X-Ray Fluorescence Equipment and Materials Characterization for RoHS Compliances

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ABSTRACT
Environmental compliance is becoming a global effort in the electrical and electronics industry. The Directive on "Restriction of Hazardous Substances" (RoHS) in Europe, is forcing the electronics industry to develop methods for analytical testing of its components and products for regulated substances. The use of lead (Pb), mercury (Hg), cadmium (Cd), hexavalent chromium (Cr VI), and some types of brominated flame retardants (like polybrominated biphenyls, PBB, polybrominated diphenyl ethers, PBDE) in products is being regulated. The industry is convinced of the importance to fulfill this requirement and has looked for confident testing methods to guarantee that banned substances contained in their products are within permitted limits. One of the more suitable analytical methods for the industry to screen and quantify the banned substances is the Energy Dispersive X-Ray Fluorescence (XRF) because of its nondestructive, fast and result-efficient way of analysis.

Analytical techniques are required to make accurate assessments. The purpose of this paper is to discuss how we evaluated the performance of XRF analytical equipment for RoHS application for the five XRF systems including Desktop and Handheld equipment. We use standard samples and production samples for the experiments:
There were four items studied with standard samples with 10, 775 readings:

1. Cpk studies with 12 standard samples including PE, PVC, aluminum alloy, brass alloy, and solder alloy types.
2. Gage reproducibility & repeatability.
3. Stability test (five readings/day, and 10 days data collections).
4. Detection level versus acquisition time.

After testing numerous samples, we selected 11 samples with RoHS compliant, non-compliant, and inconclusive compositions to send to two outsourced laboratories. We studied the correlations between XRF and two test laboratories.

With this study, we are confident in the individual XRF capabilities and accurate test levels, capabilities and accurate test levels the individual XRF have. The results provided a good reference for us to review the production sample test results with XRF. The analytical methods will be discussed in the paper.

Key words: XRF, RoHS, Cpk, Gage R&R, Stability, Sigma.

Introduction
Since July 1, 2006 electronics manufacturing industries are required to meet RoHS directive for the six Restriction of Hazardous Substances: parts or subassemblies that contain less than 1,000mg/kg each of lead (Pb), mercury (Hg), hexavalent chromium (Cr^{6+}), polybrominated biphenyls (PBB), polybrominated diphenyls ethers (PBDE), and less than 100 mg/kg of cadmium (Cd). Recently, the EU RoHS Enforcement Guidance Document recommends: supplier certificates that declare the restricted substances are within permitted level and material declarations that declare material and substance content at the component level. The EU recommends limiting the declarations to the six RoHS substances instead of full material declarations. The following are good demonstrating compliance sequences: 1. Component compliance information from suppliers; 2. Information accepted and archived by manufacturer; 3. Product compliance information to customer; 4. Information accepted and archived by customer[1]. Therefore it becomes the responsibility of manufacturers across the entire supply chain to control the content of hazardous substances in a product. The Energy Dispersive X-Ray Fluorescence (XRF) is the ideal tool for the task of materials screening for the compliance with RoHS requirement. The fluorescent light is called the characteristic X-ray of the element. In a given element, the energies between two specific orbital shells are always the same. The photons that are emitted when an electron moves between these two levels will always have the same energy. Therefore it is possible to determine the identity of that element by determining the energy of the X-ray light (photons). There are two types of XRF: handheld and desktop from different vendors. In order to know individual XRF capabilities and accurate levels, we did this study in two-phases. Phase 1: Evaluate five XRF systems with standard samples; compare Cpk; Gage R & R; stability test and detection level versus acquisition time. Phase 2: Correlation study of production sample results from XRF against XRF or ICP method from outside two laboratories. The section of experiments and analysis describes how experiment design, data collection, and analysis that included the results from 5 XRF equipments and two test laboratories. The last part of this paper is a summary including consideration.

The purpose of this paper is not to indicate which equipment is better than the other; the purpose is to show each XRF analyzer's technical performance and what level their results compare with the external test laboratories. This study can help electronics manufacturing industries achieve compliance with RoHS requirements with accurate measurement data and minimum cost and time.

Experiments and Analysis

We selected two handheld and three desk top XRF spectrometers because of their main specifications, performance and cost. They are: Vendor1-D, Vendor2-D, Vendor3-D, Vendor4-H, and Vendor5-H**.** We used this XRF equipment for Cpk, Stability, Gage R & R, Detection level versus acquisition time studies with 12 standard samples, and correlation studies with 11 production samples.

A. Cpk

Twelve standard samples as (shown in Figure 1) including polyethylene, polyvinyl chloride (PVC), aluminum alloy, brass alloy, solder alloy were used for Cpk study. The restriction of hazardous substances (ppm) of these twelve standard samples is listed in Table 1.

Figure 1 - Twelve standard samples for Cpk study

Table 1 - The restriction of hazardous substances (ppm) for twelve standard samples

	#	Standard Sample	Cr	Cd	Hg	Pb	Br
Polyethylene (PE)	1	SP3 PE (ppm)	86	44	95	91	97
	2	SP4 PE (ppm)	274	66	302	297	303
	3	SP5 PE (ppm)	544	88	590	589	589
	4	EC 680 (ppm)	114.6	140.8	25.3	107.6	808
	5	EC 681 (ppm)	17.1	21.7	4.5	13.8	98
PVC	6	PVC-H-02A (ppm)	999	300	1099	1200	1100
Aluminum Alloy	7	GAL5 (ppm)	140	170	-	1200	-
	8	GAL6 (ppm)	170	130	-	540	-
Brass Alloy	9	GBR5-2 (ppm)	110	130	-	1260	-
	10	GBR6-1 (ppm)	150	140	-	490	-
Solder Alloy	11	74X HB (ppm)	-	80	-	800	-
	12	74X AM (ppm)	-	65	-	1740	-

For each standard sample, 20 readings were collected. The average (x), standard deviation (σ), and Cpk were calculated. The definition of Cpk (a process capability) is described in equation 1. The XRF equipment standard deviation 3S obtained from blank sample testing (no RoHS banned substance means blank[2]) from the vendors. The average of standard deviation 3S from the vendors was used for this study. (X+3S) and (X-3S) are USL (upper specification limit) and LSL (lower specification limit) respectively for Cpku and Cpkl.

$$\begin{aligned} Cpk &= \min(Cpku,\ Cpkl) \\ Cpku &= [(X + 3S) - x] / (3\sigma) \\ Cpkl &= [x - (X - 3S)] / (3\sigma) \end{aligned} \qquad \textbf{Equation 1}$$

Where:

x: Average of XRF testing results from this study

σ: Standard deviation from XRF testing data from this study

X: Standard sample contents, or analytical testing results

S: Average XRF equipment standard deviation obtained from blank sample testing (no RoHS banned substance means blank) from the vendors

Table 2 lists XRF test result with desktop equipment (Vendor 1) with SP3 PE standard sample. The score 0, 1, 2, 3, 4, 5 and 6 represents Cpk ≤ 0.1, 0.5, 0.8, 1.2, 1.4, 1.6 and > 1.6 respectively. The Cpk value of > 1 and 1.6 correspond good and excellent respectively. We compared these results with five XRF, and the sum of the score is high with good capabilities. Table 3 lists all 5 XRF performances (scores) with 12 standard samples. The desktop XRF from Vendor 1 and handheld XRF from Vendor 4 have excellent performance.

Table 2 - The SP3 PE standard sample test result from one desktop XRF

Cd=44ppm, n=20		Cr=86ppm, n=20		Hg=95ppm, n=20		Pb=91ppm, n=20		Br=97ppm, n=20	
1	48.7604	1	93.3510	1	98.2729	1	83.7187	1	99.3656
2	51.2759	2	87.5217	2	92.4711	2	86.1567	2	103.4919
3	57.1590	3	91.0595	3	96.0223	3	81.7925	3	100.7245
4	46.7928	4	107.2358	4	103.9826	4	86.8810	4	101.1411
5	45.3981	5	97.8398	5	104.5030	5	90.7016	5	103.5808
6	44.9766	6	87.4506	6	103.3950	6	88.5064	6	96.9575
7	56.1494	7	89.0216	7	85.4060	7	82.2992	7	106.9537
8	48.6759	8	91.1613	8	91.7078	8	83.8525	8	103.2328
9	55.4988	9	92.7122	9	103.3873	9	87.5195	9	98.5461
10	54.0898	10	86.2576	10	96.6766	10	85.2304	10	91.1983
11	46.3105	11	91.9181	11	97.3077	11	83.9933	11	104.6903
12	56.8454	12	70.2981	12	92.7032	12	82.7015	12	95.7878
13	46.5040	13	91.9893	13	98.7609	13	90.6012	13	97.6172
14	47.6432	14	103.8083	14	100.3738	14	87.3768	14	98.1141
15	52.5409	15	78.0221	15	88.9643	15	87.4257	15	92.3964
16	54.3516	16	97.3175	16	89.6248	16	86.9174	16	96.7420
17	63.9794	17	71.1750	17	94.8126	17	86.1281	17	95.5904
18	49.5839	18	67.1267	18	101.0931	18	90.6794	18	97.0566
19	51.6710	19	76.2817	19	103.1446	19	79.8634	19	99.3513
20	56.5412	20	85.2062	20	108.1189	20	89.1033	20	95.5052
Average	51.74	Average	87.84	Average	97.54	Average	86.07	Average	98.90
Standard dev (σ)	**5.04**	**σ**	**10.73**	**σ**	**6.08**	**σ**	**3.11**	**σ**	**4.08**
Diff w/ standard value %	**17.58**	**Diff %**	**2.14**	**Diff %**	**2.67**	**Diff %**	**-5.41**	**Diff %**	**1.96**
CpkU=	0.56		1.10		0.49		1.47		1.13
CpkL=	1.58		1.21		0.76		0.42		1.44
score	2		3		1		1		3

Table 3 - Five XRF Vendors' performances with 12 standard samples

Standard sample performance	Sample number												Total Score	Rank	
	1	2	3	4	5	6	7	8	9	10	11	12			
Vendor1-D	10	6	3	1	11	1	9	9	5	3	6	3	67	1	excellent
Vendor2-D	8	2	6	0	15	0	5	5	1	1	2	0	45	3	medium
Vendor3-D	13	7	5	3	10	1	3	2	6	5	0	1	56	2	good
Vendor4-H	8	4	3	17	18	5	1	1	5	7	2	0	71	1	excellent
Vendor5-H	9	1	0	5	11	0	5	5	0	0	3	3	42	4	medium

B. Stability

Because XRF can facilitate our routine process analysis and screening RoHS compliant and non-compliant components, the usage is quite frequent. To determine the stability performance of the XRF spectrometer, we evaluated the total variation in the measurement obtained with the measurement system on the sample over an extended time period. One standard sample (PVC-H-02A) was used for the study. Five readings from the sample were taken everyday for duration of ten days. Table 4 only lists several days' data from one handheld XRF. Each element average and standard deviation was calculated from the 50 data that is shown in Table 4. The target number for each element is also listed on the first row of Table 4. The difference percentage (calculated using equation 2) indicates how big the difference is between the XRF measurement average and standard sample content (target reading).

Difference percentage = [(x - X)/ X] * 100%
Where X: standard sample content, or target reading
x: average of XRF testing results from this study by each XRF **Equation 2**

Table 4 - The stability data for standard sample PVC-H-02A from one handheld XRF

Standard sample ppm	Cr(999)	Cd (300)	Hg (1099)	Pb (1200)	Br (1100)	day
1	888.11	299.96	1057.08	1219.68	1161.69	
2	986.32	307.66	1094.31	1250.13	1193.64	
3	940.29	280.29	1081.74	1201.88	1163.94	**1**
4	1092.68	307.71	1050.26	1217.01	1136.13	
5	913.7	296.55	1087.59	1216.02	1141.77	
6	904.4	288.98	1104.17	1242.71	1182.75	
7	990.67	295.27	1083.51	1236.2	1164.79	
8	970.17	284.07	1065.28	1217.91	1132.96	**2**
9	1068.64	279.23	1081.58	1230.7	1150.69	
10	1020.16	283.09	1118.88	1232.19	1163.51	
41	980	276.95	1140.81	1253.69	1204.97	
42	971.14	283.86	1059.51	1201.05	1130.4	
43	1065.3	274.25	1071.38	1206.12	1142.27	**9**
44	965.62	301.96	1081.06	1200.45	1170.14	
45	860.5	289.58	1079.05	1207.15	1120.64	
46	1014.08	296.33	1059.81	1257.37	1172.3	
47	985.03	313.94	1107.97	1244.88	1149.31	
48	937.16	289.26	1057.66	1195.01	1143.96	**10**
49	1047.57	281.89	1118.38	1257.32	1171.18	
50	1035.29	290.46	1094.97	1254.82	1188.94	
Average	994.73	289.95	1087.62	1230.00	1162.07	
Std DEV	68.11	11.51	27.15	20.79	20.91	

Table 5 - The stability results for standard sample PVC-H-02A from five XRF

Element	Standard Deviation （σ）					Percentage of Difference					Total Rank
	Cr	Cd	Hg	Pb	Br	Cr	Cd	Hg	Pb	Br	
Vendor1-D	206.92	12.66	49.98	62.01	60.16	21.30	-16.67	-7.46	-21.22	0.42	4
Vendor2-D	65.94	20.12	56.94	62.13	39.14	-0.68	-0.82	10.28	11.13	6.03	3
Vendor3-D	36.79	9.12	23.19	42.29	21.70	16.69	-2.97	-37.20	-29.36	-23.07	2
Vendor4-H	68.11	11.51	27.15	20.79	20.91	-0.43	-3.35	-1.04	2.50	5.64	1
Vendor5-H	54.66	34.86	25.61	21.38	46.22	-10.61	37.33	-30.45	-34.31	7.39	4

We compared standard deviation （σ） and the different percentages for these five XRF for their performance rank. The analysis results are listed in Table 5, less than 30% difference between XRF average and target data for most XRF for most elements. The handheld XRF from Vendor 4 shows relatively smaller different percentage and standard deviation for all five XRF.

C. Gage R & R

The Gage Repeatability and Reproducibility (Gage R & R) was studied using the same area for the ten same yellow capacitors as shown in Figure 2. Three appraisers tested the components three time each, for a total of ninety measurements. We use MINITAB to calculate Gage R & R with three sigma tolerance. Table 6 lists Gage R & R results for elements Pb and Br from XRF Vendor 1, and where SD and %SV stand for standard deviation and percentage study variation, respectively. The %SV is 100 times the study variation for the source divided by the total variation. From the Table 6 the Gage R & R results of percentage study variation are less than 30% for the Pb and Br element for XRF from Vendor 1. The Gage R & R results for the remaining four XRF (listed in Table 7) did not meet our expectation.

Figure 2 - The production yellow capacitor sample for Gage R & R study

Table 6 - The XRF (Vendor 1) Gage R & R results for Pb and Br from MINITAB

Gage R & R Vendor 1 Desktop XRF (Pb)

Source	Var Comp	%Contribution (of VarComp)
Total Gage R&R	2396.6	6.41
Repeatability	2387	6.38
Reproducibility	9.6	0.03
Part-To-Part	34994.9	93.59
Total Variation	37391.5	100

Source	StdDev (SD)	Study Var (3 * SD)	%Study Var (%SV)
Total Gage R&R	48.955	146.865	25.32
Repeatability	48.857	146.57	25.27
Reproducibility	3.098	9.294	1.6
Part-To-Part	187.069	561.208	96.74
Total Variation	580.107	580.107	100

Gage R & R Vendor 1 Desktop XRF (Br)

Source	Var Comp	%Contribution (of VarComp)
Total Gage R&R	76104	1.91
Repeatability	73626	1.84
Reproducibility	2478	0.06
Part-To-Part	3918727	98.09
Total Variation	3994831	100

Source	StdDev (SD)	Study Var (3 * SD)	%Study Var (%SV)
Total Gage R&R	275.87	827.61	13.8
Repeatability	271.34	814.02	13.58
Reproducibility	49.78	149.35	2.49
Part-To-Part	1979.58	5938.73	99.04
Total Variation	1998.71	5996.12	100

Table 7 - The XRF Gage R & R results for Pb and Br from for five XRF

Vendor #	Vendor1-D		Vendor2-D		Vendor3-D		Vendor4-H		Vendor5-H	
Element	Pb	Br	Pb	Br	Pb	Br	Pb	Br	Pb	Br
Total Gage R&R	25.32	13.8	58.54	85.05	86.88	98.11	39.48	74.58	86.07	97.23
Repeatability	25.27	13.58	54.44	83.51	48.32	52.61	38.61	72.4	67.64	73.05
Reproducibility	1.6	2.49	21.54	16.12	72.21	82.82	8.28	17.87	53.22	64.17

D. Detection Level versus Acquisition Time

One sample (SP4 PE) was used for detection level versus acquisition time study. We took measurement data every 1 second for time period 5-10 seconds, every 2 seconds for time period 10-20 seconds, every 5 seconds for time period 20-50 seconds, every 10 seconds for the time period 50-100 seconds. Five readings were taken for every measurement, and their average was listed on each cell of the Table 8. The average measurement and standard deviation results for one handheld XRF are listed in Table 8. The desk top and handheld XRF for detection level versus acquisition time for Pb and Hg are shown in Figures 3-6 respectively. From the figures, it indicated that Vendor 1 measurement has less dependence with acquisition time for desk top XRF, and Vendor 4 measurement data has less dependence with acquisition time for handheld XRF. We compared different percentage and standard deviation for each element as shown in Table 9. The standard deviation for most elements is less than 20% compared to the target SP4 PE number except for one handheld XRF. We use the equation 2 to calculate the difference between measurement data and the target number for the detection level versus acquisition time. The percentage of difference for every element is less than 15% for Vendor 1 XRF as shown in Table 9. The performance rank is listed in Table 9 for all five XRF.

Table 8 - The handheld XRF results for detection level versus acquisition time study

Time (sec)	Cr (ppm)	Cd (ppm)	Hg (ppm)	Pb (ppm)	Br (ppm)
5	509.39	0.00	407.34	347.24	317.95
6	460.86	0.00	397.16	363.40	321.30
7	425.28	0.00	393.58	349.69	311.59
8	398.50	55.04	383.24	345.69	329.49
9	464.66	0.00	396.65	351.90	329.82
10	426.77	27.25	392.50	364.63	331.55
12	468.57	23.28	395.85	353.51	327.36
14	435.14	0.00	387.70	344.81	339.68
16	456.05	17.97	401.08	344.60	319.81
18	460.63	47.64	391.30	351.05	326.89
20	455.73	38.59	398.78	359.51	334.38
25	430.02	15.58	391.21	354.72	325.37
30	440.13	83.06	393.58	349.64	326.33
35	466.80	78.81	390.85	357.02	323.71
40	439.96	65.87	392.04	350.57	326.18
45	468.75	13.39	389.21	354.47	322.70
50	451.13	68.76	388.73	350.20	328.56
60	462.86	63.96	390.23	354.61	330.13
70	455.94	62.39	387.81	354.92	329.39
80	444.86	76.17	390.45	357.12	326.18
90	451.18	76.99	388.07	357.87	329.85
100	454.85	71.31	391.37	351.93	325.44
110	460.03	71.49	396.29	355.07	327.71
120	445.47	70.45	397.39	355.66	326.24
Average	451.40	42.83	393.02	353.33	326.57
Maximum	509.39	83.06	407.34	364.63	339.68
Minimum	398.50	0.00	383.24	344.60	311.59
Std. Dev.	20.82	30.81	5.15	5.23	5.57

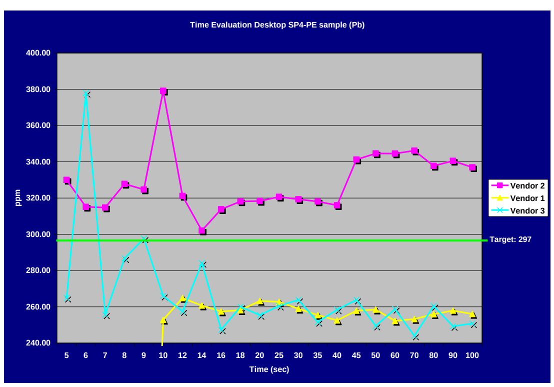

Figure 3 - The desk top XRF Pb element results for detection level versus acquisition time study

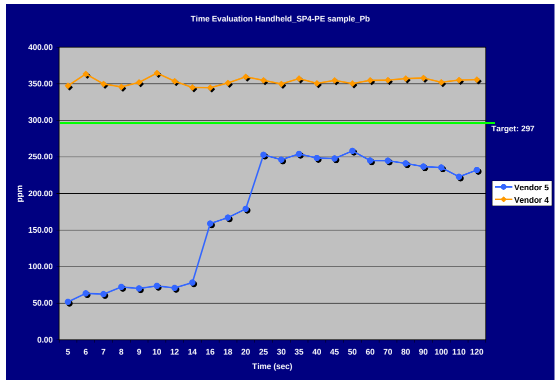

Figure 4 - The handheld XRF Pb element results for detection level versus acquisition time study

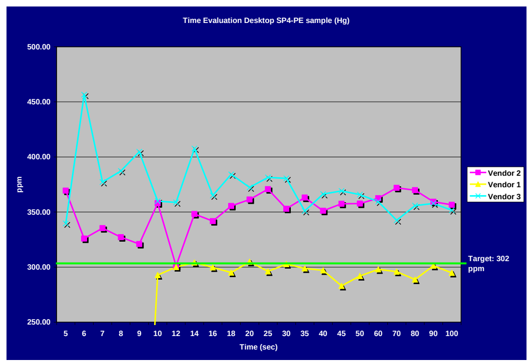

Figure 5 - The desk top XRF Hg element results for detection level versus acquisition time study

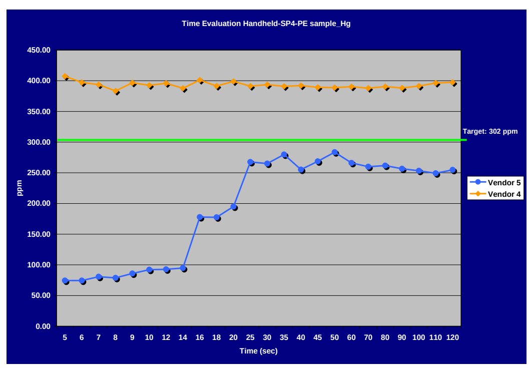

Figure 6 - The handheld XRF Hg element results for detection level versus acquisition time study

Table 9 - The detection level versus acquisition time results for standard sample SP4 PE from five XRF

Element	Standard deviation (σ)					Percentage of Difference					Total Rank
	Cr	Cd	Hg	Pb	Br	Cr	Cd	Hg	Pb	Br	
Vendor1-D	10.92	5.47	5.61	3.79	8.03	2.98	2.58	-1.74	-13.28	0.68	1
Vendor2-D	50.01	22.87	18.39	16.66	24.05	5.74	-43.83	16.16	10.66	17.32	3
Vendor3-D	8.84	6.97	25.73	28.11	8.71	-11.28	-32.02	23.32	-10.25	-40.19	2
Vendor4-H	20.82	30.81	5.15	5.23	5.57	64.74	-35.10	30.14	18.97	7.78	2
Vendor5-H	80.32	33.30	83.64	82.04	121.73	-227.63	-559.12	-9.34	-136.47	-561.53	4

E. XRF results correlation against different test laboratories

The correlation study was done with eleven different samples tested with the five XRF. In addition, all these samples were sent to external laboratories to measure. Lab 1 uses inductive coupled plasmas (ICP) optical emission spectrometry (OES), and Lab 2 uses with ICP atomic emission spectrometry (AES) analysis method. The eleven samples are list in Table 10 and Figure 7. We calculate the percentage of difference between the XRF test results and reference data (target reading) using equation 3. The reference data was obtained from the average of two external test laboratories.

Percentage of Difference = $[(x - X)/ X] * 100\%$
Where X: reference data or target reading
x: result obtained with XRF equipment **Equation 3**

Sample 1 is lead –free solder bar (SAC 305), however all XRF and ICP-AES (OES) test results indicated the lead content to be above 1000ppm as shown in Table 11. Table 12 listed the score for XRF difference percentage range, and we use the score to summarize the eleven samples.

Table 10 - Eleven production samples list

Sample #	DESCRIPTION	Comment
1	Lead - Free solder Bar SAC 305	Solder
2	Solder paste Lead-Free	Solder
3	PCBA product	Solder mask
4	Orange button Flex product	Plastic part
5	Green button Flex product	Plastic part
6	Red probe clipper (isolate)	Plastic cover
7	Red probe clipper (wire)	Plastic cover
8	Multi-meter red probe (wire)	Plastic cover
9	Multi probe -point	Plastic cover
10	Multi probe -cover point	Plastic cover
11	Cutting pliers red handle	Plastic part

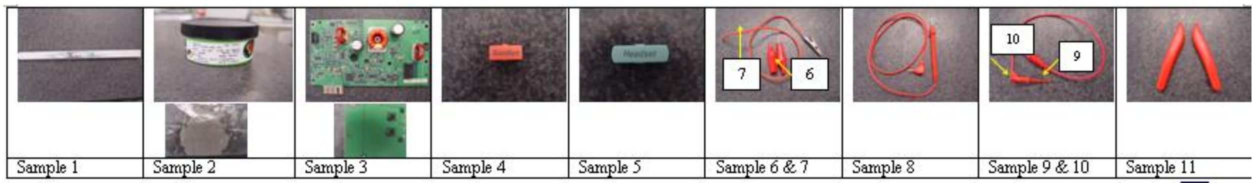

Figure 7 - Eleven production sample images

Table 11 - Test results for Sample 1

Equipment	Test Method	**Pb** (sample 1)		Score
		ppm	Diff %	
Vendor 1-D	XRF	1988.36	-13.66	4
Vendor 2-D	XRF	4838.18	110.08	0
Vendor 3-D	XRF	1818.10	-21.06	3
Vendor 4-H	XRF	2602.67	13.01	4
Vendor 5-H	XRF	2100.00		4
External Lab 1	ICP-OES	2370	-	-
External Lab2	ICP-AES	2303	-	-
Reference Data		**2336.5**		

Table 12 - Score definition

Score	Difference % range
5	0<d≤10
4	10<d≤20
3	20<d≤30
2	30<d≤40
1	40<d≤50
0	50<d

Table 13 - The test results for Sample 2

Equipment	Test Method	**Pb** (sample 2)		Score	**Br**(sample 2)		Score
		Ppm	Diff %		ppm	Diff %	
Vendor 1-D	XRF	2.36	-97.65	0	3799.25	399.90	0
Vendor 2-D	XRF	0.00	-100.00	0	0.00	-100.00	0
Vendor 3-D	XRF	0.00	-100.00	0	0.00	-100.00	0
Vendor 4-H	XRF	312.73	211.17	0	0.00	-100.00	0
Vendor 5-H	XRF	100.00	-0.50	5	0.00	-100.00	0
External Lab 1	ICP-OES	120	-	-		-	-
External Lab 2	ICP-AES	81	-	-	760	-	-
Reference Data		**100.5**			**760***		

Table 14 - Test results for Sample 3

Equipment	Test Method	Pb		Score
		ppm	Diff %	
Vendor 1-D	XRF	116.04	-99.00	0
Vendor 2-D	XRF	0.00	-100.00	0
Vendor 3-D	XRF	0.00	-100.00	0
Vendor 4-H	XRF	12466.88	7.01	5
Vendor 5-H	XRF		-100.00	0
External Lab 1	ICP-OES	12800	-	-
External Lab2	ICP-AES	10500	-	-
Reference Data		**11650**		

Table 15 - The test results for Sample 8

Equipment	Test Method	**Cd** (sample 8)		Score	**Pb** (sample 8)		Score
		ppm	**Diff %**		**ppm**	**Diff %**	
Vendor 1-D	XRF	95.78	-17.07	4	797.15	-33.21	2
Vendor 2-D	XRF	290.41	151.44	0	746.38	-37.46	2
Vendor 3-D	XRF	21.50	-81.39	0	418.00	-64.98	0
Vendor 4-H	XRF	65.32	-43.45	1	1870.30	56.71	0
Vendor 5-H	XRF	0.00	-100.0	0	757.00	-36.57	2
External Lab 1	ICP-OES	114	-	-	900	-	-
External Lab 2	ICP-AES	117	-	-	1487	-	-
Reference Data		**115.5**			**1193.5**		

Table 16 - Test results for Sample 9

Equipment	Test Method	**Cd** (sample 9)		Score
		ppm	**Diff %**	
Vendor 1-D	XRF	2318.24	-9.51	5
Vendor 2-D	XRF	3080.17	20.23	3
Vendor 3-D	XRF	519.00	-79.74	0
Vendor 4-H	XRF	3263.56	27.38	3
Vendor 5-H	XRF	3217.00	25.57	3
External Lab 1	ICP-OES	2320	-	-
External Lab 2	ICP-AES	2804	-	-
Reference Data		**2562**		

Table 17 - The test results for Sample 11

Equipment	Test Method	**Cd** (sample 11)		Score	**Pb** (sample 11)		Score
		ppm	**Diff %**		**ppm**	**Diff %**	
Vendor 1-D	XRF	234.48	-2.30	5	359.49	27.03	3
Vendor 2-D	XRF	834.81	247.84	0	281.77	-0.43	5
Vendor 3-D	XRF	110.50	-53.96	0	246.00	-13.07	4
Vendor 4-H	XRF	306.34	27.64	3	334.48	18.19	4
Vendor 5-H	XRF	374.00	55.83	0	293.00	3.53	5
External Lab 1	ICP-OES	201	-	-	190	-	-
External Lab 2	ICP-AES	279	-	-	376	-	-
Reference Data		**240**			**283**		

Sample 2 is lead -free solder paste, and all XRF and ICP-AES (OES) test results indicated the lead content meets RoHS as shown in Table 13. The XRF measurement result from the Vendor 4 has large difference than others, but the result including add measurement deviation still meets the RoHS limit. The Br measurement data is very different with XRF and ICP-AES

(OES) from different XRF and test laboratories. It is noted that the sample should be measured for Br with infrared spectroscopy (IR) or high performance liquid chromatography (HPLC) method due to Br> 350ppm[3-4].

Sample 3 is PCBA product, and we measure solder mask. The XRF and ICP-AES (OES) test results are shown in Table 14. The ICP readings for Pb from two laboratories were close, however data is largely different between five XRF tests. The XRF measurement result from Vendor 4 is close to ICP test results.

Sample 8 is multimeter red probe wire, and test results are listed in Table 15. For Cd, four XRF results meet the RoHS except Vendor 2, but ICP results showed Cd is out of the RoHS limit. For Pb, four XRF readings and one ICP result are below 1000pm, but one XRF and one laboratory result are out of RoHS.

Sample 9 is multi probe point, and test results are listed in Table 16. All results from XRF and two external test laboratories indicated Cd ppm to be above RoHS limit (Cd 100ppm). However these data have big difference from individual equipment.

Sample 11 is cutting pliers red handle, and test results are listed in Table 17. From the table, all measurement data for Cd do not meet RoHS. However all Pb test results meet RoHS.

From Table 11-17, it is obvious to see there is significant difference for individual XRF tests, and ICP-AES, ICP-OES measurement from outside test laboratories. The samples 4, 5, 6, 7, 10 have similar results. The performance rank is listed in Table 18. Desktop XRF from Vendor 1 has better performance than others.

Table 18 - Performance Rank for 11 production samples

Production sample performance	Sample number																	Total Score	Rank	
	1	2	2	3	4	4	5	6	6	7	7	8	8	9	10	11	11			
Vendor1-D	4	0	0	0	3	0	3	4	3	0	0	4	2	5	5	5	3	41	1	Excellent
Vendor2-D	0	0	0	0	0	0	0	0	1	0	1	0	2	3	0	0	5	12	5	poor
Vendor3-D	3	0	0	0	3	0	4	0	0	0	0	0	0	0	0	0	4	14	4	poor
Vendor4-H	4	0	0	5	0	0	0	5	3	0	4	1	0	3	4	3	4	36	2	good
Vendor5-H	4	5	0	0	0	0	4	0	5	0	0	0	2	3	0	0	5	28	3	medium

In some samples Performance Rank was measured for more than one element. In this case the sample number will be repeated, for example: Sample 2 and Sample 2, which means the first one is for Pb and second one is for Br.

Summary

1. Energy Dispersive X-Ray Fluorescence (XRF) is one of the more suitable analysis methods for the industry to screen because of its nondestructive, fast and result-efficient way of analysis.
2. Each XRF has a different accurate level to measure banned substances. We suggest obtaining deviation (different) results for main elements of the XRF so that we know which samples need to be sent to an outside test laboratory for further analysis to confirm whether or not the samples are RoHS compliant.
3. In general desk top XRF have better performance than handheld XRF, however handheld XRF from Vendor 4 has better performance than some desktop XRF. The Table 19 list summarizes these five XRF performances.

Table 19 - Summary for five XRF performances

Suppliers / Evaluation	*Vendor 1-D*	*Vendor 2-D*	*Vendor 3-D*	*Vendor 4-H*	*Vendor 5-H*
Standard Samples Analysis	□	□	□	□	□
Equipment Stability	□	□	□	□	□
Equipment Gage R&R	□	□	□	□	□
Detection Level Versus Acquisition Time	□	□	□	□	□
Production Samples	□	□	□	□	□

Performance Graphic Score	
□	Excellent
□	Good
□	Medium
□	Poor
□	Bad

4. Choose the reliable test laboratory for identifying samples which are inconclusive (between RoHS compliant and non-compliant range).

5. The experiment results listed in the paper are primary studies with XRF for RoHS enforcement. The results obtained from this evaluation showed the equipments' capability to quantify banned substances by RoHS initiative and demonstrated that XRF technique is a feasible testing method to have in a manufacturing area to perform quick verifications. However a safety margin has to be chosen to prevent equipment uncertainty from affecting final decision.

6. Despite the benefits of this technique there are important limitations to consider such as the inability to quantify PBB and PBDE as well as chromium VI, inability to detect banned substances in the inner part of a thick component/part, inability to differentiate the banned substance contents of a non-homogeneous component/part (the XRF result is a sum of different homogeneous materials), etc.. It is highly recommended to have an operation trial run to study its effectivity before we finally approve it. Also a well trained operator is required to carefully judge the results.

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1. Rob Rowland, "Demonstrating RoHS Compliance User Perspective", SMT web presentation, August 31, 2006.
2. Environmental standardization for electrical and electronics products and systems (IEC 62321, ED. 1, 2005)
3. Flextronics XRF evaluation report, (September 2005).
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XRF Equipment and Materials Characterization for RoHS Compliance

FLEXTRONICS

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February 2007

Introduction

- Environmental Protection
- RoHS Initiative
- Regulated Substances
- The Industry Approach

Introduction

- Analytical Methods

  - ICP (AES) Inductive Coupled Plasma atomic emission spectrometry
  - ICP (OES) Inductive Coupled Plasma optical emission spectrometry
  - ASS Atomic Absorption spectrometry
  - WDXRF Wavelength Dispersive X ray fluorescents spectrometry
  - XRF Energy Dispersive X ray fluorescents spectrometry
  - IC Ion Chromatography
  - GC Gas Chromatography

Introduction

- The purpose of this article is to present the evaluation results of XRF technique used to verify RoHS compliance for products and materials by characterizing the performance of five equipments available in the market

- The evaluation included Handheld Instruments and Desktop instruments

- The test vehicles used were:
  - Standards samples
  - Production samples

Introduction

➢The evaluation test were split in two stages:

Stage One

- Cpk
- Stability test
- Gage Reproducibility and Repeatability
- Detection level versus acquisition time

Stage Two

- Correlation results from XRF against two external Laboratories.

Cpk Study Standard Samples

- Twelve Standard Samples were used for Cpk study

	#	Standard Sample	Cr	Cd	Hg	Pb	Br
PE Standard type	1	SP3 PE (ppm)	86	44	95	91	97
	2	SP4 PE (ppm)	274	66	302	297	303
	3	SP5 PE (ppm)	544	88	590	589	589
	4	EC 680 (ppm)	114.6	140.8	25.3	107.6	808
	5	EC 681 (ppm)	17.1	21.7	4.5	13.8	98
PVC Standard type	6	PVC-H-02A (ppm)	999	300	1099	1200	1100
Aluminum Alloy	7	GAL5 (ppm)	140	170	-	1200	-
	8	GAL6 (ppm)	170	130	-	540	-
Brass Alloy	9	GBR5-2 (ppm)	110	130	-	1260	-
	10	GBR6-1 (ppm)	150	140	-	490	-
Solder Alloy	11	74X HB (ppm)	-	80	-	800	-
	12	74X AM (ppm)	-	65	-	1740	-

1 2 3 4 5 6 7 8 9 10 11 12

Cpk Analysis Method

- From each standard 20 readings were collected and the average (x) standard deviation (σ) and Cpk was calculated

Cpk	Score
Cpk <= 0.1	0
Cpk <= 0.5	1
Cpk <= 0.8	2
Cpk <= 1.2	3
Cpk <= 1.4	4
Cpk <= 1.6	5

$$Cpk = \min(Cpku, Cpkl)$$
$$Cpku = [(X + 3S) - x] / (3\sigma)$$
$$Cpkl = [x - (X - 3S)] / (3\sigma)$$

x: Average of XRF testing results from this study
σ: Standard deviation from XRF testing data from this study
X: Standard sample contents, or analytical testing results
S: Average XRF equipment standard deviation obtained from blank sample testing (no RoHS banned substance means blank) from the vendors

- The resulted Cpk was scored according the table

Cpk Study Readings examples

- XRF reading examples from PE (SPE3) std

Cd=44ppm, n=20		Cr=86ppm, n=20		Hg=95ppm, n=20		Pb=91ppm, n=20		Br=97ppm, n=20	
1	48.7604	1	93.3510	1	98.2729	1	83.7187	1	99.3656
2	51.2759	2	87.5217	2	92.4711	2	86.1567	2	103.4919
3	57.1590	3	91.0595	3	96.0223	3	81.7925	3	100.7245
4	46.7928	4	107.2358	4	103.9826	4	86.8810	4	101.1411
5	45.3981	5	97.8398	5	104.5030	5	90.7016	5	103.5808
6	44.9766	6	87.4506	6	103.3950	6	88.5064	6	96.9575
7	56.1494	7	89.0216	7	85.4060	7	82.2992	7	106.9537
8	48.6759	8	91.1613	8	91.7078	8	83.8525	8	103.2328
9	55.4988	9	92.7122	9	103.3873	9	87.5195	9	98.5461
10	54.0898	10	86.2576	10	96.6766	10	85.2304	10	91.1983
11	46.3105	11	91.9181	11	97.3077	11	83.9933	11	104.6903
12	56.8454	12	70.2981	12	92.7032	12	82.7015	12	95.7878
13	46.5040	13	91.9893	13	98.7609	13	90.6012	13	97.6172
14	47.6432	14	103.8083	14	100.3738	14	87.3768	14	98.1141
15	52.5409	15	78.0221	15	88.9643	15	87.4257	15	92.3964
16	54.3516	16	97.3175	16	89.6248	16	86.9174	16	96.7420
17	63.9794	17	71.1750	17	94.8126	17	86.1281	17	95.5904
18	49.5839	18	67.1267	18	101.0931	18	90.6794	18	97.0566
19	51.6710	19	76.2817	19	103.1446	19	79.8634	19	99.3513
20	56.5412	20	85.2062	20	108.1189	20	89.1033	20	95.5052
Average	51.74	Average	87.84	Average	97.54	Average	86.07	Average	98.90
Standard dev (σ)	**5.04**	**σ**	**10.73**	**σ**	**6.08**	**σ**	**3.11**	**σ**	**4.08**
Diff w/ standard value %	**17.58**	**Diff %**	**2.14**	**Diff %**	**2.67**	**Diff %**	**-5.41**	**Diff %**	**1.96**
CpkU=	0.56		1.10		0.49		1.47		1.13
CpkL=	1.58		1.21		0.76		0.42		1.44
score	2		3		1		1		3

Cpk Study Results

- Vendor 1-D and Vendor 4-H showed the better results

Group	#	Standard Sample	Desktop XRF Score			Handheld XRF Score	
			Vendor 1	Vendor 2	Vendor 3	Vendor 4	Vendor 5
PE Standard	1	SP3 PE	10	8	13	8	9
PE Standard	2	SP4 PE	6	2	7	4	1
PE Standard	3	SP5 PE	3	6	5	3	0
PE Standard	4	EC 680	1	0	3	17	5
PE Standard	5	EC 681	11	15	10	18	11
PVC Standard	6	PVC-H-02A	1	0	1	5	0
Aluminum Alloy	7	GAL5	9	5	3	1	5
Aluminum Alloy	8	GAL6	9	5	2	1	5
Brass Alloy	9	GBR5-2	5	1	6	5	0
Brass Alloy	10	GBR6-1	3	1	5	7	0
Solder Alloy	11	74X HB	6	2	0	2	3
Solder Alloy	12	74X AM	3	0	1	0	3
		Total Score	67	45	56	71	42
			Excellent	Medium	Good	Excellent	Medium

Stability Study

- To determine the Stability performance of XRF equipments it was evaluated the total variation in the measurement obtained with the measurement system on the same parts over an extended time period

- One standard sample (PVC-H-02A) was selected for stability study

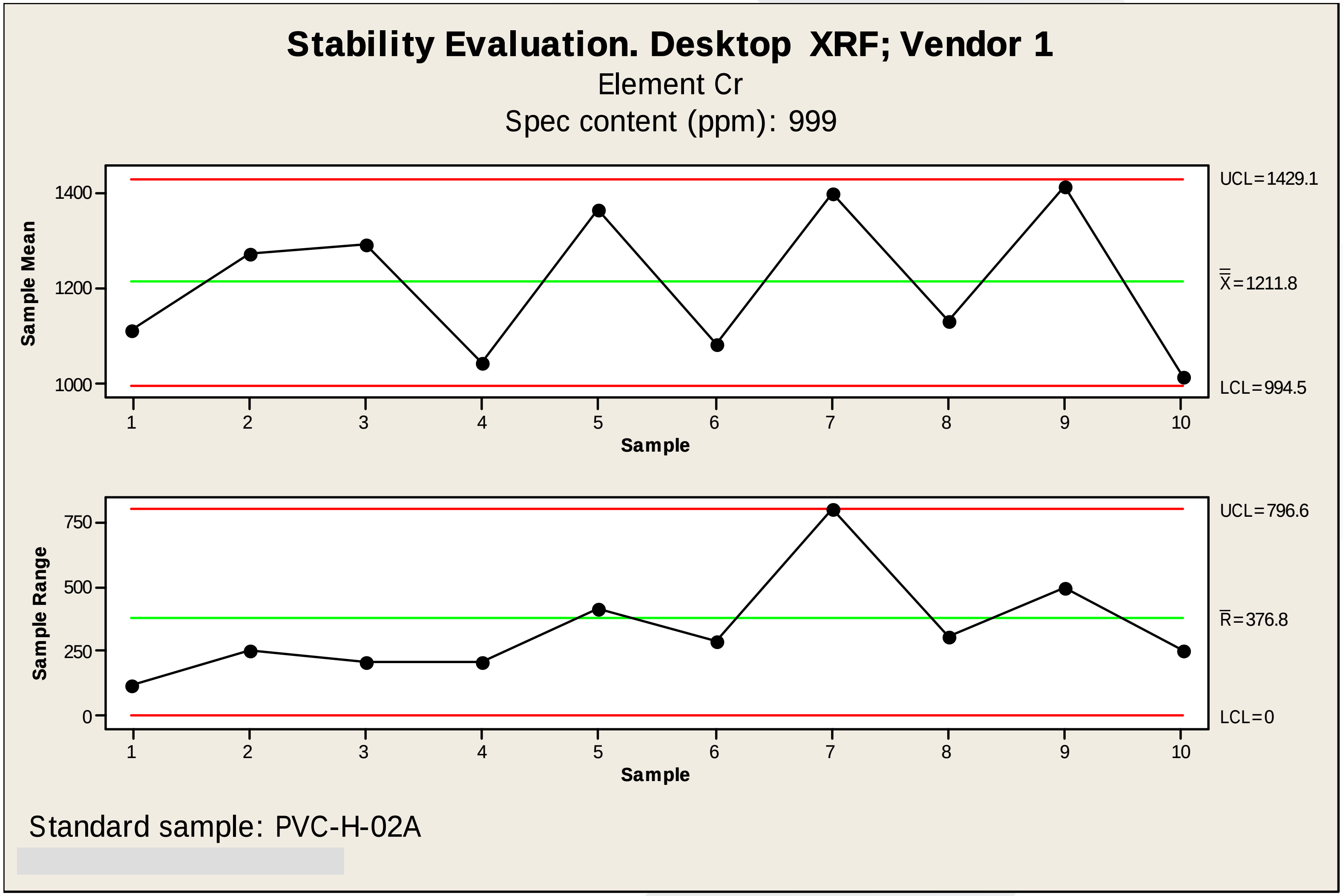
Element content	Cr	Cd	Hg	Pb	Br
Standard: PVC-H-02A (ppm)	999	300	1099	1200	1100

- Five readings were taken every day during 10 days giving a total of 50 readings by equipment.

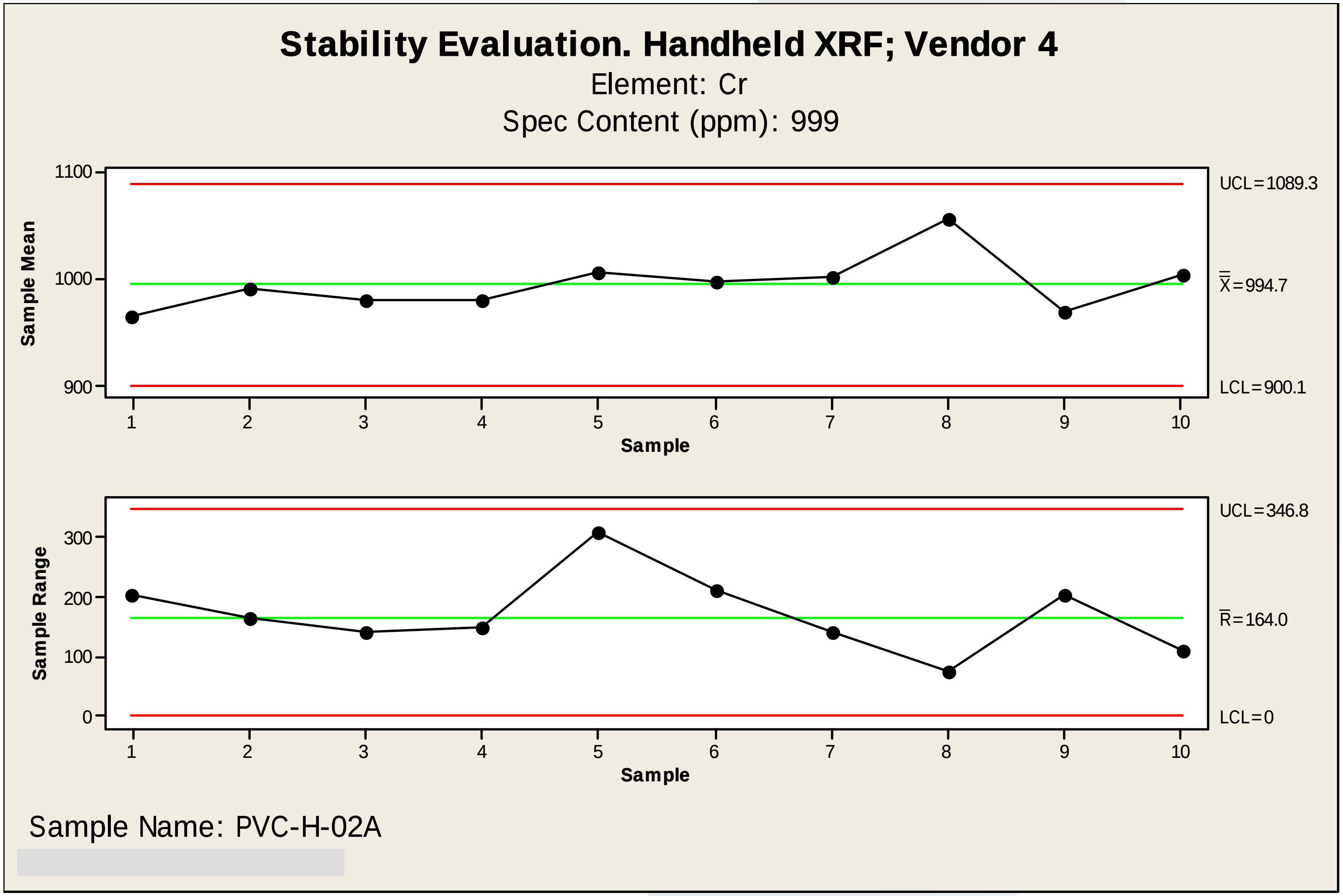
Stability Study Data

Standard sample ppm	Cr(999)	Cd (300)	Hg (1099)	Pb (1200)	Br (1100)	day
1	888.11	299.96	1057.08	1219.68	1161.69	1
2	986.32	307.66	1094.31	1250.13	1193.64	
3	940.29	280.29	1081.74	1201.88	1163.94	
4	1092.68	307.71	1050.26	1217.01	1136.13	
5	913.7	296.55	1087.59	1216.02	1141.77	
6	904.4	288.98	1104.17	1242.71	1182.75	2
7	990.67	295.27	1083.51	1236.2	1164.79	
8	970.17	284.07	1065.28	1217.91	1132.96	
9	1068.64	279.23	1081.58	1230.7	1150.69	
10	1020.16	283.09	1118.88	1232.19	1163.51	
41	980	276.95	1140.81	1253.69	1204.97	9
42	971.14	283.86	1059.51	1201.05	1130.4	
43	1065.3	274.25	1071.38	1206.12	1142.27	
44	965.62	301.96	1081.06	1200.45	1170.14	
45	860.5	289.58	1079.05	1207.15	1120.64	
46	1014.08	296.33	1059.81	1257.37	1172.3	10
47	985.03	313.94	1107.97	1244.88	1149.31	
48	937.16	289.26	1057.66	1195.01	1143.96	
49	1047.57	281.89	1118.38	1257.32	1171.18	
50	1035.29	290.46	1094.97	1254.82	1188.94	
Average	994.73	289.95	1087.62	1230.00	1162.07	
Std DEV	68.11	11.51	27.15	20.79	20.91	

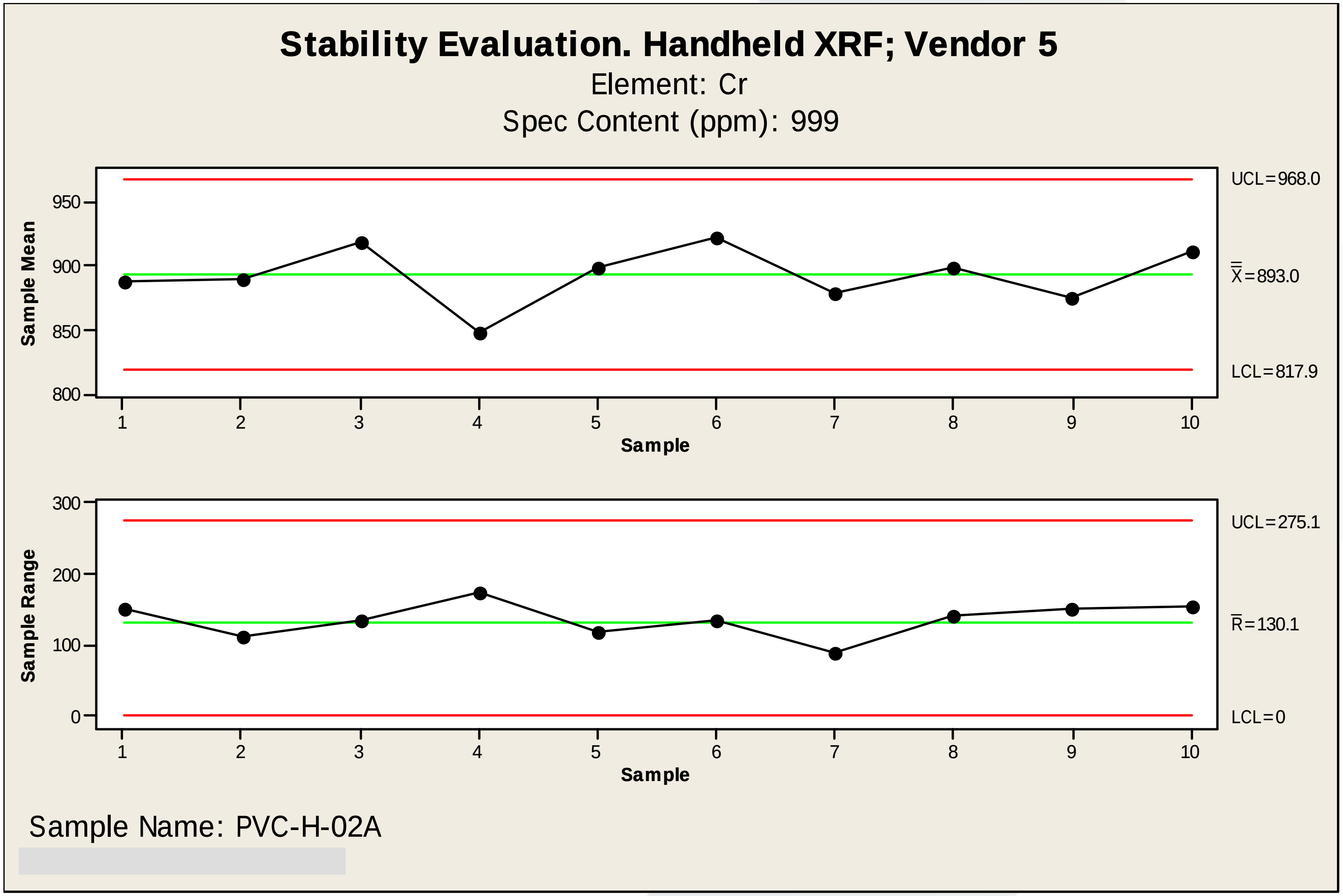
Stability Study Vendor 1 (Cr)



Stability Study Vendor 4 Charts (Cr)



Stability Study Vendor 5 Charts (Cr)



Stability Study Evaluation

- After got the average and standard deviation from 50 readings, The difference % was calculated. Then ranked the XRF per scores from difference % and standard deviation.

Definition of Difference %

Difference %= [(x' - x)/ x]100

where x : standard sample content, or analytical testing results

x' : average of XRF testing results

Stability Results

➢ Vendor 4-H showed the better results for stability test with less percentage of difference against standard values

Element	Standard Deviation (σ)					Percentage of Difference					Total Rank
	Cr	Cd	Hg	Pb	Br	Cr	Cd	Hg	Pb	Br	
Vendor1-D	206.92	12.66	49.98	62.01	60.16	21.30	-16.67	-7.46	-21.22	0.42	4
Vendor2-D	65.94	20.12	56.94	62.13	39.14	-0.68	-0.82	10.28	11.13	6.03	3
Vendor3-D	36.79	9.12	23.19	42.29	21.70	16.69	-2.97	-37.20	-29.36	-23.07	2
Vendor4-H	68.11	11.51	27.15	20.79	20.91	-0.43	-3.35	-1.04	2.50	5.64	1
Vendor5-H	54.66	34.86	25.61	21.38	46.22	-10.61	37.33	-30.45	-34.31	7.39	4

Gage R&R Study

- XRF gage R&R was evaluated with a yellow capacitor sample; Three appraisers tested the components three times each, for a total of ninety measurements. The elements evaluated were Pb and Br.

Gage R & R Vendor 1 Desktop XRF (Pb)

Source	Var Comp	%Contribution (of VarComp)
Total Gage R&R	2396.6	6.41
Repeatability	2387	6.38
Reproducibility	9.6	0.03
Part-To-Part	34994.9	93.59
Total Variation	37391.5	100

Source	StdDev (SD)	Study Var (3 * SD)	%Study Var (%SV)
Total Gage R&R	48.955	146.865	25.32
Repeatability	48.857	146.57	25.27
Reproducibility	3.098	9.294	1.6
Part-To-Part	187.069	561.208	96.74
Total Variation	580.107	580.107	100

Gage R & R Vendor 1 Desktop XRF (Br)

Source	Var Comp	%Contribution (of VarComp)
Total Gage R&R	76104	1.91
Repeatability	73626	1.84
Reproducibility	2478	0.06
Part-To-Part	3918727	98.09
Total Variation	3994831	100

Source	StdDev (SD)	Study Var (3 * SD)	%Study Var (%SV)
Total Gage R&R	275.87	827.61	13.8
Repeatability	271.34	814.02	13.58
Reproducibility	49.78	149.35	2.49
Part-To-Part	1979.58	5938.73	99.04
Total Variation	1998.71	5996.12	100

Gage R&R Results

➢ Vendor 1-D showed the better results with less than 30% of total variation

Vendor #	Vendor1-D		Vendor2-D		Vendor3-D		Vendor4-H		Vendor5-H	
Element	Pb	Br	Pb	Br	Pb	Br	Pb	Br	Pb	Br
Total Gage R&R	25.32	13.8	58.54	85.05	86.88	98.11	39.48	74.58	86.07	97.23
Repeatability	25.27	13.58	54.44	83.51	48.32	52.61	38.61	72.4	67.64	73.05
Reproducibility	1.6	2.49	21.54	16.12	72.21	82.82	8.28	17.87	53.22	64.17

Detection Level versus Acquisition Time Study

- One sample (SP4 PE) was used for detection Level versus Acquisition Time study.

SP4 PE Element Content	Cr	Cd	Hg	Pb	Br
Average (ppm)	274	66	302	297	303

- From time period 5-10 seconds, we measured every second; From 10-20 seconds every 2 seconds; From 20-50 seconds every 5 seconds, From 50-100 seconds every 10 seconds.

<u>Definition of Difference %</u>

Difference %= [(x' - x)/ x]100

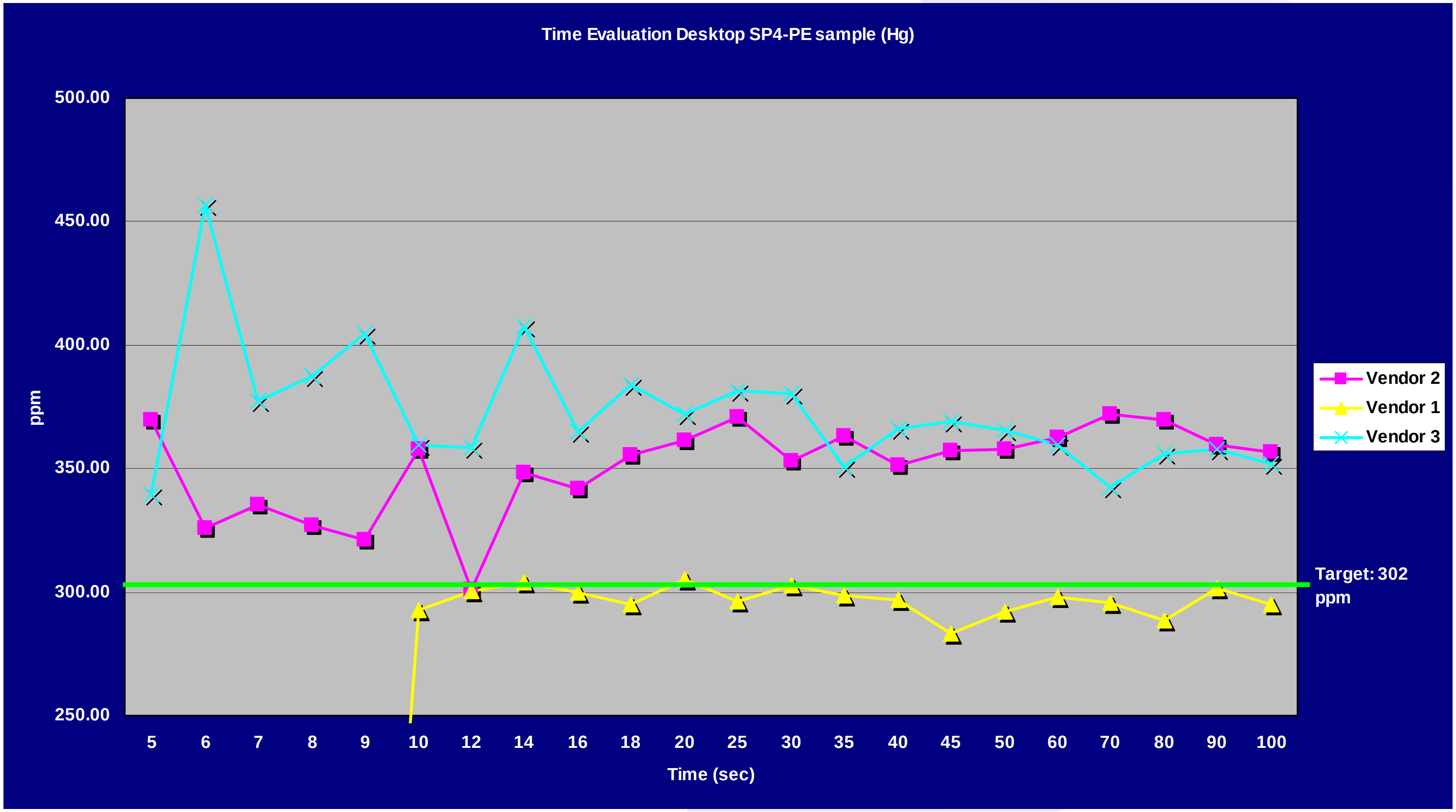
where x : standard sample content, or analytical testing results

x' : average of XRF testing results

- Five readings were taken for every measurement and calculated the average. Then the difference and standard deviation were compared.

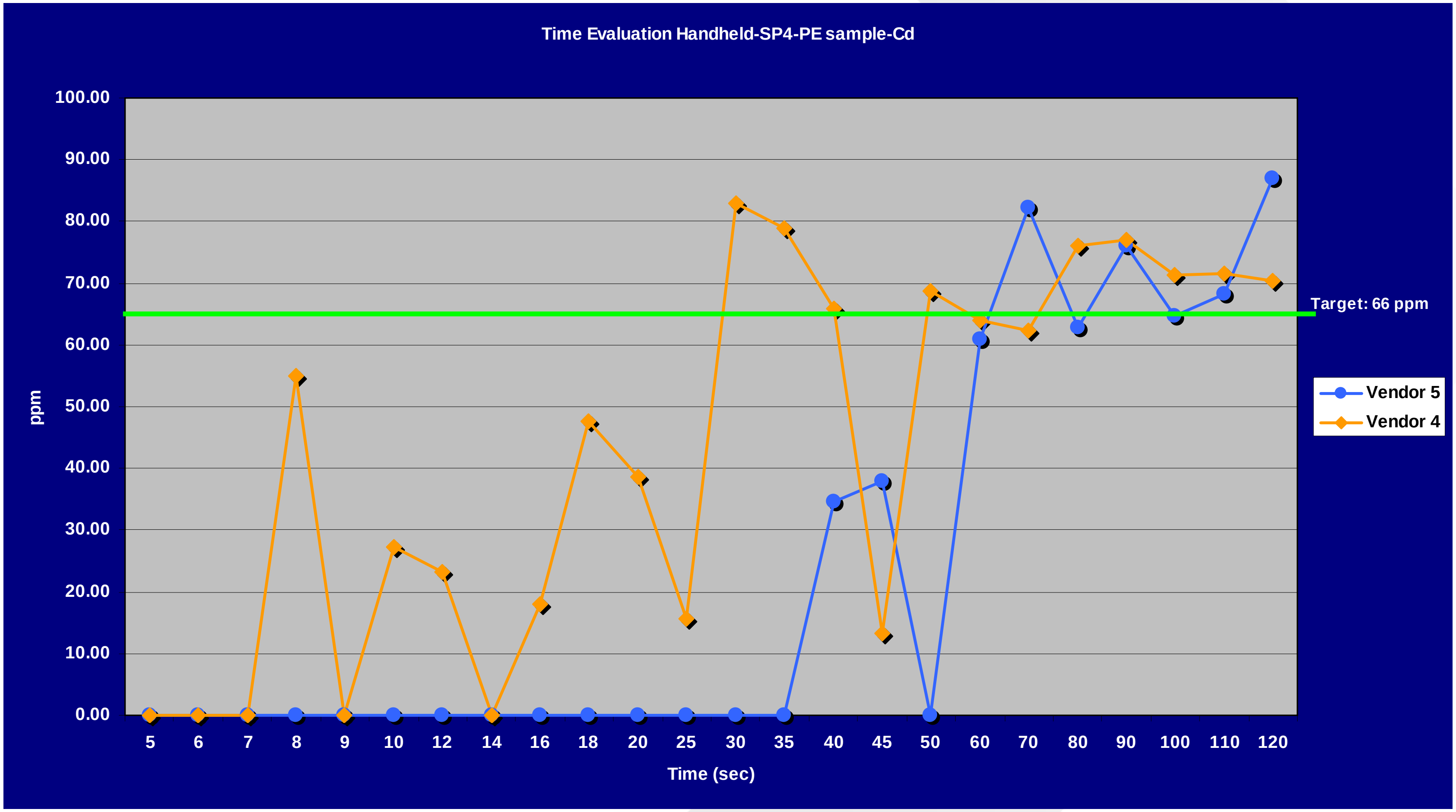
Detection Level versus Acquisition Time Study

- Desktop results for Hg



Detection Level versus Acquisition Time Study

- Handheld results for Cd



Detection Level versus Acquisition Time Results

➢ Results summary

Element	Standard deviation (σ)					Percentage of Difference					Total Rank
	Cr	Cd	Hg	Pb	Br	Cr	Cd	Hg	Pb	Br	
Vendor1-D	10.92	5.47	5.61	3.79	8.03	2.98	2.58	-1.74	-13.28	0.68	1
Vendor2-D	50.01	22.87	18.39	16.66	24.05	5.74	-43.83	16.16	10.66	17.32	4
Vendor3-D	8.84	6.97	25.73	28.11	8.71	-11.28	-32.02	23.32	-10.25	-40.19	2
Vendor4-H	20.82	30.81	5.15	5.23	5.57	64.74	-35.10	30.14	18.97	7.78	2
Vendor5-H	80.32	33.30	83.64	82.04	121.73	-227.63	-559.12	-9.34	-136.47	-561.53	5

Correlation results from XRF against two external Laboratories

- The correlation study was done with eleven different samples tested with the five XRF instruments.

- Those samples were analyzed by two external laboratories with other analyzing techniques, mainly ICP

<u>Definition of Difference %</u>
Difference %= [(x' - x)/ x]100
where x : average of Laboratory 1 and Laboratory 2 testing results
x' : result obtained with XRF equipment

- The resulted Difference % was rated according this table.

Score	Diff range
5	2<d<10
4	10<d<20
3	20<d<30
2	30<d<40
1	40<d<50
0	50<d

Samples Selected for Correlation Study








Sample #	DESCRIPTION	Comment
1	Lead - Free solder Bar SAC 305	Solder
2	Solder paste Lead-Free	Solder
3	PCBA product	Solder mask
4	Orange button Flex product	Plastic part
5	Green button Flex product	Plastic part
6	Red probe clipper (isolate)	Plastic cover
7	Red probe clipper (wire)	Plastic cover
8	Multi-meter red probe (wire)	Plastic cover
9	Multi probe -point	Plastic cover
10	Multi probe -cover point	Plastic cover
11	Cutting pliers red handle	Plastic part

Correlation Study Results

- Sample ID #1 FS21 Lead Free Solder Bar

Sample Identification	**#1 FS21 Lead Free Solder Bar**
Element analyzed (ppm)	**Pb**
Average (Laboratory 1 & Laboratory 2)	**2336.5**

Equipment	**Test Method**	**Pb**		**Score**
		ppm	Diff %	
Vendor 1-D	XRF	1988.358	-13.66	4
Vendor 2-D	XRF	4838.18	10.08	0
Vendor 3-D	XRF	1818.10	-21.06	3
Vendor 4-H	XRF	2602.67	13.01	4
Vendor 5-H	XRF	2100	-10.12	4
Laboratory 1	(ICP-OES)	2370	-	-
Laboratory 2	(ICP-AES)	2303	-	-

Correlation Study Results

- Sample ID #9 FS103 Multi Probe Point

Sample Identification	**#9 FS103 Multi Probe Point**
Element analyzed (ppm)	**Cd**
Average (Laboratory 1 & Laboratory 2)	**2562**

Laboratory	Test Method	Cd		Score
		ppm	Diff	
Vendor 1-D	XRF	2318.24	-9.51	5
Vendor 2-D	XRF	3080.17	20.23	3
Vendor 3-D	XRF	519	-79.74	0
Vendor 4-H	XRF	3263.56	27.38	3
Vendor 5-H	XRF	3217	25.57	3
Laboratory 1	(ICP-OES)	2320	-	-
Laboratory 2	(ICP-AES)	2804	-	-

Correlation Study Results

- Sample ID #11 FS103 Plastic Cover From Pliers

Sample Identification	#11 FS107 Pliers	
Element analyzed (ppm)	Cd	Pb
Average (Laboratory 1 & Laboratory 2)	240	283

Laboratory	Test Method	Cd		Score	Pb		Score
		ppm	Diff %		ppm	Diff %	
Vendor 1-D	XRF	234.48	-2.30	5	359.49	27.03	3
Vendor 2-D	XRF	834.81	247.84	0	281.77	-0.43	5
Vendor 3-D	XRF	110.5	-53.96	0	246	-13.07	4
Vendor 4-H	XRF	306.34	27.64	3	334.48	18.19	4
Vendor 5-H	XRF	374	55.83	0	293	3.53	5
Laboratory 1 Analysis	(ICP-OES)	201	-	-	190	-	-
Laboratory 2 analysis	(ICP-AES)	279	-	-	376	-	-

Correlation Study Results

- Results summary, Vendor 1-D showed the best performance

Production sample performance	Sample number																	Total Score	Rank	
	1	2	2	3	4	4	5	6	6	7	7	8	8	9	10	11	11			
Vendor1-D	4	0	0	0	3	0	3	4	3	0	0	4	2	5	5	5	3	41	1	Excellent
Vendor2-D	0	0	0	0	0	0	0	0	1	0	1	0	2	3	0	0	5	12	5	poor
Vendor3-D	3	0	0	0	3	0	4	0	0	0	0	0	0	0	0	0	4	14	4	poor
Vendor4-H	4	0	0	5	0	0	0	5	3	0	4	1	0	3	4	3	4	36	2	good
Vendor5-H	4	5	0	0	0	0	4	0	5	0	0	0	2	3	0	0	5	28	3	medium

Conclusions

- Test Results Summary from five XRF Vendors

Suppliers Evaluation	*Vendor 1-D*	*Vendor 2-D*	*Vendor 3-D*	*Vendor 4-H*	*Vendor 5-H*
Standard Samples Analysis	Excellent	Medium	Good	Excellent	Medium
Equipment Stability	Medium	Good	Good	Excellent	Medium
Equipment Gage R&R	Good	Poor	Poor	Medium	Poor
Detection Level Versus Acquisition Time	Excellent	Medium	Medium	Medium	Poor
Correlation Ext Lab	Excellent	Poor	Poor	Good	Medium

Performance Graphic Score

- **Excellent**
- **Good**
- **Medium**
- **Poor**
- **Bad**

Conclusions

- The results obtained from this evaluation demonstrated that XRF technique is a feasible testing method for factories to perform “spot checks” on the incoming materials, components and sub-assemblies to ensure RoSH compliance

- A Desktop Equipment presented the best performance but one of the handheld instruments demonstrated to be a good tool too.

- Gage R&R study revealed the opportunity of improvement for Equipment Repeatability; only the vendor 1-D showed acceptable results with a total variation of 25%. This result help to establish the confident limits to use this tool

Cr, Hg, Pb < 750ppm Cd < 75 ppm	125 > Cd > 75 1250 > Pb, Hg > 750 Cr > 750 ppm	Hg, Pb >1250ppm Cd > 125 ppm
RoHS Compliant	**Inconclusive**	**RoHS NonCompliant**

Conclusions

- When the result obtained is inconclusive it is recommended to analyze the samples with other techniques like ICP

- The handheld instruments finds its main application in large samples or samples that can not be transported to testing area

- Other advantage of XRF is the low cost and non destructive method of analysis

- Despite the benefits of XRF technique there are important limitations to consider like.

  - The inability to quantify PBB and PBDE as well as Chromium VI.
  - Only homogeneous samples can be analyzed
  - The analysis is done at the surface of samples
  - You have to select the recipes to analyze Plastic, Metals, Solders or Alloys
  - In addition a well trained operator is required to judge results

Thank You!