EVALUATION OF PORTABLE X-RAY FLUORESCENCE FOR THE DETERMINATION OF CHLORINE IN THE ENVIRONMENT AFTER CHLORINE RELEASES AT JACK RABBIT II

CSAC 16-004

Prepared by:

Mark T. Whitmire
Noblis
3150 Fairview Park Drive South
Falls Church, VA 22042

John F. Schneider, Ph.D.
Threat Detection & Analysis Group
Materials Science Division
Argonne National Laboratory. Lemont, IL 60439

For

Shannon B. Fox, Ph.D.
Chemical Security Analysis Center
Science & Technology Directorate
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Familiarization, testing, and evaluation of the hand-held Innov-X Delta Premium X-Ray Fluorescence (XRF) detector with tantalum X-ray tube, model number DP-4000, was completed during Jack Rabbit II chlorine chemical release experiments at Dugway Proving Ground, UT in August and September 2015. The hand-held XRF was used to examine common indoor surfaces exposed to infiltrating chlorine gas, and the reaction of chlorine gas and aerosols with examples of materials that may be found near a chlorine spill or used in a response to it. The standardization and analysis method requires some changes before it may be used successfully in subsequent chemical release projects.

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For

Shannon B. Fox, Ph.D.
Chemical Security Analysis Center
Science & Technology Directorate
U.S. Department of Homeland Security
Aberdeen Proving Ground, MD 21010

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February 2016

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DISCLAIMER

List of Abbreviations and Acronyms

ABBREVIATIONS/ ACRONYMS	DEFINITIONS
AA	aged asphalt
AL	aluminum
AS	asphalt shingle
CA	coated aluminum
CU	copper
DPG	Dugway Proving Ground
DSTL	Defence Science and Technology Laboratory
GS	galvanized steel
HO	nylon over rubber hose
ITM	International Technical Meeting
JRI	Jack Rabbit I
JRII	Jack Rabbit II
keV	kiloelectronvolt
LBNL	Lawrence Berkeley National Laboratory
MDST	mountain daylight savings time
NA	new asphalt
NaCl	sodium chloride
ND	Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV
ppm	parts per million
ppmw	parts per million by weight
PVC	polyvinylchloride
PY	pyrolite
R_c	capture resistance
RP	nylon braided rope
RR	railroad tie
TR	rubber tire
SAG	Scientific Advisory Group
ST	steel
TIH	toxic inhalation hazard(s)
TP	telephone pole
UK	United Kingdom
UT	Utah

List of Abbreviations and Acronyms (cont.)

ABBREVIATIONS/ ACRONYMS	DEFINITIONS
UVU	Utah Valley University
VY	PVC Pipe
WB	Witness Board
WD	wood
WG	Working Group
Wt% Cl	weight percent chlorine
XRF	X-Ray Fluorescence

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

Page

Abstract

Familiarization, testing, and evaluation of the Innov-X Delta Premium hand-held X-Ray Fluorescence (XRF) detector, model number DP-4000 equipped with a tantalum X-ray tube was completed during Jack Rabbit II (JRII) chlorine chemical release experiments at Dugway Proving Ground (DPG), Utah (UT) in August and September 2015. The hand-held XRF was used to examine common indoor surfaces exposed to infiltrating chlorine gas, and the reaction of chlorine gas and aerosols with examples of materials that may be found near a chlorine spill or used in a response to it. The results demonstrate that the analysis method requires some changes before it may be used successfully in subsequent chemical release projects.

1.0 Background

The Jack Rabbit II[1] (JRII) project is the second part of a series of compressed chlorine gas release experiments performed at Dugway Proving Ground (DPG), Utah (UT). JRII leverages and extends the work of Jack Rabbit I[2] (JRI) which developed, tested, and evaluated a mechanism for the controlled, rapid release of liquefied, pressurized gases; observed the physiochemical characteristics of the disseminated vapor and aerosol cloud; and investigated toxic inhalation hazard (TIH) vapor transport, dispersion, and mitigation via deposition and reactions with water and soil. The project also evaluated instruments, test methods, and strategies that may be used to study future industrial scale tests. Two 'pilot' tests and 8 'record' tests of either 1 or 2 tons each of either chlorine or ammonia were completed in 2010. The results demonstrated:

- Downwind transport and turbulent mixing are initially resisted by a dense persistent gas/aerosol cloud.
- Rapid phase transition eruptions present a previously unobserved chlorine spill hazard.
- Source phenomena was non-linear with increasing release volumes.
- Reactivity with soil containing water and organic matter is an important removal mechanism for chlorine.

The goals of JRII are to collect data regarding the release source, cloud transport and dispersion, chemical reactions with the environment, exposure effects on equipment and infrastructure, and urban impacts using a mock urban test-bed. The program proposes to collect the data in real time via ground based and unmanned aerial system video and spectroscopic instruments, in situ point detectors, path-integrated detectors, and concentration- and dosage-determination instruments, and then share the data with all project participants in prescribed and common formats. The generated data and findings will drive

improved understanding of the basic science, improved operational hazard prediction modeling, more effective emergency response and training, national preparedness, and mitigation strategies.

As part of the JRII planning, the JRII Chlorine Reactivity and Deposition Working Group (WG) proposed a series of experiments to assist in the determination of important chemical deposition parameters. The parameters included the capture resistance (Rc) of soil, vegetation, and man-made surfaces used to calculate deposition velocity. The Rc represents the net effect of surface uptake effectiveness which depends on the surface composition and characteristics of the surface material.[1] The relative chemical reactivity with the surface is important, because even if the material is brought to the surface by turbulent transport, it will not deposit unless it reacts with or is adsorbed by the surface.

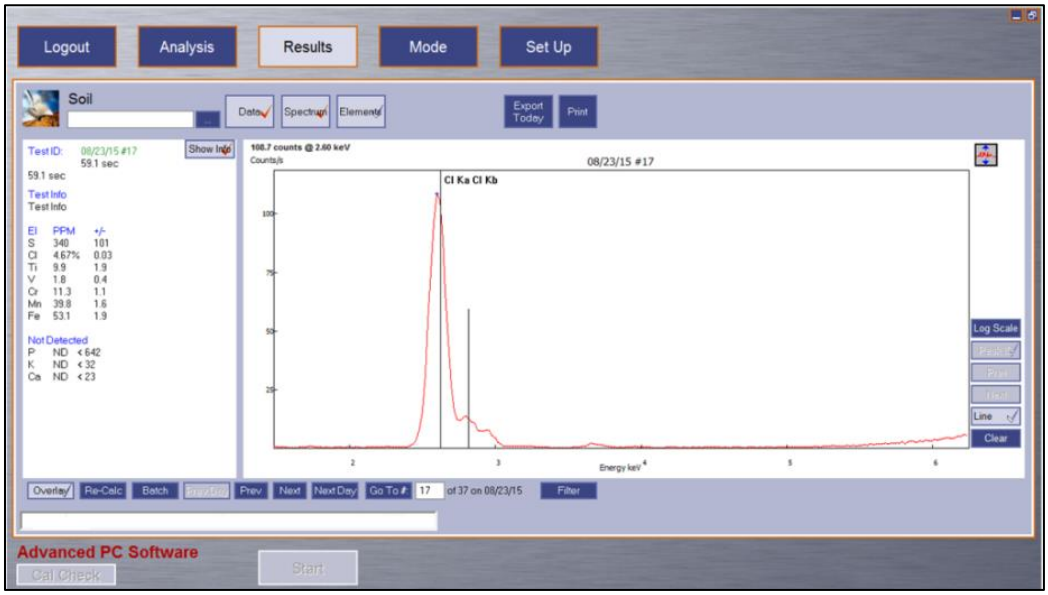
2.0 The Innov-X Delta Premium XRF, Model Number DP-4000

Reactivity and deposition experiments that the project Scientific Advisory Group (SAG) had originally scheduled for 2015 were postponed until 2016, so project scientists used the 2015 test releases to evaluate and familiarize themselves with some of the techniques and equipment that may be used for those experiments. The equipment included the hand-held Innov-X Delta Premium X-Ray Fluorescence (XRF) detector, model number DP-4000. The instrument was evaluated for its usefulness as a sensitive and quantitative chlorine detector. It is equipped with a tantalum X-ray tube for excitation and a large area silicon drift detector as shown in **Figure 1** (Serial Numbers 510828 and 510580).[3]

NOTE: Photo from http://www.olympus-ims.com/en/xrf-xrd/delta-handheld/delta-env/

Figure 1. Innov X Delta Premium Model Number DP-4000

The XRF uses an X-ray tube source to irradiate samples with X-rays. The incident radiation dislodges electrons from the innermost shells of the atom, creating vacancies. The electron vacancies are filled by other electrons cascading down from higher energy electron shells, thus emitting fluorescent energy characteristic of the element. A detector in the unit accumulates the returned energy signal and represents it as a peak centered near 2.6 kiloelectronvolt (keV); an example spectrum is shown in **Figure 2**. Depending on the sample material, the analyzer's incident beam is limited in its depth of penetration. Further, materials without a uniform composition may return a misleading result. For example, based on some weight percent chlorine (Wt% Cl) result, it would be incorrect to conclude that gypsum board exposed to chlorine would be penetrated throughout its thickness with reacted chlorine; and not limited to the paper surface.



NOTE: For quantitation, the peak height may be divided by the slope of a response vs. concentration instrument calibration.

Figure 2. An Accumulated Fluorescent Signal Centered near 2.6 keV Represents the Sample Chlorine Concentration

3.0 Activities

The XRF was used to supplement experiments and inform data gathered by Dr. Mike Sohn and Dr. Woody Delp from Lawrence Berkeley National Laboratories (LBNL).[4] They were investigating infiltration and exfiltration of chlorine relative to indoor environments. Their results using a bubbler system and Hach DR-1900 Portable Spectrophotometer (visible range, 340 to 800 nm) to investigate outgassing from exposed surfaces may be compared to the XRF examination of exposed drywall and carpet results.

The XRF was also used to support experiments completed by Mr. Andy Byrnes and his team from Utah Valley University (UVU); they were investigating the reaction of chlorine gas and aerosols with examples of materials that may be found near a chlorine spill or used in a response to it. For example, sections of creosote treated telephone poles and railroad ties, new and aged asphalt, and steel and copper coupons representing the materials of construction used in emergency response equipment. UVU had only proposed to make observations of the reaction of chlorine with each of the items, but the XRF was able to quantitate the amount of the reaction.

Aside from those efforts, scientists from the Defence Science and Technology Laboratory (DSTL), United Kingdom (UK) tested soil, vegetation, clothing, and hair samples at small scale chlorine exposure test sites at each of ten locations in tests 1 and 2 located adjacent to point monitors and on arcs inside the urban test grid. The samples were collected after each test and returned to DSTL for analysis; the project may expect to receive a report.

4.0 Procedure and Instrument Familiarization

The hand held XRF instrument was delivered with a single beam default environmental method used for the standards and sample analysis. A sample is analyzed by placing the instrument's tip in direct contact with the sample; or using the manufacturer's recommendations for divided samples:

- Prepare samples cups to contain at least 0.5" (usually 4-8 grams) of packed samples.
- When analyzing bagged samples, ensure that sufficient sample material exists in the bag to create a sample thickness of a minimum of 15 mm for a spot size that is larger than the analyzer's measurement window.
- When using bags, bags with thinner plastic walls are best

Chlorine standards were prepared from ordinary sugar and table salt weighed on an analytical balance and recorded to 5 decimal places. The balance calibration was checked with certified standard weights before

each use. The weight percent chlorine (Wt% Cl) was calculated from the following equation (**Equation 1**):

$$\text{Wt\% Cl} = 100\% \times \text{Mass NaCl} \times 0.607/\text{Total Mass NaCl and Sugar}$$

Equation 1

The result was recorded to 3 significant figures; 0.607 is the molecular weight fraction of chlorine in table salt. The salt and sugar were not dried before weighing, and the standards were not kept in a desiccator between uses. The details are presented in **Table 1**.

Table 1. Chlorine Standards Prepared August 23, 2015

MASS NaCl*	TOTAL MASS NaCl AND GRANULATED SUGAR	WT% Cl**
0.03538	10.37975	0.207
0.13181	10.00412	0.800
0.08662	10.13678	0.519
0.16672	10.09900	1.00
1.66450	10.00081	10.1
3.36750	10.06220	20.3
0.33187	9.99320	2.02
0.82729	9.98103	5.03
2.48897	10.00030	15.1

NOTE: *NaCl = Sodium Chloride; **WT% Cl = weight percent chlorine.

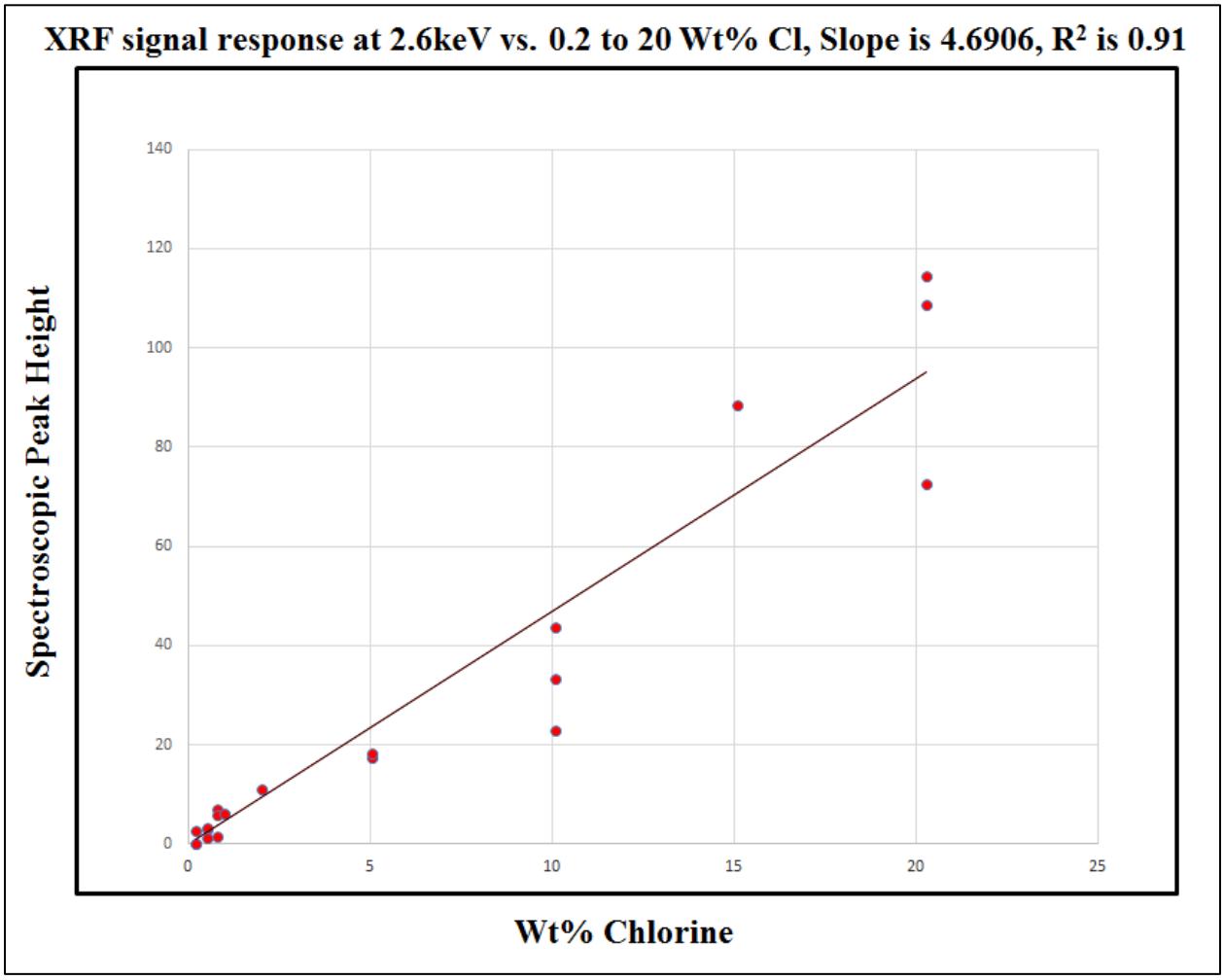
Once prepared, the standards were placed in polypropylene bags and analyzed in triplicate, at least for this initial set of standards. To analyze a standard, the salt and sugar mixture was gathered in a corner of the polypropylene bag and gently pressed against a hard surface beneath the instrument window tip to about 1 cm thickness. The analysis is started by operating the trigger on the instrument, and it is completed in 1 minute. The analysis time may be adjusted via the software or instrument interface. The instrument S/N is 510828, the results are presented in **Table 2** and plotted in the accompanying graph (**Figure 3**). The slope is 4.6909, "R^2" is 0.91. "R^2" is the coefficient of determination; it is the certainty with which one may predict the spectroscopic peak height from the standard concentration (Wt% Cl). "R" is the linear regression correlation coefficient; it is a measure of the strength and direction of the linear relationship between the standard concentration (Wt% Cl) and the spectroscopic peak height. For every subsequent calibration, the plot is similar differing only in the slope. It ranges

from 4.0614 to 5.6223. R^2 is never less than 0.91. The mean of the slope is 4.6693, standard deviation is 0.4863.

Table 2. Calibration Data Collected August 23, 2015

INSTRUMENT ANALYSIS NUMBER	STANDARD CONCENTRATION WT% Cl*	CHLORINE PEAK HEIGHT
#1	Manufacturer Calibration Check	Passed
#2	0.210	0.0
#3	0.210	2.7
#4	0.210	0.0
#5	0.800	1.5
#6	0.800	6.9
#7	0.800	5.8
#8	0.520	3
#9	0.520	3.4
#10	0.520	1.3
#11	1.00	4
#12	1.00	1.6
#13	1.00	1.7
#14	10.1	44
#15	10.1	23
#16	10.1	33
#17	20.3	110
#18	20.3	120
#19**	20.3	73
#33	1.00	6.1
#34	2.02	11
#35	5.03	17
#36	5.03	18
#37	15.1	89

NOTE: Slope is 4.6909, R^2 0.91; *WT% Cl = weight percent chlorine; **Background analysis of Lawrence Berkley National Laboratory's Trailers 3 and 4, gypsum drywall and carpet sample analyses 20-31.



NOTE: The relatively wide response distribution with concentration is typical of every subsequent calibration.

Figure 3. Initial XRF Calibration Before Baseline and Sample Analysis August 24

5.0 Gypsum Drywall, Carpet, and Witness Board Items; Baseline Analysis

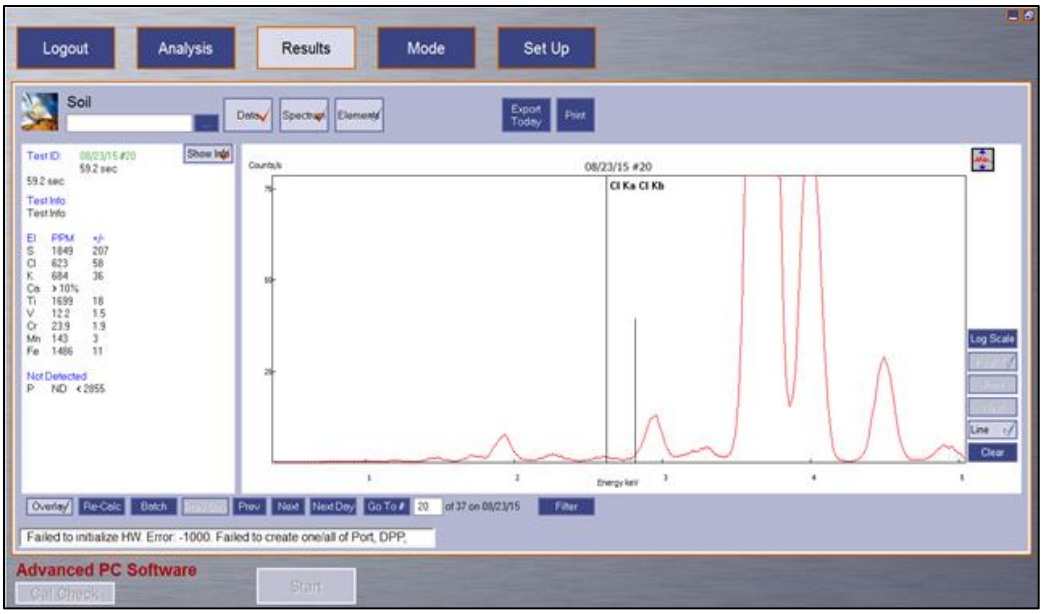
During preparation for Test Release 1 on August 24 the indoor gypsum drywall and carpeted floor of the LBNL test trailers 3 and 4 were examined at specific locations and in triplicate to serve as a Wt% Cl baseline for those surfaces. The results are presented in **Table 3.**

Table 3. Pre Release Analyses Collected August 23, 2015

INSTRUMENT ANALYSIS NUMBER	SAMPLE NAME	CHLORINE PEAK HEIGHT	WT% Cl*
#20	LBNL** Trailer 3, Wall 1	ND***	ND
#21	LBNL Trailer 3, Duplicate	ND	ND
#22	LBNL Trailer 3, Triplicate	ND	ND
#23	LBNL Trailer 3, Carpet 1	ND	ND
#24	LBNL Trailer 3, Duplicate	ND	ND
#25	LBNL Trailer 3, Triplicate	ND	ND
#26	LBNL Trailer 4, Wall 1	ND	ND
#27	LBNL Trailer 4, Duplicate	ND	ND
#28, #29	LBNL Trailer 4, Triplicate	ND	ND
#30	LBNL Trailer 4, Carpet 1	ND	ND
#31	LBNL Trailer 4, Duplicate	ND	ND
#32	LBNL Trailer 4, Triplicate	ND	ND

NOTE: *WT% Cl = weight percent chlorine; **LBNL = Lawrence Berkeley National Laboratory; ***ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.

Examples of the wall and carpet sample spectra in the chlorine region are shown in the **Figure 4** and **Figure 5.** The taller vertical line in each figure at 2.6 keV indicates where the chlorine spectral peak should occur if a detectable level of chlorine was present.



NOTE: The vertical lines are supplied by the software, and indicate where peaks corresponding to fluorescent electron transitions would appear if chlorine had been detected.

Figure 4. Example of the Baseline, Pre-Release Analysis of the Gypsum Drywall Inside the LBNL Indoor Environment

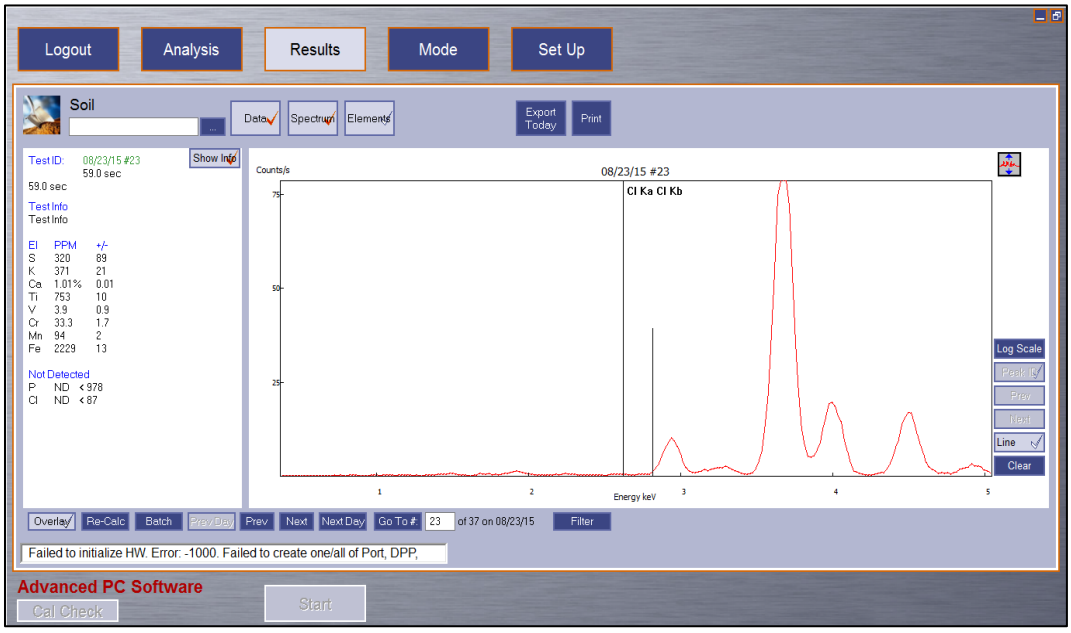


Figure 5. Example of the Baseline, Pre-Release Analysis of the Carpeted Floor Inside the LBNL Indoor Environment

The XRF was also used to complete the baseline analysis of all Witness Board (WB) items and four corresponding items from WB2; the Witness Boards were placed on the grid by UVU researchers near chlorine point monitors. Witness Board 2 is shown in **Figure 6**.

NOTE: The XRF was used to analyze the surface of each item after the Witness Board was exposed to the chlorine cloud, then recovered after a test release.

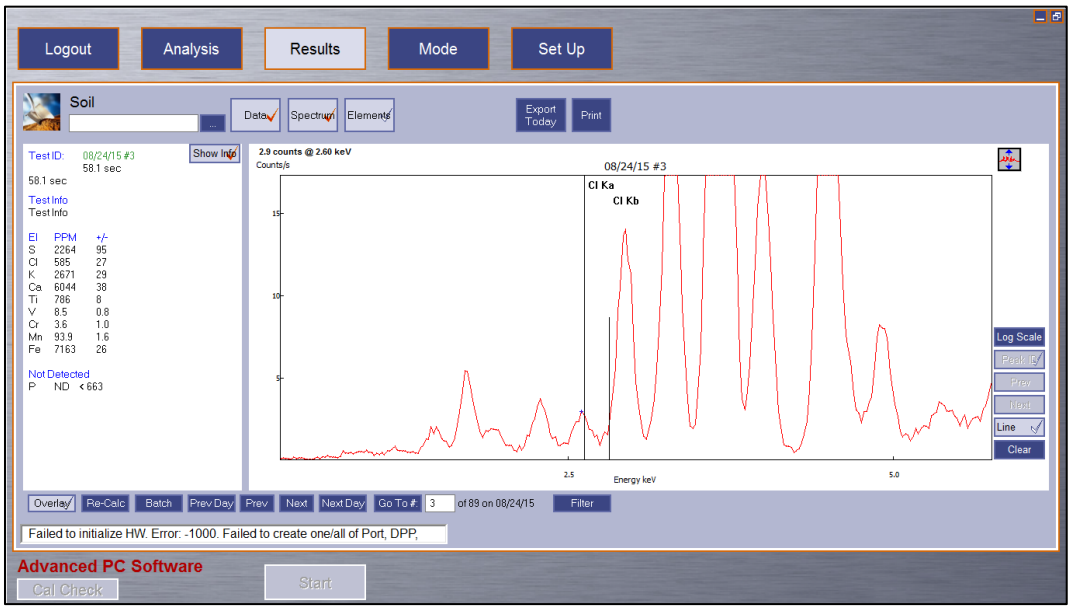
Figure 6. Utah Valley University Witness Board 2

The results are presented in **Table 4**. Detail of the XRF spectra for Instrument Reading #3, WB1 Railroad Tie is shown in **Figure 7** as an example analysis; the chlorine peak is indicative of pentachlorophenol or other chlorinated organic used as a wood preservative.

Table 4. Pre Release Analyses Collected August 24, 2015

INSTRUMENT 510828 NUMBER	SAMPLE NAME*	CHLORINE PEAK HEIGHT	WT% Cl**
#2	WB1,TP	2.7	0.58
#3	WB1, RR	2.9	0.62
#4	WB1, AA	ND***	ND
#5	WB1, NA	ND	ND
#6	WB1, AS	ND	ND
#7	WB1, VY	1051	-
#8	WB1, WD	ND	ND
#9	WB1, GS	ND	ND
#10	WB1, CU	0.9	0.19
#11	WB1, AL	ND	ND
#12	WB1, CA	ND	ND
#13	WB1, ST	ND	ND
#14	WB1, TR	ND	ND
#15	WB1, PY	ND	ND
#16	WB1, HO	ND	ND
#17	WB1, RP	4.3	0.92
#18	WB2, GS	ND	ND
#19	WB2, CU	ND	ND
#20	WB2, AL	ND	ND
#21	WB2, CA	ND	ND

NOTE: *Witness Board (WB); Telephone Pole (TP), treated with a chlorinated organic as preservative; Railroad Tie (RR) similarly treated; Aged Asphalt (AA); New Asphalt (NA); Asphalt Shingle (AS); PVC Pipe (VY); Wood (WD); Galvanized Steel (GS), zinc coating on steel; Copper (CU); Aluminum (AL); Coated Aluminum (CA), coating is titanium white paint; Steel (ST); Rubber Tire (TR); Pyrolite (PY), a material that may be used in an emergency response equipment coupling; nylon over rubber Hose (HO); and nylon braided Rope (RP); **WT% Cl = weight percent chlorine; ***ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.



NOTE: The chlorine peak is indicative of pentachlorophenol or other chlorinated organic used as a wood preservative.

Figure 7. Detail of the XRF Spectra from the Baseline Analysis of a Railroad Tie Completed Before the Chlorine Exposure

6.0 Calibration for Test Release 1 and Sample Analysis, August 24, 2015

Test release 1 (5 t) occurred on Monday August 24, 2015 at 07:36 mountain daylight savings time (MDST). An instrument calibration was completed before any LBNL indoor sites and UVU Witness Board materials were analyzed. The calibration data is presented in **Table 5**. As before, the poorly correlated concentration vs. response points may be seen up to about 1.0 Wt% Cl; above that, and including all of the points and the origin the slope is 5.0167, R^2 is 0.95.

Table 5. Calibration Data Collected August 24, 2015

INSTRUMENT 510828 NUMBER	STANDARD CONCENTRATION WT% Cl*	CHLORINE PEAK HEIGHT
#23	0.21	0.0
#24	0.52	4.4
#25	0.80	5.2
#26	1.00	2.4
#27	2.02	3.7
#28	5.03	20
#29	10.1	36
#30	15.1	68
#31	Data Lost	
#32	Data Lost	
#33	Calibration Check	
#34	1.00	12
#35	20.3	120
#36	2.02	2.6
#37	2.02	11
#38	0.21	ND**
#39	2.02	11
#40	2.02	5.8

NOTE: Slope is 5.0167, R^2 0.95; *WT% Cl = weight percent chlorine;**ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.

The results of the UVU Witness Boards 1 and 2 analysis are presented in **Table 6** and **Table 7**, respectively; the chlorine peak height is divided by the calibration line slope equal to 5.0167 to calculate the sample Wt% Cl. The witness boards were separated by a considerable lateral distance on the same grid arc. The UVU team used video cameras to closely monitor the materials during the test, and interestingly, observed that the sample railroad tie (RR) was smoking from the heat of the reaction with chlorine.

Table 6. Post Release Analyses Collected August 24, 2015

INSTRUMENT 510828 NUMBER	SAMPLE NAME*	CHLORINE PEAK HEIGHT	WT% Cl**
#41	WB1 , TP	11	2.1
#42	WB1, RR	12	2.3
#43	WB1, AA	3.2	0.64
#44	WB1, NA	6.6	1.3
#45	WB1, AS	3.6	0.72
#46	WB1, VY	1076	-
#47	WB1, WD	6.1	1.2
#48	WB1, GS	ND***	ND
#49	WB1, CU	61	12
#50	WB1, AL	1.3	0.26
#51	WB1, CA	ND	ND
#52	WB1, ST	119	24
#53	WB1, TR	14	2.8
#54	WB1, PY	3.4	0.68
#55	WB1, HO	7.2	1.4
#56	WB1, RP	5.8	1.2

NOTE: *Witness Board (WB); Telephone Pole (TP), treated with a chlorinated organic as preservative; Railroad Tie (RR) similarly treated; Aged Asphalt (AA); New Asphalt (NA); Asphalt Shingle (AS); PVC Pipe (VY); Wood (WD); Galvanized Steel (GS), zinc coating on steel; Copper (CU); Aluminum (AL); Coated Aluminum (CA), coating is titanium white paint; Steel (ST); Rubber Tire (TR); Pyrolite (PY), a material that may be used in an emergency response equipment coupling; nylon over rubber Hose (HO); and nylon braided Rope (RP); **WT% Cl = weight percent chlorine;***ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.

Table 7. Post Release Analyses Collected August 24, 2015

INSTRUMENT 510828 NUMBER	SAMPLE NAME*	CHLORINE PEAK HEIGHT	WT% Cl**
#57	WB2 , TP	5.9	1.2
#58	WB2, RR	21	4.2
#59	WB2, AA	4.0	0.80
#60	WB2, NA	2.8	0.56
#61	WB2, AS	ND***	ND
#62	WB2, VY	994	-
#63	WB2, WD	4.2	0.84
#64	WB2, GS	4.3	0.86
#65	WB2, CU	68.5	14
#66	WB2, AL	1.1	0.22
#67	WB2, CA	16.8	3.3
#68	WB2, ST	27.9	5.6
#69	WB2, TR	5.4	1.1
#70	WB2, PY	ND	ND
#71	WB2, HO	9.4	1.9
#72	WB2, RP	4.9	0.98

NOTE: *Witness Board (WB); Telephone Pole (TP), treated with a chlorinated organic as preservative; Railroad Tie (RR) similarly treated; Aged Asphalt (AA); New Asphalt (NA); Asphalt Shingle (AS); PVC Pipe (VY); Wood (WD); Galvanized Steel (GS), zinc coating on steel; Copper (CU); Aluminum (AL); Coated Aluminum (CA), coating is titanium white paint; Steel (ST); Rubber Tire (TR); Pyrolite (PY), a material that may be used in an emergency response equipment coupling; nylon over rubber Hose (HO); and nylon braided Rope (RP); **WT% Cl = weight percent chlorine; ***ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.

The results of the LBNL indoor sites are presented in **Table 8**, the chlorine peak height is divided by calibration line slope equal to 5.0167 to calculate the sample Wt% Cl.

Table 8. Post Release Analyses Collected August 24, 2015

INSTRUMENT 510828 NUMBER	SAMPLE NAME	CHLORINE PEAK HEIGHT	WT% Cl*
#73	LBNL** Trailer 3, Wall Analysis	4.4	0.88
#74	LBNL Trailer 3, Wall Duplicate	4.0	0.80
#75	LBNL Trailer 3, Wall Triplicate	4.1	0.82
#76	LBNL Trailer 3, Carpet Analysis	ND***	ND
#77	LBNL Trailer 3, Carpet Duplicate	1.1	0.22
#78	LBNL Trailer 3, Carpet Triplicate	1.1	0.22
#79	LBNL Trailer 4, Wall Analysis	4.4	0.88
#80	LBNL Trailer 4, Wall Duplicate	3.7	0.74
#81	LBNL Trailer 4, Wall Triplicate	4.1	0.82
#82	LBNL Trailer 4, Carpet Analysis	ND	ND
#83	LBNL Trailer 4, Carpet Duplicate	ND	ND
#84	LBNL Trailer 4, Carpet Triplicate	ND	ND

NOTE: *WT% Cl = weight percent chlorine; **LBNL = Lawrence Berkeley National Laboratory; ***ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.

Another series of standards was prepared on August 26 to replace or be used with the existing standards to investigate the instrument's poor linearity, and variable and lower than expected response. The data is presented in **Table 9**.

Table 9. Supplemental and Replacement Standards Prepared August 26, 2015

MASS NaCl	TOTAL MASS NaCl AND GRANULATED SUGAR	WT% Cl*
0.25490	10.03306	1.54
0.03511	10.05319	0.210
0.08881	10.00945	0.540
0.13328	9.99562	0.81
0.16842	10.01835	1.02
0.25848	10.01520	1.57
0.16616	10.02643	1.00

NOTE: *WT% Cl = weight percent chlorine.

7.0 Calibration for Test Release 2 and Sample Analysis, August 28, 2015

Test release 2 (9 t) occurred on August 28, 2015 at 09:24 MDST. XRF instrument S/N 510828 was abandoned because of intermittent but progressively more frequent instrument analysis failures. Instrument serial number 510580 was used for the remainder of the project.

A seven point instrument calibration was completed in triplicate on August 28 before analysis of the LBNL indoor sites and UVU Witness Board materials were analyzed after Test Release 2. The calibration data is presented in **Table 10**.

Incidentally, though it was collected on August 28, the data is officially recorded as having occurred on August 29 because of a peculiarity of the instrument and Innov-X software. That is, regardless of the date it was collected, the reported date is the date that the data is downloaded from the hand held instrument. So, in this instance, despite being calibrated before data collection on August 28 after test release 2, the data was not downloaded until after additional calibration and sample data was collected after test release 3 on August 29. Further and unexpectedly, the data is not time stamped. If it were, and if the stability and sensitivity issues were resolved, the instrument could conceivably be used to determine chlorine off gassing rates.

Table 10. Calibration Data Collected August 28, 2015

INSTRUMENT 510580 NUMBER	STANDARD CONCENTRATION, WT% Cl*	CHLORINE PEAK HEIGHT
#17	1.01	8.9
#18	1.54	3.5
#19	2.02	3.5
#20	5.03	19.6
#21	10.1	25.3
#22	15.1	77.2
#23	20.3	160
#24	1.01	15.8
#25	1.54	8.1
#26	2.02	6.5
#27	5.03	18.2
#28	10.1	30.5
#29	15.1	73.0
#30	20.3	19.1
#31	1.01	12.6
#32	1.54	5.4
#33	2.02	3.7
#34	5.03	24.5
#35	10.1	43.5
#36	15.1	65.4
#37	20.3	86.6

NOTE: Data is officially and misleadingly date stamped August 29; slope is 4.2784, R^2 is 0.93; *WT% Cl = weight percent chlorine.

The results of the UVU Witness Boards analysis are presented in **Table 11** and **Table 12**; the chlorine peak height is divided by slope equal to 4.2784 to calculate the sample Wt% Cl. The witness boards 3 and 4 were separated by a considerable lateral distance on the same grid arc.

Table 11. Post Release Analyses Collected August 28, 2015

INSTRUMENT 510580 NUMBER	SAMPLE NAME*	CHLORINE PEAK HEIGHT	WT% Cl**
#38	WB3 , TP	8.4	2.0
#39	WB3, RR	3.9	0.91
#40	WB3, AA	3.6	0.84
#41	WB3, NA	6.9	1.6
#42	WB3, AS	3.2	0.75
#43	WB3, VY	1032	-
#44	WB3, WD	6.2	1.4
#45	WB3, GS	7.2	1.7
#46	WB3, CU	24.8	5.8
#47	WB3, AL	1.7	0.40
#48	WB3, CA	ND***	ND
#49	WB3, ST	ND	ND
#50	WB3, TR	9.4	2.2
#51	WB3, PY	2.7	0.63
#52	WB3, HO	6.0	1.4
#53	WB3, RP	2.5	0.58

NOTE: Data is officially and misleadingly date stamped August 29; *Witness Board (WB); Telephone Pole (TP), treated with a chlorinated organic as preservative; Railroad Tie (RR) similarly treated; Aged Asphalt (AA); New Asphalt (NA); Asphalt Shingle (AS); PVC Pipe (VY); Wood (WD); Galvanized Steel (GS), zinc coating on steel; Copper (CU); Aluminum (AL); Coated Aluminum (CA), coating is titanium white paint; Steel (ST); Rubber Tire (TR); Pyrolite (PY), a material that may be used in an emergency response equipment coupling; nylon over rubber Hose (HO); and nylon braided Rope (RP); **WT% Cl = weight percent chlorine; ***ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.

Table 12. Post Release Analyses Collected August 28, 2015

INSTRUMENT 510580 NUMBER	SAMPLE NAME*	CHLORINE PEAK HEIGHT	WT% Cl**
#54	WB4, TP	10.2	2.4
#55	WB4, RR	12.8	3.0
#56	WB4, AA	6.1	1.4
#57	WB4, NA	9.8	2.3
#58	WB4, AS	4.3	1.0
#59	WB4, VY	1033	-
#60	WB4, WD	4.2	1.0
#61	WB4, GS	5.9	1.4
#62	WB4, CU	48.7	11
#63	WB4, AL	1.5	0.35
#64	WB4, CA	ND***	ND
#65	WB4, ST	ND	ND
#66	WB4, TR	6.7	1.6
#67	WB4, PY	ND	ND
#68	WB4, HO	11.8	2.8
#69	WB4, RP	4.8	1.1

NOTE: Data is officially and misleadingly date stamped August 29; *Witness Board (WB); Telephone Pole (TP), treated with a chlorinated organic as preservative; Railroad Tie (RR) similarly treated; Aged Asphalt (AA); New Asphalt (NA); Asphalt Shingle (AS); PVC Pipe (VY); Wood (WD); Galvanized Steel (GS), zinc coating on steel; Copper (CU); Aluminum (AL); Coated Aluminum (CA), coating is titanium white paint; Steel (ST); Rubber Tire (TR); Pyrolite (PY), a material that may be used in an emergency response equipment coupling; nylon over rubber Hose (HO); and nylon braided Rope (RP); **WT% Cl = weight percent chlorine; ***ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.

The results of the LBNL gypsum dry wall and carpet analysis are presented in **Table 13**; the chlorine peak height is divided by slope equal to 4.2784 to calculate the sample Wt% Cl. The witness boards 3 and 4 were separated by a considerable lateral distance on the same grid arc.

Table 13. Post Release Analyses Collected August 28, 2015

INSTRUMENT ANALYSIS NUMBER	SAMPLE NAME	CHLORINE PEAK HEIGHT	WT% Cl*
#70	LBNL** Trailer 3, Wall Analysis	6.0	1.4
#71	LBNL Trailer 3, Wall Duplicate	6.5	1.5
#72	LBNL Trailer 3, Wall Triplicate	6.0	1.4
#73	LBNL Trailer 3, Carpet Analysis	1.6	0.37
#74	LBNL Trailer 3, Carpet Duplicate	1.6	0.37
#75	LBNL Trailer 3, Carpet Triplicate	1.6	0.37
#76	LBNL Trailer 4, Wall Analysis	4.2	0.98
#77	LBNL Trailer 4, Wall Duplicate	4.7	1.1
#78	LBNL Trailer 4, Wall Triplicate	4.6	1.1
#79	LBNL Trailer 4, Carpet Analysis	1.3	0.30
#80	LBNL Trailer 4, Carpet Duplicate	1.5	0.35
#81	LBNL Trailer 4, Carpet Triplicate	1.3	0.30

NOTE: Data is officially and misleadingly date stamped August 29; *WT% Cl = weight percent chlorine; **LBNL = Lawrence Berkeley National Laboratory.

8.0 Continue Analysis after Test Release 3 and Complete Calibration, August 29, 2015

Test release 3 (5 t) occurred on Saturday, August 29, 2015 at 07:56 MDST. The XRF analyses continued without an intervening calibration; the results of the analysis of Witness Board 5 and 6 items are presented in **Table 14** and **Table 15**. The chlorine peak height is divided by slope equal to 4.0614, R^2 equals 0.96, to calculate the sample Wt% Cl. The slope is determined from a straight line fit of a line drawn through the data points from a post sample calibration. An analysis of the LBNL trailer surfaces was not completed after test release 3.

Table 14. Post Release Analyses Collected August 29, 2015

INSTRUMENT ANALYSIS NUMBER	SAMPLE NAME*	CHLORINE PEAK HEIGHT	WT% Cl**
#82	WB5, TP	6.4	1.6
#83	WB5, RR	32.4	8.0
#84	WB5, AA	3.0	0.74
#85	WB5, NA	4.2	1.0
#86	WB5, AS	2.3	0.57
#87	WB5, VY	1117	-
#88	WB5, WD	3.4	0.84
#89	WB5, GS	3.8	0.94
#90	WB5, CU	62.0	15
#91	WB5, AL	ND***	ND
#92	WB5, CA	ND	ND
#93	WB5, ST	ND	ND
#94	WB5, TR	4.3	1.1
#95	WB5, PY	1.9	0.47
#96	WB5, HO	6.2	1.5
#97	WB5, RP	4.3	1.1

NOTE: *Witness Board (WB); Telephone Pole (TP), treated with a chlorinated organic as preservative; Railroad Tie (RR) similarly treated; Aged Asphalt (AA); New Asphalt (NA); Asphalt Shingle (AS); PVC Pipe (VY); Wood (WD); Galvanized Steel (GS), zinc coating on steel; Copper (CU); Aluminum (AL); Coated Aluminum (CA), coating is titanium white paint; Steel (ST); Rubber Tire (TR); Pyrolite (PY), a material that may be used in an emergency response equipment coupling; nylon over rubber Hose (HO); and nylon braided Rope (RP); **WT% Cl = weight percent chlorine; ***ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.

Table 15. Post Release Analyses Collected August 29, 2015

INSTRUMENT ANALYSIS NUMBER	SAMPLE NAME*	CHLORINE PEAK HEIGHT	WT% Cl**
#98	WB6, TP	5.4	1.3
#99	WB6, RR	5.1	1.3
#100	WB6, AA	3.5	0.86
#101	WB6, NA	4.2	1.0
#102	WB6, AS	2.1	0.52
#103	WB6, VY	1093	-
#104	WB6, WD	4.6	1.1
#105	WB6, GS	ND***	ND
#106	WB6, CU	24.6	6.1
#107	WB6, AL	ND	ND
#108	WB6, CA	ND	ND
#109	WB6, ST	ND	ND
#110	WB6, TR	6.2	1.5
#111	WB6, PY	2.2	0.54
#112	WB6, HO	4.5	1.1
#113	WB6, RP	4.3	1.1

NOTE: *Witness Board (WB); Telephone Pole (TP), treated with a chlorinated organic as preservative; Railroad Tie (RR) similarly treated; Aged Asphalt (AA); New Asphalt (NA); Asphalt Shingle (AS); PVC Pipe (VY); Wood (WD); Galvanized Steel (GS), zinc coating on steel; Copper (CU); Aluminum (AL); Coated Aluminum (CA), coating is titanium white paint; Steel (ST); Rubber Tire (TR); Pyrolite (PY), a material that may be used in an emergency response equipment coupling; nylon over rubber Hose (HO); and nylon braided Rope (RP); **WT% Cl = weight percent chlorine; ***ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.

A calibration was completed at the end of the Witness Board analysis; the results are presented in **Table 16**, in which the slope of the current calibration line is 4.0614, R^2 is 0.96.

Table 16. Calibration Data Collected August 29, 2015

INSTRUMENT ANALYSIS NUMBER	STANDARD CONCENTRATION WT% Cl*	CHLORINE PEAK HEIGHT
#114	1.01	13.8
#115	1.54	5.4
#116	2.02	3.9
#117	5.03	18.8
#118	10.1	40.8
#119	15.1	61.5
#120	20.3	144
#121	0.21	0.0
#122	0.54	1.0
#123	0.81	2.7
#124	1.02	5.5
#125	1.57	11.6

NOTE: Slope is 4.0614, R^2 0.96; *WT% Cl = weight percent chlorine.

9.0 Supplementary Analysis, August 31, 2015

Before the release the XRF was used to examine the concrete surface at the points represented in the accompanying diagram (**Figure 8**). After so many tests the concrete was likely saturated with chlorine, but the data was collected with the expectation that it may be useful. The results are in **Table 17**. The chlorine peak height is divided by slope equal to 4.6656, R^2 equals 0.94, to calculate the sample Wt% Cl. The slope is determined from a straight line fit of a line drawn through the data points from the September 1 calibration, the data is presented below.

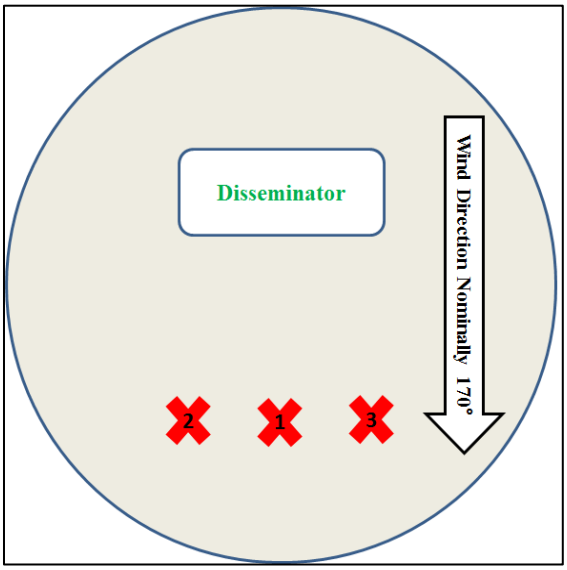


Figure 8. Schematic of Concrete Pad and XRF Sampling Locations

Table 17. Pre Release Analyses of Already Exposed Concrete

INSTRUMENT ANALYSIS NUMBER	SAMPLE NAME	CHLORINE PEAK HEIGHT	WT% Cl*
#3	Concrete Pad 1	24.4	5.2
#4	Concrete Pad 2	10.0	2.1
#5	Concrete Pad 3	15.6	3.3

NOTE: Collected August 31, 2015; *WT% Cl = weight percent chlorine.

10.0 Test Release 4, September 1, 2015

Test release 4 (7.7 t) occurred on Tuesday September 1, 2015 at 08:38 MDST.

A calibration was completed before the samples were analyzed; the calibration results are presented in **Table 18**. The slope of the line is 4.6656, R^2 is 0.94. The current calibration slope differs from the average of the current and previous slopes by +6.9%.

Table 18. Calibration Data Collected September 1, 2015

INSTRUMENT ANALYSIS NUMBER	STANDARD CONCENTRATION WT% Cl*	Cl PEAK HEIGHT AT 2.6 keV**
#2	1.01	ND***
#3	1.54	3.4
#4	2.02	8.6
#5	5.03	13.5
#6	10.1	44.6
#7	15.1	69.4
#8	20.3	106
#9	0.21	ND
#10	0.54	ND
#11	0.81	3.0
#12	1.02	13.6
#13	1.57	9.0
#14	1.01	2.3
#15	1.54	8.5
#16	2.02	4.4
#17	5.03	17.7
#18	10.1	20.2
#19	15.1	66.3
#20	20.3	107
#21	0.21	ND
#22	0.54	6.3
#23	0.81	1.8
#24	1.02	14.6
#25	1.57	5.2

NOTE: Slope is 4.6656, R^2 0.94; *WT% Cl = weight percent chlorine; **keV = kiloelectronvolt; ***ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.

Post-release analysis of the concrete pad was completed within hours of the end of the release. The chlorine peak height is divided by slope equal to 4.6656, R^2 is 0.94, to calculate the sample Wt% Cl. There is only a nominal change in chlorine concentration on the concrete surface where liquid chlorine had previously washed over it (see **Table 19**).

Table 19. Post Release Analyses Collected September 1, 2015

INSTRUMENT ANALYSIS NUMBER	SAMPLE NAME	CHLORINE PEAK HEIGHT	WT% Cl*
#27	Concrete Pad 1	19.4	4.2
#28	Concrete Pad 2	13.2	2.8
#29	Concrete Pad 3	26.6	5.7

NOTE: *WT% Cl = weight percent chlorine.

The post release results of the LBNL gypsum dry wall and carpet analysis are presented in **Table 20**, **Table 21**, and **Table 22**. The chlorine peak height is divided by slope equal to 4.6656, R^2 is 0.94, to calculate the sample Wt% Cl. The wall and carpet contamination doesn't seem to be changing appreciably even after many repeated exposures.

Table 20. Post Release Analyses Collected September 1, 2015

INSTRUMENT ANALYSIS NUMBER	SAMPLE NAME	CHLORINE PEAK HEIGHT	WT% Cl*
#30	LBNL** Trailer 3, Wall Analysis	5.6	1.2
#31	LBNL Trailer 3, Wall Duplicate	3.2	0.7
#32	LBNL Trailer 3, Wall Triplicate	5.9	1.3
#33	LBNL Trailer 3, Carpet Analysis	1.5	0.3
#34	LBNL Trailer 3, Carpet Duplicate	ND***	ND
#35	LBNL Trailer 3, Carpet Triplicate	1.7	0.4
#36	LBNL Trailer 4, Wall Analysis	7.3	1.6
#37	LBNL Trailer 4, Wall Duplicate	8.1	1.7
#38	LBNL Trailer 4, Wall Triplicate	7.8	1.7
#39	LBNL Trailer 4, Carpet Analysis	2.4	0.5
#40	LBNL Trailer 4, Carpet Duplicate	1.7	0.4
#41	LBNL Trailer 4, Carpet Triplicate	1.6	0.3

NOTE: *WT% Cl = weight percent chlorine; **LBNL = Lawrence Berkeley National Laboratory; ***ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.

Table 21. Post Release Analyses Collected September 1, 2015

INSTRUMENT ANALYSIS NUMBER	SAMPLE NAME*	CHLORINE PEAK HEIGHT	WT% Cl**
#42	WB7 , TP	8.4	1.8
#43	WB7, RR	Sample Lost	
#44	WB7, NA	6.7	1.4
#45	WB7, AS	9.2	2.0
#46	WB7, VY	1098	-
#47	WB7, WD	11.5	2.5
#48	WB7, GS	9.1	2.0
#49	WB7, CU	49.4	10.6
#50	WB7, AL	1.7	0.4
#51	WB7, CA	ND***	ND
#52	WB7, ST	76.3	16.4
#53	WB7, TR	22.3	4.8
#54	WB7, PY	2.2	0.5
#55	WB7, HO	10.3	2.2
#56	WB7, RP	5.1	1.1

NOTE: *Witness Board (WB); Telephone Pole (TP), treated with a chlorinated organic as preservative; Railroad Tie (RR) similarly treated; Aged Asphalt (AA); New Asphalt (NA); Asphalt Shingle (AS); PVC Pipe (VY); Wood (WD); Galvanized Steel (GS), zinc coating on steel; Copper (CU); Aluminum (AL); Coated Aluminum (CA), coating is titanium white paint; Steel (ST); Rubber Tire (TR); Pyrolite (PY), a material that may be used in an emergency response equipment coupling; nylon over rubber Hose (HO); and nylon braided Rope (RP); **WT% Cl = weight percent chlorine; ***ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.

Table 22. Post Release Analyses Collected September 1, 2015

INSTRUMENT ANALYSIS NUMBER	SAMPLE NAME*	CHLORINE PEAK HEIGHT	WT% Cl**
#57	WB8, TP	13.4	2.9
#58	WB8, RR	99.2	21.3
#59	WB8, AA	12.9	2.8
#60	WB8, NA	37.5	8.0
#61	WB8, AS	15.0	3.2
#62	WB8, VY	1085	-
#63	WB8, WD	22.3	4.8
#64	WB8, GS	23.2	5.0
#65	WB8, CU	26.8	5.7
#66	WB8, AL	1.7	0.4
#67	WB8, CA	ND***	ND
#68	WB8, ST	176	37.7
#69	WB8, TR	37.5	8.0
#70	WB8, PY	8.5	1.8
#71	WB8, HO	21.8	4.7
#72	WB8, RP	5.0	1.1

NOTE: *Witness Board (WB); Telephone Pole (TP), treated with a chlorinated organic as preservative; Railroad Tie (RR) similarly treated; Aged Asphalt (AA); New Asphalt (NA); Asphalt Shingle (AS); PVC Pipe (VY); Wood (WD); Galvanized Steel (GS), zinc coating on steel; Copper (CU); Aluminum (AL); Coated Aluminum (CA), coating is titanium white paint; Steel (ST); Rubber Tire (TR); Pyrolite (PY), a material that may be used in an emergency response equipment coupling; nylon over rubber Hose (HO); and nylon braided Rope (RP); **WT% Cl = weight percent chlorine; ***ND = Not Detected - no discernable peak corresponding to chlorine fluorescence was detected at ~ 2.6 keV.

An instrument calibration check was completed after the samples were analyzed. The calibration results are presented in **Table 23**, the slope of the line is 5.6223, and R^2 is 0.93. The current calibration slope differs from the average of the current and previous slopes by +29%.

Table 23. Calibration Data Collected September 1, 2015

INSTRUMENT ANALYSIS NUMBER	STANDARD CONCENTRATION, WT% Cl*	Cl PEAK HEIGHT AT 2.6 keV**
#73	1.01	11.6
#74	1.54	3.3
#75	2.02	16.3
#76	5.03	12.1
#77	10.1	51.7
#78	15.1	93.2

NOTE: Slope 5.6223, R^2 0.93; *WT% Cl = weight percent chlorine; **keV = kiloelectronvolt

11.0 Test Release 5, September 3, 2015

Test release 5 (9.0 t) occurred on Tuesday September 3, 2015 at 07:28 MDST. A calibration was completed before the samples were analyzed; the calibration results are presented in **Table 24**. The slope of the line is 4.3469, R^2 is 0.97. The current calibration slope differs from the average of the current and previous slopes by +6.9%.

Table 24. Calibration Data Collected September 3 2015

INSTRUMENT ANALYSIS NUMBER	STANDARD CONCENTRATION, WT% Cl*	CHLORINE PEAK HEIGHT
#2	1.02	6.3
#3	1.57	9.3
#4	2.02	10.0
#5	5.03	15.6
#6	10.1	43.2
#7	15.1	74.8
#8	20.3	83.0
#9	0.21	0.0
#10	0.54	0.0
#11	0.81	8.0
#12	1.01	12.5
#13	1.54	3.9
#14	0.21	3.4
#15	0.54	0.0
#16	0.81	0.0
#17	1.01	13.9
#18	1.54	9.5
#19	0.54	0.0
#20	1.54	9.4

NOTE: Slope is 4.3469, R^2 0.97; *WT% Cl = weight percent chlorine.

The post release results of the LBNL gypsum dry wall and carpet analysis are presented in **Table 25**. The chlorine peak height is divided by slope equal to 4.3469, R^2 is 0.97, to calculate the sample Wt% Cl. The witness board sample were not analyzed as in previous tests, they had been removed from the site.

Table 25. Post Release Analyses Collected September 3, 2015

INSTRUMENT ANALYSIS NUMBER	SAMPLE NAME	CHLORINE PEAK HEIGHT	WT% Cl*
#21	LBNL** Trailer 3, Wall Analysis	9.8	2.3
#22	LBNL Trailer 3, Wall Duplicate	9.4	2.2
#23	LBNL Trailer 3, Wall Triplicate	8.7	2.0
#24	LBNL Trailer 3, Carpet Analysis	1.8	0.4
#25	LBNL Trailer 3, Carpet Duplicate	2.3	0.5
#26	LBNL Trailer 3, Carpet Triplicate	1.9	0.4
#27	Missing		
#28	LBNL Trailer 4, Wall Analysis	6.0	1.4
#30	LBNL Trailer 4, Wall Duplicate	5.9	1.4
#31	LBNL Trailer 4, Wall Triplicate	Failed	-
#32	LBNL Trailer 4, Carpet Analysis	6.0	1.4
#33	LBNL Trailer 4, Carpet Duplicate	1.8	0.4
#34	LBNL Trailer 4, Carpet Triplicate	1.3	0.3
#35	LBNL Trailer 4, Wall Analysis	1.2	0.3

NOTE: *WT% Cl = weight percent chlorine; **LBNL = Lawrence Berkeley National Laboratory.

A subsequent calibration was completed to bracket the data for quality control purposes, the slope was 5.1288, R^2 was 0.97. The results are presented in **Table 26**.

Table 26. Calibration Completed to Bracket September 3 Testing

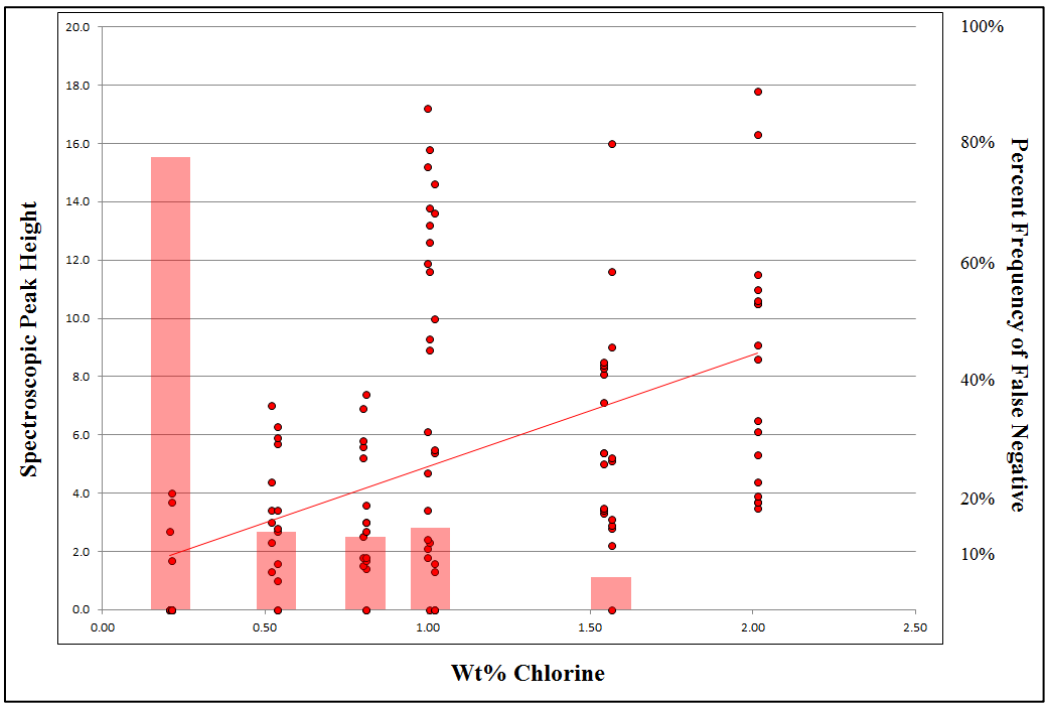
INSTRUMENT ANALYSIS NUMBER	STANDARD CONCENTRATION WT% Cl*	CHLORINE PEAK HEIGHT
#36	1.02	7.0
#37	1.57	12.4
#38	2.02	16.1
#39	5.03	18.9
#40	10.1	47.5
#41	15.1	81.3

NOTE: *WT% Cl = weight percent chlorine.

12.0 Conclusions

The manufacturer states that the detection limit is on the order of 200 parts per million by weight (ppmw) (0.02 Wt% Cl), but the instrument was not capable of detecting chlorine in mixtures of common table salt and sugar below about 2000 ppmw, ten times the manufacturer's detection limit.[A]

The results of each of the standard analyses are shown in the following graph (**Figure 9**) as a plot of concentration in Wt% Cl versus response. There is a considerable amount of uncertainty at each concentration. For example, at 1.0 Wt% Cl, the chlorine signal was 8.4 height units tall, but the standard deviation was 7.2. The bar graph represents the fraction of times that a false negative was recorded; that is, despite some true level of chlorine, the chlorine was not detected. At 200 parts per million (ppm) the instrument returned a false negative 78% of the time. From 0.5-1.0 Wt% Cl the false negatives were reduced to about 15%; above that the instrument detected chlorine in each of the standards each time they were analyzed. The simplicity and specificity of the analysis suggests that false positives are unlikely; that is, that the instrument would indicate the presence of chlorine where there is none.



NOTE: The plot illustrates the instrument variability at each concentration. The bar graph represents The fraction of times that a false negative was recorded; that is, despite some known chlorine concentration, the chlorine was not detected.

Figure 9. Plot of Every Standard Analysis, Response vs. Concentration

[A] M. Deveney (Personal Communication, 11/24/2015: "The Cl LOD is dependent on both test length and matrix. Our LOD of 200 ppm is reported for a 120 second test in a SiO2 background.").

Interestingly, and contrary to the calibration standard analysis, the data from the XRF triplicate analysis of the Lawrence Berkeley trailers' gypsum drywall and carpet samples may demonstrate the actual reproducibility of the instrument. There, and after each analysis of the drywall or carpet, the XRF was moved within inches of the previous test point; the agreement is very good between each analysis, and even between trailers 3 and 4. However, considering the variability and poor sensitivity of the standard analysis, nothing may necessarily be said of the drywall and carpet chlorine concentration, but that it has been contaminated with chlorine. Similarly for the remaining witness board and concrete slab analyses; a user should not have much confidence in the quantitative results despite a reported concentration.

In an e-mail on November 30 to discuss the explanation, Innov-X scientists write, "It is very difficult to gauge how deeply the excitation x-rays will penetrate into any given sample because it is based on the density of the sample. In steel the beam may penetrate only a matter of microns; in a liquid it may travel several centimeters. But just because it travels several centimeters and excites an element, it does not mean the resulting fluorescence has the energy to travel the several centimeters back to the detector to be measured. That is, it is unrealistic to know exactly how deep the x-ray is exciting and collecting, and above some sample thickness the sample may be regarded as infinitely thick. Innov-X recommends an air background for samples that may not be infinitely thick. While a centimeter of salt/sugar mixture sounds reasonable [Innov-X] for detection, if [the x-rays] were exciting the table behind it could have [effectively] been adding mass to the analysis, [thus diluting the sample concentration]."[B]

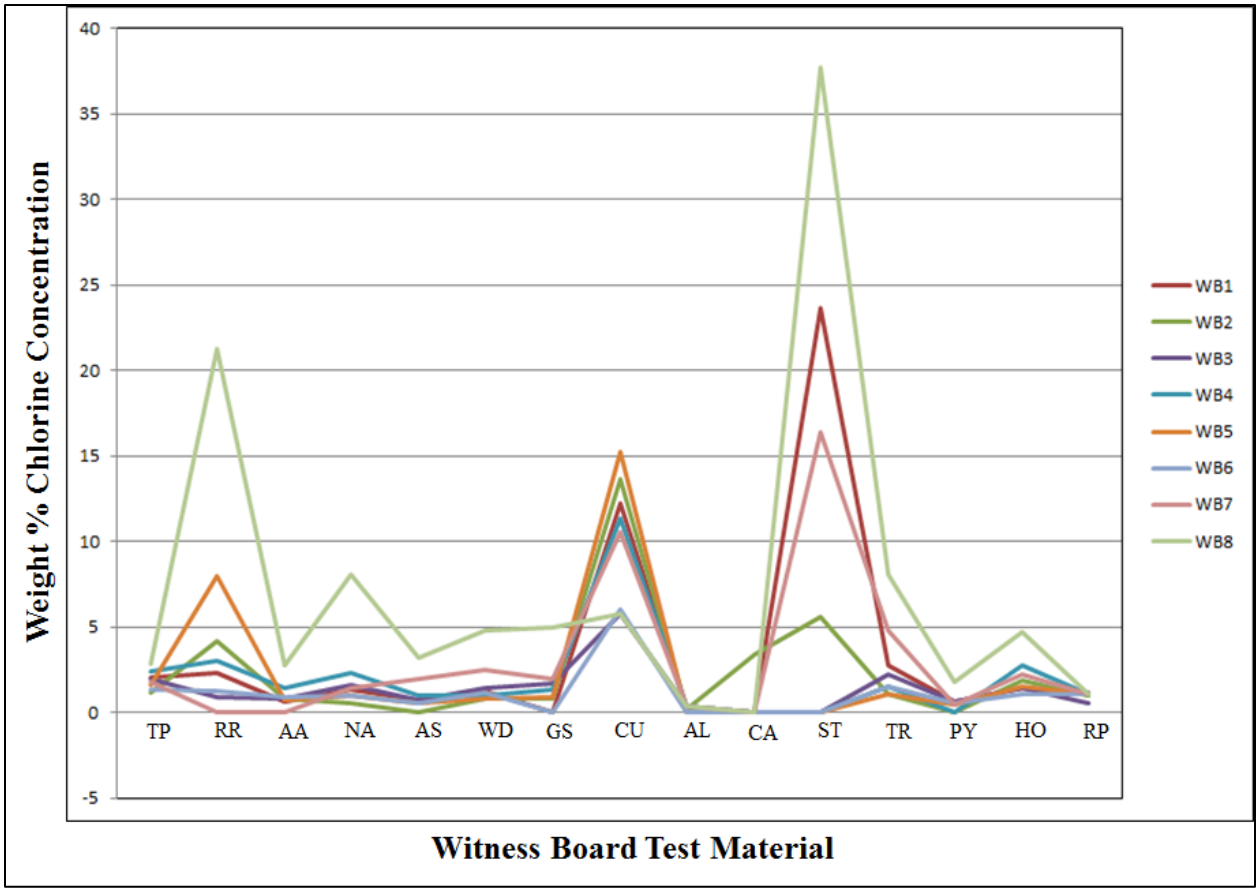
The reliability, reproducibility, and sensitivity of the instrument may change with composition and physical properties of the chlorine contaminated sample substrate. Consequently, standards must be prepared to match each type of sample analyzed, and the analyst must demonstrate with a secondary method that the XRF method may be applied to the samples he may encounter. The technique for completing the standard analysis rather than any instrument capability is the likely source of the errors. Crystal stratification in the standards based on differing crystal sizes of the sugar and salt used to prepare the standards was eliminated as a possibility by agitating the standard before each analysis, and by grinding each standard mixture to uniform crystal size with a mortar and pestle.

As an alternative, and if interference with the table top used to back the samples during analysis is the source of the problem, Innov-X offers sample cups that may eliminate the problem. Otherwise, the salt and sugar mixture may be melted and assayed by an alternate method.

[B] M. Deveney (Personal Communication, 11/24/2015, Subject:3-beam XRF analyzer).

To easily view the data and spectra, and otherwise prepare a spreadsheet data before analysis, the data file for each analysis must be downloaded from the handheld instrument. The data is not time stamped. And though it is date stamped, the date stamp may be misleading. For example, data collected on August 28 is officially recorded as having occurred on August 29 because regardless of the date it was collected, the reported date is the date that the data is downloaded from the hand held instrument. So, in this instance, despite being calibrated before data collection on August 28 after test release 2, the data was not downloaded until after additional calibration and sample data was collected after test release 3 on August 29.

Some trends may be seen from the accumulated witness board data in **Figure 10**.



NOTE: Each colored line represents a Witness Board with 16 items, but only 15 are shown because the polyvinyl chloride item is not included. Two Witness Boards were placed on the grid for each of 5 trials, but the items on the Witness Boards 9 and 10 for trial 5 were not analyzed. Thus, only 8 Witness Board analyses are shown.
Witness Board Materials: Telephone Pole (TP), treated with a chlorinated organic as preservative; Railroad Tie (RR) similarly treated; Aged Asphalt (AA); New Asphalt (NA); Asphalt Shingle (AS); PVC Pipe (VY); Wood (WD); Galvanized Steel (GS), zinc coating on steel; Copper (CU); Aluminum (AL); Coated Aluminum (CA), coating is titanium white paint; Steel (ST); Rubber Tire (TR); Pyrolite (PY), a material that may be used in an emergency response equipment coupling; nylon over rubber Hose (HO); and nylon braided Rope (RP);

Figure 10. Accumulated Witness Board Data

For example, in the series of Witness Board Analyses, the copper was contaminated in most instances at about the same level despite the varying levels of exposure. That is, the reaction is limited by chlorine-copper reactivity and saturation, not chlorine concentration, exposure time, and transport to the copper surface. The contrary example is steel; it seems to be exposure time and concentration dependent; that is, a higher concentration and longer exposure would dramatically affect it. Either of those may be true for the remaining materials; but it is more difficult to observe because of their lower reactivity, and uncertainty regarding the instrument's sensitivity and variability. The contrary example is the gypsum dry wall and carpet analysis for the indoor experiments. Despite the very low signal, the results are very precise even between the trailers.

The PVC pipe results are not listed because it is an unreactive polymer with about 60% chlorine. That is, it is a relatively unreactive material with a chlorine background signal so high that any small change may not be discerned.

13.0 References

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