White Paper -- Inorganic Wildfire Chemistry Methods

SUPPLEMENTAL CHEMICAL TESTS FOR THE ANALYSIS OF WILDFIRE ASH AND CORROSION POTENTIAL USING pH, CONDUCTIVITY, AND SCANNING ELECTRON MICROSCOPY / DISPERSIVE X-RAY ANALYSIS

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The data presented in this paper is a "draft" document summarizing our development of new and practical methods to measure the potential for corrosion and chemical alteration associated with wildfire debris. The paper is being revised when new information becomes available

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Daniel M. Baxter – Environmental Analysis Associates, Inc. – 2019

1.0 BACKGROUND

The current analytical method used to determine the presence and relative concentration of wildfire soot, char, and ash indoors following a wildfire is Optical Microscopy (Transmitted and Reflected Light). Because the identification of particles subjected to pyrolysis (burning) requires simultaneous examination of their transmitted and reflected light properties, a wide range of magnifications and microscopic illumination methods are required to ensure proper detection and quantification. These methods include reflected light, reflected light dark field, reflected polarized light, transmitted light, and transmitted polarized light. This is especially important for evaluating “ash” or colored opaque debris found in wildfire samples. Even when the lab is equipped with the proper microscopic capabilities, there are still limitations and interferences that can prevent a full and accurate sample analysis. More importantly, microscopy methods cannot directly quantify the potential for corrosion “damage” as a result of the changed chemical properties found in combustion samples. This additional chemistry information can readily be measured using alkalinity (pH) and conductivity analysis; and Scanning Electron Microscopy (SEM) combined with X-ray elemental analysis to measure the soluble cation/anions found in combustion ash, that may be responsible for potential corrosion. These methods are addressed in this paper.

Electron Microscopy (SEM and TEM) in general, have very limited and specific uses for analyzing fire-related carbonaceous particles. The SEM and dispersive X-ray capabilities are not suitable for detecting fine aciniform soot particles, however, they are essential in differentiating non-carbonaceous look-alike (interference) particles from “char” particles in cases where they cannot be resolved by Optical Microscopy methods alone. Although being offered as a test method for analysis of wildfire soot by some laboratories, the ASTM D6602[25] Transmission Electron Microscopy (TEM) method has only limited additional value in assessing carbonaceous “soot” or other interference particles. Large soot clusters commonly associated with vegetation/wild fires are more easily observed and quantified by using Optical Microscopy analysis. TEM analysis results are often both inconclusive and misleading for several reasons.

1. Wildfire and structure fire “soot” residues are generated at lower temperatures and contain both fully combusted (non-soluble and non-volatile) and partially combusted (semi-soluble and semi-volatile) aciniform soot particles. The partially combusted soot particles can comprise a large percentage of soot generated by vegetation burning, and often form large resinous 5-50µm size clusters and chains (especially in structure fires) that are not carbon black.

2. The ASTM D6602[25] TEM method was designed specifically for the analysis and differentiation of carbon black from other “non-volatile” fugitive industrial or automotive aciniform combustion emissions. The ASTM sample preparation and analysis procedures are by design only capable of analyzing and differentiating those “non-soluble” and “non-volatile” pure carbon soot particles, from other aciniform soot sources that may contain percent levels of sulfur or other elements (primarily heavy metals).

3. The sample preparation method requires the collected wipe samples to be ultra-sonicated in a solvent (chloroform or acetone) to remove and disperse the soot particles from the collection media. This sampling procedure is designed to evenly break up aggregate particles in a solvent so that small sub-samples can be uniformly transferred drop-wise onto a TEM specimen mount (grid) and evaporated.

As a result, the preparation procedure can alter the identifying features of soot and other particles associated with vegetation burning (i.e. large aciniform clusters). An unknown percentage of the "semi-volatile" soot particles will also be dissolved into residues that are no longer recognizable as "soot" (even before they are placed into the TEM for analysis).

4. Once the remaining fine soot and other particles are placed in the high vacuum required for TEM analysis, additional particle loss can occur through sublimation and vaporization by the electron beam.

5. Additionally, the analysis method is only marginally helpful in differentiating the <u>non-volatile</u> portion of wildfire "soot" particles (if present) from the many other environmental sources that have both a similar morphology and elemental chemistry.

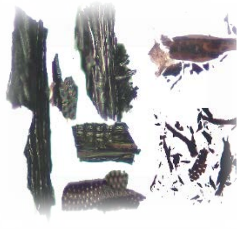
Based on these uncertainties, the TEM (and SEM) methods cannot reliably detect the semi-volatile soot particles commonly associated with wildfires or structure fires (even when they are present). Furthermore, the remaining "non-volatile" soot particles cannot be accurately quantified or differentiated from a wildfire or other background sources without manually performing a comprehensive particle-by-particle X-ray analysis. Since <u>automated</u> X-ray analysis cannot be performed in a TEM, a thorough analysis is very labor intensive, subjective, and costly. It is also a fact that large (10-50μm) soot clusters and chains (a characteristic of wildfire soot) can occasionally infiltrate buildings when in close proximity to the fire. These soot clusters, however, can routinely be detected and quantified on tape lift samples using current Optical Microscopy methods <u>without a concern for sample loss in the preparation or analysis procedure, or the need for the high magnifications provided by the Transmission Electron Microscope</u>.

If an investigation requires the assessment of potential "damage", microscopy analyses in general are inadequate and cannot provide any direct chemical or physical measurements for corrosion chemistry or "damage". Furthermore, there is no measurement that could show the dust chemistry is significantly different than the normal background dust. The most appropriate chemical tests for this purpose are acidity/alkalinity (pH), conductivity, and elemental composition of the dust and soluble ions (i.e. cation/anions) using SEM/X-ray analysis. These chemical tests can also provide an additional confirmation of the presence of wildfire "ash" when the Optical Microscopy methods may be inconclusive.

2.0 THE DEFINITION OF WILDFIRE RESIDUE

There are morphologically particle categories associated with combustion (pyrolysis) in general (soot, char, and ash), as well recognizable vegetation derived particles and elemental chemistry that can help differentiate "wildfire" particles from other combustion debris. The identification of combustion particles using microscopy methods is not a precise science and is based on the morphological classification of particles. All fire combustion particles are transitional in nature and their composition is determined by the source material, combustion temperature, and decomposition over time. Because char, aciniform soot, and especially "ash" can rapidly degrade over time due to weathering, biologic decomposition, and water / humidity impact; differentiation using Optical Microscopy can become more subjective and less reliable over time. Optical Microscopy methods do not address the odors and organic compounds that are associated with incomplete combustion and may remain within the pore structure of soot and char particles. Some of these compounds have a very short residence time (days–weeks), while others may linger for weeks to months. The organic compounds need to be addressed using other analysis methods. The difference in chemistry between "fresh" fire residues and older re-suspended residues can also be significantly different. As a result, the potential impact (e.g. visual damage, corrosion potential, and even health effects) can be significantly different over time. These differences cannot be readily determined by Optical Microscopy methods alone. There are also known interferences that can complicate the analysis.

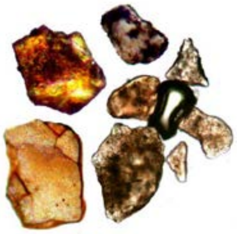
Optical Micrographs of the common types of wildfire residue particles are shown below:

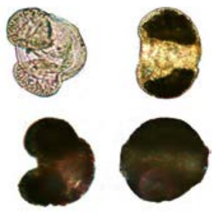

Char


Ash


Aciniform soot


Burned Phytoliths/Ash


Burned mineral grains


Un-burned – burned pollen

The definition and characteristics of each type of wildfire combustion particle are described below:

a. **Ash**[1,2,32] – The brown to silver/gray alkali "semi-soluble" salt residues (primarily Calcium, Potassium and Magnesium, oxides) consisting of partial to fully combusted (decarbonized) vegetation debris and plant phytoliths (silica and Calcium oxide crystals). Although "ash" particles can retain the morphology remnants of the plant structure, and micro-crystalline birefringence properties, they can also resemble other commonly found optically diffuse and porous minerals such as drywall dust. As a result, accurate quantification by Optical Microscopy can be difficult and highly variable. Furthermore, a high percentage of ash particles are fragile and highly soluble. They can easily break apart when subjected to physical manipulation and placed in refractive index oils, stain, solvents, or water. Ash from vegetative combustion has a distinct "alkali" chemistry primarily from highly soluble potassium salts, and the absence of buffering chloride (Cl^-) anions. This chemistry is useful as an indicator for the presence of ash, and determining the soluble cations / anions that are responsible for elevated pH.

b. **Char**[1,2] – Partially burned and angular black/brown vegetation debris that still retains characteristics of the original plant or cellulosic material. This material consists of angular and fractured cell membrane/walls. Because the particles can be optically opaque and appear black in transmitted light microscopy, the identification of residual vegetative structure often requires reflected light dark field microscopic illumination to see the plant structure. The pH of vegetation char particles is relatively neutral to weakly basic (pH 6.5-7.8) because of the lower concentration of "soluble" cations and anions that are still "bound" in the plant structure.

c. **Aciniform Soot particles**[1,2,25] – Small dark black/brown/gray aciniform clusters of sub-micron to 50 micron spherical particles clusters composed of approximately more than 80% carbon. Most soot particle "clusters" associated with condensed material on indoor surfaces can be visually identified with Optical Microscopy at magnifications of 200–1,000x. Soot particles from outdoor vegetative burning are typically "blown off" in the crown of the fire, are generated at a lower temperature, and are pH neutral because of the low concentration of "soluble" cations and anions. "Soot" particles are not found as a significant portion of infiltrated or settled wildfire particles. Soot particles are the major fire particle category usually associated with indoor fires.

d. **Burned/carbonized clays & mineral grains**[32] - Soil particles (clays, mineral grains) that exhibit partial combustion / heating during intense fires. The changes in surface coloration, texture, and carbon deposition, can be recognized by using both transmitted and reflected light (dark field) optical microscopy.

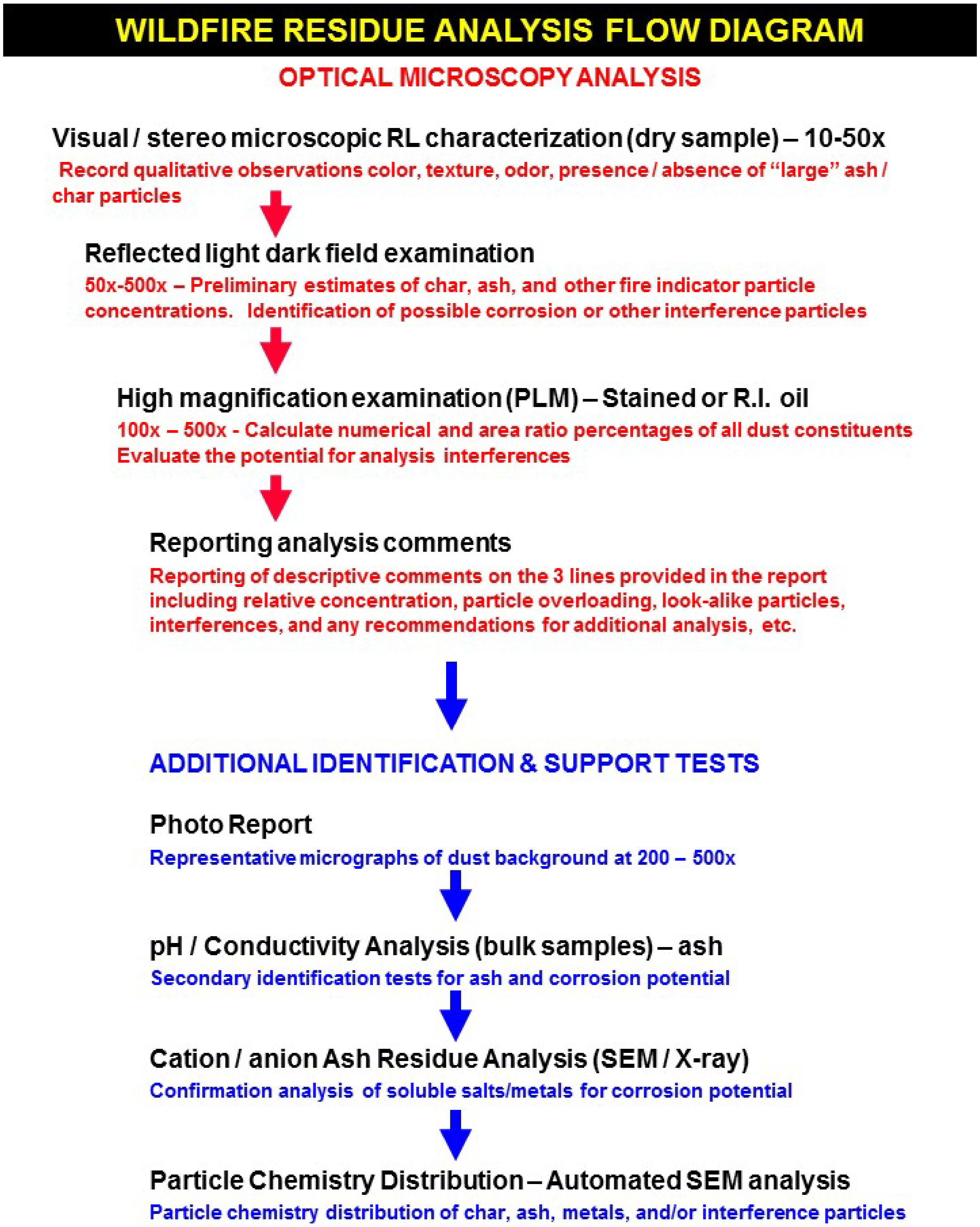
e. **Burned plant phytoliths**[4,5,6,7,8,9,10,11] – Distinct Calcium oxide and silica crystals remaining after combustion of the cellulosic cell wall structure of vegetation. The burned vegetation source can sometimes identified by the type of phytoliths present.

f. **Burned pollen grains**[1] **-** Pollen grains with carbonized or "singed" surfaces clearly different than "decayed" pollen. Detection of burned pollen grains in multiple microscopic fields-of-view is considered significant. The burned vegetation source can sometimes be identified by the type of pollen present.

3.0 INTEGRATION OF OPTICAL MICROSCOPY AND CHEMISTRY METHODS

Optical Microscopy[1,2,23] is the recommended method used to first evaluate the presence or absence of wildfire or structure fire residue in the sample. When "char" and "ash" concentrations are relatively high (e.g. >10%), employing the additional chemical tests may not be necessary unless there are specific "damage" claims being made, or more precise identification of the fire source is in question. When fire residue levels are marginally elevated (e.g. 3-5%), additional analysis methods can differentiate "atypical" fire impacted samples from background dust or inferences from corrosion or other look-alike particles.

A flow diagram for the various and integrated fire analysis methods provided by EAA is illustrated below.



WILDFIRE RESIDUE ANALYSIS FLOW DIAGRAM

OPTICAL MICROSCOPY ANALYSIS

Visual / stereo microscopic RL characterization (dry sample) – 10-50x

Record qualitative observations color, texture, odor, presence / absence of "large" ash / char particles

Reflected light dark field examination

50x-500x – Preliminary estimates of char, ash, and other fire indicator particle concentrations. Identification of possible corrosion or other interference particles

High magnification examination (PLM) – Stained or R.I. oil

100x – 500x - Calculate numerical and area ratio percentages of all dust constituents
Evaluate the potential for analysis interferences

Reporting analysis comments

Reporting of descriptive comments on the 3 lines provided in the report including relative concentration, particle overloading, look-alike particles, interferences, and any recommendations for additional analysis, etc.

ADDITIONAL IDENTIFICATION & SUPPORT TESTS

Photo Report

Representative micrographs of dust background at 200 – 500x

pH / Conductivity Analysis (bulk samples) – ash

Secondary identification tests for ash and corrosion potential

Cation / anion Ash Residue Analysis (SEM / X-ray)

Confirmation analysis of soluble salts/metals for corrosion potential

Particle Chemistry Distribution – Automated SEM analysis

Particle chemistry distribution of char, ash, metals, and/or interference particles

When additional information is required to determine the fire residue chemistry, the pH, Conductivity, and cation/anion chemistry can be determined from micro-vacuum or bulk dust samples. Tape lift samples cannot be used for these procedures. Tape samples are the preferred collection method for obtaining the particle chemistry distribution using automated SEM/X-Ray analysis.

4.0 CHEMICAL PROPERTIES OF VEGETATION CHAR AND ASH

The chemistry of wildland fires is best described in a research paper published in Earth-Science Reviews entitled "*Wildland Fire Ash: Production, Composition, and Eco-Hydro-Geomorphic Effects*[33]. Under most wildland fire conditions combustion is incomplete and only some of the fuel is actually charred. This incomplete combustion generates pyrogenic organic compounds formed or transformed during the fire and includes a continuum of C-rich solid organic materials from charred vegetation biomass. At low combustion completeness (typically >450^{0}C), most organic carbon is volatilized and the remaining is composed of mineral ash. The ash is composed mainly of Calcium, Magnesium, Sodium, Potassium, Silicon, and Phosphorous in the form of inorganic carbonates, whereas at temperatures >580^{0}C the most common forms are oxides (and hydroxides) that have an elevated pH when placed in solution. The chemical reactions for the most common ash mineral residues are described below:

Ash Combustion Chemical Production:

$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$ (600-840^{0}C)

$K_2CO_3 + \text{heat} \rightarrow K_2O + CO_2$ (1100-1400^{0}C)

$MgCO_3 + \text{heat} \rightarrow MgO + CO_2$ (580-630^{0}C)

When subjected to hydration, atmospheric moisture, CO_2, and degradation over time, the reactive oxides and hydroxides (responsible for the elevated pH of "fresh" ash) are converted into carbonates, bi-carbonates, and more neutral salts. Empirical measurements have shown the hydroxides of Potassium (K) have the greatest impact on the soluble pH. These reactions are described below:

Ash Rehydration and Degradation:

$CaO + H_2O \rightarrow CaO + Ca(OH)_2$ (strong base 12.3 # 1mM/liter)

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$

$K_2O + H_2O \rightarrow 2\ KOH$ (strong base = 11.95 @ 1mM/liter)

$MgO + H_2O \rightarrow Mg(OH)_2$ (neutral buffer, pH ~7.0)

Major temperature thresholds that determine the char, ash, and soil chemistry produced during a wildfire is graphically represented below in Figure 1 from the publication *Wildland Fire Ash: Production, Composition, and Eco-Hydro-Geomorphic Effects*[33].

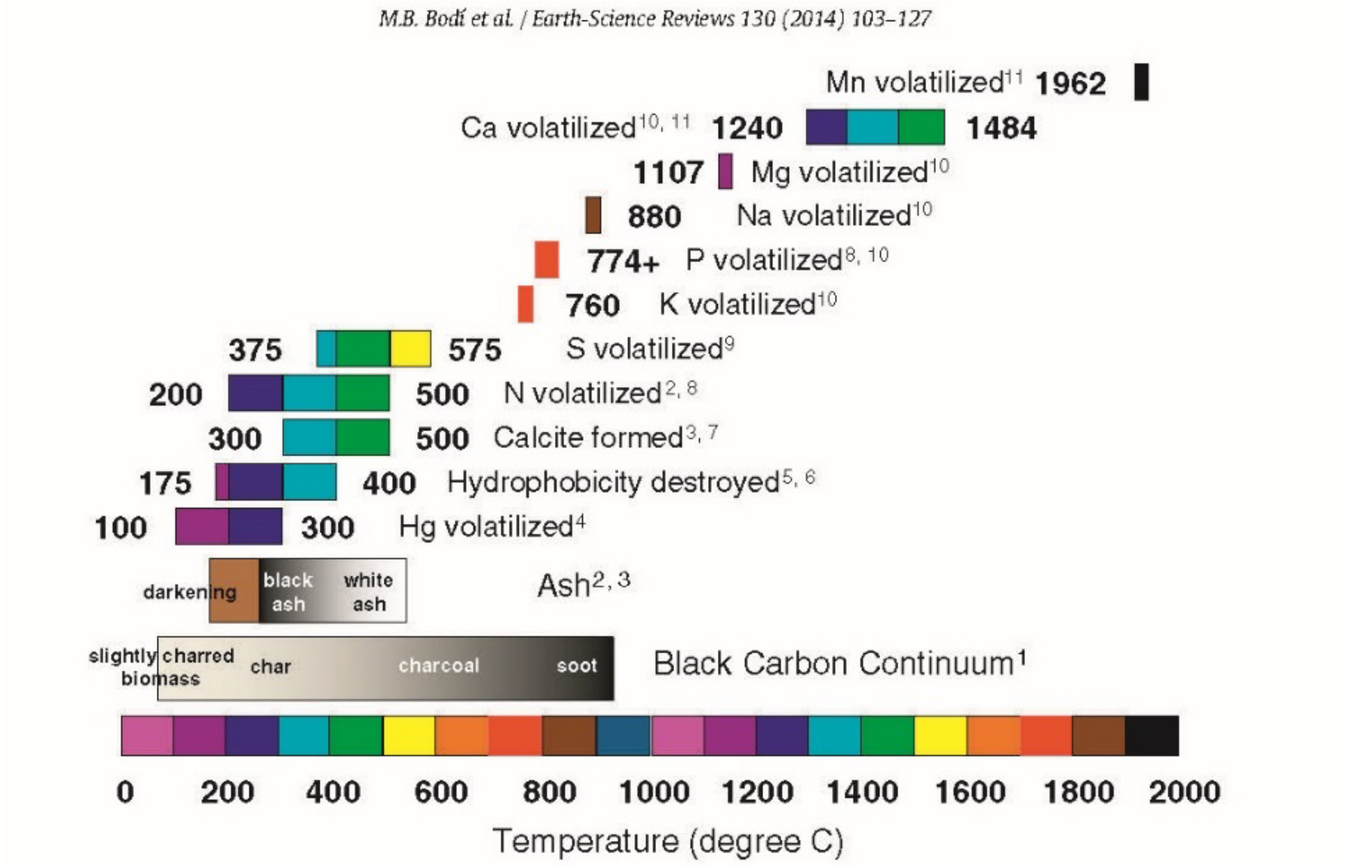


Figure 1 – Major temperature thresholds that affect ash and soil chemistry.

Other physical properties of the temperature char and ash continuum are given below in Table 1.

Table 1. Other Physical and Chemical Properties Based on Combustion Temperature

Temp ^{0}C	Classification	Common Color	Size	Density ~g/cc	Elemental / Chemical Transition
<350	Char	Brown - reddish	coarse	1.0 – 2.0	Water/ low density char/ iron oxide
350 - 700	Char/Ash	gray/brown	finer	2.0 – 2.5	Transition to calcite / other elements
500 - 700	Ash	gray	fine	2.5 – 2.7	Primarily silica and carbonates
>900	Ash	light gray/white	fine/dense	~2.8	Primarily silica and oxides

Fresh wildfire (vegetation) ash combusted above ~600^{0}C that has not been subjected to water hydration or degradation over time will likely contain elevated pH levels ranging from 8.5 to 12.0 due primarily to the presence of Calcium (Ca) and Potassium (K) as a hydroxides (O^{H-}). Typical background levels for pH and Conductivity of water, indoor dust, and fire residues are given below in Table 2.

5.0 ACIDITY/ALKALINITY (pH) AND CONDUCTIVITY ANALYSIS OF DUST SAMPLES

The chemical tests used by EAA and described below include pH, conductivity, and soluble cation/anion chemistry. Acid/Alkali content, i.e. pH analysis, is performed using a modified ASTM D4972-01 Method[24] originally developed for soil analysis. EAA uses this method as another tool to help determine the presence or absence of wildfire or structure fire ash in indoor dust samples. It can also be used as a direct measure of the corrosion potential of settled dust. The presence of an elevated pH combined with elevated conductivity from specific cations and anions can indicate "corrosive" properties associated with ash from recently burned vegetation or indoor combustion sources. Normal indoor dust is weakly acid to weakly alkali with a "normal" pH range of 6.5–7.8. It also has a low to moderate conductivity range from ~200 at high water dilution, to ~7,000 ppm at maximum dust / water saturation or "Water Holding Capacity^{31}". The water holding capacity (WHC) will be discussed further in Section 8.2. The pH and conductivity of indoor dust is primarily due to the salts found in human dander, the most common indoor dust particles found. The salts normally present in indoor dust (NaCl, KCl, $CaCl_2$) have a neutral ionic potential with a pH around 7.0. High concentrations of these salts tend to act as a buffer for indoor dust that has not been impacted by a structure or wildfire. As a result, pH measurements below ~6.0 can be used as a potential indicator of a recent structure fire. Conversely, pH measurements above ~8.5 can be used as potential indicator of a recent wildfire.

Table 2. Typical pH and Conductivity Background Levels in Solutions and Dust Samples.

Solution	pH	Conductivity -- (mS/cm)	TDS ppm
RO water		--	25-50
Domestic tap water	6.5–8.0	0.5 - 0.8	250-400
Potable water (Max.)	NS	1.055	528
Sea water	~8.3	56.0	~28,000
Brackish water	>8.3	100	~50,000
Dust type (Diluted with distilled water)			
San Diego soil <62µm fraction (0.02g/ml)	7.72	0.60	432
Indoor dust (0.02g/ml water)	6.5 - 7.8	0.3 - 1.5	~100-500
Oak/pine log ash (0.02g/ml water)	10 - 13		
Oak/pine leaf/twig ash (0.02g/ml)	10.5 - 11.0	~0.24	~170
Montecito fire char/ash mix (0.02g/ml)	8.7 - 11.3	0.2 - 0.64	~115-400
Structure fire ranges (estimated)	3.8 – 6.5	~1.0 – 4.0	500 - 3000

As a result, this method can be used as an indicator for the presence or absence of fresh fire-related ash, and the resulting potential for corrosive "damage". To precisely determine the type of cation salts present and exact source, the SEM/X-ray cation method can be utilized (see below in Section 7.0).

6.0 METHOD LIMITATIONS OF pH ANALYSIS

The ASTM D4972^{24} Standard Test Method was specifically designed to measure the pH of soils using a standardized 1:1 soil weight to water volume ratio (10grams/10ml water). This dilution ratio is not practical or possible with surface "dust" samples due to the fine grained size distribution, composition, and low density (specific gravity) of indoor dust. Also, micro-vacuum or bulk "dust" samples submitted from the field rarely contain more than 0.50 grams, therefore, the pH measurements obtained must always be based on more "dilute" samples with dust/water volume (g/ml) ratios ranging from 0.2:1 to 0.001:1. For this reason, data interpretation needs to be based upon threshold concentration ranges. The pH measurements of ash samples performed by the modified method will also be lower than a pH measurement conducted closer to the dilution ratios prescribed by the ASTM method. It is also important to note, that "degraded" or leeched ash can be present with a more neutral pH (i.e. <8.5). As a result, "high" pH measurements are a direct indicator of the presence "fresh" or recent ash. This also means the test can help determine if the Optical Microscopy measurements may represent the most recent fire event (i.e. high pH), or whether or not the measured fire residue (char and ash) is more likely from a historical fire event (i.e. pH lower than 8.5).

In spite of some limitations, the method is useful because samples containing even low concentrations of "fresh" wildfire "ash" are typically alkali. This is due to Potassium cations (present as a hydroxide O^{H-}), that can be easily detected even in highly diluted water samples because of the high pH. When significant "fresh" or unaltered or degraded fire residues are present, the pH will usually exceed a pH of 8.5 even when low ash concentrations of less than 10% are present in dust samples containing less than 0.001grams (total weight). Because dust samples are usually submitted with limited material, the EAA modified procedure is performed with a minimum volume of distilled water (e.g. 3 ml) and a maximum weight of collected dust not to exceed ~0.050 grams. In some samples with low ionic concentrations and neutral pH, accurate pH readings may not be possible. However, when reading drift prevents accurate analysis, this condition is still an indication of the absence of significant fire ash residue.

7.0 pH AND CONDUCTIVITY ANALYSIS – MICRO-VACUUM OR BULK DUST SAMPLES

The analysis of pH and conductivity can be performed on bulk samples or samples vacuumed from the surface. Wipe samples can be used, however, the results are not as accurate as from bulk dust samples. There is insufficient material on tape lift samples to provide an accurate analysis.

7.1 Preparation and Analysis Procedure

The analysis is conducted by weighing and placing 0.05grams of dust in a 15mm screw-top disposable centrifuge tube. Distilled water is added to contain a total volume of 3 ml. The sample is then shaken for 15 seconds and allowed to sit for a minimum of 10 minutes to allow the particulate to settle prior to analysis. The pH and conductivity meters are calibrated, and measurements are collected by placing the electrodes into the centrifuge tube. This same dust/water solution can then be used to perform the cation/anion analysis described below if deemed necessary.

Wipe samples require an additional preparation step that includes removing the dust from the wipe sample with ultra-sonication. The weight of the dust used in the calculation is less accurate because it is obtained indirectly by subtracting the weight of the wipe (after ultra-sonication and drying) from the initial weight of the combined wipe and collected sampled dust.

7.2 Interpretation of results

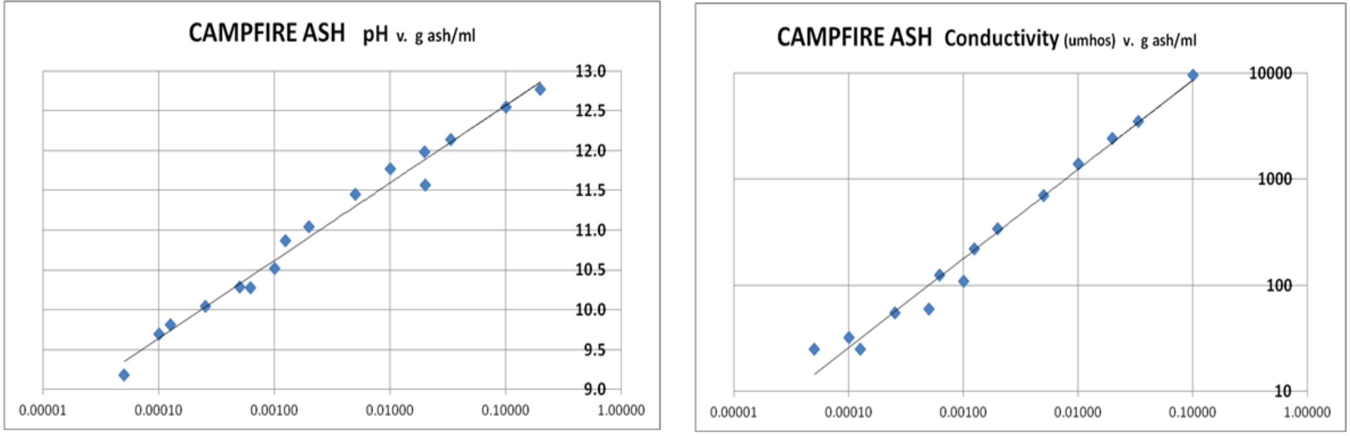
Wildfire Residues

In fresh wilfire “ash” samples (mixed Oak and Pine with a high pH of 10-13), the actual measurement can be expected to vary more than 2.0 pH units over an entire 1000-fold water dilution range of 0.0001 to 0.10 grams/ml of dust. Using only trace amounts of fresh wildfire ash (0.0001 grams / ml) can raise the pH to a value greater than 8.5 in a neutral indoor dust sample. The normal variation of expected pH concentrations has been determined using actual measured fire ash concentrations comprised of oak and pine logs, as well as with ash collected from specific fires. These results will be discussed below. The mixed oak and pine log samples were combusted for a full 24 hours. Serial dilutions of ash were prepared and the range of pH and conductivity levels were determined. The results are summarized below in in Figures 2 and 3.

Structure Fire Residues

Structure fire residues are analyzed by same procedure as described above. “Fresh” fire residues tend have a pH below 6.0 and have higher anion elemental ratios of chlorides due to the combustion of plastics and synthetic fibers from fabrics and carpeting. As of the data of this document, not as much information is available on pH, conductivity, or cation/anion ranges of indoor fires.

Figures 2 & 3 – Decrease of Campfire Ash pH and Conductivity with Increasing Serial Dilution of Distilled Water



Based on this analysis, the pH of fully combusted ash concentrations of less than 0.0001 grams per ml in distilled water should easily be measured above 9.0, and “detectable” in indoor dust samples. Furthermore, the high conductivity of the mixed oak and pine fire ash provide relatively stable alkali pH measurements over a very wide 1000-fold serial dilution range of ash concentrations. Because the change in pH and conductivity follows a predictable dilution curve that can mathematically be calculated, these measurements can also be standardized to a specific mass concentration value for inter-sample comparison, even when different dust weights and dilutions are used. These parameters are used to calculate the Maximum Corrosion Potential analysis discussed in Section 8.2.

In order to determine the difference between the soluble and insoluble composition, the campfire ash sample was filtered through a 0.2µm polycarbonate filter. The remaining ash residue on the filter (insoluble filtrate), and the evaporated salts from the supernatant liquid (soluble) were analyzed. The measured conductivity (umhos, i.e. mS/cm) of fire ash, and differentiation between the soluble ions responsible for elevated pH in the supernatant are given below in Table 3. SEM micrographs and X-ray spectra are given in Figures 4 and 5.

Table 3. Campfire Ash (Mixed Oak & Pine) Elemental Weight Percent Summary

	Elemental Weight %										
Description	C	N	O	Na	Mg	Al	Si	P	S	Cl	K	Ca
Solid filtrate	11	--	40	0.1	3.2	0.4	2.1	--	--	0.1	0.8	38
Soluble Supernatant	20	--	32	2.9	--	--	0.7	--	0.9	1.7	42	--

The differentiation between the soluble and non-soluble components of campfire ash are given below in Figure 4, X-ray filtrate, and Figure 5, soluble supernatant ash residues.

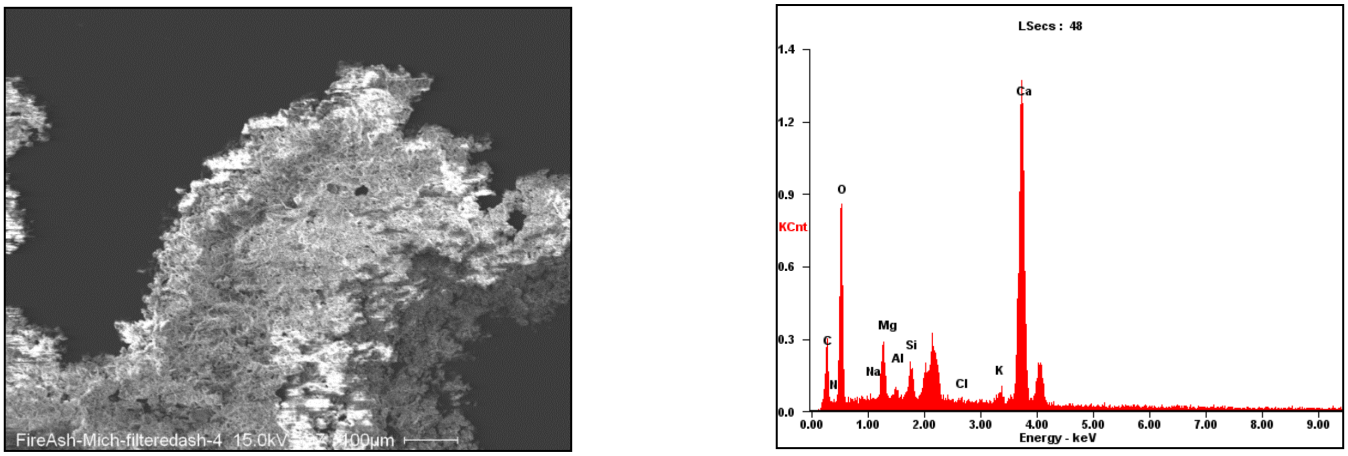
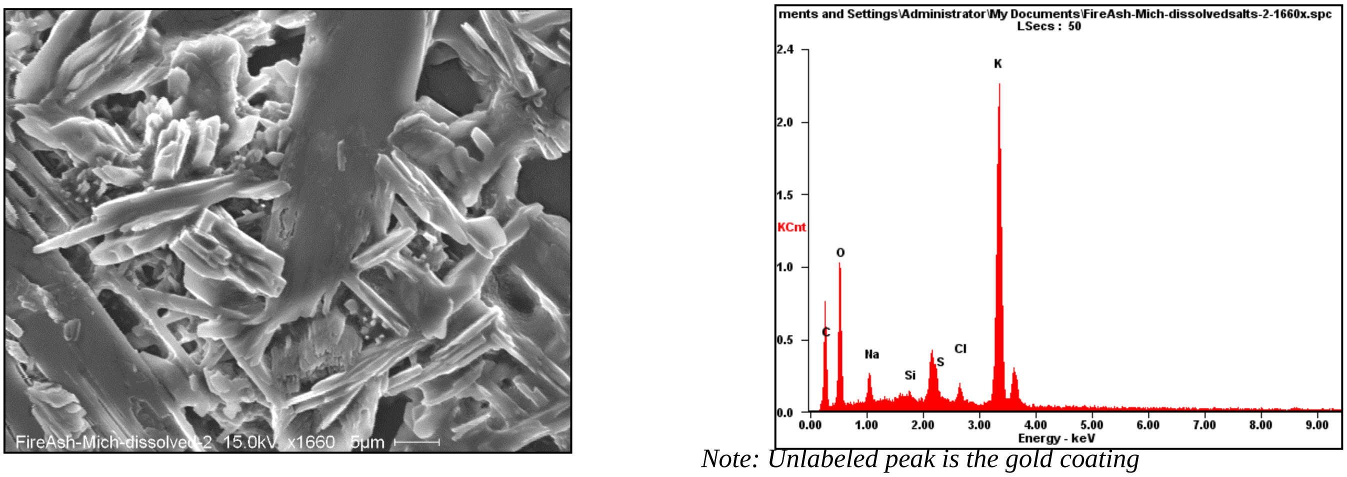


Figure 4. – X-ray Composition of the Fire Ash Filtrate Solids after a Triple Rinse of Distilled Water



Note: Unlabeled peak is the gold coating

Figure 5. – X-ray Composition of the Fire Ash Supernate Solution Crystals after Evaporation

For interpretation purposes, EAA uses the measured pH guideline ranges given in Table 4 (based on approximate 0.05g dust/3ml of distilled water, e.g. ~0.02g/ml) to characterize normal verses atypical (high) pH measurements. Because soils in marine coastal areas, and carbonate rich soils can produce alkaline dust with pH ranges up to ~7.8, this pH is used for an initial threshold of the upper "normal" range for indoor dust samples.

Table 4. Recommended Interpretation Guidelines for pH Analysis of Indoor dust.

pH Range	Relative Level Range of Indoor Dust Samples
6.5 - 7.8	Normal / neutral pH - (typical background)
8.0 - 8.5	Low-moderate alkalinity, potential fire "ash" or other conditions present
8.5 - 9.0	Moderate alkalinity - potential fire "ash" (confirm with SEM/X-ray cation/anion analysis)
> 9.0	High alkalinity - fire "ash" present (confirm with SEM / X-ray cation/anion analysis)
>10.0	Very high alkalinity - "ash" present (confirm with SEM / X-ray cation/anion analysis)

8.0 CATION / ANION ANALYSIS USING BULK SEM / X-RAY ELEMENTAL ANALYSIS

As discussed above, the identification and quantification of fire "ash" residues by optical microscopy is often the most difficult, variable, and under-reported part of the analysis. The major cations and anions found in vegetation ash are known to be chemically alkali and potentially “damage” or alter the surfaces they settle upon. The SEM/X-ray cation /anion analysis method developed by EAA is most effective when combined with the pH analysis as an additional test to 1). Confirm the presence or absence of vegetation fire “ash” in settled dust, and 2). Provide an indicator of the corrosion potential of the settled dust particles. There is significant literature supporting this analysis approach to determine the trace mineral salts within vegetation, and also to address the impact of “soft” metal cations on the corrosion of metals including aluminum alloys and building components[20]. Historical scientific approaches for assessing plant nutrients and SEM / X-ray analysis techniques can directly be applied to the assessment of fire ash residue samples for these purposes[12,13,14,15,16,17,20,21].

8.1 Background - Significance and Basis for the Cation/Anion Test Method

This method is used to confirm the presence or absence of “fresh” wildfire or structure fire ash, and the corrosion potential based on the soluble cation and anion chemistry. The method relies on a combination of pH, conductivity, and the elemental weight percent and/or atomic percent of the evaporated soluble cations and anions as analyzed by SEM / X-ray analysis. When used together these methods can determine the presence, absence, or the source of combustion; and also provide critical chemical data regarding the corrosion potential of the dust. When assessing corrosion potential, this method must be combined with other engineering and corrosion tests that are outside the scope of this specific laboratory analyses.

The method developed by EAA separates the soluble from insoluble constituents by filtering out the particulate phase, and analyzing the remaining solution (supernatant) of the dust sample previously analyzed for pH and conductivity. Approximately 0.5 ml of the supernatant is transferred to a 5-10ml syringe with a 0.2um syringe filter. The filtered solution is placed drop-wise onto a heated glass microscope slide and allowed to evaporate. The evaporated residue is then transferred to an SEM specimen mount and analyzed using the Scanning Electron Microscope and Dispersive X-ray analysis to determine the relative elemental composition (weight percent). The analysis can determine the exact ratios of different cations and anions that are associated with normal indoor environments, and those more likely associated with vegetation ash or other sources. The results can also be used as an indicator for the potential corrosion impact. The method analyzes the cations and anions most commonly associated with fire corrosion chemistry.

Common Cations – Na^+, Mg^{2+}, K^+, Ca^{2+} Common Anions – Cl^-, SO_4^-, PO_4^-, NO_4^-

The analysis is based on using the known distribution of cation mineral content (specifically Potassium) found in the residual ash of trees and other plants. Sodium and Potassium are alkali element cations found in ash that are responsible for the high pH. Alkali Sodium (present as Sodium hydroxide NaO^{H-}) is very low (i.e. <1%) and not a factor in changing the ash pH. Alkali Potassium (present as Potassium hydroxide (KO^{H-}) is typically 10-30% of the weight of residual ash, whereas other minerals including Sodium and Phosphorus are ~2-3% (see The Sodium, Potassium and Phosphorus Contents of Tree Species Grown in Close Stands, p. 277[13] given in Figure 7 below).

Figure 7. Sodium, Potassium, and Phosphorous Concentrations in Tree Ash

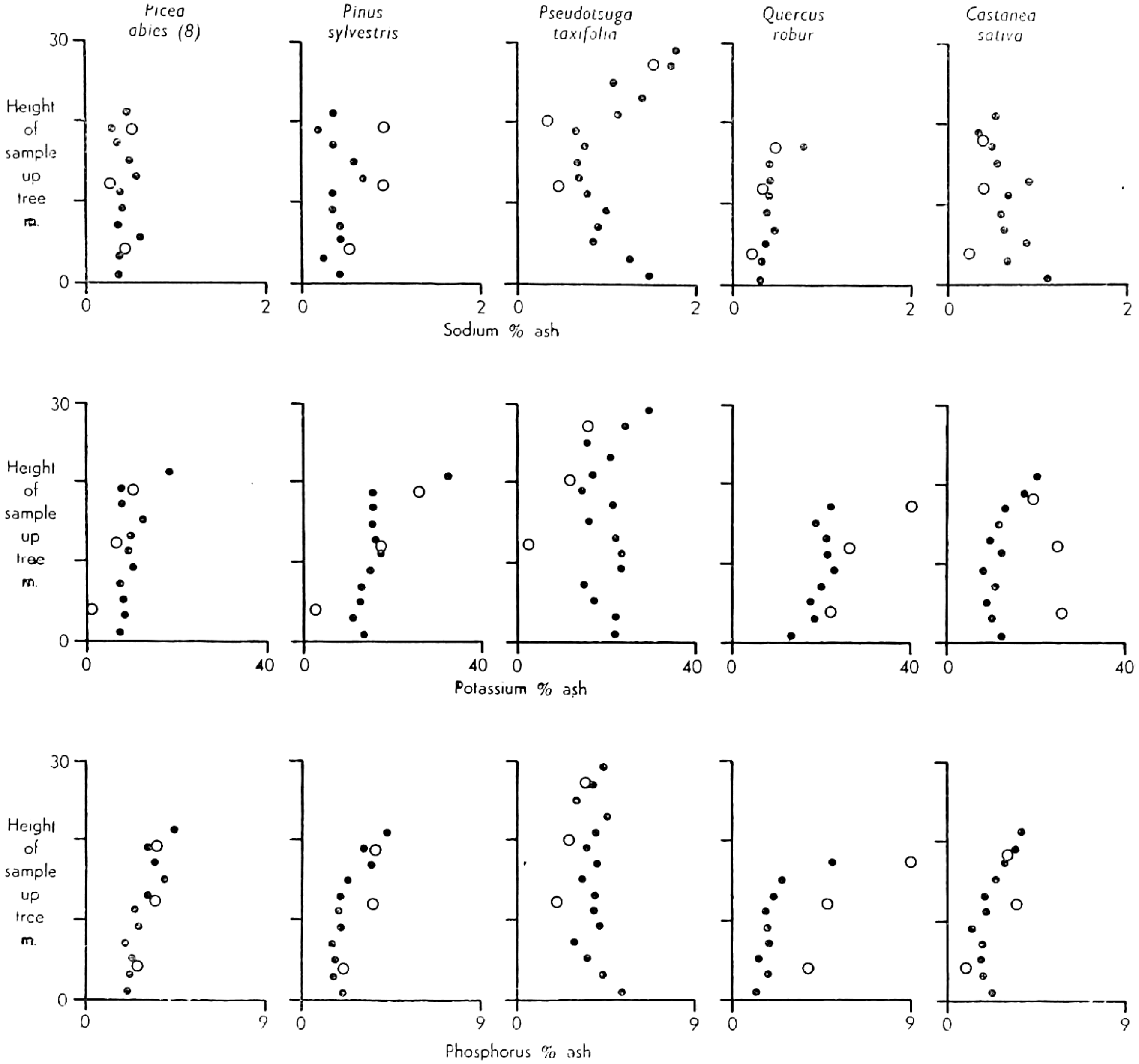


Fig. 2. The sodium, potassium and phosphorus content (as per cent of the ash) of the boles and canopies of some of the sample trees at Abbotswood. ● = bole, O = canopy.

Analysis of the elemental ash composition of various wood “fuels” is given in Table 1 of the publication “Ash-related Problems during Biomass Combustion and Possibilities for a Sustainable Ash Utilisation[17]”. This table is listed below as Table 5 and shows the major elements found in burned vegetation. The elemental order of abundance is approximately Ca > K > Mg > Si > P > Al. There are different elemental concentrations depending on the type of wood, and the location within the tree (bark or interior trunk). It is important to note there are low levels of Sodium (Na^+), and an absence of Chlorine (Cl^-) in wood ash residues. These levels are significantly different than levels found in indoor dust samples. As will be discussed later, Na^+, K^+, and Cl^- are the major ionic elements found in indoor dust, however, they are typically present as “chlorides” and not “hydroxides”. This difference in elemental ratios (especially chlorine) and the ionic potential, can help differentiate an “indoor dust” chemical distribution from a dust sample contaminated with wildfire ash.

Table 5. Typical Mean Values for the Chemical Composition of Wood Fuels (Article Table 1)

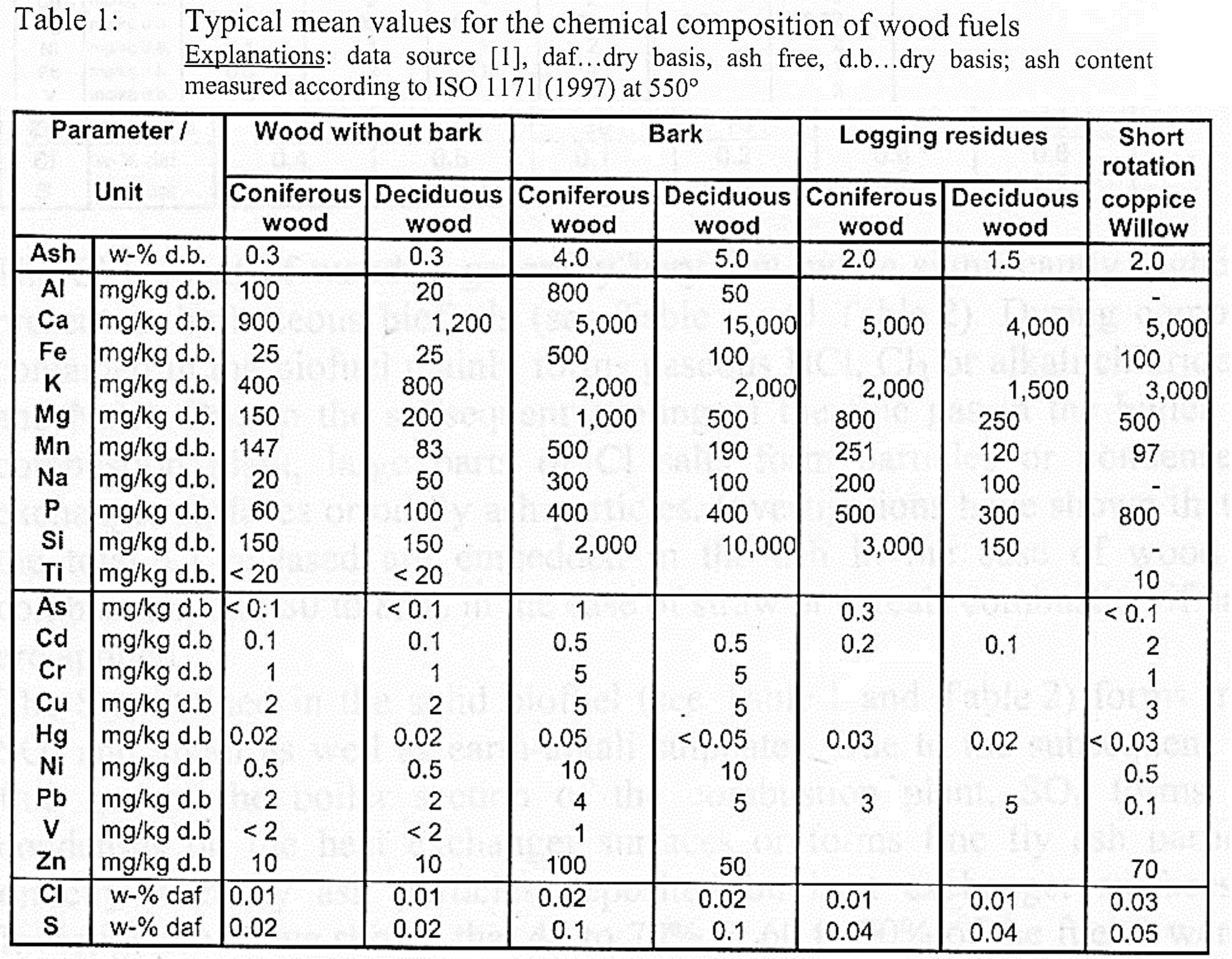


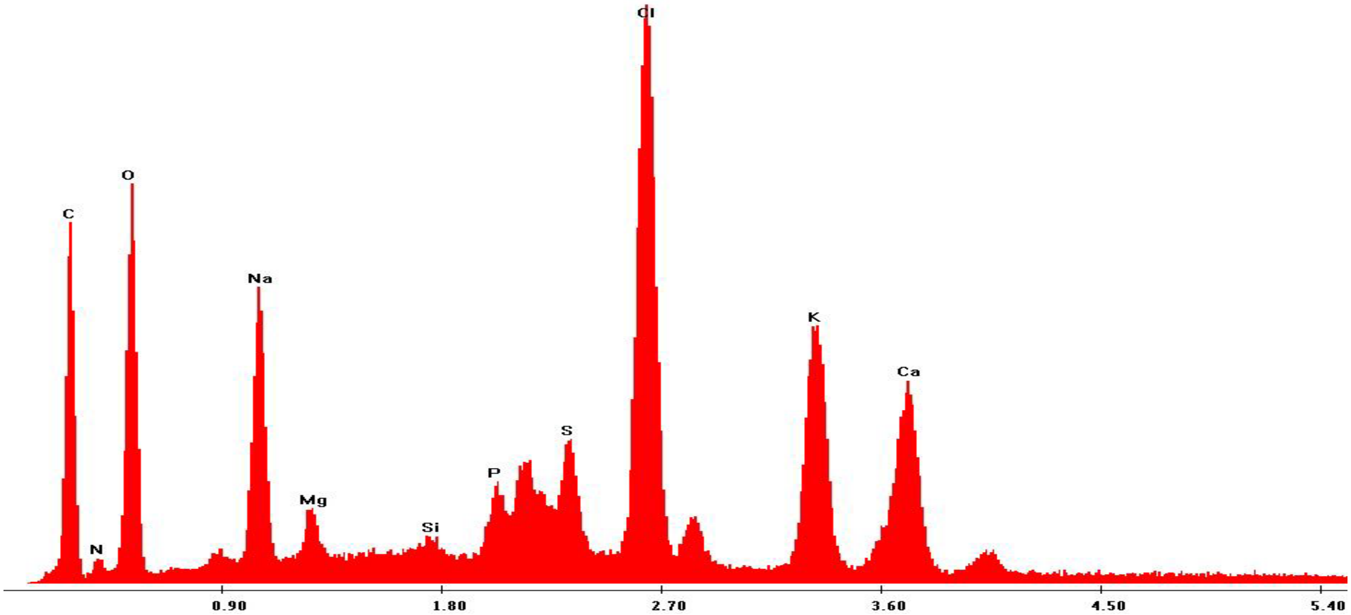
Table 1: Typical mean values for the chemical composition of wood fuels

Explanations: data source [1], daf...dry basis, ash free, d.b...dry basis; ash content measured according to ISO 1171 (1997) at 550°

Parameter /	Unit	Wood without bark		Bark		Logging residues		Short rotation coppice Willow
		Coniferous wood	Deciduous wood	Coniferous wood	Deciduous wood	Coniferous wood	Deciduous wood	
Ash	w-% d.b.	0.3	0.3	4.0	5.0	2.0	1.5	2.0
Al	mg/kg d.b.	100	20	800	50			-
Ca	mg/kg d.b.	900	1,200	5,000	15,000	5,000	4,000	5,000
Fe	mg/kg d.b.	25	25	500	100			100
K	mg/kg d.b.	400	800	2,000	2,000	2,000	1,500	3,000
Mg	mg/kg d.b.	150	200	1,000	500	800	250	500
Mn	mg/kg d.b.	147	83	500	190	251	120	97
Na	mg/kg d.b.	20	50	300	100	200	100	-
P	mg/kg d.b.	60	100	400	400	500	300	800
Si	mg/kg d.b.	150	150	2,000	10,000	3,000	150	-
Ti	mg/kg d.b.	< 20	< 20					10
As	mg/kg d.b	< 0.1	< 0.1	1		0.3		< 0.1
Cd	mg/kg d.b	0.1	0.1	0.5	0.5	0.2	0.1	2
Cr	mg/kg d.b	1	1	5	5			1
Cu	mg/kg d.b	2	2	5	5			3
Hg	mg/kg d.b	0.02	0.02	0.05	< 0.05	0.03	0.02	< 0.03
Ni	mg/kg d.b	0.5	0.5	10	10			0.5
Pb	mg/kg d.b	2	2	4	5	3	5	0.1
V	mg/kg d.b	< 2	< 2	1				
Zn	mg/kg d.b	10	10	100	50			70
Cl	w-% daf	0.01	0.01	0.02	0.02	0.01	0.01	0.03
S	w-% daf	0.02	0.02	0.1	0.1	0.04	0.04	0.05

Normal “indoor” dust is slightly acidic or pH neutral (e.g. pH 6.5-7.5), and a pH above 7.8 is rarely encountered. The ionic elements in indoor dust are primarily composed of neutral or weakly acidic Sodium, Potassium, and Calcium present as chloride salts. The high amount of chloride, carbonic acid (and other anions) normally found in normal indoor dust have a tendency to buffer the sample and keep the pH relatively neutral and stable throughout a wide range of dust concentrations when diluted in distilled water. Typically, the conductivity of indoor dust is higher than wildfire ash due to the presence of Sodium, Potassium, and Calcium Chloride salts. Because indoor dust is typically pH neutral, the measurements typically drift and are not precise at low dust concentrations. As a result, the correlation coefficient between dust weight and water volume in a serial water dilution in typical indoor dust samples is non-existent (i.e. $R^2 = 0.04$). Elemental analysis using dispersive X-ray (Figure 8) and pH calculations from serial dilutions of dust in distilled water (Figure 8) are given below.

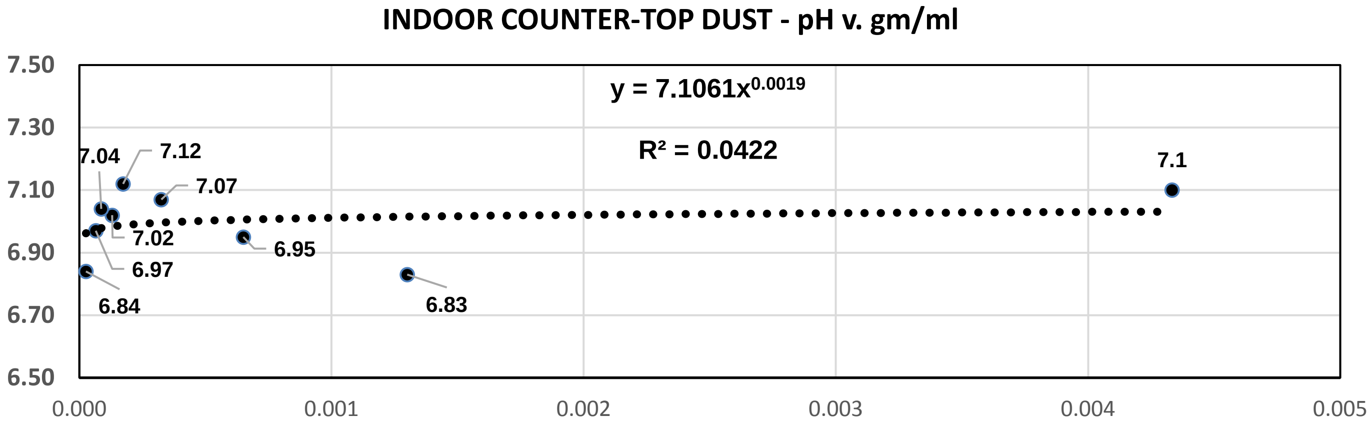
Figure 8. Indoor office dust – Elemental X-Ray Spectra of the soluble cations / anions.



Note: The cations of Na$^{+,}$ Mg^{2+},K^{+}, and Ca^{2+} are typically found in indoor dust as neutral or weakly acidic chlorides (Cl^{-}). The dust sample also contains minor amounts of Sulfur (S), phosphorous (P), and Nitrogen (N) that are also other likely anions buffering the dust sample. The presence of Potassium (K+) in indoor dust is partially associated with the soluble minerals in infiltrated soil clay minerals from the decayed vegetation (see Figure 9) and as discussed below.

The serial dilution curve of pH verses dust concentration (g/ml) given in Figure 8 shows the correlation to be very low (R^2=0.04) due to a neutral pH (~7.0), and the relatively low conductivity of dust at these low concentrations. As mentioned above, Sodium, Potassium, Magnesium, Carbon, and Calcium (in indoor dust) are found in solution as neutral chlorides, sulfates, or weak acids. The pH changes less than 0.3 pH units (6.8-7.1) over a 150-fold serial dilution (.0045g/ml – 0.00003g/ml).

Figure 9. pH of Indoor Office Dust Collected from Counter Top Surfaces



As mentioned above, the indoor dust (pH, conductivity, and soluble cations/anions) can be influenced by a contribution of infiltration clay minerals in close proximity to the building. A soil sample representing areas of native vegetation within 100 feet of indoor dust sample was also analyzed for pH, conductivity, and soluble cations and anions. The analysis results are shown below in Table 6 and Figure 9 respectively.

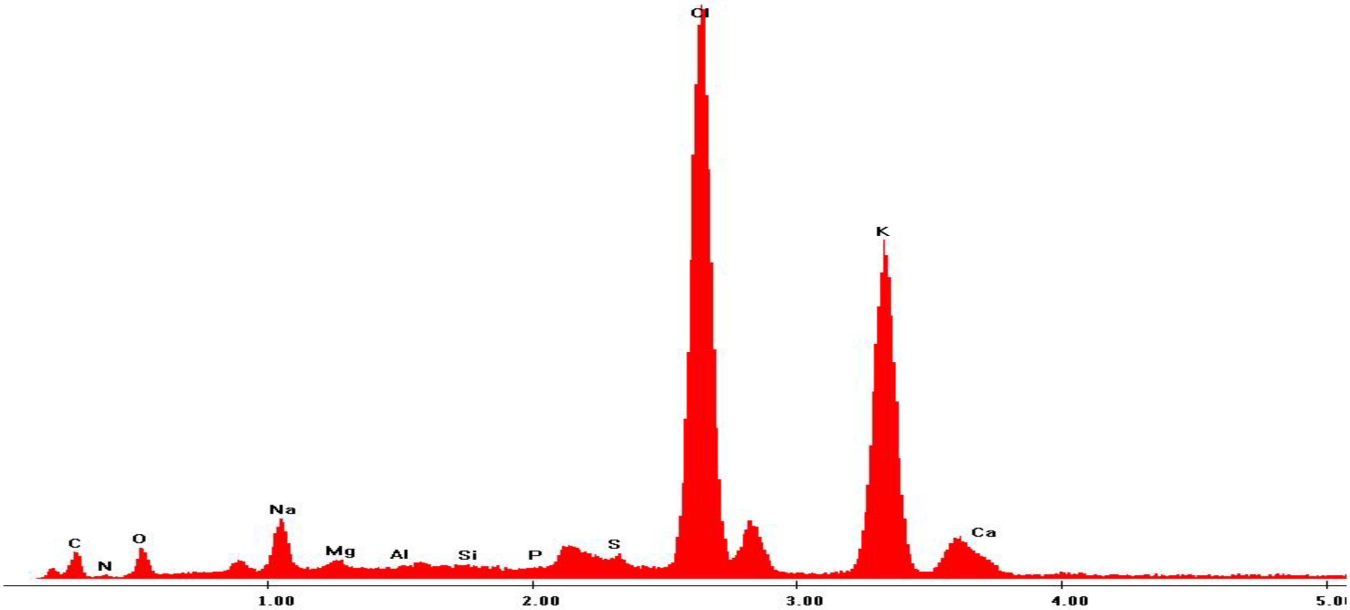
Table 6 summarizes the pH, conductivity and X-Ray chemistry (weight %) of the soil sample.

Table 6. San Diego Native Soil Sample - pH, Conductivity, and Elemental Weight% Soluble Ash Cations/anions.

	Conductivity		Weight %											
pH	mS/cm	ppm	C	N	O	Na	Mg	Al	Si	P	S	Cl	K	Ca
7.72	0.60	432	11.8	2.1	6.3	4.5	1.2	0.7	0.7	0.6	1.3	**36.8**	**31.8**	2.2

The soil sample (<62µm size fraction) is slightly alkali (pH ~7.7) with a moderate conductivity (0.60 mS/cm, ~430ppm). The predominant ions present are Chlorine and Potassium. Figure 10 shows the X-ray spectra (soluble cations/anions) of the same soil sample.

Figure 10. Elemental X-Ray Spectra of the <62um San Diego Soil Sample Soluble Cations/Anions.



The infiltration of outdoor soil (clays <62µm) can significantly affect the indoor dust chemistry, and both the influence and difference between indoor dust chemistry and fire ash chemistry can clearly be seen. Although the Potassium level in the native San Diego soluble soil sample fraction is high (31.8%), it is present as Potassium chloride (K^+ = 31.8%, Cl^- = 36.8%), and not as a hydroxide (i.e. Oxygen is only 6.3%). Sodium (4.5% Na^+) and Calcium (2.2% Ca^{2+}) are also very low. The soluble cations and anion composition is very different from the chemistry of fire ash as described below.

Measured Vegetation Char Chemistry

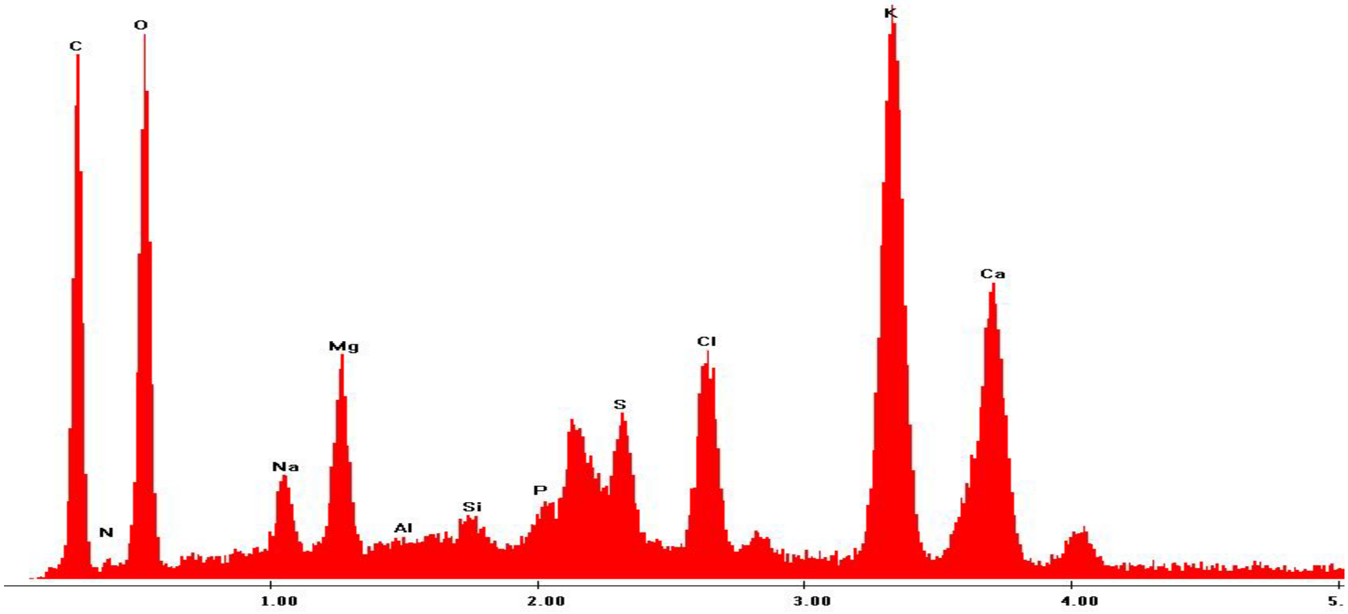
Wildfire or vegetation fire char and ash residues are comprised of both insoluble and soluble material. Char is visually black and composed of primarily hydrophobic partially combusted cellulose materials, residual organic resins, and relatively small concentrations of soluble cations and anions (when compared to ash). Oak char is weakly alkali (pH around 7.7-7.8). An example of the elemental composition of soluble cations and anions found in Oak "char" is given below in Table 7.

Table 7. Oak “Char” - pH, Conductivity, and Elemental Weight% Soluble Ash Cations/anions (0.02g/ml).

	Conductivity		Weight %											
pH	mS/cm	ppm	**C**	**N**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**
7.8	--	488	28.3	1.7	28.5	2.3	3.8	0.0	0.5	1.0	2.9	4.7	16.5	10.0

The “char” sample still retains significant concentrations of Carbon, Oxygen, Sodium, Magnesium, Potassium, Phosphorus, and Sulfur (likely as chlorides). During continuing combustion, the cations are driven off as a mixture of hydrogen chlorides (HCL) and other acidic (CO_2, O_3, etc.) and other corrosive gases. The fully combusted (decarbonized) and remaining ash contains primarily insoluble carbonates, oxides, and a much higher weight percentage of soluble alkali cations and anions. The elemental X-ray spectra for an oak char sample is given below in Figure 11.

Figure 11. Oak “Char” (black) - Elemental X-ray Spectra of Soluble Ash Cations/anions.



Measured Vegetation “Ash” Chemistry

In fully combusted “Ash” samples, the insoluble fraction is primarily composed of Magnesium oxides, Calcium oxides/oxalates, Calcium carbonate, and Silica oxides as plant phytoliths and other solids. The “soluble” supernatant fraction (after being placed in distilled water) is primarily composed of Potassium and Magnesium hydroxides that are the major source of the alkali pH. The exact elemental composition and pH of the soluble cations and anions is determined by the type of vegetation and combustion temperature. The chemical composition of fire ash will be different for grasses, leaf and twigs from various types of trees, and also different within the bark of trees which may contain higher proportional concentrations of Calcium of up to 80-90%[12,17]. Even with this high variation in potential ash composition, the pH is strongly influenced by very low concentrations of soluble Potassium (K^+) hydroxide (O^{H-}). As a result, very low concentrations of fire ash in indoor dust samples can significantly elevate pH levels from neutral to over 10.0 over a wide range of very low dust concentrations (<0.00001 g/ml) to moderate dust concentrations (0.05 g/ml in distilled water). The significant presence of soluble Potassium and sometimes Magnesium cations (i.e. weight% >10% total) in the absence of other buffering salt anions (e.g. Cl^-, S^-, etc.) is also an identifying fingerprint for the presence of vegetation ash. Because vegetation ash residues are <u>strongly alkali</u> and have moderate conductivity, the pH measurements are relatively accurate from very low to very high dilutions. As a result, the correlation coefficient verses concentration is relatively high ($R^2 > .90$). The "soft" cations of K^+ and Mg^{2+} are also known to be more corrosive to some metals (especially Aluminum) than other cations[20]. Elemental analysis of cation/anion chemistry using dispersive X-ray, and pH serial dilution profiles verses dust concentration are illustrated below in Figure 12 for an oak & pine log campfire "ash" sample. The mixed "char/ash" sample collected in the 2018 Montecito fire burn zone is also shown in Figures 13 and 14.

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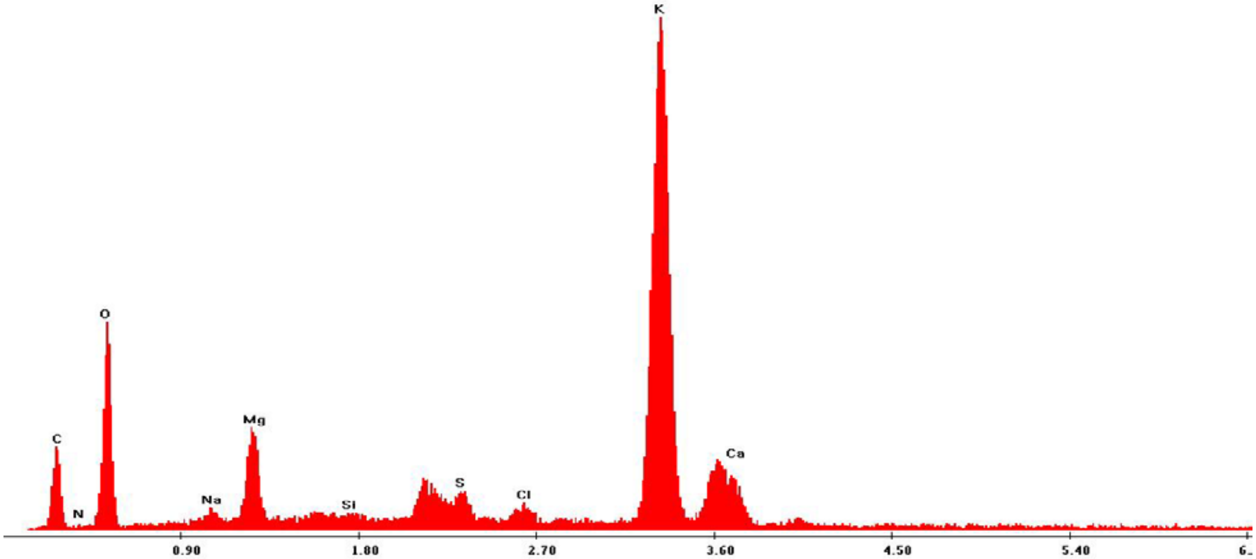
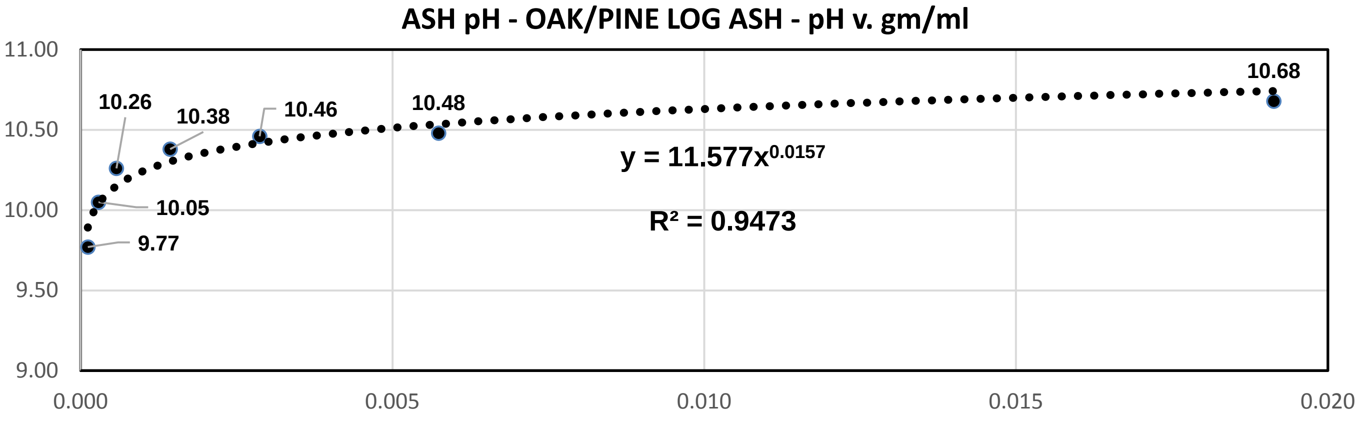
Figure 12. Elemental X-ray Spectra of an Oak / Pine Log "Ash" Sample - Soluble Cations/Anions



The 2017 oak and pine log supernatant analysis (Figure 9) contains over 90% ash as analyzed by Optical Microscopy. The X-ray elemental analysis spectra shows primarily K^+ and O^{H-}. Minor amounts of Mg^{2+}, and Ca^{2+} are present, and Na^+ and Cl^- are essentially absent.

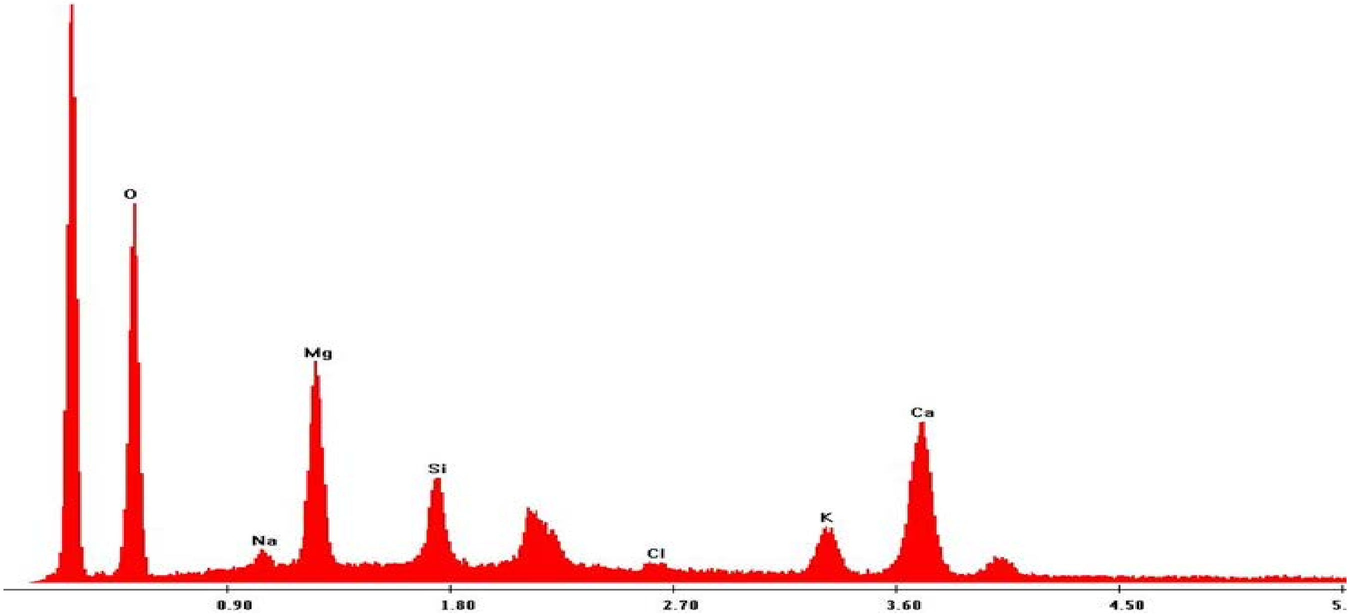
A serial dilution curve for the oak and pine log ash sample (Figure 13) shows the pH to change less than 1 pH unit (9.8-10.7) over a 180-fold serial dilution (.018g/ml – 0.0001g/ml).

Figure 13. pH analysis verses Ash Concentration (g/ml) From Oak and Pine Log Ash



The X-ray analysis of soluble cations/anions from the 2018 Montecito fire burn zone is shown below in Figure 14.

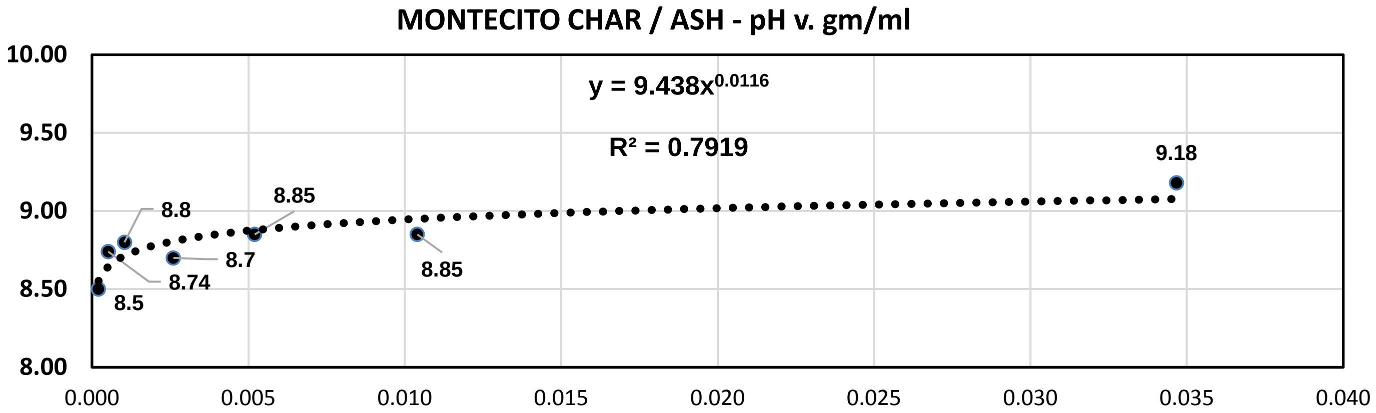
Figure 14. 2018 Montecito Fire Ash – Elemental X-ray Spectra of The Mixed char and ash sample (~60% char, <30% ash)



This is an example of settled wildfire debris that contains a lower percentage of ash as measured by Optical Microscopy (~60% char, <30% ash). Even though this sample contained relatively moderate ash by an Optical Microscopy analysis, the sample still contained the predominant cations C (unlabeled peak to the left), Mg^{2+}, Ca^{2+}, and K^{+}, <u>in the absence of Na^{+}, Cl^{-}, S^{-}, and N^{-} anions</u>.

Based on a serial dilution curve (Figure 15), the pH changes less than 1 pH unit (9.8-10.7) over a 90-fold serial dilution (.018g/ml – 0.0002g/ml).

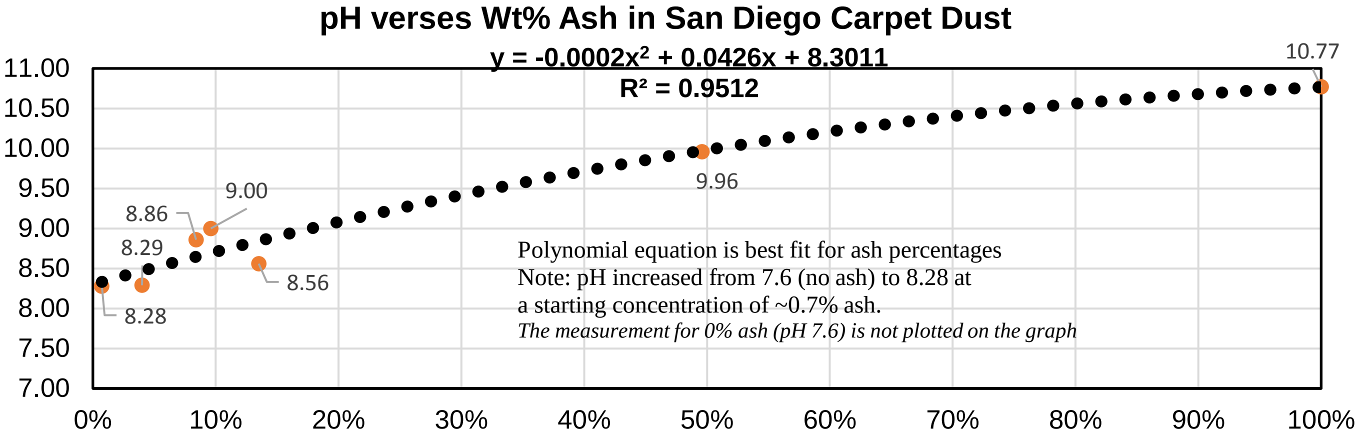
Figure 15. 2018 Montecito fire – Serial Dilution Curve of a Mixed Char and Ash Sample.



The pH level was found to change less than 1 pH unit (i.e. 8.5-9.2) over a 175-fold serial dilution change from <0.0002 g/ml to 0.035 g/ml.

In order to determine the pH detection and impact range in an indoor carpet dust sample, various concentrations of Michigan twig/leaf fire ash (Oak and Pine) were added to a San Diego carpet dust sample. Cation/anion wt% ratios, pH, and conductivity were then measured. The pH, conductivity, and cation/anion ratios were calculated at ash concentrations of 0.0% (no ash), 0.7%, 4.0%, 8.4%, 9.6%, 13.5%, 49.6%, and 100% ash. The initial carpet dust sample (without the addition of fire ash) had a measured pH of 7.6. All samples were analyzed at dilution volumes of ~.02g/ml (total weight). Figure 16 shows that a leaf and twig ash sample with a measured pH of ~10.8 will increase the pH in a carpet dust sample from an initial pH of 7.6 (no ash), to a pH >8.2 with an ash concentration as low as 0.7%.

Figure 16. pH Verses Weight Percent Ash in a San Diego Carpet Dust Sample.



Polynomial equation is best fit for ash percentages
Note: pH increased from 7.6 (no ash) to 8.28 at a starting concentration of ~0.7% ash.
The measurement for 0% ash (pH 7.6) is not plotted on the graph

The carpet dust sample used for this test is similar to the hundreds of other samples analyzed from homes where fire residue impact was determined to be absent. The normal pH measured in surface dust samples typically ranges from a low of 6.5 to a high of 7.7. Based on the data collected from historical indoor dust samples, pH measurements of non-fire impacted indoor dust are rarely higher than 7.8. In these isolated cases, the source of the increase in pH can be usually be determined by using the SEM/X-ray analysis method described below. The data given in the above tests confirms the following:

1. The elevated alkali Potassium (i.e. KO^{H-}) and Magnesium (Mg^{2+}) cations found in vegetation ash are good pH and chemical indicators for the presence or absence of fresh or unaged wildfire “ash” in indoor dust samples.

2. The dust concentrations used to perform the test do not significantly change the measured pH over a 10-fold range. This means that pH measurements from very low (highly diluted) indoor dust concentrations (<0.001g/ml) can reliably be used as an indicator of “fresh” wildfire vegetation ash even when the ash mass weight percentages are as low as 1-5%.

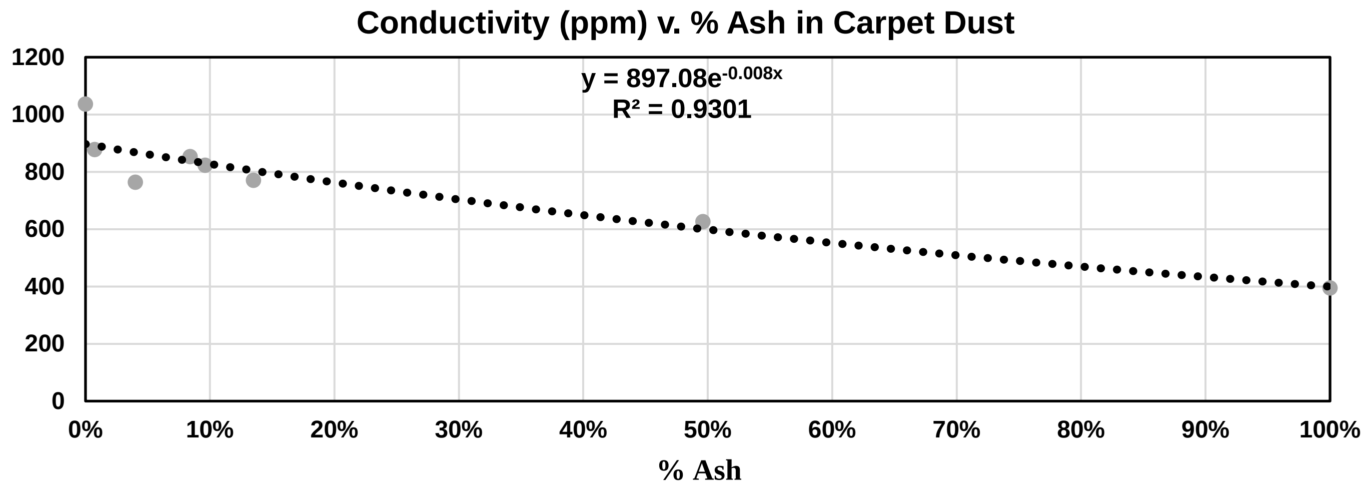
3. pH measurements above 9.0, are a strong indicator for the presence of “fresh” or “unaged” wildfire ash.

4. The soluble cation/anion chemistry in indoor dust and outdoor soil samples is significantly different than the soluble chemistry found in “fresh” fire ash residues. Fire ash residues are predominantly hydroxides of Potassium whereas, indoor dust and most soil samples are weakly acidic or neutral and usually Sodium and Potassium chloride salts.

Based on the ash concentration analysis in indoor carpet dust shown in Figure 17 and Table 8, the conductivity of vegetation fire ash is less than measured in indoor carpet dust samples. The conductivity of carpet dust samples decreased with increasing ash concentration from a high of ~900ppm with no ash present, to a low of 400ppm in a sample containing 100% ash. This is due to the high concentration of

Na^+ and Cl^- neutral salt ions found in normal carpet dust, and not found in vegetation ash.

Figure 17. Conductivity (ppm) Verses Weight Percent Ash in San Diego Carpet Dust Sample.



SEM/X-ray analysis from the filtered supernatant of the same samples (Table 8) shows the relationship between pH, and elemental cation/anion composition, and weight% of fire ash in the sample.

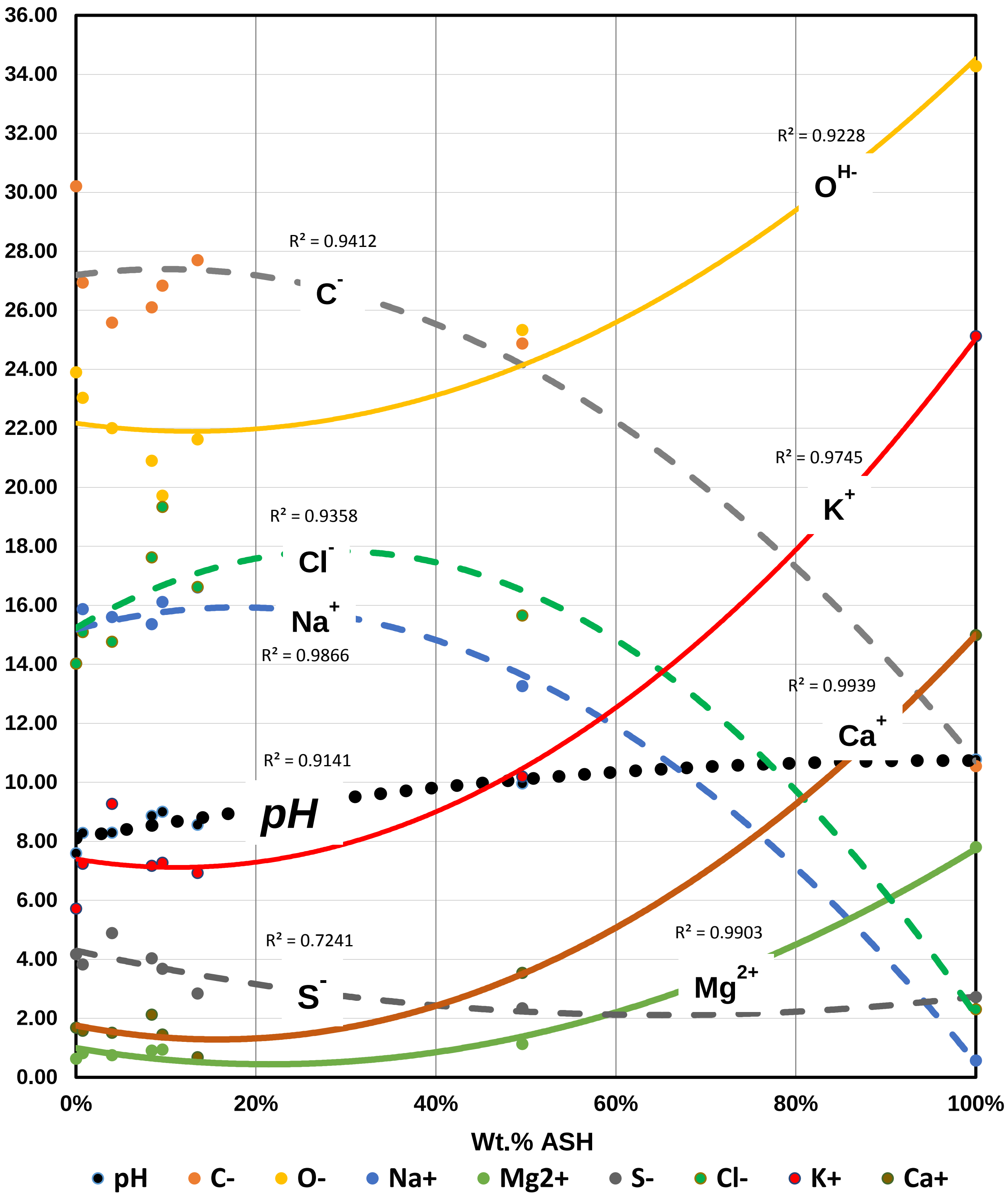
Table 8. pH and Elemental Concentration for Wt% of Twig/Leaf Ash in San Diego Carpet Dust

	WEIGHT % ASH V. CATION/ANION CONCENTRATION						
Sample #	1	7	8	2	4	3	5	6
Cation/anion	0.0 wt.%	0.7 wt.%	4.0 wt.%	8.4 wt.%	9.6 wt.%	13.5 wt.%	49.6 wt.%	100 wt.%
pH	7.59	8.28	8.29	8.86	9.00	8.56	9.96	10.77
C^-	**30**	**27**	**26**	**26**	**27**	**28**	**25**	**11**
N^-	**4**	**4**	**4**	**4**	**4**	**6**	**3**	**1**
O-	**24**	**23**	**22**	**21**	**20**	**22**	**25**	**34**
Na^+	**14**	**16**	**16**	**15**	**16**	**17**	**13**	**1**
Mg^{2+}	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**8**
Si	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
P^-	**1**	**1**	**1**	**1**	**1**	**0**	**0**	**0**
S^-	**4**	**4**	**5**	**4**	**4**	**3**	**2**	**3**
Cl^-	**14**	**15**	**15**	**18**	**19**	**17**	**16**	**2**
K^+	**6**	**7**	**9**	**7**	**7**	**7**	**10**	**25**
Ca^+	**2**	**2**	**2**	**2**	**1**	**1**	**4**	**15**

The pH analyses were all conducted at a dust concentration weight of 0.02 g/ml in distilled water. A graphical representation using a polynomial curve fit shows the change in elemental cations verses the weight percent of fire ash added to the San Diego carpet dust sample. The correlation coefficient (R^2) for the change in elemental concentrations is greater than 0.90 with the exception of Sulfur (see Figure 16).

Figure 18 shows the changing cation / anion concentrations with increasing weight percentages of fire ash added to a carpet dust sample.

Figure 18. Elemental Cation/Anion Wt.% verses Wt.% Ash Added to San Diego Carpet Dust - Polynomial curve fit



The changes in the soluble cation/anion elemental X-ray concentrations verses the weight percent ash are shown below in Figures 19-26.

Figure 19. 0.0% Ash in carpet dust

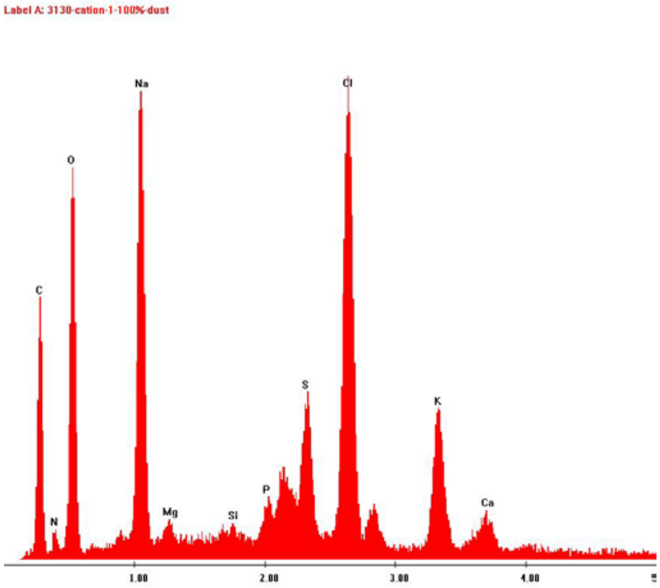


Figure 20. 0.7% Ash in carpet dust

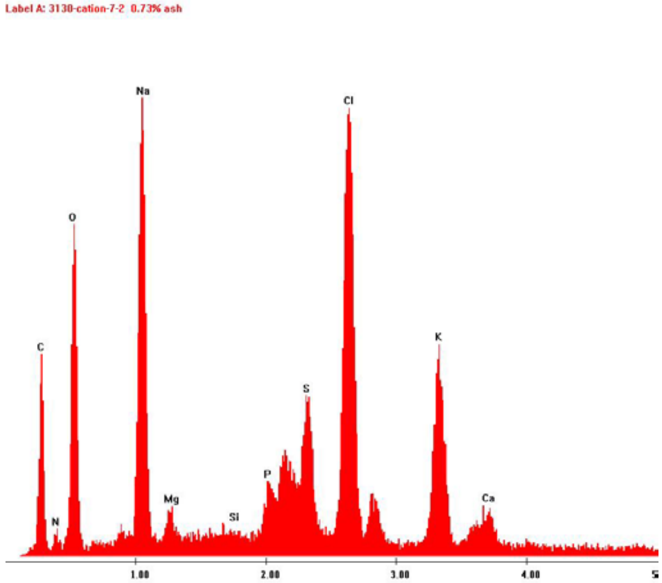


Figure 21. 4.0% Ash in carpet dust

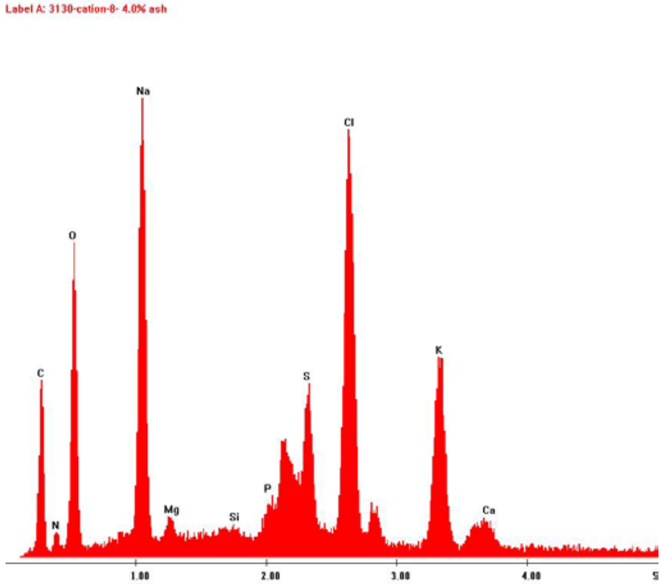


Figure 22. 8.4% Ash in carpet dust

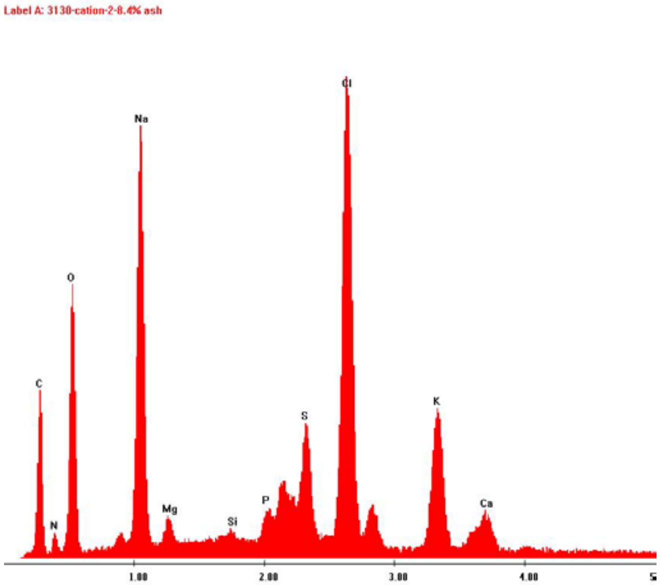


Figure 23. 9.6% Ash in carpet dust

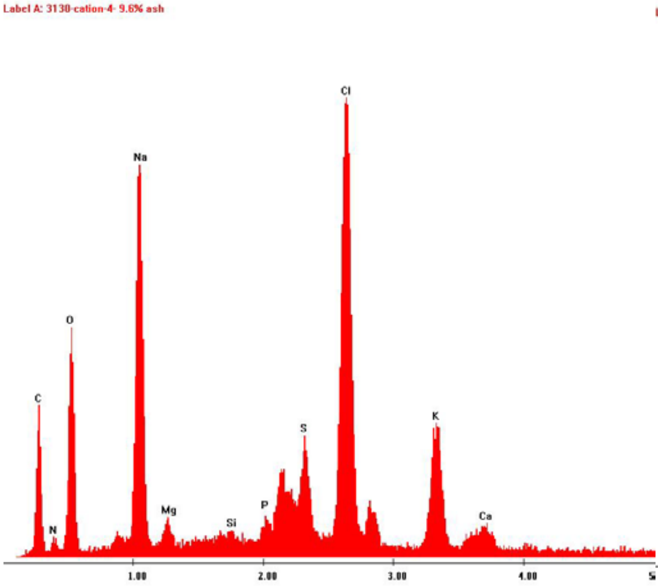


Figure 24. 13.5% Ash in carpet dust

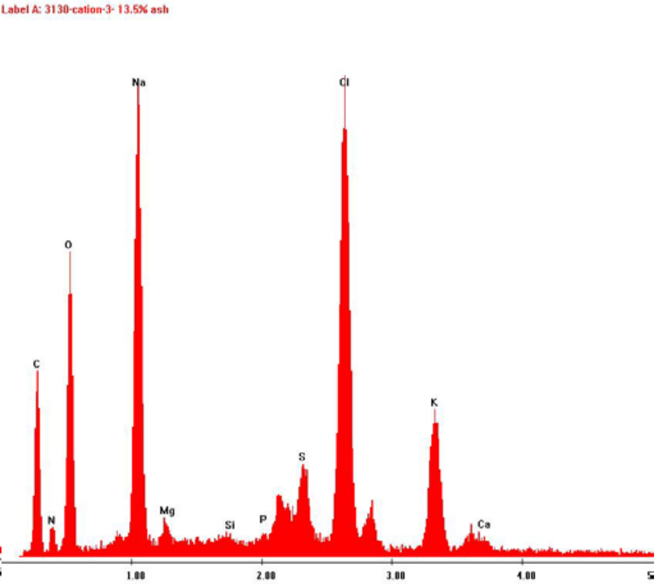


Figure 25. 49.6% Ash in carpet dust

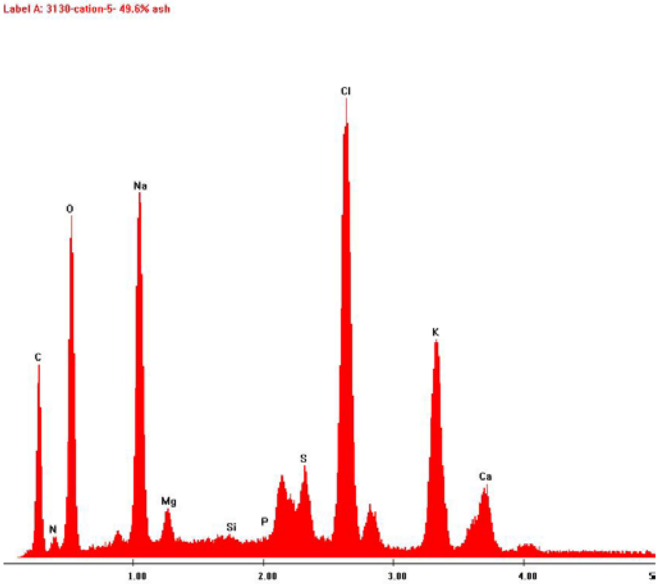
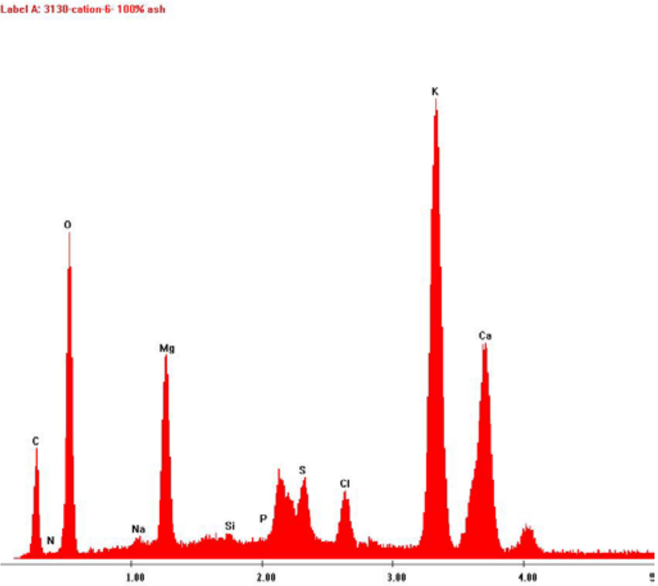


Figure 26. 100% Ash, no carpet dust



Although the changes in elemental cation composition (Wt.%) are subtle at concentrations below ~20% ash weight (see Table 8 and Figure 18), the proportionally larger increase in pH can be directly attributed to very minor changes in soluble Potassium (K^+) and Calcium (Ca^{2+}) that are present as a hydroxide (O^{H-}). The increase of Magnesium (Mg+) likely present as Magnesium hydroxide $Mg(OH)_2$ is also an indicator of vegetation ash in the sample, however, it has a neutral pH and does not impact the pH of the sample. The anionic state, strength, of Oxygen (O^{H-}), a primary criterion for high pH, cannot be directly determined by the X-ray elemental analysis alone. The elevated presence of Magnesium (Mg^{2+}) is also an indicator of vegetation ash, however, it does not have a direct impact on the sample pH because it is relatively insoluble. The changes in cation/anion weight percentages in mixed ash and carpet dust (although complex) are accompanied with a simultaneous decrease in the weight% ratios of Sodium, Chlorine, Sulfur, and Carbon (likely present as chlorides, sulfates, and carbon present as carbonic acid). As described above, the presence of very low vegetation ash concentrations as low as ~0.7% will increase the pH of the carpet dust from a background measurement (no ash) of 7.6, to a pH of 8.3 in a distilled water dilution ratio of ~0.02 g/ml (total sample weight). The ash wt% concentration in the serial dilution sample comprising 0.7% ash was 0.00014 g/ml.

These tests indicate that a pH measurement exceeding 8.0 (in this carpet dust sample) is a potential indicator of low percent concentrations (~1%) of "fresh" vegetation "ash" in the dust sample. Other potential sources need to be excluded or accounted for at this pH concentration. Dust samples with a pH above 8.5 likely contain significant levels of "fresh" or "unaged" wildfire ash (i.e. ~5-10%). It is also important to note that "old" or "aged" ash residues may be present, but the pH may be significantly lower due to a chemical change or the removal of soluble Potassium in the form of a hydroxide. Additional research work is required to determine if ash percentages can be reliably estimated using the pH measurement. SEM/X-ray analysis of the residual supernatant solution used for pH analysis can then be used as confirmatory test for the presence or absence of vegetation ash. In other words measuring a pH above 8.5, when combined with the weight % measurements >10% of the primary cations of K^+ and often Mg^{2+}, indicate significant vegetation / wildfire ash is present.

8.2 Measurement of the Maximum pH and Conductivity Corrosion Potential

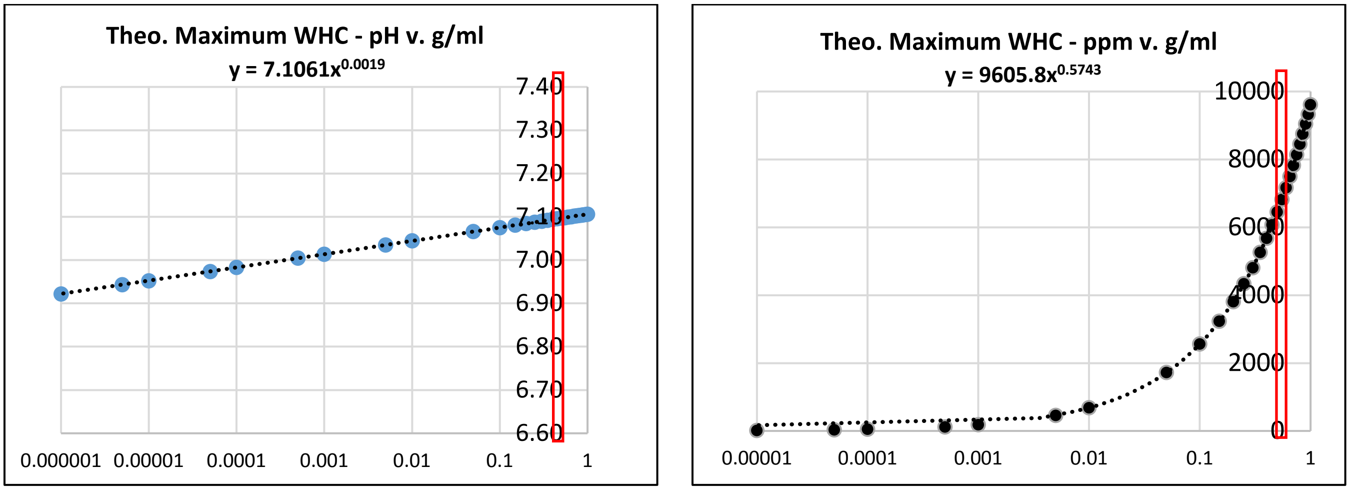
Although there is no simple formula or test to determine the corrosion potential[19,20,21] of wildfire ash on various materials, the maximum impact will occur when "fresh" ash has settled on susceptible surfaces and becomes saturated with water. This water-saturated condition is known as Available Water Capacity[30] or Water Holding Capacity[31]. The Water Holding Capacity definition used in this paper (and the EAA analysis method) is the measured water volume that can be added to a known weight of dry dust (defined in g/ml) until the sample is thoroughly saturated, and no excess water is present. The maximum pH and conductivity at the maximum Water Holding Capacity (WHC) of a dust sample can be calculated from the serial dilution data (as shown in the fire and indoor dust examples in Figures 25-26 below). The maximum theoretical pH, and conductivity can then be estimated by using a best fit equation. Soil samples are significantly different than settled dust samples because of their larger grain size, lower porosity, and lower surface area. The theoretical maximum saturation (WHC) calculations are shown below (Figures 24-29) for up to a theoretical maximum of 1.0g/ml for indoor carpet dust, Montecito fire ash, and oak/pine twig and leaf campfire ash. Based on actual empirical tests, the red rectangles show the actual maximum WHC for indoor dust samples is 0.5g/ml. Indoor dust and fire residues (average mass mean particle size of <20µm) are far different than typical clay sized soil particles infiltrating into the indoor environment (mass mean size <62µm). Native clay sized soil particles are primarily composed of a mixture (in decreasing order of abundance) of Aluminum silicate clays, quartz, feldspar minerals, carbonates, iron oxide, carbonaceous debris, and salts from both soil leeching and decomposing vegetation. For comparison, the measured WHC for a San Diego native coastal soil sample (sieved size fraction of <62um) is ~3.0g/ml in distilled water.

Indoor dust samples are primarily composed of fine grained, fluffy, and porous carbonaceous debris, skin cell fragments, cellulosic fabric fibers, and soil clay particles infiltrating from outdoors. The measured dry specific gravity is approximately 0.3g/cc even after being slightly compacted. The dry specific gravity for indoor dust samples is at least 10-fold lower than the average soil/sediment sample (~2.5g/cc) for which the ASTM pH Method was originally designed. At the same time the higher porosity and available surface area of indoor dust particles increases the potential adsorption of salts and water retention over

100-fold as compared to a typical soil sample. In fact there is no way to conduct an “ASTM” pH measurement on indoor dust at the 1:1 weight / volume ratio (as prescribed by the method). This is due to the fine grain size and low specific gravity if indoor dust (~0.3g/ml), and a higher maximum WHC value of ~0.5g/ml. The modified EAA procedure, even while using a lower dust weight to water volume ratio, is at least 10-fold more sensitive for determining the pH of indoor dust samples as compared to applying the method to soil samples.

Based on initial tests, the maximum saturation weight/water volume ratio (WHC) for a carpet dust sample was approximately 0.5 g/ml of water. The extrapolated pH and conductivity values at water saturation for indoor carpet dust are given in Figures 27 and 28.

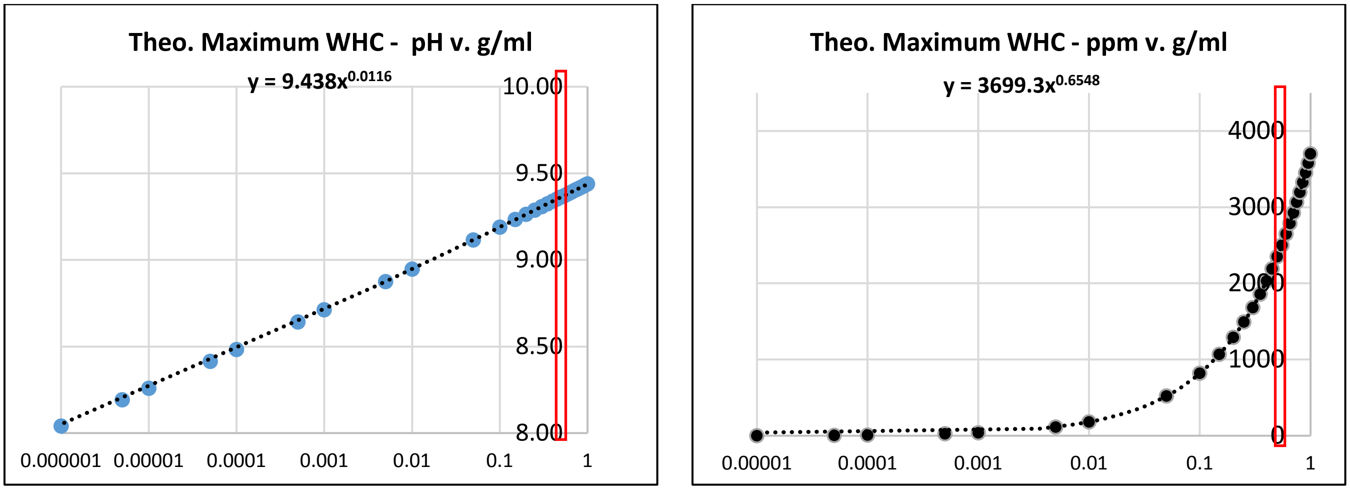
Figures 27 & 28. Indoor Carpet Dust Extrapolated pH and Conductivity at Saturation (WHC)



The pH and conductivity extrapolated to a maximum WHC of 0.5g/ml are 7.10 (pH), and >7,000 ppm respectively (red rectangle).

The pH and conductivity extrapolated to a maximum saturation (WHC) for the Montecito wildfire ash sample are given in Figures 29 and 30.

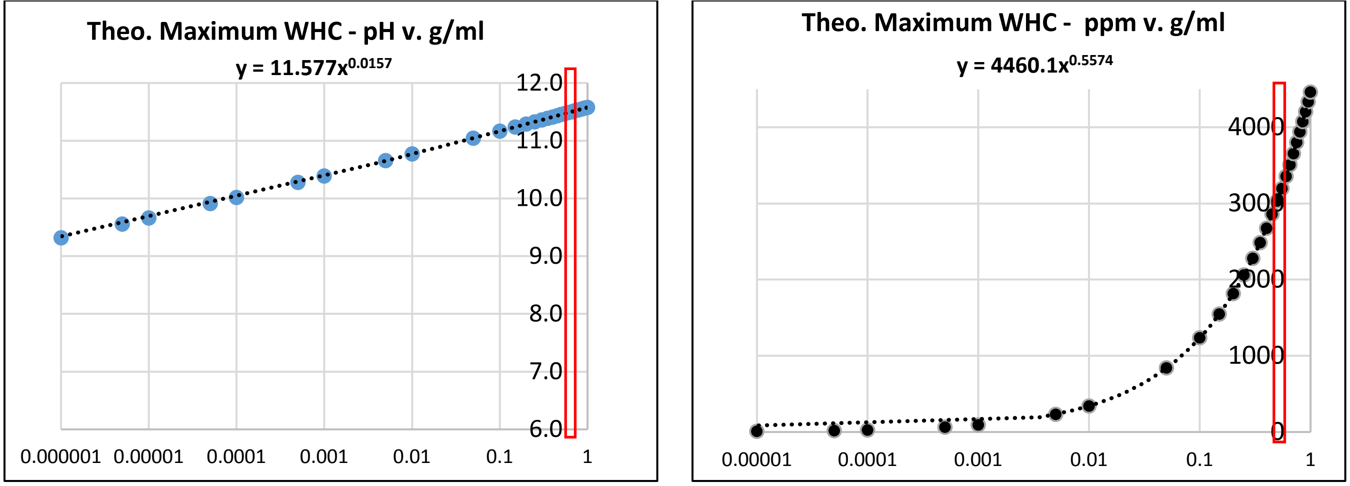
Figures 29 & 30. Montecito Fire Ash Extrapolated pH and Conductivity at Saturation (WHC)



The pH and conductivity extrapolated to a maximum WHC of 0.5g/ml are ~9.4 (pH), and ~ 2,500 ppm respectively (red rectangle).

The pH and conductivity extrapolated to a maximum WHC for pure oak/pine twig and leaf ash sample are given in Figures 31 and 32.

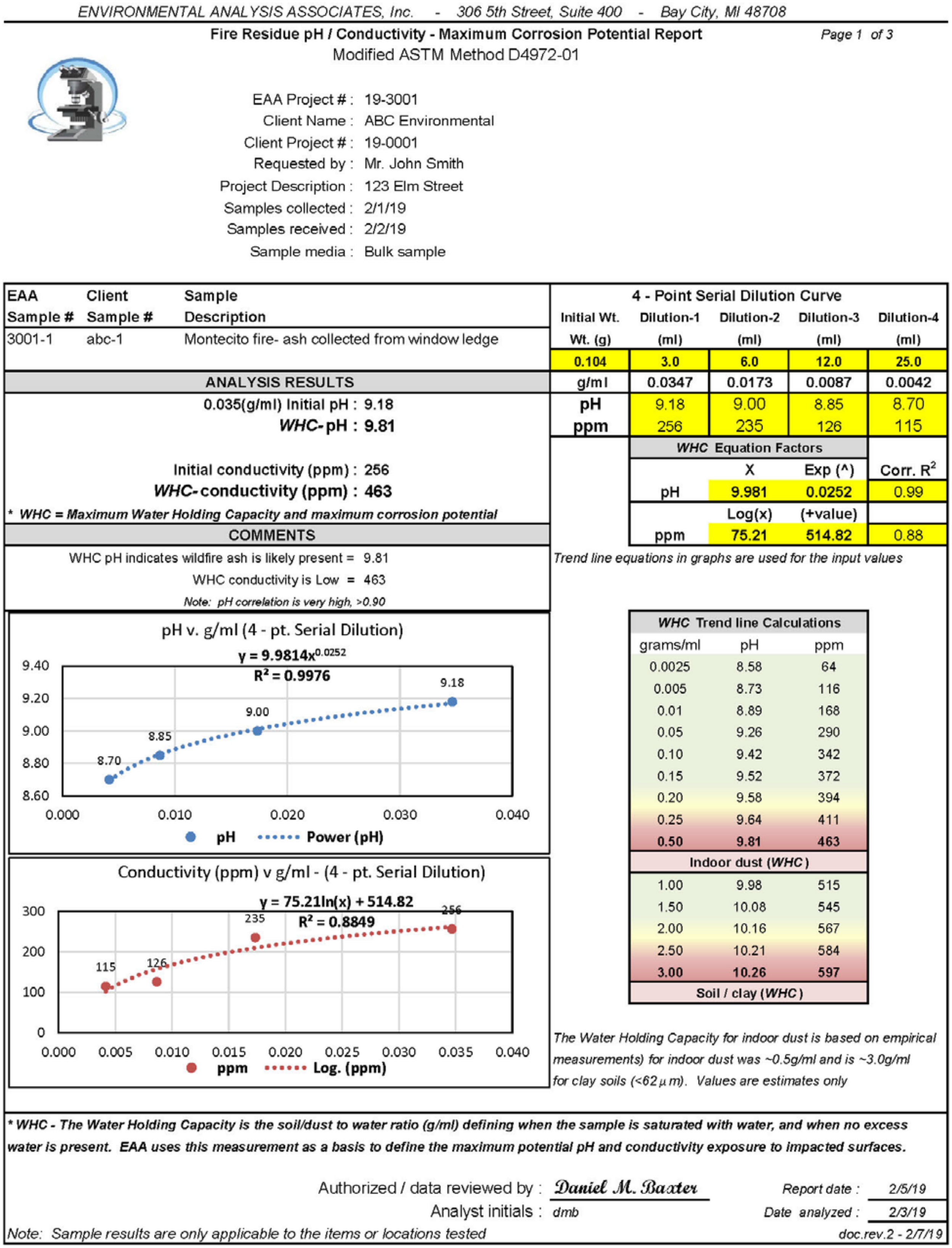
Figures 31 & 32. Oak/Pine Twig and Leaf Ash Extrapolated pH and Conductivity (g/ml) at saturation (WHC)



The pH and conductivity (Oak/Pine Twig and Leaf Ash) extrapolated to a maximum WHC of 0.5g/ml are ~11.5 (pH), and ~3200 ppm respectively (red rectangle). Based on the existing data, the maximum WHC pH for a typical "fresh" wildfire ash can range from a pH of 9.4 to potentially over 11.5. The maximum conductivity can range up to 3,000 ppm (based on a maximum WHC value of 0.5g/ml). In contrast, the normal indoor dust pH range is from 6.9 to 7.1, with higher measured conductivity approaching 7,000ppm due to the presence of Sodium and Chlorine ions.

An example of the EAA fire residue pH / Conductivity Maximum Corrosion Potential Report is given in Figure 33 on the following page. The report provides the initial measured pH and conductivity measurements at the analysis dilution rate of 0.5g/3ml, and then uses a four (4) point serial dilution curve (3ml, 6ml, 12ml, and 25ml respectively) to measure and obtain a best fit line equation. The trend line graphs and line equations for pH and conductivity are given in the report. The line equation values are used to calculate the maximum theoretical pH and conductivity at the maximum Water Holding Capacity (WHC). These values are reported in the "Analysis Results" section of the report and represent the "worst case" corrosion potential. When combined with cation /anion report, the information can be provided to engineering and/or corrosion experts to determine the potential impact on various surfaces and materials.

Figure 33. Example Maximum pH and Conductivity Corrosion Potential Report



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Fire Residue pH / Conductivity - Maximum Corrosion Potential Report

Page 1 of 3

Modified ASTM Method D4972-01

EAA Project # :	19-3001
Client Name :	ABC Environmental
Client Project # :	19-0001
Requested by :	Mr. John Smith
Project Description :	123 Elm Street
Samples collected :	2/1/19
Samples received :	2/2/19
Sample media :	Bulk sample

EAA Sample #	Client Sample #	Sample Description
3001-1	abc-1	Montecito fire- ash collected from window ledge

4 - Point Serial Dilution Curve

Initial Wt. Wt. (g)	Dilution-1 (ml)	Dilution-2 (ml)	Dilution-3 (ml)	Dilution-4 (ml)
0.104	3.0	6.0	12.0	25.0
g/ml	0.0347	0.0173	0.0087	0.0042
pH	9.18	9.00	8.85	8.70
ppm	256	235	126	115

ANALYSIS RESULTS

0.035(g/ml) Initial pH : 9.18

***WHC*-pH : 9.81**

Initial conductivity (ppm) : 256

***WHC*-conductivity (ppm) : 463**

** **WHC = Maximum Water Holding Capacity and maximum corrosion potential***

WHC Equation Factors

	X	Exp (^)	Corr. R²
pH	9.981	0.0252	0.99
	Log(x)	(+value)	
ppm	75.21	514.82	0.88

Trend line equations in graphs are used for the input values

COMMENTS

WHC pH indicates wildfire ash is likely present = 9.81

WHC conductivity is Low = 463

Note: pH correlation is very high, >0.90

***WHC* Trend line Calculations**

grams/ml	pH	ppm
0.0025	8.58	64
0.005	8.73	116
0.01	8.89	168
0.05	9.26	290
0.10	9.42	342
0.15	9.52	372
0.20	9.58	394
0.25	9.64	411
0.50	**9.81**	**463**
Indoor dust (*WHC*)		
1.00	9.98	515
1.50	10.08	545
2.00	10.16	567
2.50	10.21	584
3.00	**10.26**	**597**
Soil / clay (*WHC*)		

The Water Holding Capacity for indoor dust is based on empirical measurements) for indoor dust was ~0.5g/ml and is ~3.0g/ml for clay soils (<62 µ m). Values are estimates only

**** WHC - The Water Holding Capacity is the soil/dust to water ratio (g/ml) defining when the sample is saturated with water, and when no excess water is present. EAA uses this measurement as a basis to define the maximum potential pH and conductivity exposure to impacted surfaces.***

Authorized / data reviewed by : Daniel M. Baxter

Analyst initials : *dmb*

Report date : 2/5/19

Date analyzed : 2/3/19

Note: Sample results are only applicable to the items or locations tested

doc.rev.2 - 2/7/19

8.3 Differentiating Cigarette Ash and Char from Wild Fire Ash and Char

Cigarette tobacco leaf ash can sometimes be differentiated from wildfire vegetation ash in a surface or bulk sample when found in high concentrations. This is based upon using a combination of properties found in cigarette ash including the high conductivity of salts and/or additives, the presence of Potassium nitrate crystals using optical microscopy (Figures 34-37), and elemental analysis performed by SEM / X-ray analysis (Figures 38 & 39). Initial pH and conductivity measurements of Winston cigarette ash show the pH to be approximately 10.7 and similar to wildfire ash. However, the conductivity is approximately 10-fold higher than typical wildfire ash (e.g. conductivity around 5.4 mS/cm, and 5,500 ppm), and 5-fold higher than an average indoor dust sample measured at the same weight / volume dilution. This higher conductivity is due to the elevated Chlorine and/or other salts or additives. It is important to note that the "nitrate" in Potassium nitrate (a common additive to promote slow burning) was not elevated in the X-ray spectra from either the bulk ash, leaf char, or soluble cation/anion analysis in the Winston cigarette sample.

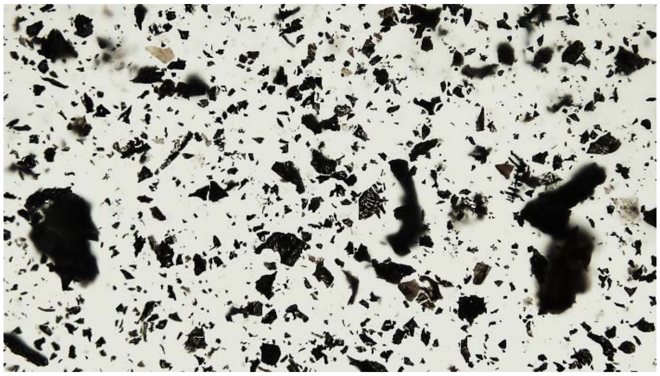


Figure 34. Cigarette ash – 200x RL – White background

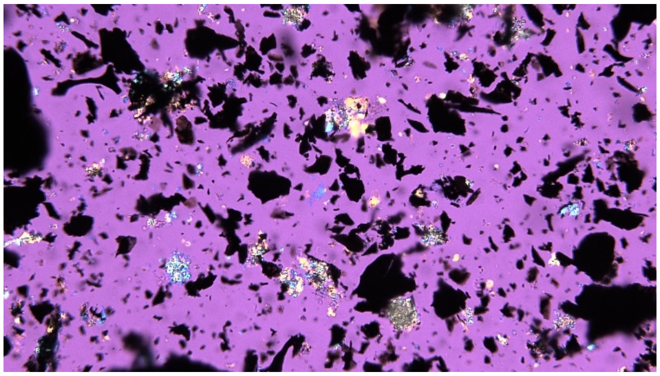


Figure 35. Cigarette ash – 200x - Polarized Light
Suspect Potassium nitrate crystals

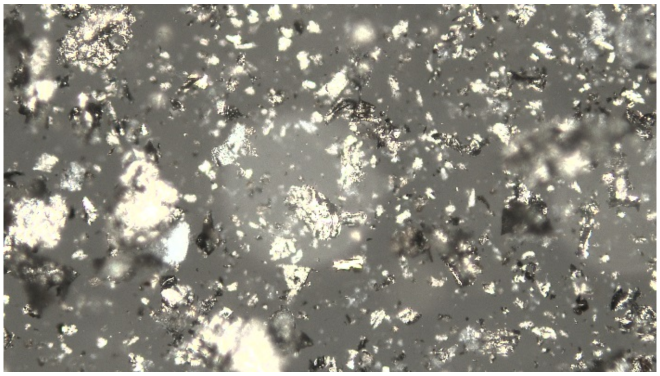


Figure 36. Cigarette ash – 200x RL – Black background
Highly reflective suspect Potassium nitrate crystals

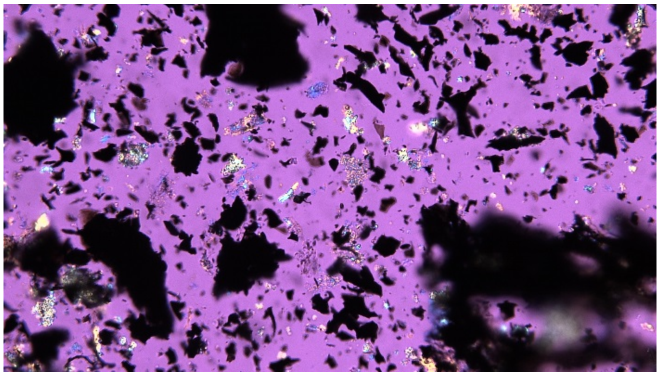


Figure 37. Cigarette ash – 200x - Polarized Light

The X-ray spectra of Winston bulk cigarette ash, a charred cigarette leaf, and the soluble cation/anions of the ash are shown in Figures 38-41. Elevated Chlorine and Potassium when found in the absence of Sodium (see Table 9) is an indicator for cigarette ash and is different than wildfire vegetation ash. The high conductivity of the cigarette ash can be attributed to elevated chloride (~ greater than 3%) present as soluble Potassium chloride (KCl).

Table 9. Comparison of Elemental Weight% For Bulk Cigarette Ash, Char, and Soluble Ash Cations/anions

Sample	**C**	**N**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**
Bulk ash-2 bkg	38.0	1.8	24.6	**0.1**	3.2	0.2	0.6	1.3	1.4	**2.9**	**12.4**	13.6
Bulk Leaf “char”	43.6	3.6	13.5	**0.3**	4.2	0.0	0.4	2.0	0.8	**5.8**	**18.6**	8.2
Cation/anion-ash *(Soluble fraction only)*	12.1	1.4	22.3	**0.7**	3.4	0.5	0.4	0.4	5.2	**9.6**	**42.2**	1.9

Figure 38. Bulk x-ray analysis of dry ash

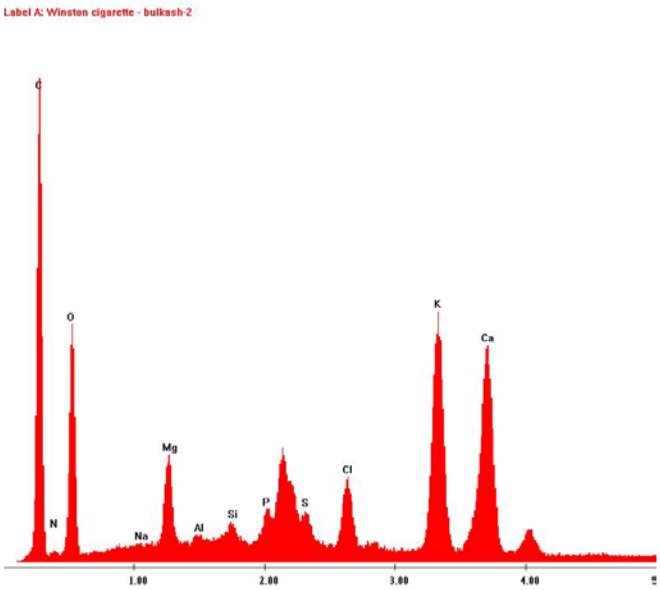


Figure 39. Soluble cation/anion X-ray analysis

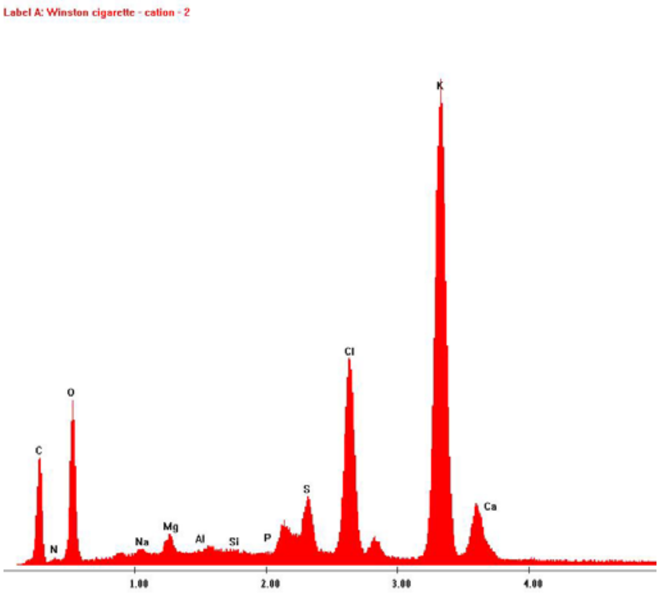


Figure 40. Micrograph of cigarette leaf char – 194x

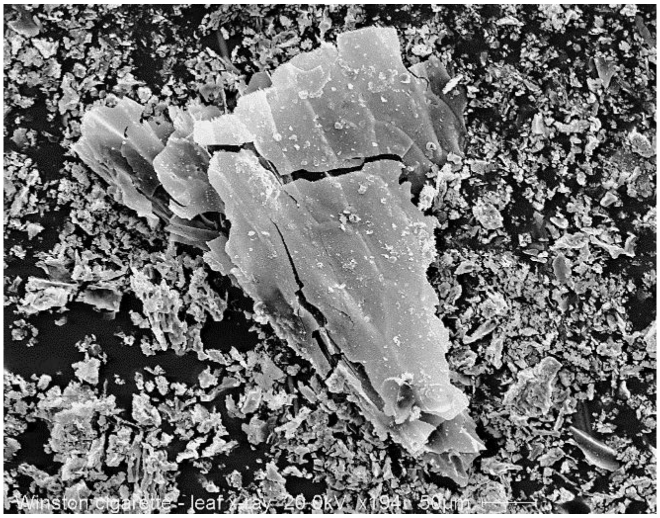
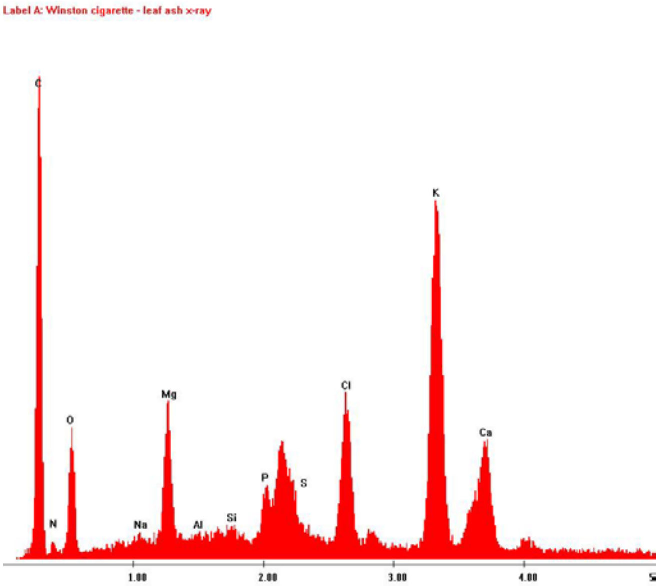


Figure 41. Bulk x-analysis of cigarette leaf char



Unlike normal vegetation “char” that is primarily carbon and oxygen, the X-ray analysis of char particles in the cigarette ash contain high levels of Potassium, Magnesium, and Chloride salts. The morphology of the tobacco leaf (using Optical and/or SEM analysis) can also be helpful in differentiating tobacco ash from other outdoor vegetation sources.

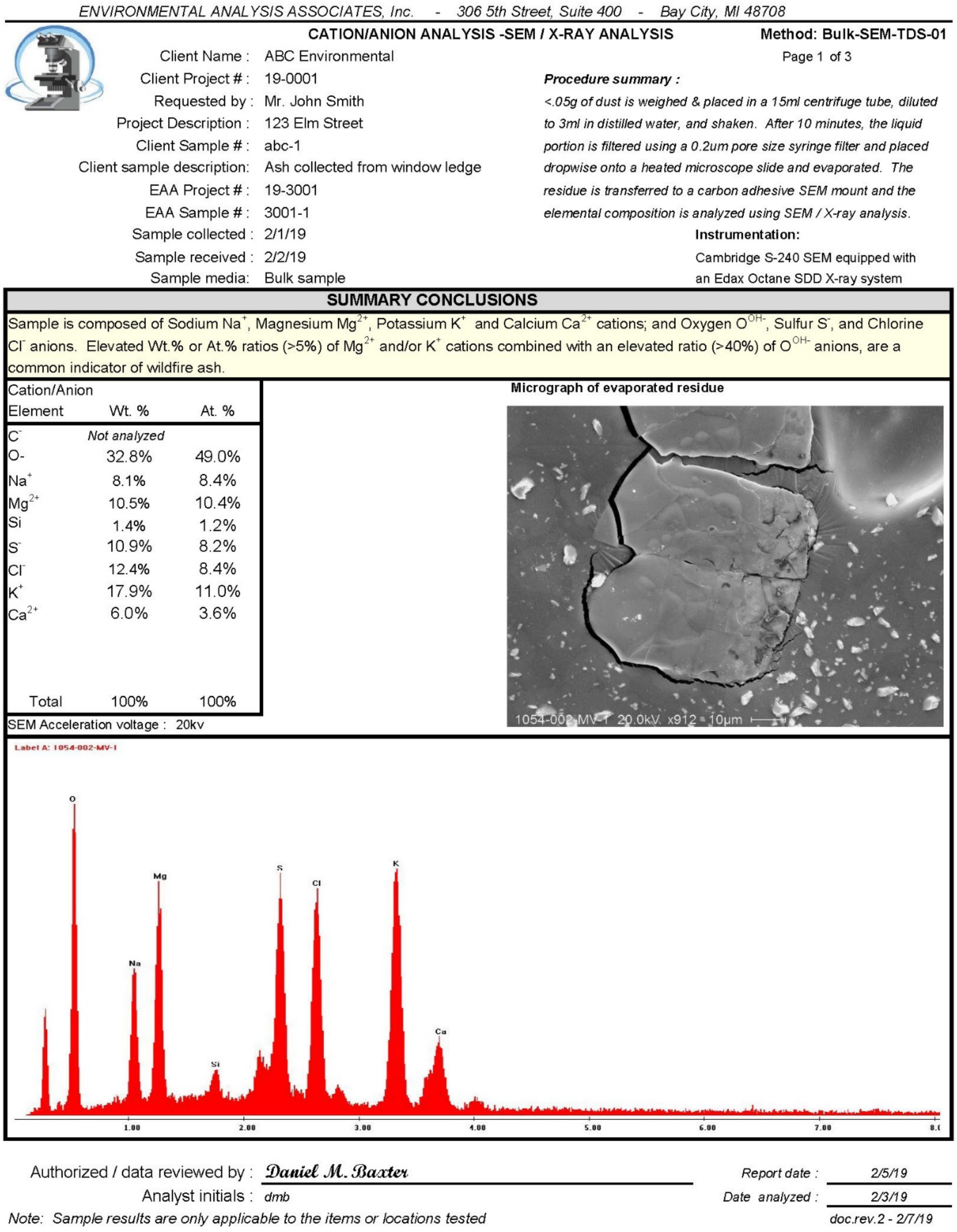
8.4 Cation/Anion Sample Preparation Procedure

The preparation procedures are summarized in this section. A known weight of ~0.05g settled dust (if sufficient material was collected) is placed in a 10ml centrifuge tube and 3ml of distilled water is added. The sample is shaken for 10 seconds. The sample is allowed to sit for 5 minutes and then shaken for 10 seconds again and allowed to settle for another 10 minutes or placed in a centrifuged to accelerate particle settling. The pH/conductivity supernatant sample can also be directly used for the cation/anion test. Approximately 2ml of the liquid is pipetted into a 5-10ml syringe with a 0.2µm syringe filter attached to the tip of the syringe. The supernatant is filtered and placed dropwise (5-10 drops at a time) onto a heated microscope slide and allowed to evaporate leaving the salt residue on the slide. Once the slide is fully dry, a pre-cleaned razor blade is used to scrape the residue from the slide and transfer it directly onto a carbon adhesive SEM specimen mount.

7.4 Cation / Anion Sample Analysis Procedure

The sample is coated with a defined thin layer using a sputter coater and placed into the Scanning Electron Microscope. A representative area of the evaporated bulk debris is analyzed by dispersive X-ray analysis at an accelerating voltage of 20kv. The report includes a micrograph of the area analyzed, the bulk dust X-ray spectrum, and the quantitative analysis for each element in weight % and atomic %. The Summary Conclusions provide a narrative interpretation of the results. An example report for the SEM/X-ray cation/anion analysis of an indoor dust sample collected from a fire impacted home from the Montecito fire is shown in Figure 42 on the following page.

Figure 42. SEM X-ray Cation/Anion Analysis of Micro-vacuum Sample - Montecito Fire.



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CATION/ANION ANALYSIS -SEM / X-RAY ANALYSIS

Method: Bulk-SEM-TDS-01

Page 1 of 3

Client Name : ABC Environmental
Client Project # : 19-0001
Requested by : Mr. John Smith
Project Description : 123 Elm Street
Client Sample # : abc-1
Client sample description: Ash collected from window ledge
EAA Project # : 19-3001
EAA Sample # : 3001-1
Sample collected : 2/1/19
Sample received : 2/2/19
Sample media: Bulk sample

Procedure summary :

<.05g of dust is weighed & placed in a 15ml centrifuge tube, diluted to 3ml in distilled water, and shaken. After 10 minutes, the liquid portion is filtered using a 0.2um pore size syringe filter and placed dropwise onto a heated microscope slide and evaporated. The residue is transferred to a carbon adhesive SEM mount and the elemental composition is analyzed using SEM / X-ray analysis.

Instrumentation:

Cambridge S-240 SEM equipped with
an Edax Octane SDD X-ray system

SUMMARY CONCLUSIONS

Sample is composed of Sodium Na^+, Magnesium Mg^{2+}, Potassium K^+ and Calcium Ca^{2+} cations; and Oxygen O^{OH-}, Sulfur S^-, and Chlorine Cl^- anions. Elevated Wt.% or At.% ratios (>5%) of Mg^{2+} and/or K^+ cations combined with an elevated ratio (>40%) of O^{OH-} anions, are a common indicator of wildfire ash.

Cation/Anion Element	Wt. %	At. %
C^-	*Not analyzed*	
O-	32.8%	49.0%
Na^+	8.1%	8.4%
Mg^{2+}	10.5%	10.4%
Si	1.4%	1.2%
S^-	10.9%	8.2%
Cl^-	12.4%	8.4%
K^+	17.9%	11.0%
Ca^{2+}	6.0%	3.6%
Total	100%	100%

SEM Acceleration voltage : 20kv

Micrograph of evaporated residue

Authorized / data reviewed by : Daniel M. Baxter
Analyst initials : *dmb*
Report date : *2/5/19*
Date analyzed : *2/3/19*

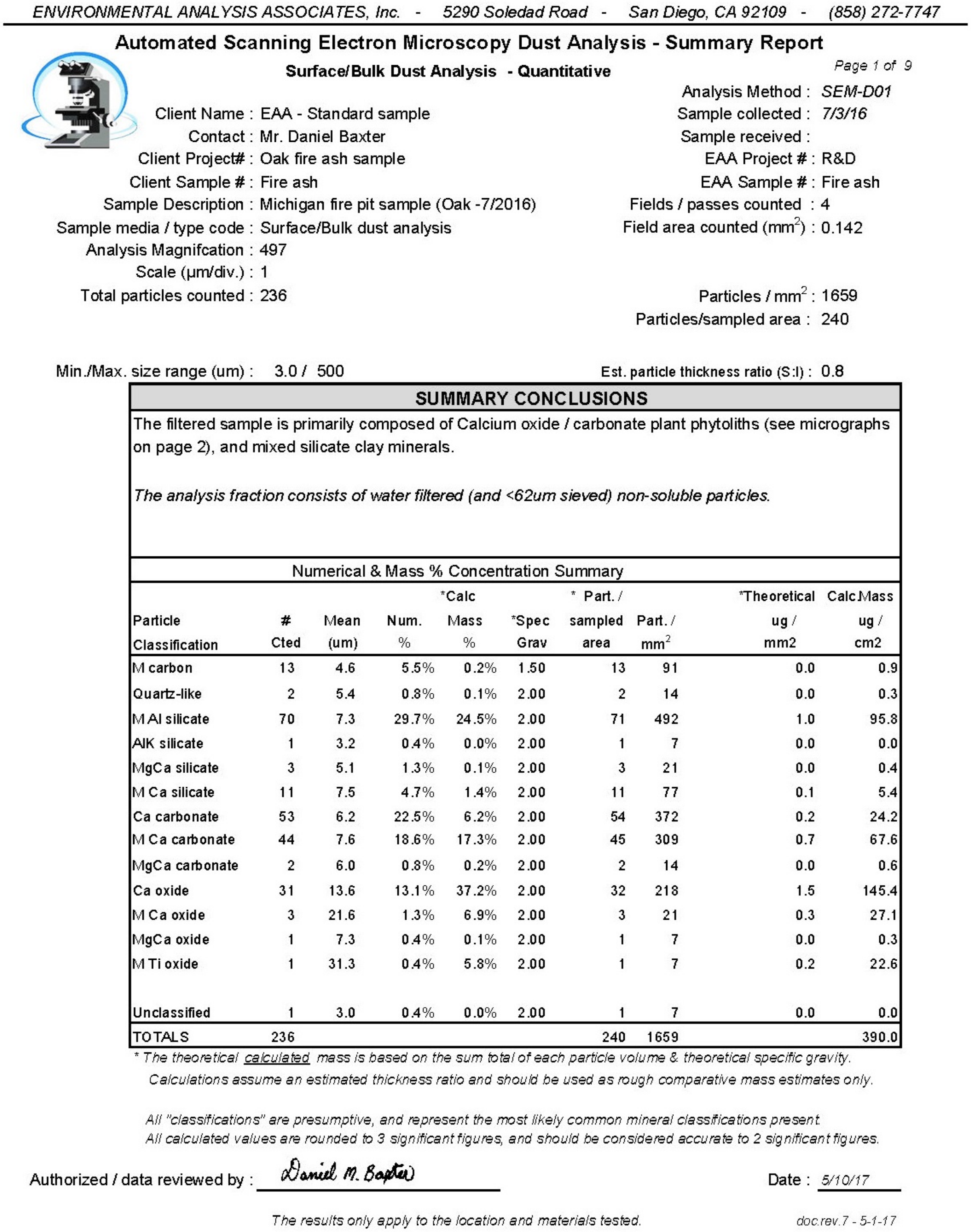
Note: Sample results are only applicable to the items or locations tested

doc.rev.2 - 2/7/19

9.0 AUTOMATED SEM / X-RAY ANALYSIS OF FIRE RESIDUE SAMPLES

EAA has developed an Automated SEM / X-ray analysis procedure that can be performed on bulk dust or surface tape lift surface samples. This analysis simultaneously identifies particles based on elemental chemistry (at one particle/second), and provides comprehensive size and mass distribution analysis of a statistically significant number of particles. This analysis can be used to differentiate wildfire particles from interference particles encountered in the Optical Microscopy analysis such as corrosion metals. Example report pages from the analysis of the non-soluble constituent Oak ash sample collected from a Michigan fire pit are given below in Figures 43-46. Figure 43 is the summary report page.

Figure 43. Example Automated SEM Analysis – Fire Report Summary Page (Non-soluble fire ash constituents)



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Automated Scanning Electron Microscopy Dust Analysis - Summary Report

Surface/Bulk Dust Analysis - Quantitative

Page 1 of 9

Analysis Method : *SEM-D01*
Sample collected : *7/3/16*
Sample received :
Client Name : EAA - Standard sample
Contact : Mr. Daniel Baxter
Client Project# : Oak fire ash sample
EAA Project # : R&D
Client Sample # : Fire ash
EAA Sample # : Fire ash
Sample Description : Michigan fire pit sample (Oak -7/2016)
Fields / passes counted : 4
Sample media / type code : Surface/Bulk dust analysis
Field area counted (mm^2) : 0.142
Analysis Magnifcation : 497
Scale (µm/div.) : 1
Total particles counted : 236
Particles / mm^2 : 1659
Particles/sampled area : 240

Min./Max. size range (um) : 3.0 / 500
Est. particle thickness ratio (S:l) : 0.8

SUMMARY CONCLUSIONS

The filtered sample is primarily composed of Calcium oxide / carbonate plant phytoliths (see micrographs on page 2), and mixed silicate clay minerals.

The analysis fraction consists of water filtered (and <62um sieved) non-soluble particles.

Numerical & Mass % Concentration Summary

Particle Classification	# Cted	Mean (um)	Num. %	*Calc Mass %	*Spec Grav	* Part. / sampled area	Part. / mm^2	*Theoretical ug / mm2	Calc.Mass ug / cm2
M carbon	13	4.6	5.5%	0.2%	1.50	13	91	0.0	0.9
Quartz-like	2	5.4	0.8%	0.1%	2.00	2	14	0.0	0.3
M Al silicate	70	7.3	29.7%	24.5%	2.00	71	492	1.0	95.8
AlK silicate	1	3.2	0.4%	0.0%	2.00	1	7	0.0	0.0
MgCa silicate	3	5.1	1.3%	0.1%	2.00	3	21	0.0	0.4
M Ca silicate	11	7.5	4.7%	1.4%	2.00	11	77	0.1	5.4
Ca carbonate	53	6.2	22.5%	6.2%	2.00	54	372	0.2	24.2
M Ca carbonate	44	7.6	18.6%	17.3%	2.00	45	309	0.7	67.6
MgCa carbonate	2	6.0	0.8%	0.2%	2.00	2	14	0.0	0.6
Ca oxide	31	13.6	13.1%	37.2%	2.00	32	218	1.5	145.4
M Ca oxide	3	21.6	1.3%	6.9%	2.00	3	21	0.3	27.1
MgCa oxide	1	7.3	0.4%	0.1%	2.00	1	7	0.0	0.3
M Ti oxide	1	31.3	0.4%	5.8%	2.00	1	7	0.2	22.6
Unclassified	1	3.0	0.4%	0.0%	2.00	1	7	0.0	0.0
TOTALS	236					240	1659		390.0

** The theoretical calculated mass is based on the sum total of each particle volume & theoretical specific gravity. Calculations assume an estimated thickness ratio and should be used as rough comparative mass estimates only.*

All "classifications" are presumptive, and represent the most likely common mineral classifications present.
All calculated values are rounded to 3 significant figures, and should be considered accurate to 2 significant figures.

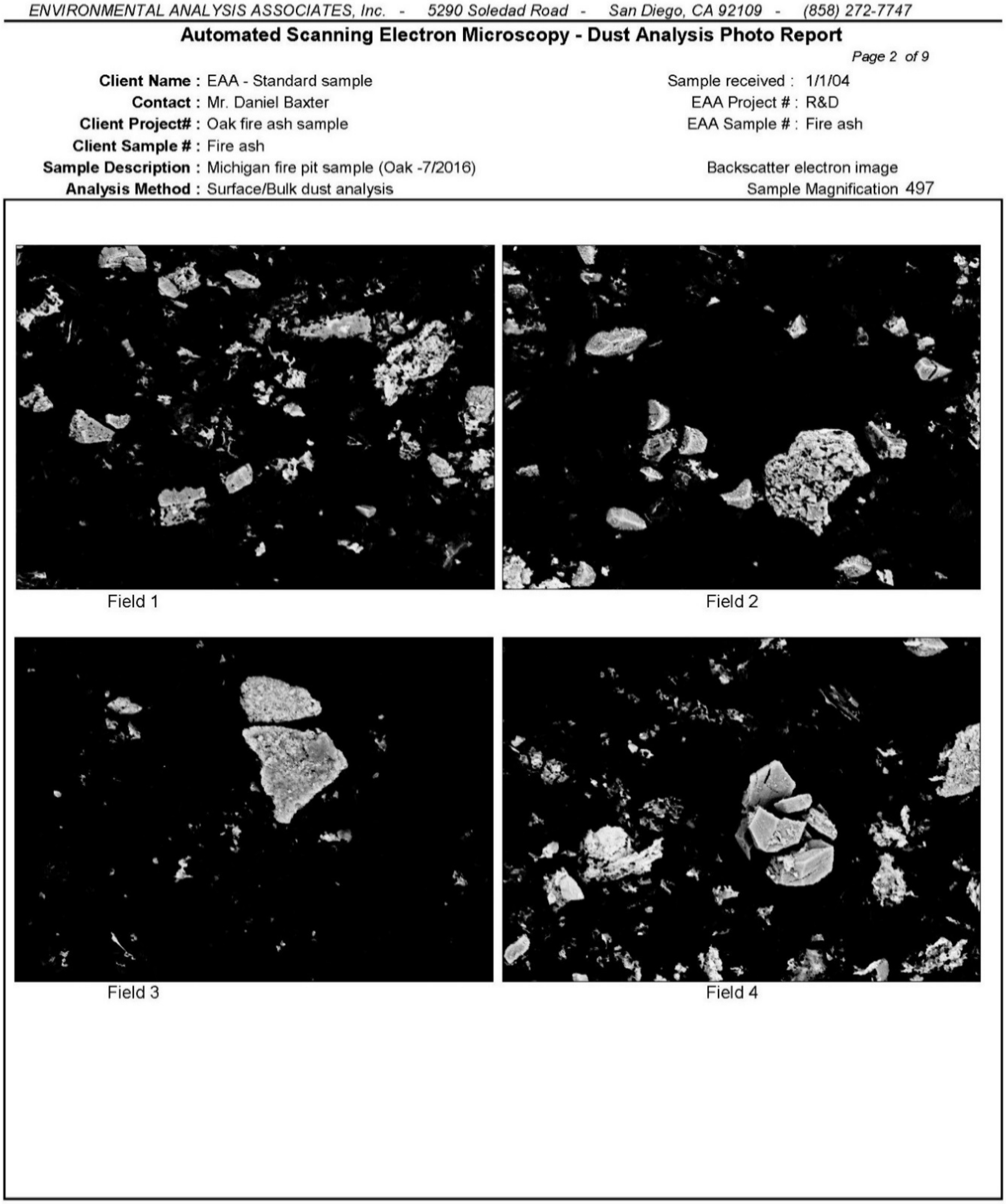
Authorized / data reviewed by : Daniel M. Baxter
Date : *5/10/17*

The results only apply to the location and materials tested.

doc.rev.7 - 5-1-17

The automated SEM / X-ray fire summary report page shows the quantitative results of a Michigan fire ash sample. The sample is primarily composed of mixed Magnesium and Calcium oxides, Calcium carbonate, and Mixed Aluminum Silicates consistent with the composition of vegetation ash. An example of the micrograph report page is given below in Figure 44.

Figure 44. Example Automated SEM Analysis – Micrograph Summary Page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Automated Scanning Electron Microscopy - Dust Analysis Photo Report

Page 2 of 9

Client Name : EAA - Standard sample
Contact : Mr. Daniel Baxter
Client Project# : Oak fire ash sample
Client Sample # : Fire ash
Sample Description : Michigan fire pit sample (Oak -7/2016)
Analysis Method : Surface/Bulk dust analysis

Sample received : 1/1/04
EAA Project # : R&D
EAA Sample # : Fire ash

Backscatter electron image
Sample Magnification 497

Field 1

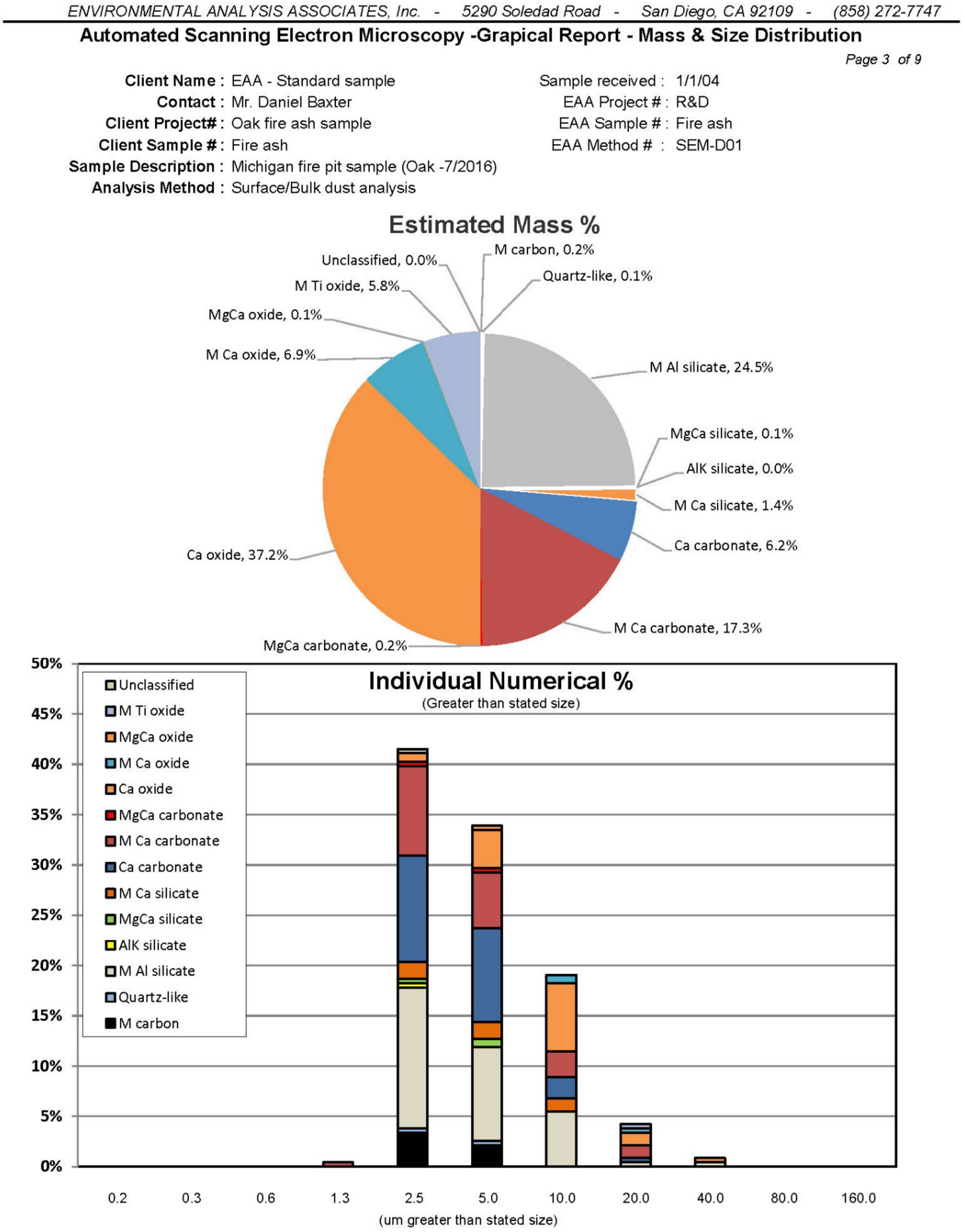
Field 2

Field 3

Field 4

The automated SEM / X-ray micrograph page shows the elemental/chemical distribution of the non-soluble ash fraction is composed of large Calcium oxide/carbonate plant phytoliths. Mass and size distribution information is also generated in a graphical summary page (see Figure 45 below).

Figure 45. Example Automated SEM / X-ray Analysis Graphical Mass and Size Distribution Page.



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Automated Scanning Electron Microscopy -Grapical Report - Mass & Size Distribution

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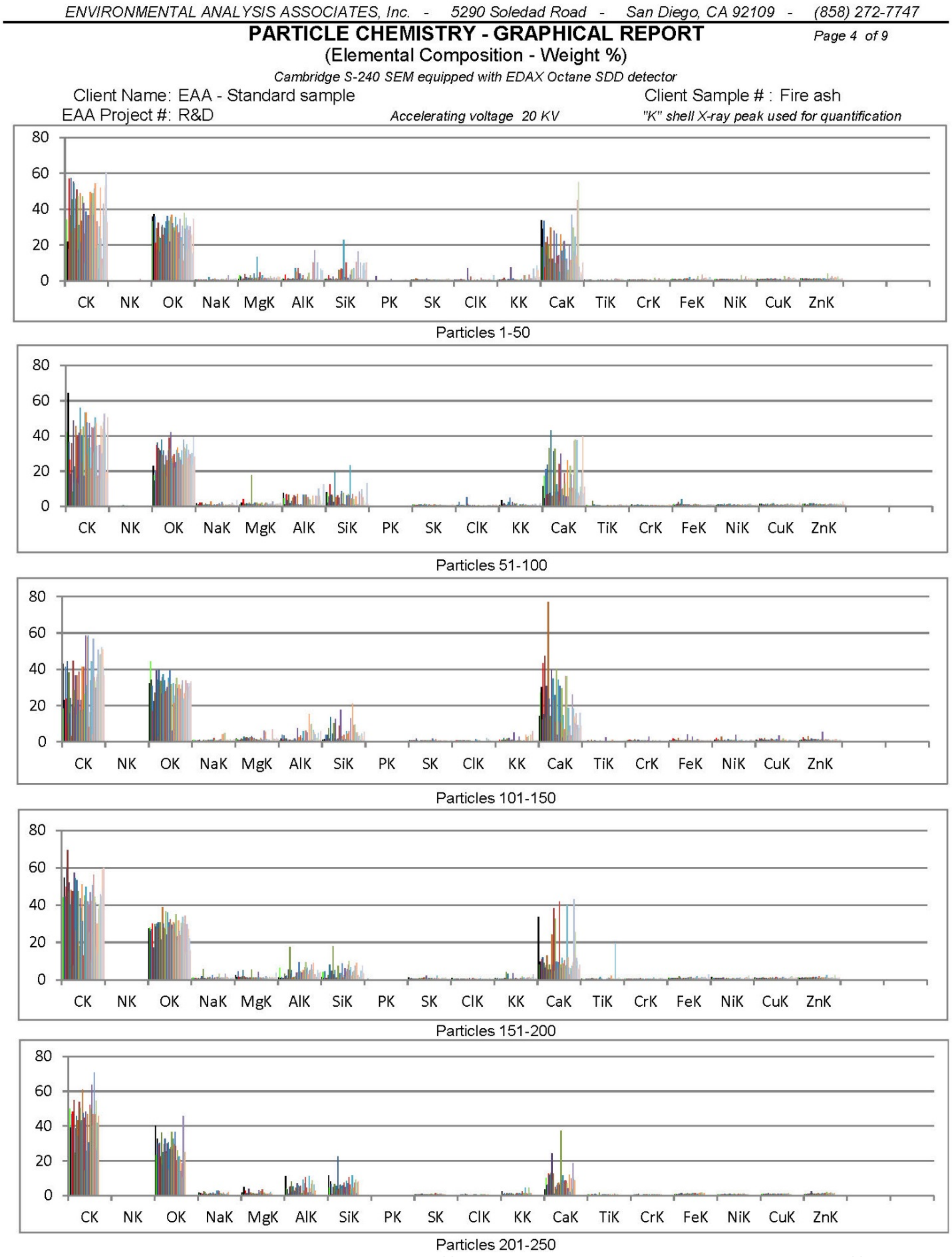
Client Name : EAA - Standard sample
Contact : Mr. Daniel Baxter
Client Project# : Oak fire ash sample
Client Sample # : Fire ash
Sample Description : Michigan fire pit sample (Oak -7/2016)
Analysis Method : Surface/Bulk dust analysis

Sample received : 1/1/04
EAA Project # : R&D
EAA Sample # : Fire ash
EAA Method # : SEM-D01

The automated SEM / X-ray analysis graphical page shows the mass size distribution of the ash sample (Primarily Mixed Calcium/Magnesium oxides and carbonates).

The elemental histogram page (Figure 46) shows the composited X-ray spectrums from each particle.

Figure 46. Example Automated SEM / X-ray Analysis Elemental Histogram Page



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PARTICLE CHEMISTRY - GRAPHICAL REPORT *Page 4 of 9*

(Elemental Composition - Weight %)

Cambridge S-240 SEM equipped with EDAX Octane SDD detector

Client Name: EAA - Standard sample
Client Sample # : Fire ash
EAA Project #: R&D
Accelerating voltage 20 KV
"K" shell X-ray peak used for quantification

Example pie charts showing the mass distribution differences between a typical San Diego office dust sample, “oak char”, and “oak ash”, are given below in Figures 47-49. The particle chemistry differences obtained by using automated SEM/X-ray analysis can clearly be seen between normal indoor dust, and mixed oak/pine twig and leaf “char”, and “ash” composition. These differences can be used to assess the dust source and potential impact from fire residue.

Figure 47. Particle Mass Distribution of an Office Dust Sample (Automated SEM/X-ray analysis)

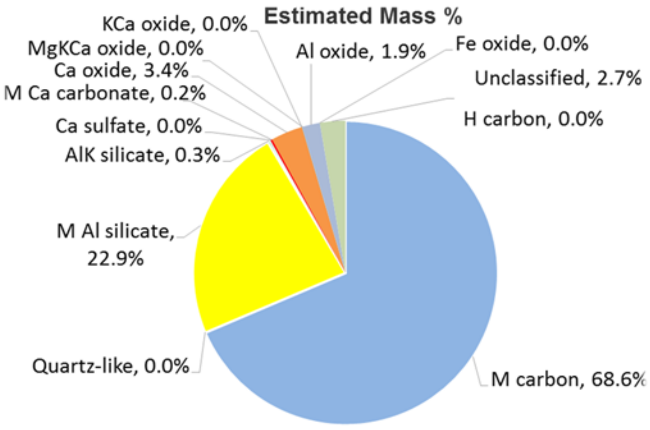
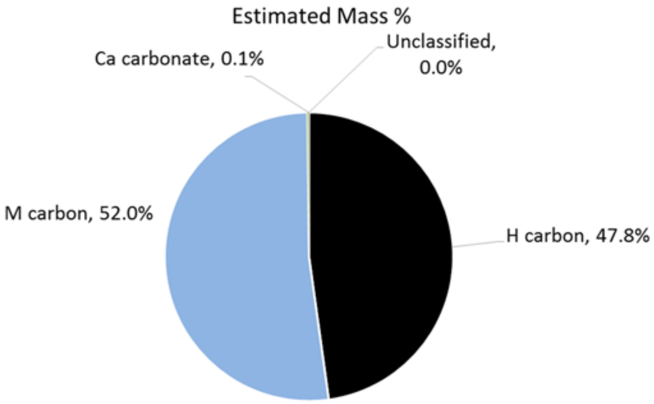
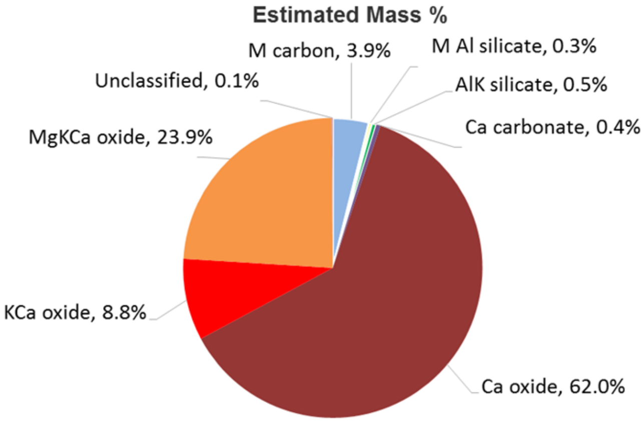


Figure 48. Particle Mass Distribution of Oak/pine "Char" Sample (Automated SEM/X-ray analysis)



It is important to note that the majority of mixed carbonaceous particles (M carbon) particles, i.e. Carbon 50-80%, are skin cell fragments in indoor dust samples. Typical char particles can be a mixture of "M carbon" and high carbonaceous particles (H carbon), i.e. Carbon >80%.

Figure 49. Particle Mass Distribution of an Oak/Pine Ash Sample. (Automated SEM/X-ray analysis)



This paper has provided an overview of additional fire residue analysis methods developed by Environmental Analysis Associates, Inc to supplement Optical Microscopy analysis. In most cases, the Optical Microscopy method is more than sufficient to differentiate non-impacted buildings from fire impacted buildings. The methods outlined above are the direct result of client requests for more comprehensive and targeted analysis methods to differentiate fire sources, determine the difference between "fresh" fire ash and historical re-entrainment, and determine the corrosion potential of wildfire and structure fire contamination claims. Keeping up with industry needs is an ongoing process at EAA and your feedback and input is important. More detailed information regarding these methods and other services offered by EAA can be obtained by contacting Mr. Daniel Baxter at 858-272-7747, or by email at dbaxter@eaalab.com.

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