaks from the blank, it also shows a strong signal from iron, likely indicating some sort of particle of steel or rust from the system.

Other than the background signals and spots which we attribute to steel or rust, there is very little to be seen in any of the SEM results that would be expected of salt solution. Figure 14 is a representative sample. Any amount of salt solution (feed or decontaminated) should dry out in the fibers of the filter to leave inorganic deposits such as aluminates, aluminosilicates, or carbonates.

Figure 13. Spectrum of CSEM Blank

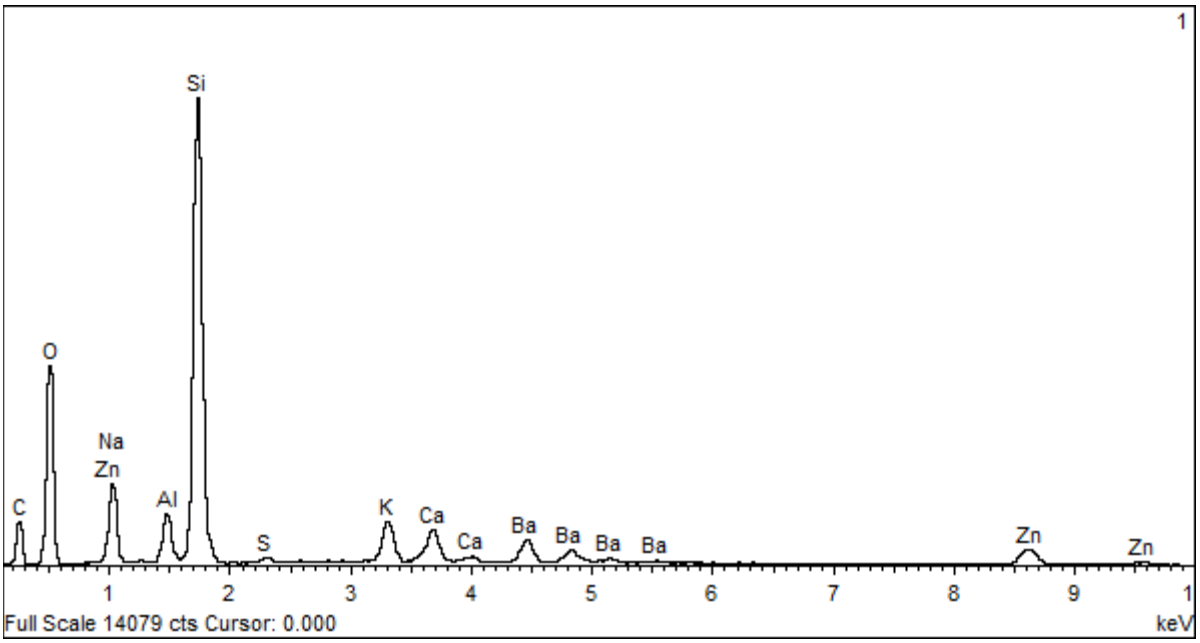
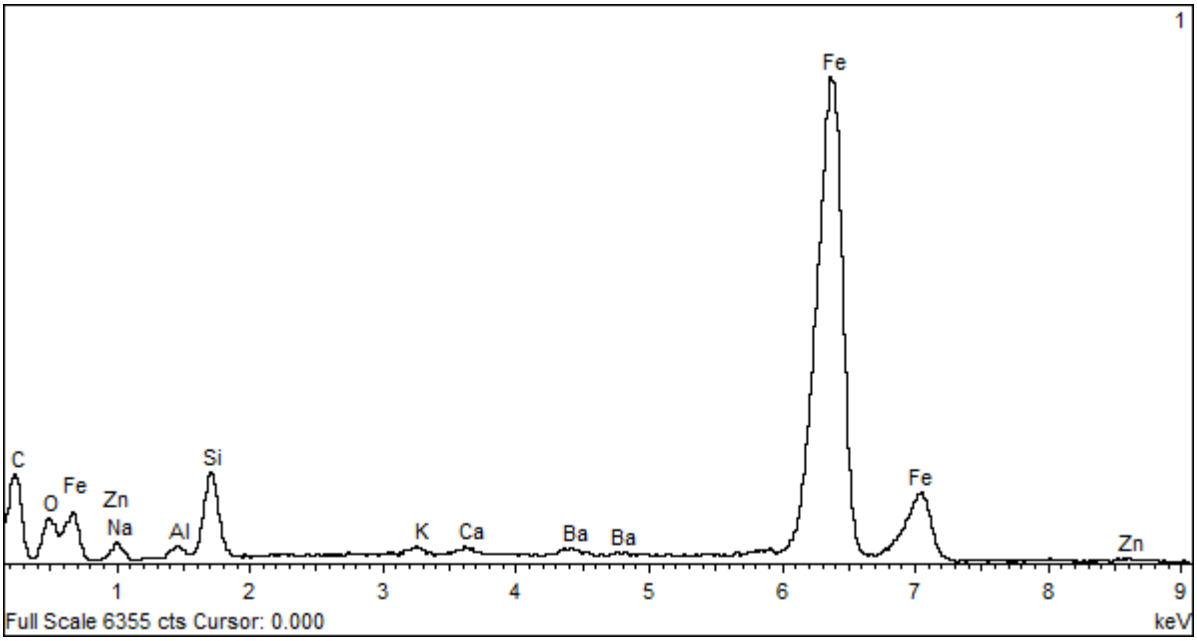


Figure 14. CSEM Spectrum of Point #1



4.0 Conclusions

A series of direct analyses on three portions (inlet, center, and outlet) of the HEPA filter material have been performed; this includes x-ray methods such as XRD, CSEM and XRF, as well as FTIR. Additionally, two leaching studies (one with water, one with dichloromethane) have been performed on three portions (inlet, center, and outlet) of the HEPA filter material, with the leachates being analyzed by ICPES, SVOA and gammascan.

In total, the analyses lead to several conclusions:

- The sample results indicate that the types of analytes are the same through the depth (inlet, center, outlet) of the HEPA filter. In fact, most of the analytes increase in concentration as outlet>center>inlet. This implies that the material intruding into the filter is wicking through the filter and then concentrating in the outlet, following the flow of air.

- As the types of analytes are consistent through the depths of the samples (point above), it is reasonable to assume that the results of the HEPA filter core are representative of the HEPA filter as a whole; there is no plausible mechanism to introduce an intruding solution to small, selected areas on the face of the filter (i.e., a compact stream of liquid), as opposed to a more diffuse mist hitting the HEPA filter face.

- There is very little intrusion of salt solution into the filter. If salt solution was entrained into the filter, there would be evidence of salt residues, such as carbonate. Furthermore, the water leaching would have provided for much higher concentrations of sodium and other cations.

- The evidence suggests small amounts of silicate material and some iron containing materials (possibly rust) are present in the filter.

- The dichloromethane leachings gave easily detectable concentrations of modifier (a component of the MCU solvent). As there is no known mechanism for modifier to be by itself without the other components of the solvent, the presence of modifier implies that bulk solvent is being introduced into the HEPA filter.

- Small concentrations (on the order of ~1E+05 dpm/mL) of ^{137}Cs are present in both leaching solutions. While it is difficult to say if the ^{137}Cs is from aqueous material or from the solvent, the low concentrations imply that raw salt solution, strip effluent (SE), and/or Cs-loaded solvent are not being loaded into the HEPA filter. Instead, cesium-depleted solvent is the most likely candidate for the material being loaded into the HEPA filter.

In summary, SRNL feels that cesium-depleted solvent is being introduced into the HEPA filter. The most likely avenue for this is mechanical aerosolization of solvent, where the aerosol is then carried along an airstream into the HEPA filter. Once introduced into the HEPA filter media, the solvent wicks throughout the material, and migrates towards the outlet end. Once on the outlet end, continual drying could cause particulate flakes to exit the filter and travel farther down the airstream path.

5.0 References

[i] P. E. Fogelman, "Analyze MCU HEPA Filter Core to Characterize Contaminants", X-TTR-H-00062, June 15, 2016.
[ii] T. B. Peters, F. F. Fondeur, "Task Technical and Quality Assurance Plan for Studies of MCU HEPA Filter", SRNL-RP-2016-00480, August 4, 2016.
[iii] Savannah River National Laboratory, "Technical Report Design Check Guidelines", WSRC-IM-2002-00011, Rev. 2.

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