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NPL REPORT MAT 4

XRF Measurement of Residual Materials in Electronics

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AUGUST 2007

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Department for **Innovation, Universities** & **Skills**

XRF Measurement of Residual Materials in Electronics

Martin Wickham and Christopher Hunt
Industry and Innovation Division

ABSTRACT

The aim of this study was to assess the suitability of using X-ray fluorescence (XRF) systems for screening electronics parts in two applications - compliance with RoHS regulations, and tin whisker mitigation. Fifteen XRF systems were evaluated using typical electronic components and assemblies, ranging from contaminated plastic components, through bulk solder alloys, to solder joints and solder-terminated components.

The results indicate that while PIN (semiconductor diode) and SiLi detector based systems are suitable for RoHS compliance measurements in plastics and solders, proportional counter based systems are not. XRF systems using PIN or SiLi detectors generally proved efficient at distinguishing between non-compliant components (containing typically 2000+ppm of restricted substances) and compliant components (typically <500ppm of restricted substances). For levels between 500ppm and 2000ppm, the use of additional techniques may be required to provide discrimination. The PIN or SiLi detectors also proved efficient at distinguishing compliant and non-compliant systems containing >1000ppm cadmium. Below this level, however, additional techniques may again be required to provide discrimination. The lower RoHS limit for cadmium of 100ppm did result in a number of false detections for this element.

Proportional counter based systems were capable of registering the presence of RoHS-banned elements at levels >3% e.g. such as found in some plastics. Below this level, however, their ability to detect any banned substances was questionable, and their use for such applications is not recommended.

For tin whisker mitigation applications, lead levels in excess of 4% are required for solder samples. All the systems successfully detected lead at or above this level, providing the sample size was large enough to fill the measurement window. Indeed, all systems proved capable of detecting/measuring lead levels above 1% in solder.

It is important to remember that the use of these instruments for both the applications studied (RoHS compliance, or tin whisker mitigation) requires the operators to have both a thorough knowledge of the instrument themselves, and a good understanding of the structure and materials involved in the test samples These are required to prevent incorrect interpretation of the data provided i.e. incorrect indications of RoHS compliance, or of tin whisker mitigation (e.g. for samples having lead in base materials beneath a lead-free metalisation). Recommendations on instrument practice to obtain meaningful, repeatable results are given.

ISSN 1754-2979

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Approved on behalf of the Managing Director, NPL,
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authorised by Director, Industry and Innovation Division

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1 INTRODUCTION

The requirement to comply with the European regulations (RoHS – Restriction of Hazardous Substances) from July 2006 (Reference 1) that restrict the use of lead, cadmium, mercury, hexavalent chromium, polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) flame retardants, is driving the adoption of a range of new materials in electronics components. A company failing to comply with RoHS is liable to be fined. Consequently, to ensure only RoHS compliant materials are supplied or used, the industry has turned to using energy-dispersive X-ray fluorescence (EDX) as a goods-in inspection tool, although the technical capabilities of the instruments are not well understood by the electronics manufacturing community.

This jointly funded by industry and the Department of Innovation, Universities & Skills (DIUS), this collaborative project brought together interested parties who needed to develop confidence in the XRF technique to deliver quantified data. The project used an inter-comparison of different XRF equipment and test sites to determine the suitability of the techniques to determine the presence of any restricted substances in typical electronics components and thus significantly improve industry's confidence in meeting the EC regulations.

X-ray fluorescence (XRF) is used throughout a wide range of industries for fast, non-destructive, elemental chemical analysis of materials. Samples are bombarded with high energy X-rays with some of the X-rays being absorbed by the atoms of the sample. If the captured X-ray is of sufficient energy, an electron will be ejected from an inner shell creating vacancies. To stabilise the atom, electrons from the outer shells fall to the inner shells, giving off another X-ray whose energy is the difference between the two binding energies of the inner and outer electron shells. As each element has a unique combination of electron shell energy levels, the spectrum of emitted X-rays is characteristic of the elements contained in the sample. The peak intensities of the emitted X-rays provide information about the concentration of the elements.

The incident X-rays can be provided by two alternative sources: X-ray tube or a radioactive isotope. The X-ray tube is inert until activated by the operator whilst the isotope source needs shielding to prevent operator exposure. Examples of both types have been included in this study. Further details of the XRF technique can be found in References 2 to 7.

The emitted X-rays are analysed using one of three types of detector.

(i) **SiLi detectors** have the best resolutions, being able to differentiate between peaks approximately 140eV apart. However, they require liquid nitrogen to allow them to be kept cool enough to maintain their stability.

(ii) **Si-PIN photodiodes** (formed from p-type / intrinsic / n-type semiconductor) can be cooled using Peltier devices. They are less expensive and do not have as a good a resolution as the SiLi detectors, but are still able to differentiate between peaks around 250eV apart. These detectors form the majority of the systems evaluated here.

(iii) **Proportional counters** use photo-ionization of gases within the counters, to detect the emitted X-rays. They are the least expensive of the options explored in this study but are only capable of resolving between peaks around 1000eV apart.

This project analysed a range of samples containing RoHS prohibited substances. These included Pb/Br/Cd/Hg in plastics (plasticisiers/pigments) and lead in solders (bulk and

coatings). Additionally, control samples with no contamination were included to investigate whether there were any incorrect, or false, detections of the banned substances.

In addition to those companies wishing to avoid the use of RoHS restricted materials in their assembly, a second group of interested companies was involved in the project. These comprised companies currently exempt from RoHS regulations, but seeking to gain confidence in using XRF to ensure that component terminations contained at least 4% Pb (References 8 and 9). This lead is required to inhibit tin whiskers forming during field service. A range of bulk solder and solder joint samples was included to assess instrument capability in this area.

2 METHODOLOGY

The project was undertaken in two phases. In the initial phase, a range of samples with recognised or perceived problems re RoHS compliance, were assembled. To validate the samples, one sister specimen of each sample type (i.e. from the same batch) was chemically analysed to determine its composition and the levels of any banned substances.

In phase 2, the samples chosen in phase 1 were taken to all the partners for blind evaluation using their own XRF systems. When all partners had been visited and the XRF trials completed, the actual samples used were chemically analysed to confirm composition.

2.1 SAMPLES

The samples chosen for evaluation were as detailed in Table 1. The samples were especially chosen to represent typical RoHS compliance or non-compliance, or to present XRF systems with particular challenges. The area of interest for each sample was designated and circular section samples were cut in half to ensure repeatable presentation to the instruments.

2.2 CHEMICAL ANALYSIS

All chemical analysis results are given as weight percentages.

2.2.1 Total chromium, cadmium, lead and mercury content using microwave acid Digestion by Inductively Coupled Plasma with Mass Spectrometry (ICP-MS).

This method was undertaken on samples 1 to 9 (not 1A or 5A), 12 to 14 and 34 to 36.

2.2.1.1 Preparation of samples

The solid samples were either cut, ground in a cryo-grinder, or prepared using a combination of both. Care was taken to avoid any residual contamination by scrupulous cleaning of the blades or replacement of the blades. The solder pastes were not further prepared before microwave acid digestion.

2.2.1.2 Microwave Acid Digestion

Approximately 0.1 g of each sample was accurately weighed into a high-pressure quartz digestion vessel. A mixture of concentrated nitric acid and hydrogen peroxide was added to the digestion vessel and placed in a Paar Multiwave microwave system for closed vessel

microwave digestion. Each sample was digested at 230 ºC using two different programmes to ensure full digestion of the samples. With each batch of samples a reference material and a blank solution were analysed with the samples. The samples and reference materials were diluted with high purity (18.2 mW) water, prior to analysis.

The solder pastes contained undigested white particulates. These samples were filtered through a 540 hardened ashless filter paper, and the liquid used for analysis. The filtrate was digested using high pressure teflon vessels in a Paar Multiwave microwave system using a mixed HNO_3/HF acid digest. All sample acid digestions produced clear solutions confirming that the samples had been fully digested.

Table 1: Sample list

No.	Name	Description
1	SPDY	Yellow PVC sleeve from spade terminal
1A	SPDY AS	Spade terminal with yellow PVC sleeve
2	BACK	PVC Gland adaptor back shell
3	DIN	PVC strain relief from 5-way gold-plated 180deg DIN cable plug
4	IDC	Standard grey 34-way IDC cable with PVC coating
5	NET	PVC strain relief from green Cat5e RJ45 UTP patch lead
5A	NET AS	Green Cat5e RJ45 UTP patch lead connector with PVC strain relief
6	FEET	Non-PVC black stick-on feet
7	BEV	Silvered bevel from push button
8	FUSE	Red non-PVC fitting from 32A fuse holder
9	PLUG	Red outer casing from connector plug
10	RES	1206 chip resistor
11	SCREW	Large headed bolt with zinc-passivated surface
12	SPDR	Red PVC sleeve from spade terminal
13	CBLE	PVC strain relief from connector on grey Cat5e RJ45 UTP patch lead
14	MMC	Non-PVC blue housing for 120A 600V connector
15	PB1	Sn sample with 50ppm Pb contamination
16	PB2	Sn sample with 110ppm Pb contamination
17	PB3	Sn sample with 260ppm Pb contamination
18	PB4	Sn sample with 490ppm Pb contamination
19	PB5	Sn sample with 980ppm Pb contamination
20	PB6	Sn sample with 1900ppm Pb contamination
21	PB7	Sn sample with 10000ppm Pb contamination
22	PB8	Sn sample with 20000ppm Pb contamination
23	NPL1	Lead-free SOIC soldered with SnAgCu solder paste to lead-free PCB
24	NPL2	SnPb terminated SOIC soldered with SnAgCu solder paste to lead-free PCB with resulting ~2% Pb contamination in joint
25	NPL3	As above with ~5% Pb contamination in joint
26	NPL4	As above with ~10% Pb contamination in joint
27	NPL5	As above with ~15% Pb contamination in joint
28	REL1	SnPb-terminated resistor (11% Pb) in tape
29	REL2	Tin-terminated resistor in tape
30	BGA1	SnPb BGA soldered with SnPbAg solder paste ~ 40% Pb in joint
31	BGA2	SnAgCu BGA soldered with SnPbAg solder paste ~ 10% Pb in joint
32	STCK	SnPb-terminated SOIC (36% Pb) in plastic tube
33	STCK1	Sn-terminated SOIC in plastic tube
34	PSTE1	Sn 62 (SnPbAg) solder paste in plastic tub
35	PSTE2	Pb contaminated Sn62 solder paste in plastic tub
36	PSTE3	SAC solder paste in plastic tub
37	R60L	Resistor as in 10:RES (above) soldered with SAC to ENIG PCB
38	POST	Tin-plated brass threaded spacer

2.2.1.3 Determination using Inductively Coupled Plasma with Mass Spectrometry (ICP-MS)

The measurements were carried out using an Agilent 7500ce ICP-MS instrument with an integrated sample introduction system in high sample throughput mode to minimise potential carry over effects. Samples were introduced into the ICP via a micro-flow quartz concentric nebuliser and a PTFE Scott type double pass spray chamber cooled to 2 ºC. The system was automated using a CETAC ASX-520 auto-sampler. Rhodium, tellurium and thallium were used as internal standards to correct for suppression effects. Primary mercury, cadmium, chromium and lead standards traceable to international standards (SI) were used to calibrate the ICP-MS.

2.2.2 Total cadmium (Cd) and lead (PB) using acid digestion by Inductively-Coupled Plasma – Atomic Emission Spectrometry (ICP-AES)

This method was undertaken on samples 15 to 22.

2.2.2.1 Preparation of samples

The samples were dissolved in nitric acid (in duplicate) after the removal of tin as stannic bromide. The solutions were transferred into 50ml volumetric flasks and made up to the mark with distilled water.

2.2.2.2 Determination using Inductively-Coupled Plasma – Atomic Emission Spectrometry (ICP-AES)

The solutions were analysed for cadmium and lead contents using ICP-AES, and a Varian 720 ES Instrument.

2.2.3 Qualitative determination of chromium VI

Undertaken on sample 11.

2.2.3.1 Method

A qualitative test (Reference 10) was used by reacting hydrogen peroxide with an acidic extract taken from the sample. A positive result is indicated by the formation of chromium peroxide, which has a blue colouration.

2.2.4 Total bromine content using oxygen flask combustion by ion chromatography

Undertaken on samples 2, 6, 8, 13 and 14.

2.2.4.1 Method

The bromine content was determined by combusting the prepared ground samples in an oxygen flask (Schöniger flask method). The sample was weighed out and placed in an ashless filter paper holder, which in turn was placed in a platinum basket attached to the stopper of the flask. The flask was filled with oxygen and a reacting solution, and the stopper placed in the flask. The sample was combusted and the resultant combustion products are absorbed into solution.

The solution was analysed for bromine using ion chromatography (LGC SOP EA/NW/6R) and a Dionex DX-500 ion chromatography System. Reference materials and a certified working standard LGC 4008 (4-bromobenzoic acid) were used to confirm recovery and accuracy of determinations.

2.2.5 Energy-dispersive X-ray analysis (EDX)

Undertaken on samples 10, 23 to 29, 32 to 33, 37 and 38.

2.2.5.1 Method

For samples where there was insufficient material for chemical analysis, the detection and analysis of the characteristic X-ray of various elements were obtained using an EDX system attached to a scanning electron microscope (SEM). This technique is similar in principal to XRF but atom excitation is achieved by bombardment with electrons rather than X-rays. Typically this technique has a shallower penetration depth than XRF, of around 1μm, depending on material examined. The limit of detection is considered to be around 0.1%.

2.3 XRF Analysis

Each sample was presented to the XRF systems three times, with the sample being removed from the equipment between tests. XRF system parameters were set by each end-user/supplier to his best practice for each sample type. Typical spot sizes used for each system are shown in Table 2. Details of whether the system was bench-top or portable and the type of detector used are given in Table 3. In total fifteen systems were tested, eleven bench-tops (seven Si-PIN, one SiLi and three proportional counters) and four portables (all Si-PIN). All used X-ray tubes as a source for the incident X-rays except one system, which used a Co57 source. In all twelve partners and 11 different systems were evaluated. All XRF analysis results are given as weight percentages.

Table 2: Typical spot sizes and test times for test systems (Φ indicates diameter of circular spot)

		Plastics		Metals	
Partner	System	SpotSize	TestTime	SpotSize	TestTime
A	P	0.2-2mmΦ	340s	0.2-2mmΦ	210s
B	P	1-2mmΦ	340s	1-2mmΦ	205s
A	Q	0.1-0.6mmΦ	340s	0.1-0.6mmΦ	210s
C	Q	0.1-0.6mmΦ	350s	0.1-0.6mmΦ	95s
D	Q	0.3-0.6mmΦ	360s	0.3-0.6mmΦ	210s
E	Q	0.6mmΦ	200s	0.1-0.6mmΦ	100s
F	R	3x3mm	180s	3x3mm	30s
F	S	1.2mmΦ	120s	1.2mmΦ	280s
G	T	0.5-2mmΦ	120s	0.4-0.5mmΦ	20-100s
H	U			0.3mmΦ	15s
J	V	3mmΦ	120s	3mmΦ	100-200s
J	W	10x20mm	120s	10x20mm	200s
L	X	1mmΦ	200s	0.3-1mmΦ	210s
M	Y	0.4mmΦ	30s	0.08-0.4mmΦ	30s
N	Z	3mmΦ	120s	3mmΦ	60s

Table 3: Test system comparison for benchtop/portable and detector types

Partner	System	Bench Top	Portable	*SiLi*	*PIN*	*Prop. Count.*
A	**P**	X			X	
B	**P**	X			X	
A	**Q**	X			X	
C	**Q**	X			X	
D	**Q**	X			X	
E	**Q**	X			X	
F	**R**		X		X	
F	**S**	X		X		
G	**T**	X				X
H	**U**	X				X
J	**V**		X		X	
J	**W**		X		X	
L	**X**	X			X	
M	**Y**	X				X
N	**Z**		X		X	

3 RESULTS FOR PLASTIC COMPONENTS

Summary results are given graphically in the Sections below. The summaries show averages of three instrument readings except where stated. For the purposes of averaging, where a system returned a "not detected" result, it was equated to 0.

Sample 1 (SPDY) and sample 1A (SPDY AS)
Figure 1, with sample 1A SPDY AS shown as an insert. The metal insert was removed from sample 1 before both XRF and chemical analyses. Sample 1A was another component from the same batch as sample 1, but was tested with the metal insert included.

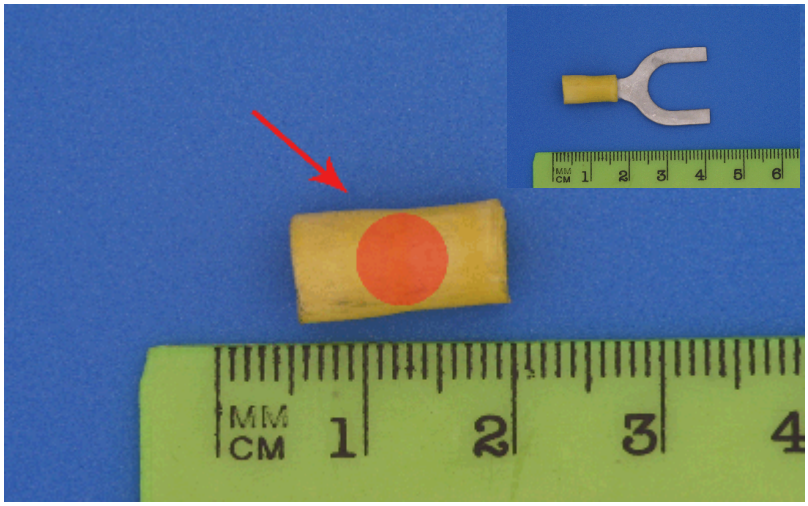

Figure 1: Sample 1 (SPDY) with sample 1A (SPDY AS) as an insert

3.1.1 SPDY Chemical Analysis Results

SPDY	Bromine %	Cadmium%	Mercury %	Lead %	Chromium %
	Not tested	<0.001	<0.001	2.634	0.039
	Not tested	<0.001	<0.001	3.311	0.052
Average		**<0.001**	**<0.001**	**2.973**	**0.046**

3.1.2 SDPY Proportional Counter Results

For all three proportional counter based instruments, a lead peak was present in the spectra. One system (GT) gave an automatically calculated average Pb content of 0.147%. This is sufficient to mark the component as non-compliant with the RoHS requirements, but significantly different from the average chemical analysis result (~3.0%). No other RoHS restricted contaminants were noted. In particular, there was no evidence for chromium (~0.05% by chemical analysis) in the spectra obtained.

3.1.3 SDPY PIN/SiLi Results

The results for the PIN/SiLi detector systems are shown in Figures 2 to 5. All the detector systems indicated the sample was RoHS non-compliant for lead (>0.1% Pb), but compliant for chromium (Figure 3) and mercury and bromine (Figure 4). One system (EQ) falsely indicated the presence of cadmium. A comparison between the results for SPDY and the SPDY AS sample with the metal insert is shown in Figure 6, and it is apparent there were no differences in the data between the lead levels in the two samples.

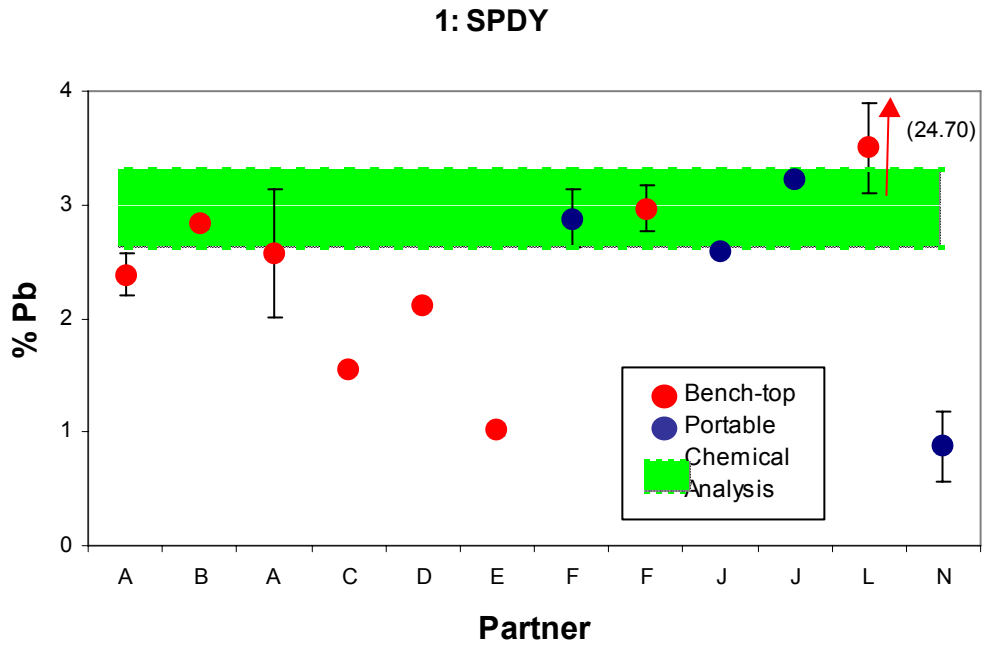

Figure 2: Results on SPDY sample for Pb (wt%) for PIN/SiLi detector systems

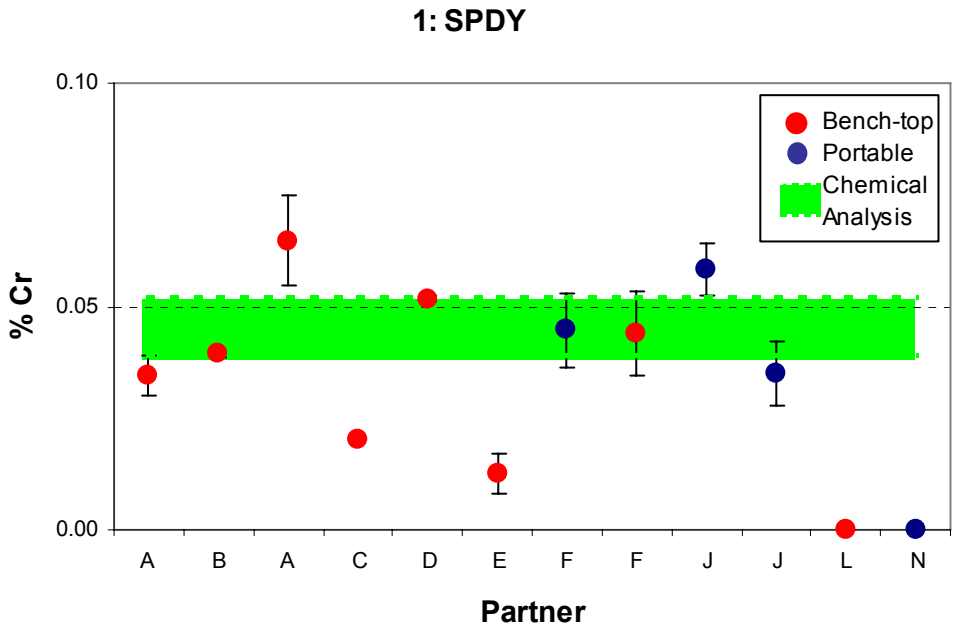

Figure 3: Results on SPDY sample for Cr (wt%) for PIN/SiLi detector systems

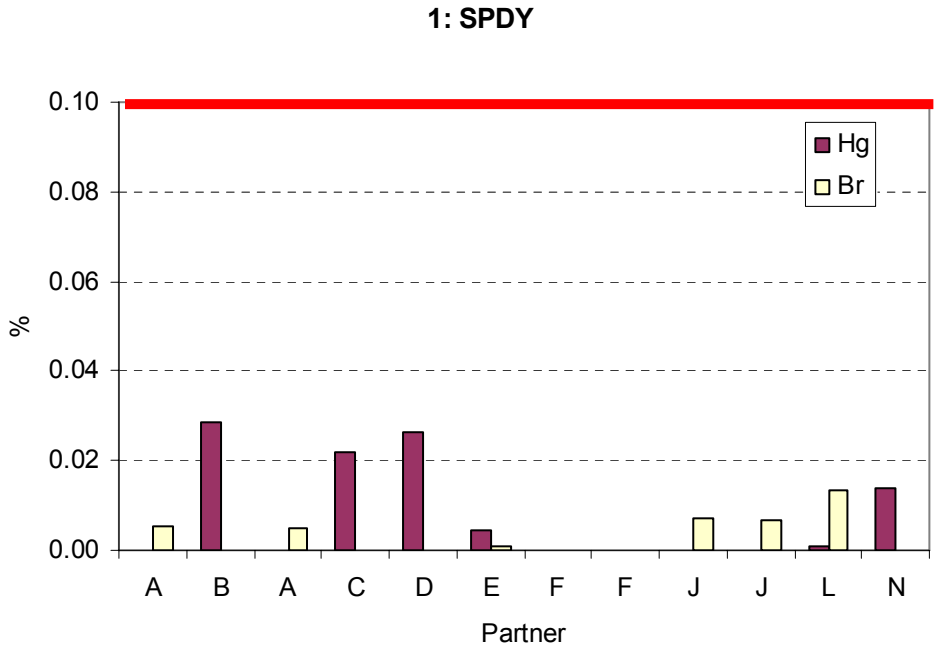

Figure 4: Results on SPDY sample for Hg and Br (wt%) for PIN/SiLi detector systems

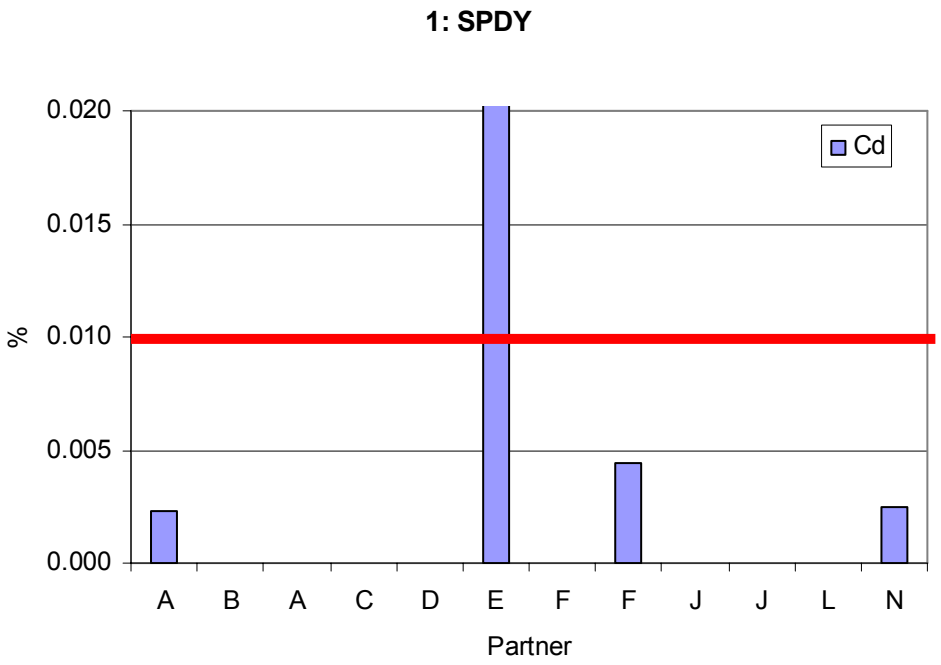

Figure 5: Results on SPDY sample for Cd (wt%) for PIN/SiLi detector systems

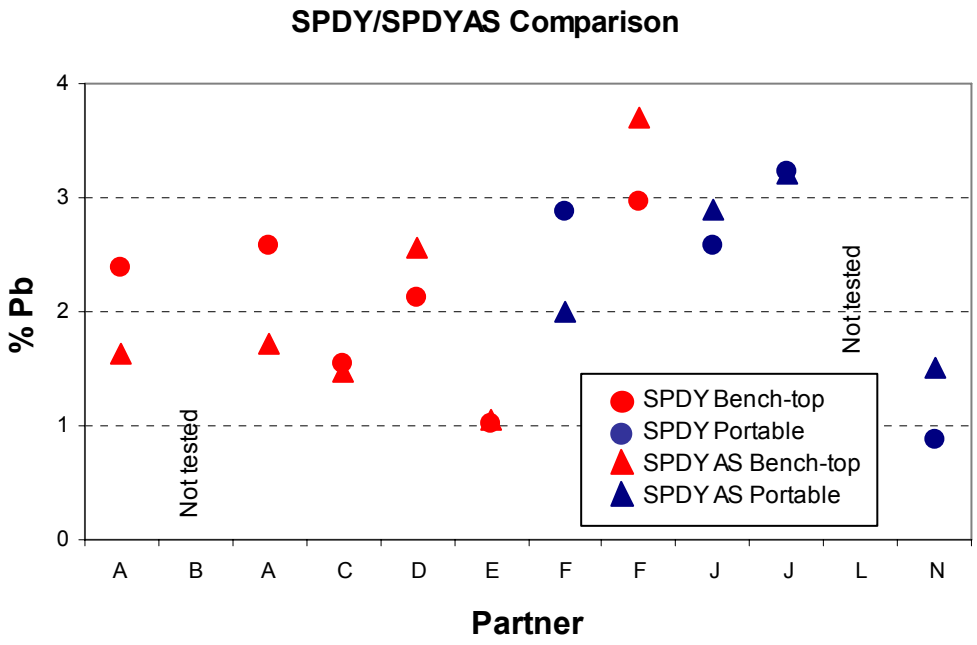

Figure 6: Comparison of PIN/SiLi detector systems' results (wt%) for SPDY and SPDY AS.

3.2 SAMPLE 2 (BACK)

Sample 2 (BACK) was a black PVC gland adaptor backshell and is shown in Figure 7.

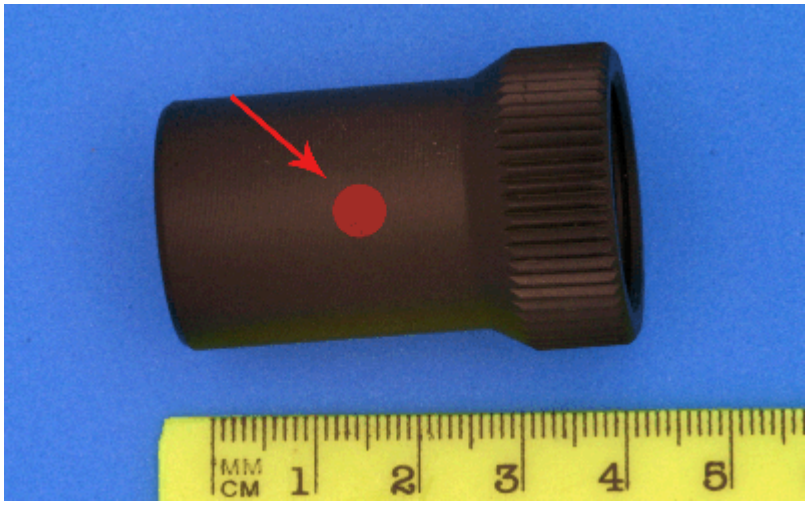

Figure 7: Sample 3 (BACK)

3.2.1 BACK Chemical Analysis Results

BACK	Bromine %	Cadmium%	Mercury %	Lead %	Chromium %
	<0.07	<0.001	<0.001	1.256	<0.001
	<0.07	<0.001	<0.001	1.285	<0.001
Average	**<0.07**	**<0.001**	**<0.001**	**1.271**	**<0.001**

3.2.2 BACK Proportional Counter Results

For all three proportional counter based instruments, a lead peak was present in the spectra. One system (GT) gave an automatically calculated average content of 0.035% Pb. This was not sufficient to mark the component as RoHS non-compliant but is was significantly different from the average chemical analysis result (~1.3% Pb). No other RoHS restricted contaminants were noted.

3.2.3 BACK PIN/SiLi Results

The results for PIN/SiLi detector systems are shown in Figures 8 to 10. All the detector systems indicated the sample was RoHS non-compliant for lead (>0.01% Pb), but compliant for chromium, mercury and bromine (Figure 9) and cadmium (Figure 10). One system (EQ) falsely indicated the presence of chromium (0.118%, not speciated). Another system (FR) gave an average cadmium content within 10% of the permitted maximum.

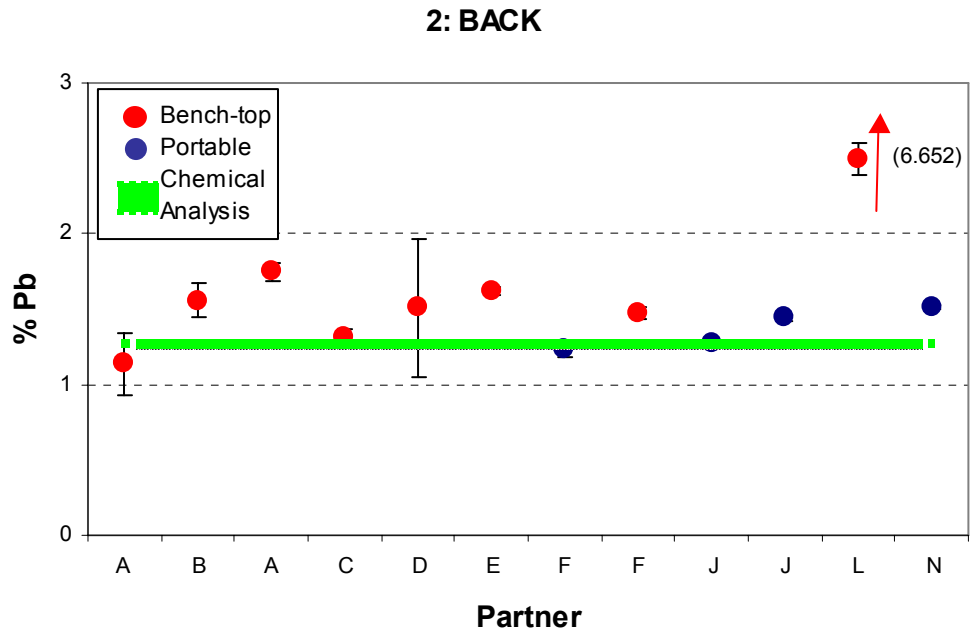

Figure 8: Results on BACK sample for Pb (wt%) for PIN/SiLi detector systems

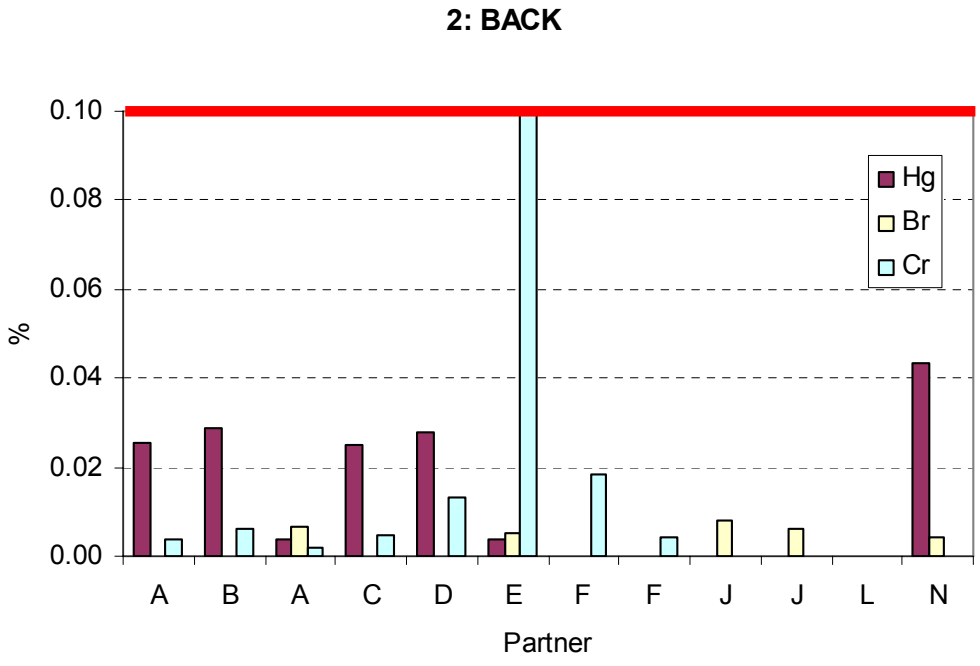

Figure 9: Results on BACK sample for Hg, Br and Cr (wt%) for PIN/SiLi detector systems

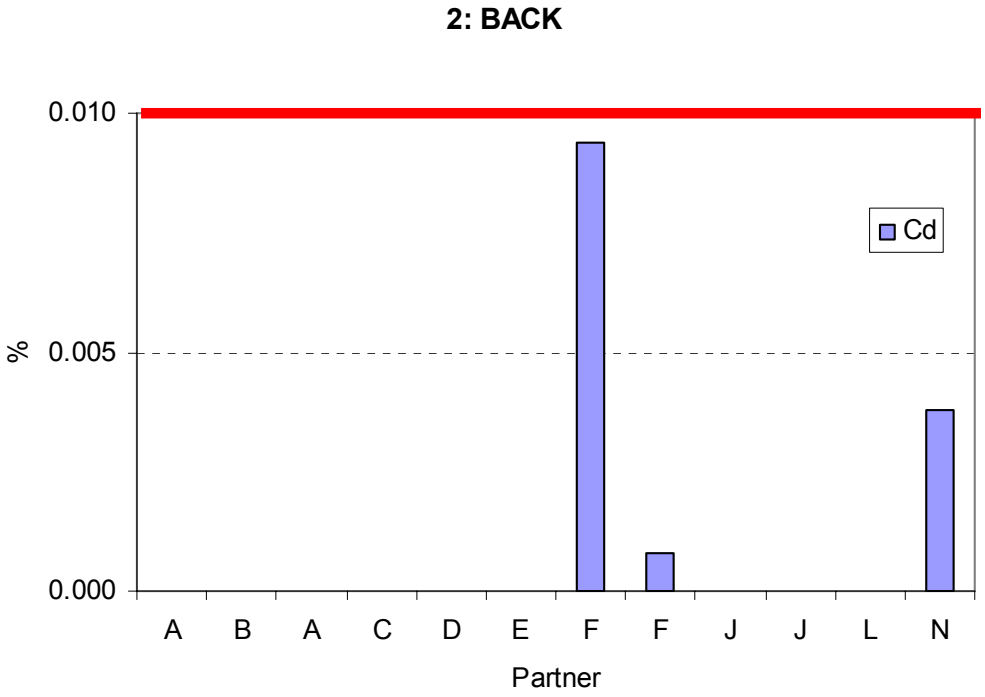

Figure 10: Results on BACK sample for Cd (wt%) for PIN/SiLi detector systems

3.3 SAMPLE 3 (DIN)

Sample 3 (DIN) was a black PVC strain relief from a 5-way gold-plated 180deg cable plug and is shown in Figure 11, with the original component before disassembly shown in the insert. The strain relief was removed from the connector body for both XRF and chemical analyses.

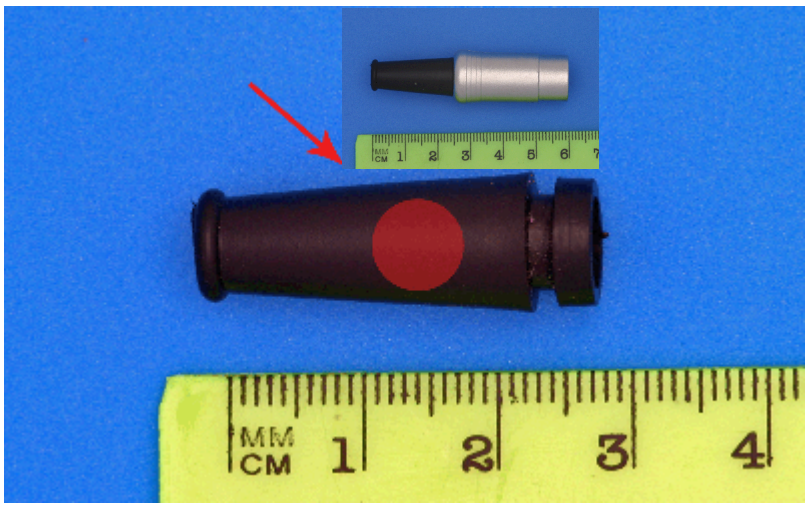

Figure 11: Sample 3 (DIN)

3.3.1 DIN Chemical Analysis Results

DIN	Bromine %	Cadmium%	Mercury %	Lead %	Chromium %
	Not tested	0.002	<0.001	1.273	0.003
	Not tested	0.002	<0.001	1.275	0.003
Average		**0.002**	**<0.001**	**1.274**	**0.003**

3.3.2 DIN Proportional Counter Results

For all three proportional counter based instruments, a lead peak was present in the spectra. One system (GT) gave an automatically calculated average lead content of 0.060% Pb. This was not sufficient to mark the component as RoHS non-compliant, but it was significantly different from the average chemical analysis result (~1.3% Pb). No other RoHS restricted contaminants were noted.

3.3.3 DIN PIN/SiLi Results

The results for PIN/SiLi detector systems are shown in Figures 12 to 14. All the detector systems indicated the sample was RoHS non-compliant for lead (>0.1% Pb), but compliant for chromium, mercury, bromine (Figure 13) and cadmium (Figure 14). One system (FR) gave an average cadmium content within 10% of permitted maximum.

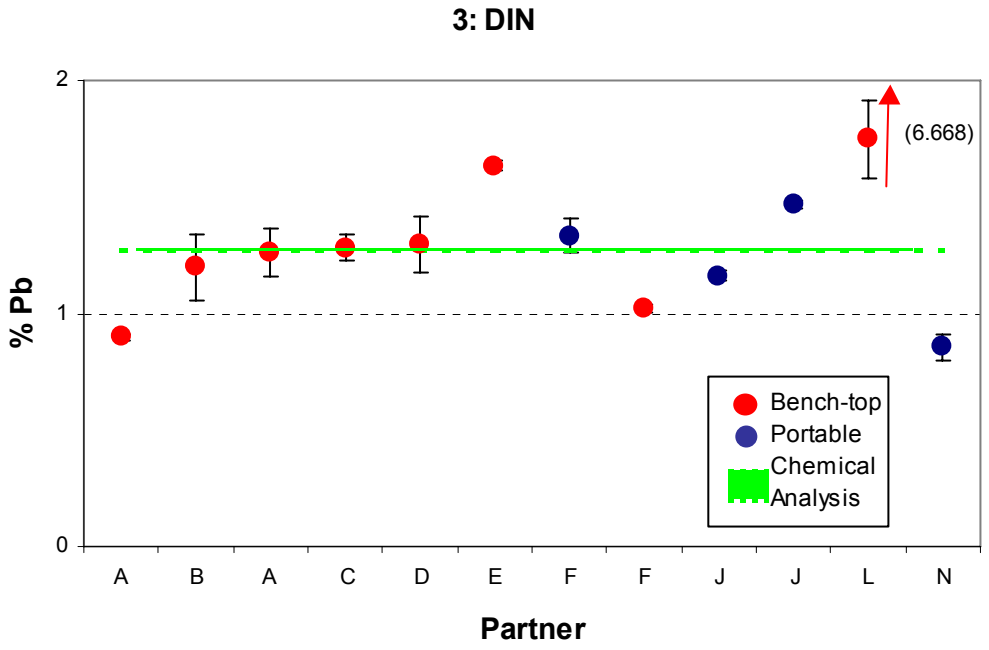

Figure 12: Results on DIN sample for Pb (wt%) for PIN/SiLi detector systems

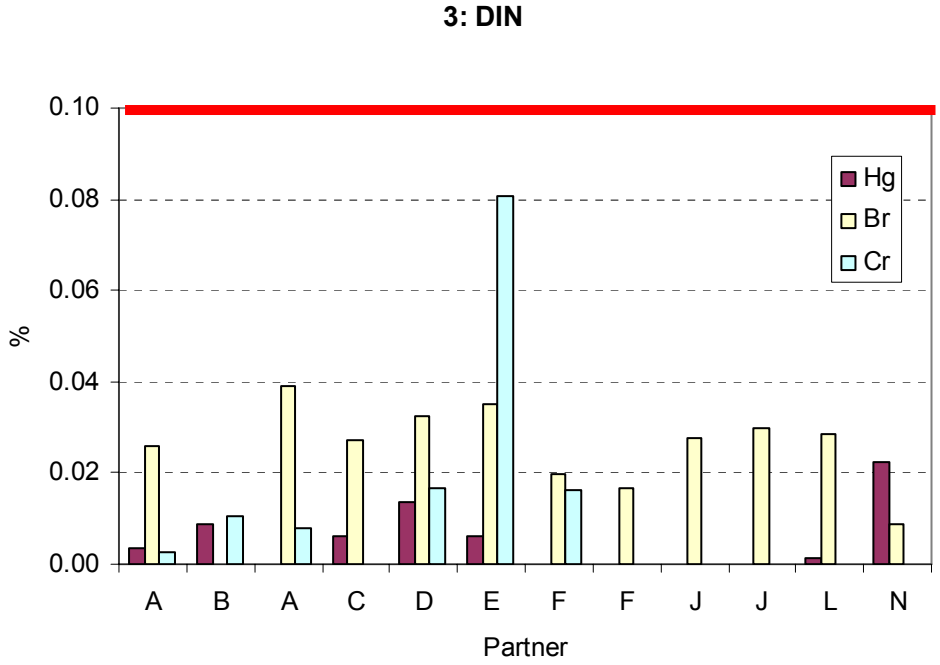

Figure 13: Results on DIN sample for Hg, Br and Cr (wt%) for PIN/SiLi detector systems

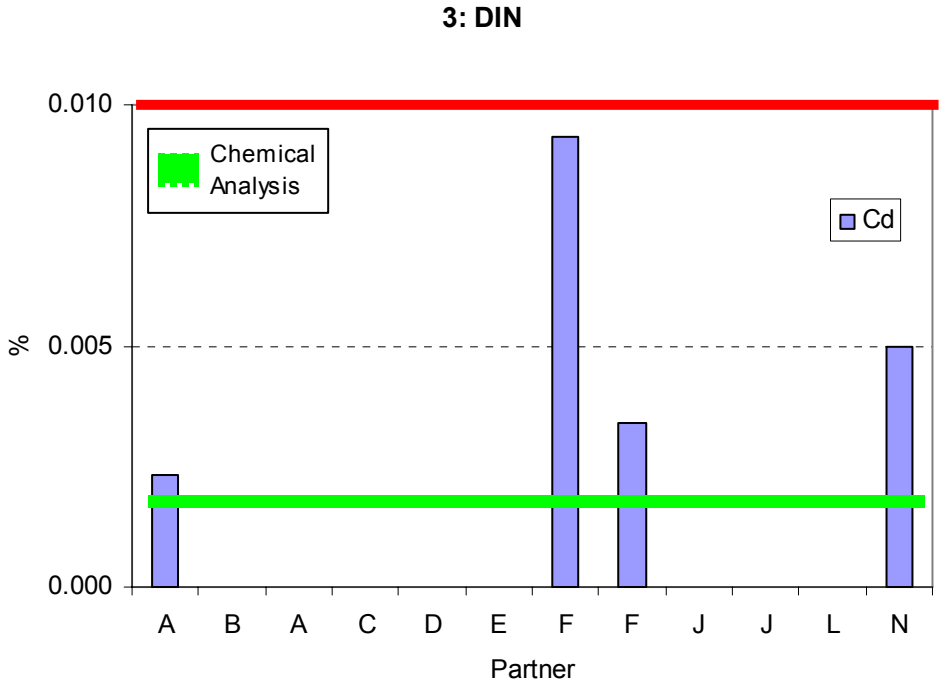

Figure 14: Results on DIN sample for Cd (wt%) for PIN/SiLi detector systems

3.4 SAMPLE 4 (IDC)

Sample 4 IDC was a grey PVC IDC cable (34-way) and is shown in

Figure 15. For XRF analysis, the whole cable including core was tested. Chemical analysis was undertaken on both the whole cable and on the sleeve only with core removed.

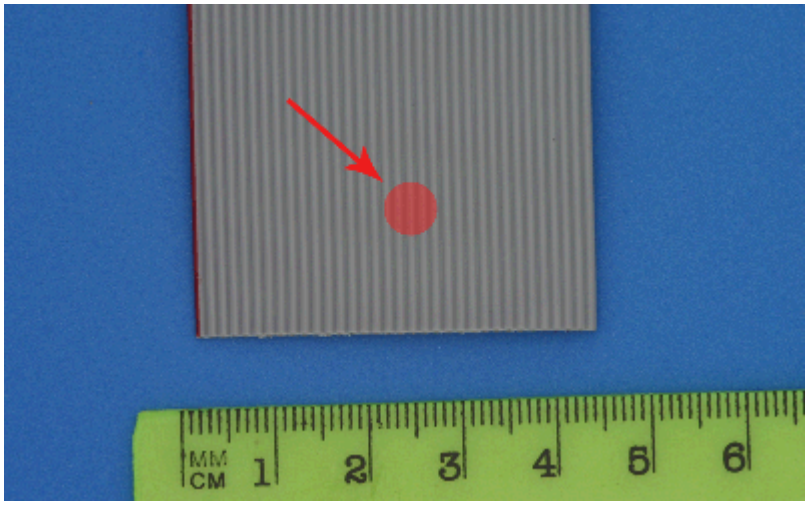

Figure 15: Sample 4 (IDC)

3.4.1 IDC Chemical Analysis Results

IDC	Bromine %	Cadmium%	Mercury %	Lead %	Chromium %
	Not tested	<0.001	<0.001	1.197	<0.001
	Not tested	<0.001	<0.001	1.214	<0.001
Average		**<0.001**	**<0.001**	**1.206**	**<0.001**
IDC	**Bromine %**	**Cadmium%**	**Mercury %**	**Lead %**	**Chromium %**
Sleeve	Not tested	<0.001	0.002	1.946	<0.001
Only	Not tested	<0.001	<0.001	1.993	<0.001
Average		**<0.001**	**0.001**	**1.970**	**<0.001**

3.4.2 IDC Proportional Counter Results

For all three proportional counter based instruments, a lead peak was present in the spectra. One system (GT) gave an automatically calculated average lead content of 0.057%. This was not sufficient to mark the component as RoHS non-compliant, but it was significantly different from the average chemical analysis result (~1.2% Pb). No other RoHS restricted contaminants were noted.

3.4.3 IDC PIN/SiLi Results

The results for PIN/SiLi detector systems are shown in Figures 16 to 18. All the detector systems indicated the sample was RoHS non-compliant for lead (>0.1% Pb – see Figure 16), but compliant for mercury, bromine and chromium (Figure 17). Two systems (BP & AQ)

indicated the sample was RoHS non-compliant for cadmium (>0.01%), and another (CQ) gave an average cadmium content within 10% of the permitted maximum. The higher kV benchtop systems tended to give lower values for lead content than the portable systems (except the isotope system N). It is likely that the higher power of these systems meant that they were sensing the metal core more than the portable systems did, thus resulting in apparently lower lead contents.

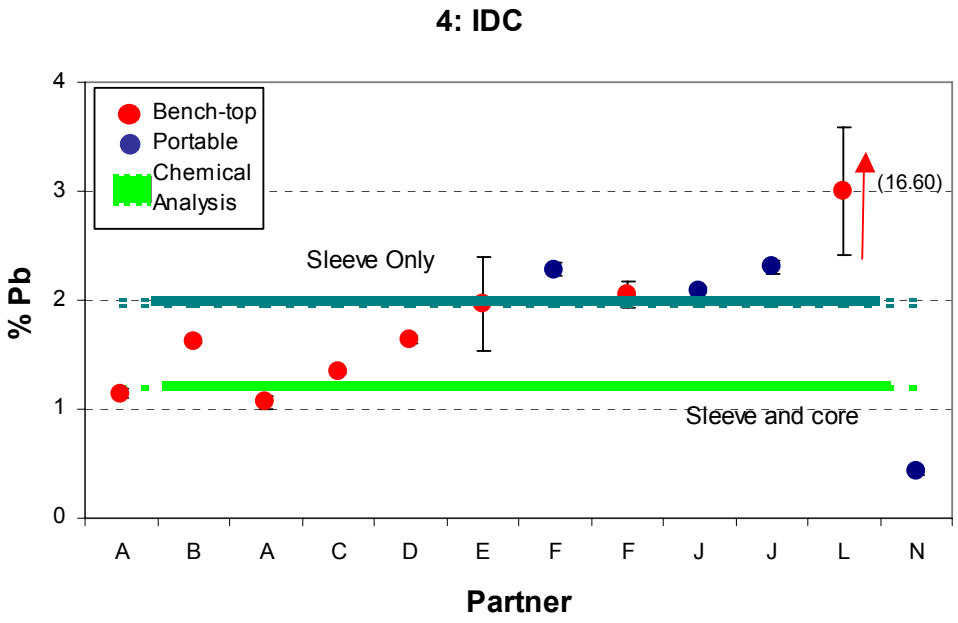

Figure 16: Results on IDC sample for Pb (wt%) for PIN/SiLi detector systems

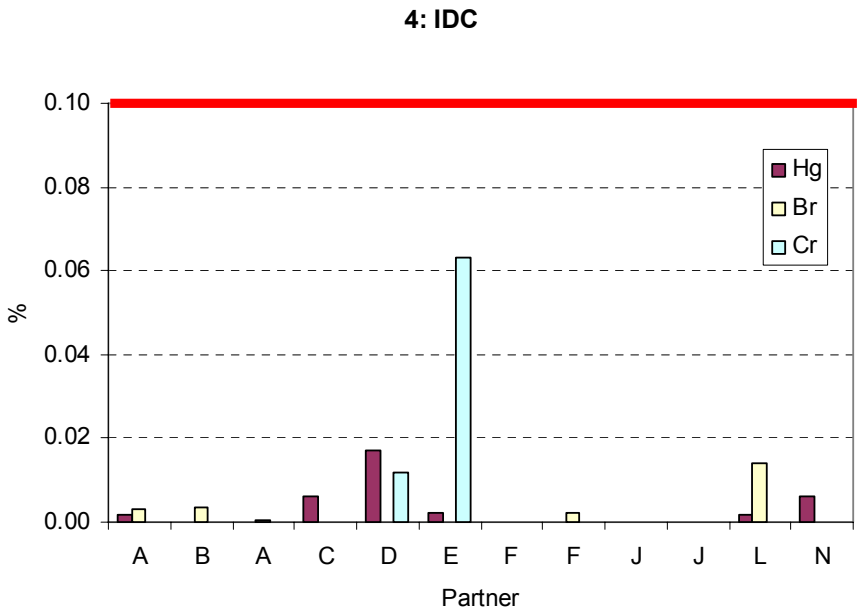

Figure 17: Results on IDC sample for Hg, Br and Cr (wt%) for PIN/SiLi detector systems

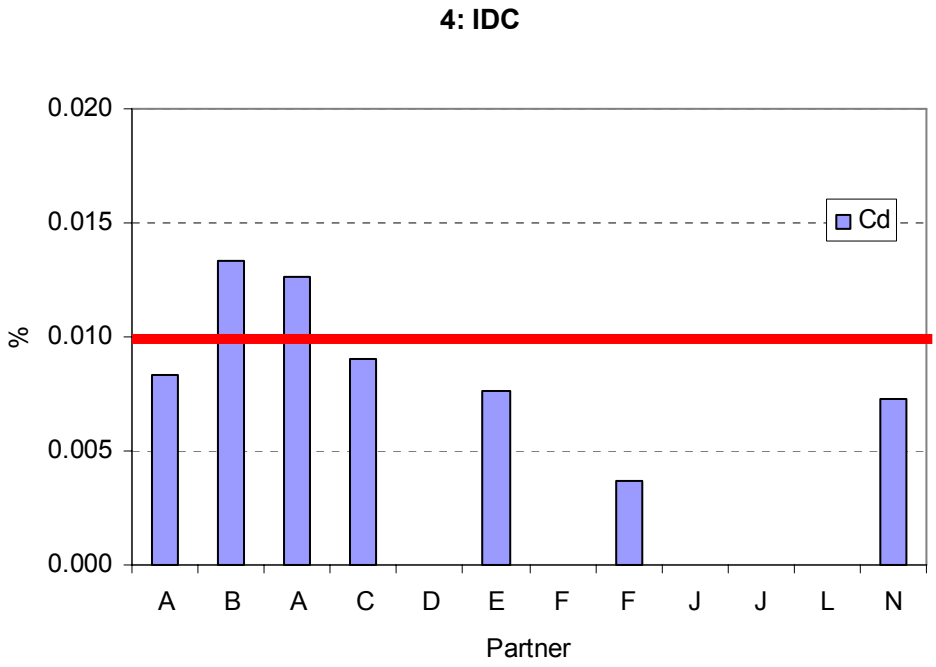

Figure 18: Results on IDC sample for Cd (wt%) for PIN/SiLi detector systems

3.5 SAMPLE 5 (NET) AND SAMPLE 5A (NET AS)

Sample 5 (NET) was the PVC strain relief from a green Cat5e RJ45 UTP patch lead and is shown in Figure 19, with Sample 5A (Net AS) before disassembly shown as an insert. This sample had the inner connector and cable removed before both XRF and chemical analyses. Sample 5A was another identical component with the inner connector and cable included.

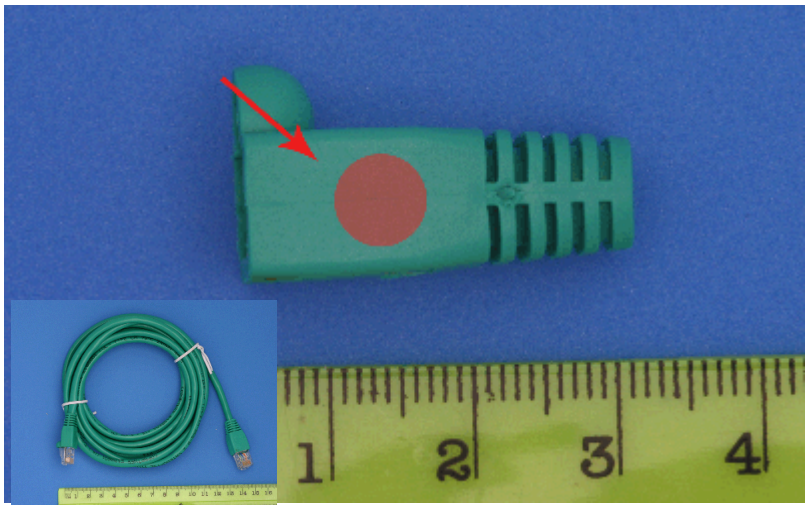

Figure 19: Sample 5 (NET)

3.5.1 NET Chemical Analysis Results

NET	Bromine %	Cadmium%	Mercury %	Lead %	Chromium %
	Not tested	<0.001	<0.001	1.167	0.008
	Not tested	<0.001	<0.001	1.167	0.009
Average		**<0.001**	**<0.001**	**1.167**	**0.009**

3.5.2 NET Proportional Counter Results

For all three proportional counter based instruments, a lead peak was present in the spectra. One system (GT) gave an automatically calculated average Pb content of 0.053%. This was sufficient to mark the component as RoHS non-compliant for lead, but it was significantly different from the average chemical analysis result (~1.2% Pb). No other RoHS restricted contaminants were noted.

3.5.3 NET PIN/SiLi Results

The results for PIN/SiLi detector systems are shown in Figures 20 to 23. All the detector systems indicated the sample was RoHS non-compliant for lead (>0.1% Pb), but compliant for mercury, bromine and chromium (Figure 21). A comparison of the lead contents of the NET and NET AS samples with the inner connector and cable included, is shown in Figure 23. It can be clearly seen that the presence of the connector and cable, diluted the Pb signal recorded by vast majority of the instruments. If the actual lead content of the strain relief had been much closer to the 0.1% limit, this phenomenon may have produced a false non-compliance result.

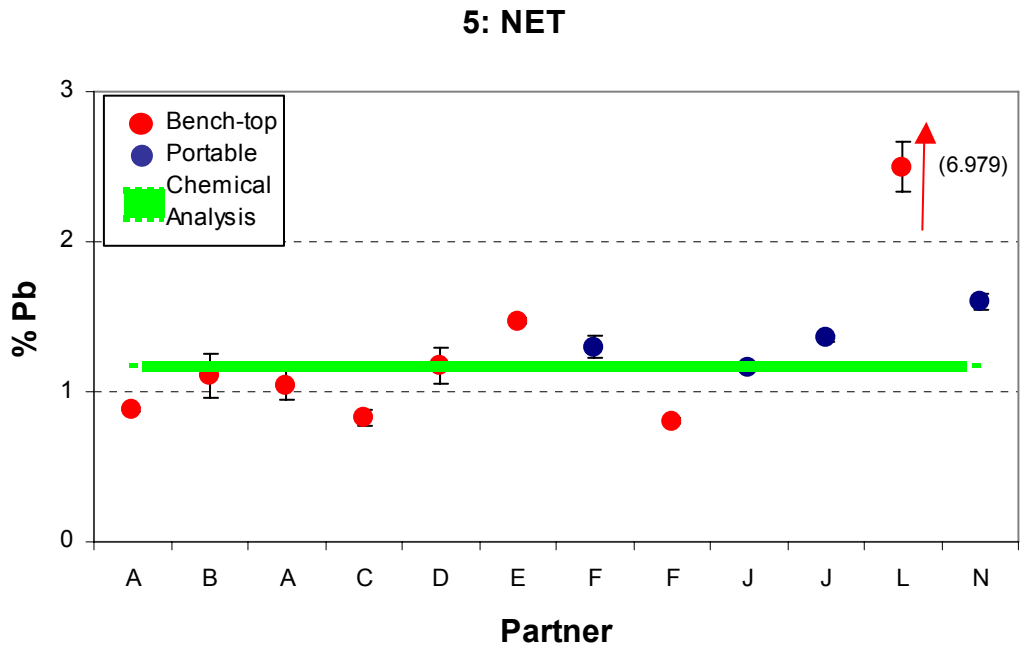

Figure 20: Results on NET sample for Pb (wt%) for PIN/SiLi detector systems

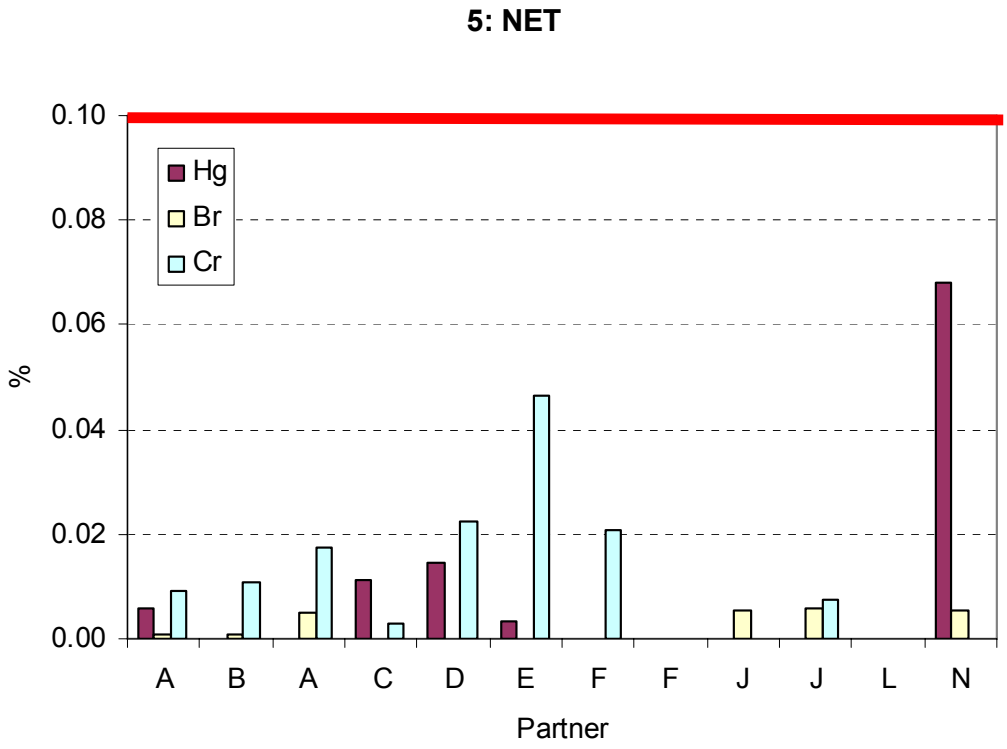

Figure 21: Results on NET sample for Hg, Br and Cr (wt%) for PIN/SiLi detector systems

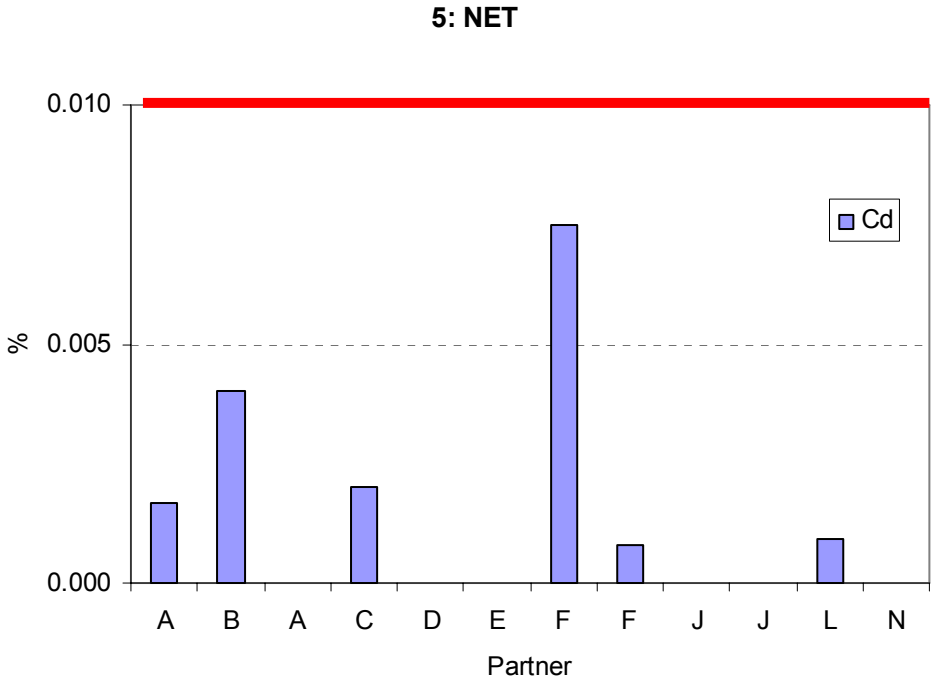

Figure 22: Results on DIN sample for Cd (wt%) for PIN/SiLi detector systems

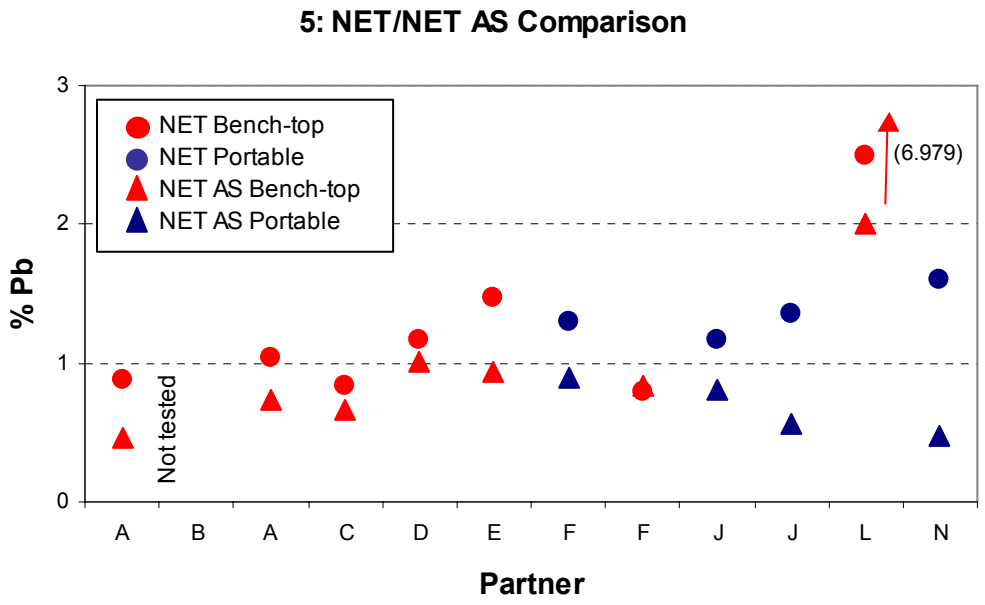

Figure 23: Comparison of PIN/SiLi detector systems results for NET and NET AS

3.6 SAMPLE 6 (FEET)

Sample 6 FEET was a non-PVC black stick-on foot and is shown in Figure 24..

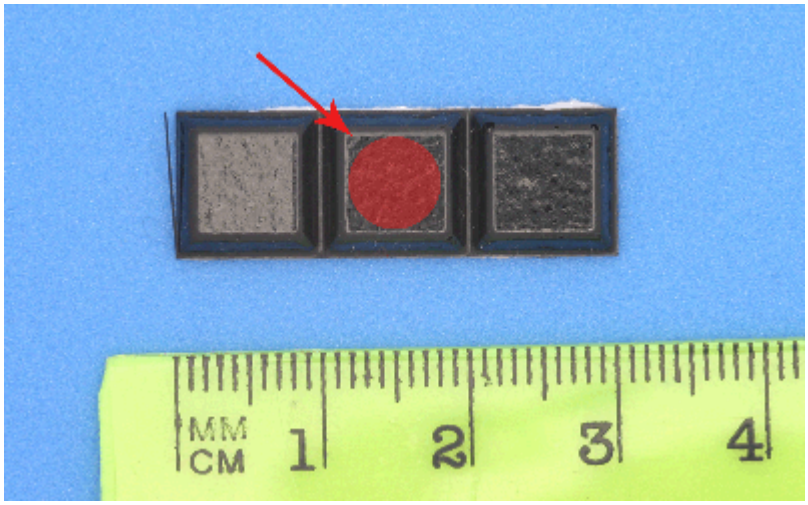

Figure 24: Sample 6 (FEET)

3.6.1 FEET Chemical Analysis Results

FEET	Bromine %	Cadmium%	Mercury %	Lead %	Chromium %
	<0.07	<0.001	0.241	<0.001	<0.001
	<0.07	<0.001	0.287	<0.001	<0.001
Average	**<0.07**	**<0.001**	**0.264**	**<0.001**	**<0.001**

3.6.2 FEET Proportional Counter Results

For all three proportional counter based instruments, a mercury peak was present in the spectra. One system (GT) gave an automatically calculated average mercury content of 0.017% Hg. This was not sufficient to mark the component as RoHS non-compliant for mercury, but was significantly different from the average chemical analysis result (0.26%). No other RoHS restricted contaminants were noted.

3.6.3 FEET PIN/SiLi Results

The results for PIN/SiLi detector systems are shown in Figures 25 to 27. All the detector systems indicated the sample was RoHS non-compliant for mercury (>0.1% Hg) but compliant for lead, bromine, chromium and cadmium (Figures 26 and 27). One system (NZ) incorrectly indicated non-compliance re chromium (>0.1% Cr, not speciated).

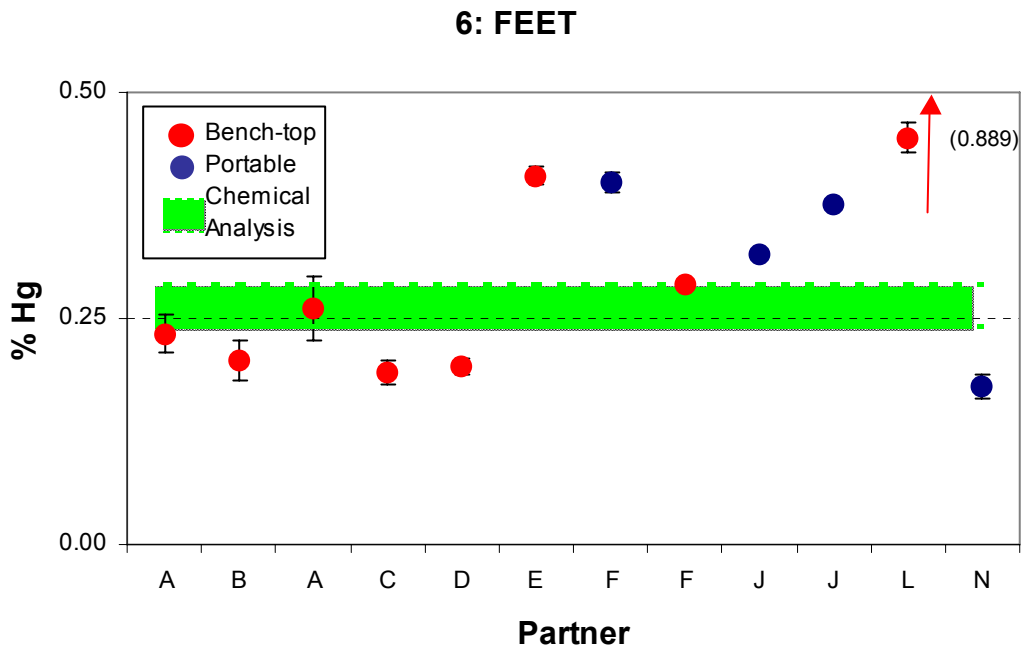

Figure 25: Results on FEET sample for Hg (wt%) for PIN/SiLi detector systems

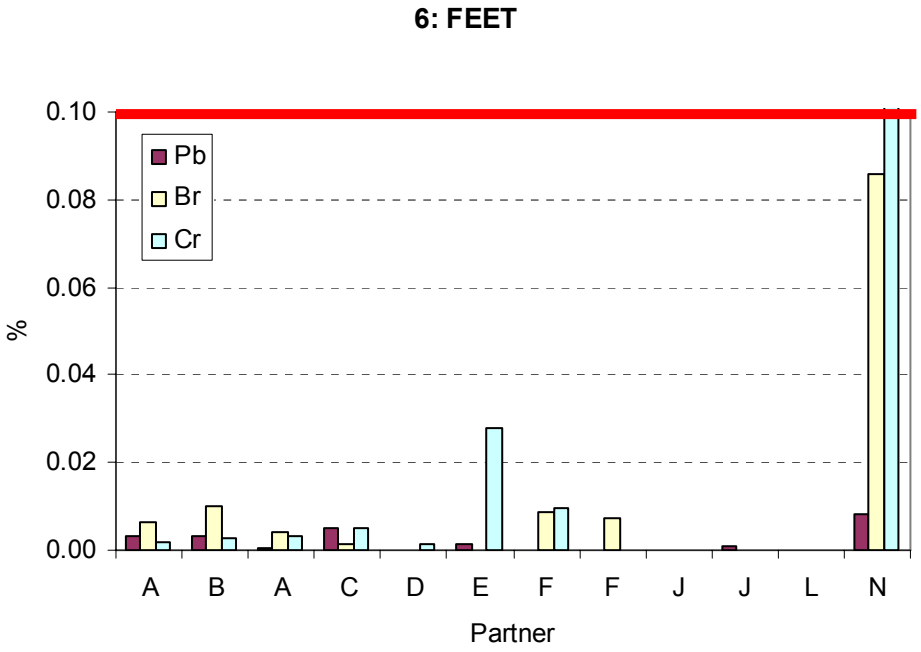

Figure 26: Results on FEET sample for Pb, Br and Cr (wt%) for PIN/SiLi detector systems

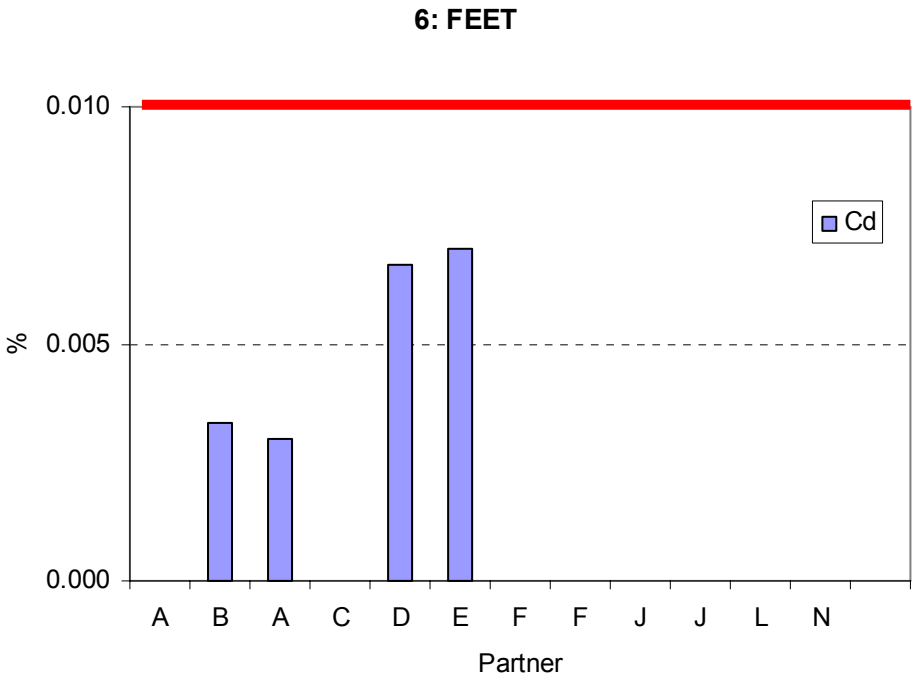

Figure 27: Results on FEET sample for Cd (wt%) for PIN/SiLi detector systems

3.7 SAMPLE 7 (BEV)

Sample 7, BEV, shown in Figure 28, was a chromium-plated push button bezel.

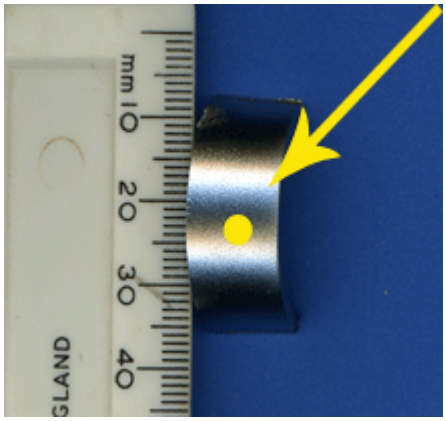

Figure 28: Sample 7 (BEV)

3.7.1 BEV Chemical Analysis Results

Analysis was undertaken on a grind of the whole sample, not a separated coating.

BEV	Bromine %	Cadmium%	Mercury %	Lead %	Chromium %
	Not tested	<0.001	<0.001	<0.001	0.135
	Not tested	<0.001	<0.001	<0.001	0.142
Average		**<0.001**	**<0.001**	**<0.001**	**0.139**

3.7.2 BEV Proportional Counter Results

Tests on BEV were undertaken on two of the proportional counter based instruments. The resulting spectra highlighted that only one instrument had detected chromium.

3.7.3 BEV PIN/SiLi Results

The results for PIN/SiLi detector systems are shown in Figure 29. Eight systems were used to examined this sample and all detected the presence of chromium. However, only five systems were able to quantify the chromium content, and the values varied from 0.6 to 2.5% Cr. No false detects were noted (Figure 30).

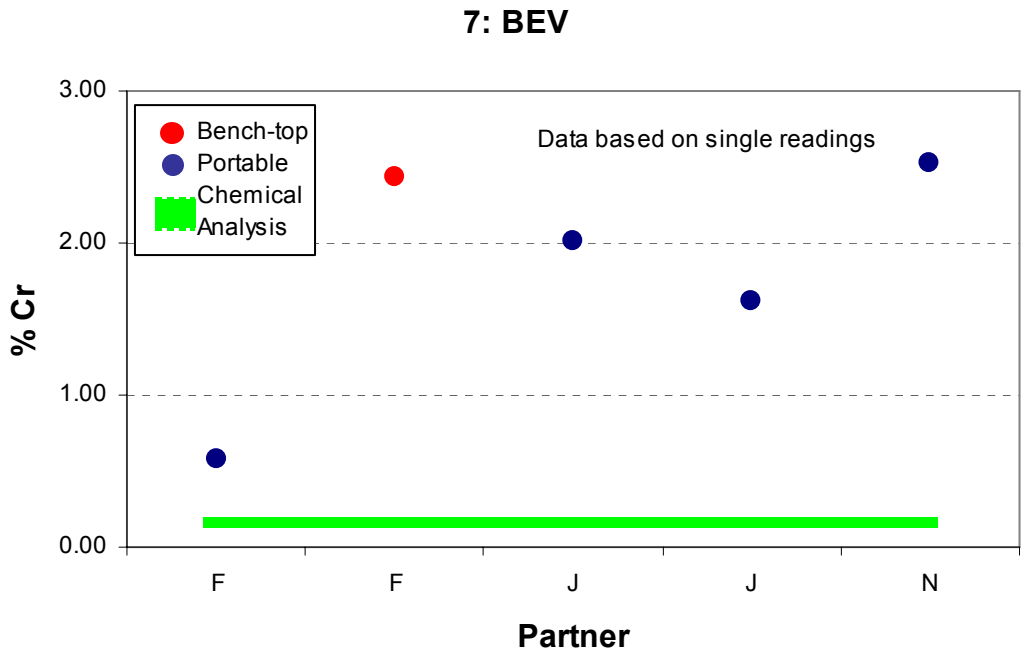

Figure 29: Results on BEV sample for Cr (wt%) for PIN/SiLi detector systems

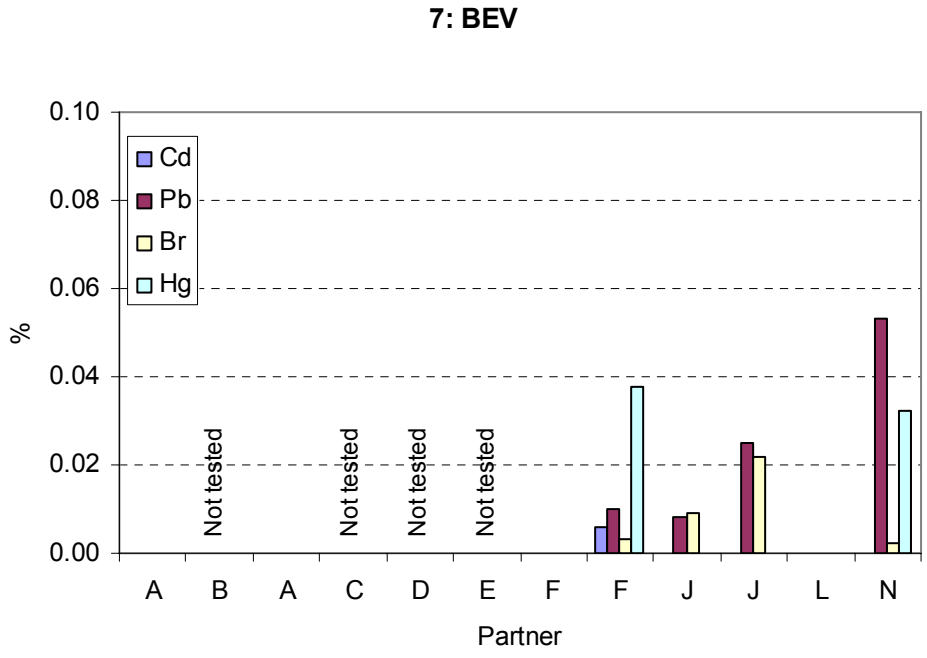

Figure 30: Results on FEET sample for Cd Pb, Br and Cr (wt%) for PIN/SiLi detector systems

3.8 SAMPLE 8 (FUSE)

Sample 8, FUSE, is shown in Figure 30, and with the original component before disassembly is shown in the insert. The sample was a non-PVC clip from a 32A fuse holder.

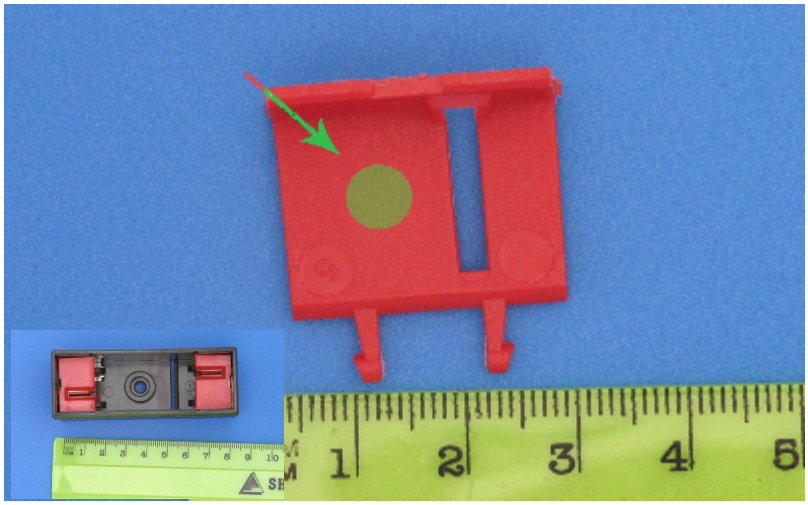

Figure 31: Sample 8 (FUSE)

3.8.1 FUSE Chemical Analysis Results

FUSE	Bromine %	Cadmium%	Mercury %	Lead %	Chromium %
	<0.07	0.213	<0.001	<0.001	<0.001
	<0.07	0.215	<0.001	<0.001	<0.001
Average	**<0.07**	**0.214**	**<0.001**	**<0.001**	**<0.001**

3.8.2 FUSE Proportional Counter Results

For two of the three proportional counter based instruments (GT & HU), a cadmium peak was present in the spectra. One system (GT) gave an automatically calculated average cadmium content of 66%. This was sufficient to mark the component as RoHS non-compliant for cadmium but significantly different from the average chemical analysis result (0.21% Cd) for the result to be questionable. The GT system recorded a mercury level of 37% and a bromine level of 0.6%.

3.8.3 FUSE PIN/SiLi Results

The results for PIN/SiLi detector systems are shown in Figures 31 to 32. All the detector systems indicated the sample was RoHS non-compliant for cadmium (>0.1% Cd), but compliant for mercury, bromine, chromium and lead (Figure 32), No false detections were noted.

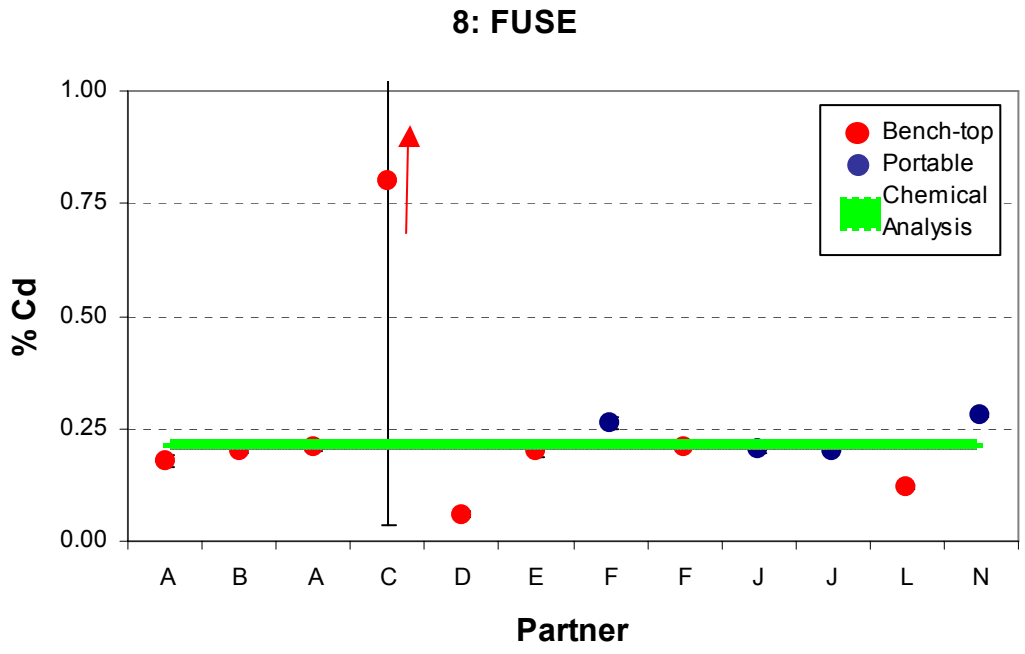

Figure 32: Results on FUSE sample for Cd (wt%) for PIN/SiLi detector systems

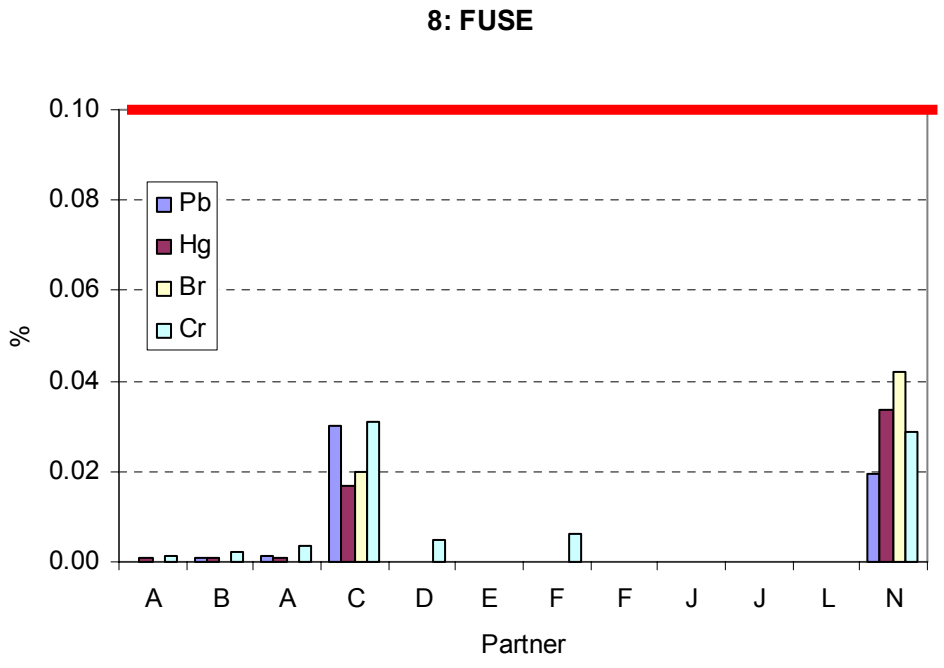

Figure 33: Results on FUSE sample for Pb, Hg, Br and Cr (wt%) for PIN/SiLi detector systems

3.9 SAMPLE 9 (PLUG)

Sample 9, PLUG, is shown in Figure 33 and was the outer casing from a connector plug.

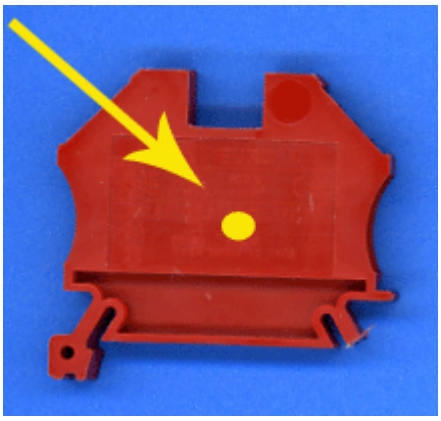

Figure 34: Sample 9 (PLUG)

3.9.1 PLUG Chemical Analysis Results

PLUG	Bromine %	Cadmium%	Mercury %	Lead %	Chromium %
	Not tested	0.237	<0.001	<0.001	<0.001
	Not tested	0.235	<0.001	<0.001	<0.001
Average		**0.236**	**<0.001**	**<0.001**	**<0.001**

3.9.2 PLUG Proportional Counter Results

For two of the three proportional counter based instruments (GT & HU), a cadmium peak was present in the spectra. One system (GT) gave an automatically calculated average cadmium content of 66%. This was sufficient to mark the component as RoHS non-compliant for cadmium, but significantly different from the average chemical analysis result (0.24%) for the result to be questionable. The GT system also showed Hg at 37%.

3.9.3 PLUG PIN/SiLi Results

The results for PIN/SiLi detector systems are shown in Figures 34 to 35. All the detector systems indicated the sample was RoHS non-compliant for cadmium (>0.01% Cd) but compliant for mercury, bromine, chromium and lead (Figure 35). No false detections were noted.

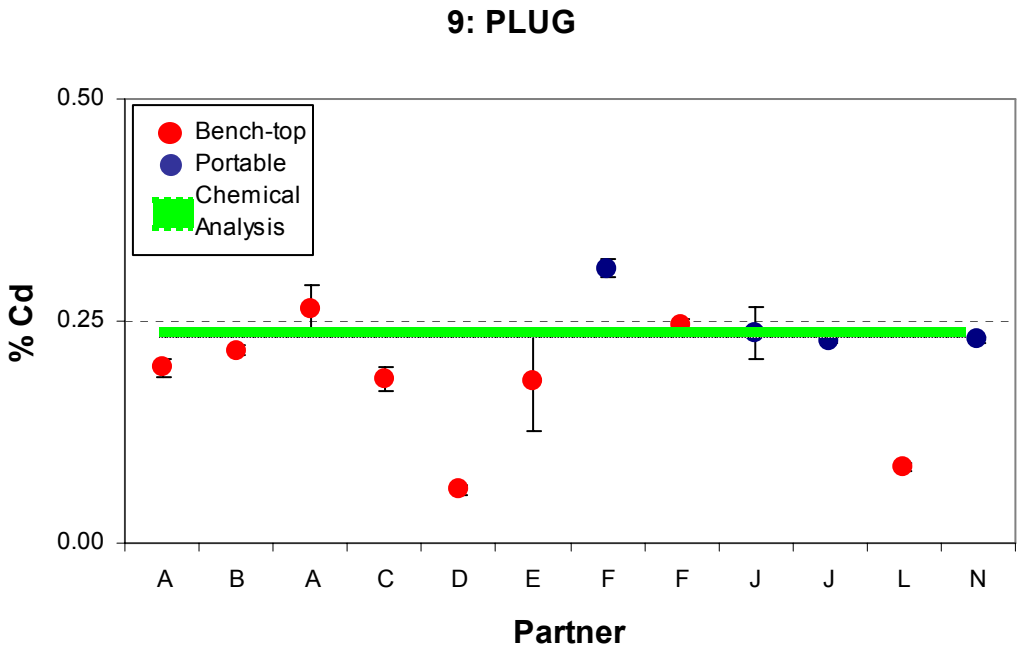

Figure 35: Results on PLUG sample for Cd (wt%) for PIN/SiLi detector systems

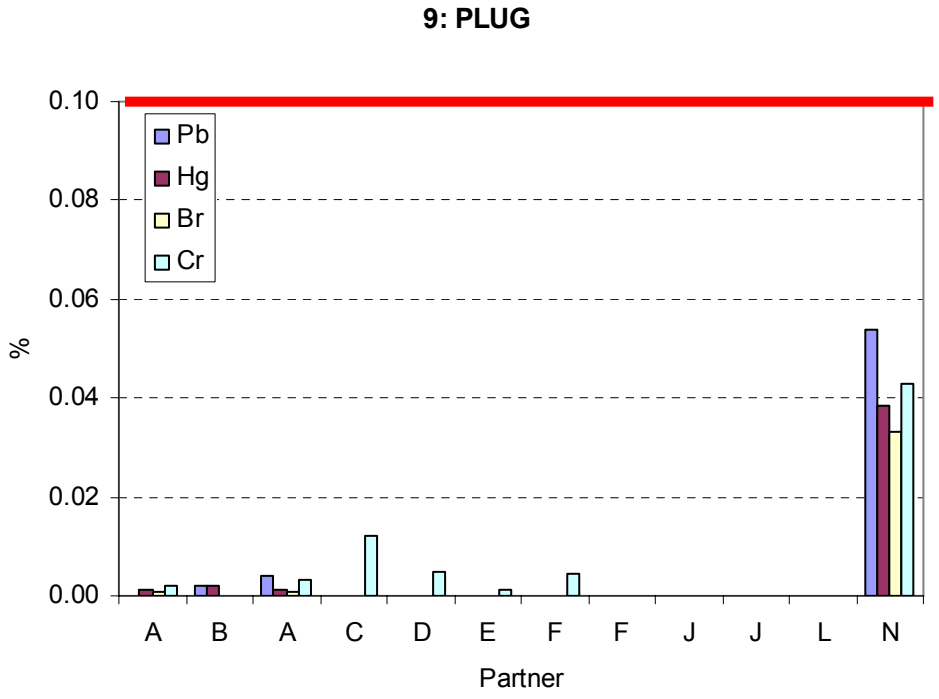

Figure 36: Results on FUSE sample for Pb, Hg, Br and Cr (wt%) for PIN/SiLi detector systems

3.10 SAMPLE 12 (SPDR)

Sample 12 SPDR was a compliant red PVC shrink sleeve from an M4 spade terminal and is shown in Figure 37, with the original component before disassembly shown in the insert. The sample had the metal insert removed before both XRF and chemical analyses.

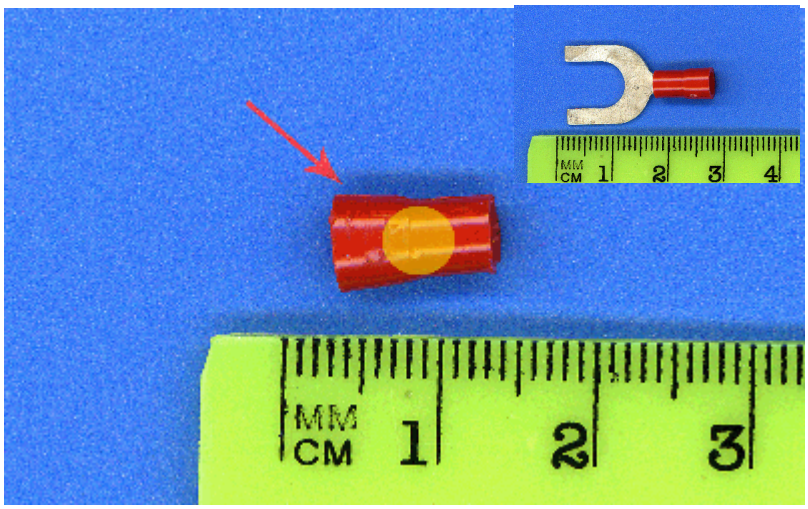

Figure 37: Sample 12 (SPDR)

3.10.1 SPDR Chemical Analysis Results

SPDR	Bromine %	Cadmium%	Mercury %	Lead %	Chromium %
	Not tested	<0.001	<0.001	0.007	<0.001
	Not tested	<0.001	<0.001	0.004	<0.001
				0.009	
Average		**<0.001**	**<0.001**	**0.007**	**<0.001**

3.10.2 SPDR Proportional Counter Results

For all three proportional counter based instruments, no peaks associated with RoHS restricted materials were present in the recorded spectra.

3.10.3 SPDR PIN/SiLi Results

The results for PIN/SiLi detector systems are shown in Figures 37 to 38. All the systems indicated the sample was RoHS compliant for mercury, bromine, chromium and lead, but one system (DQ – see Figure 38) incorrectly indicated an RoHS non-compliance for cadmium (>0.01% Cd).

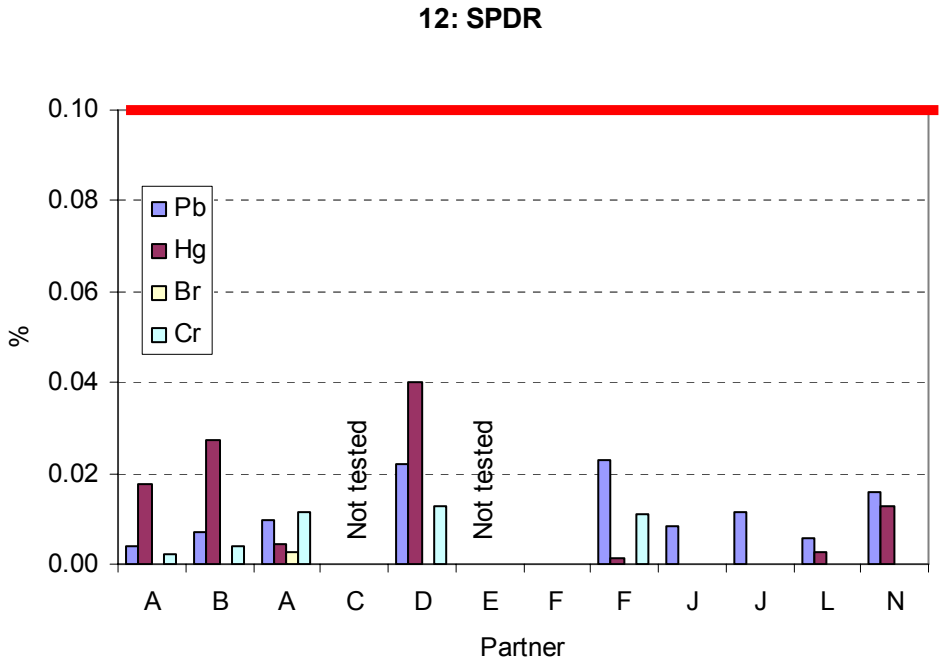

Figure 38: Results on SPDR sample for Pb, Hg, Br and Cr (wt%) for PIN/SiLi detector systems

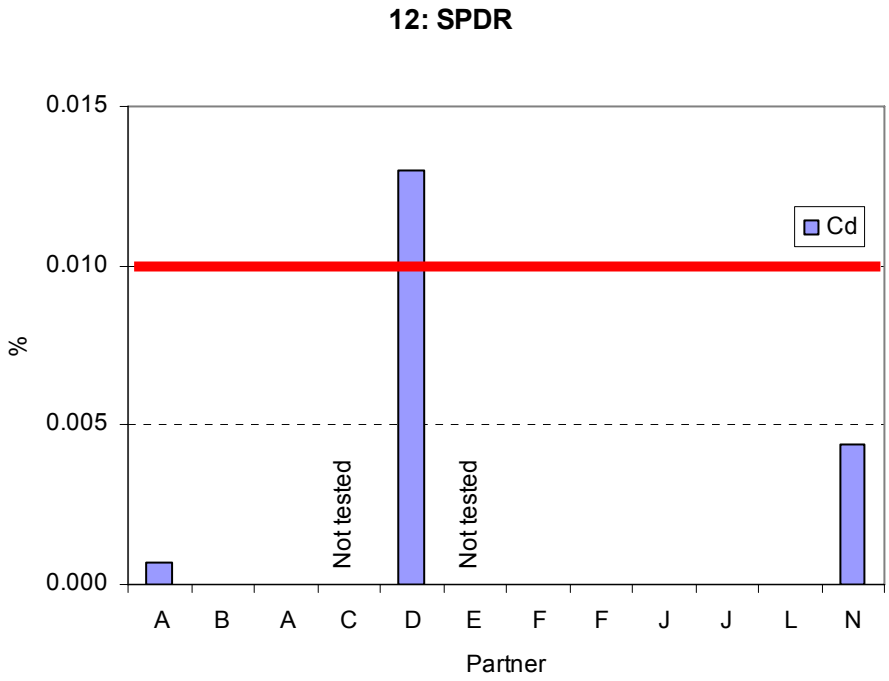

Figure 39: Results on SPDR sample for Cd (wt%) for PIN/SiLi detector systems

3.11 SAMPLE 13 (CBLE)

Sample 13 CBLE was the outer sleeve from a compliant grey brominated PVC cat5e RJ45 UTP patch cord and is shown in Figure 40, with the original component before disassembly shown in the insert. The sample had the core removed before both XRF and chemical analyses.

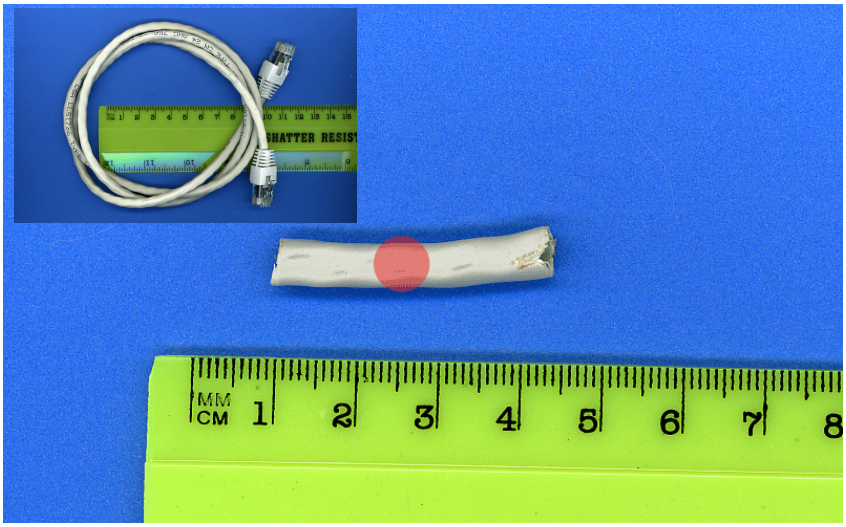

Figure 40: Sample 13 (CBLE)

3.11.1 CBLE Chemical Analysis Results

SPDR	Bromine %	Cadmium%	Mercury %	Lead %	Chromium %
	5.30	<0.001	<0.001	<0.001	<0.001
	5.10	<0.001	<0.001	<0.001	<0.001
	5.50				
Average	**5.30**	**<0.001**	**<0.001**	**<0.001**	**<0.001**

3.11.2 CBLE Proportional Counter Results

For the two proportional counter based instruments tested (GT & HU), a bromine peak was present in the spectra.. One system (GT) gave an automatically calculated average bromine content of 0.4%. This was sufficient to mark the component as RoHS non-compliant, but it was significantly different from the average chemical analysis result (5.3% Br). The GT system also showed cadmium present at a level of 0.13%.

3.11.3 CBLE PIN/SiLi Results

The results for PIN/SiLi detector systems are shown in Figures 40 to 42, and indicate the sample was RoHS compliant for lead, mercury and chromium. However, three systems (BP, AQ and NZ)) incorrectly suggested that the sample was RoHS non-compliant for cadmium (>0.01% Cd – see Figure 42).

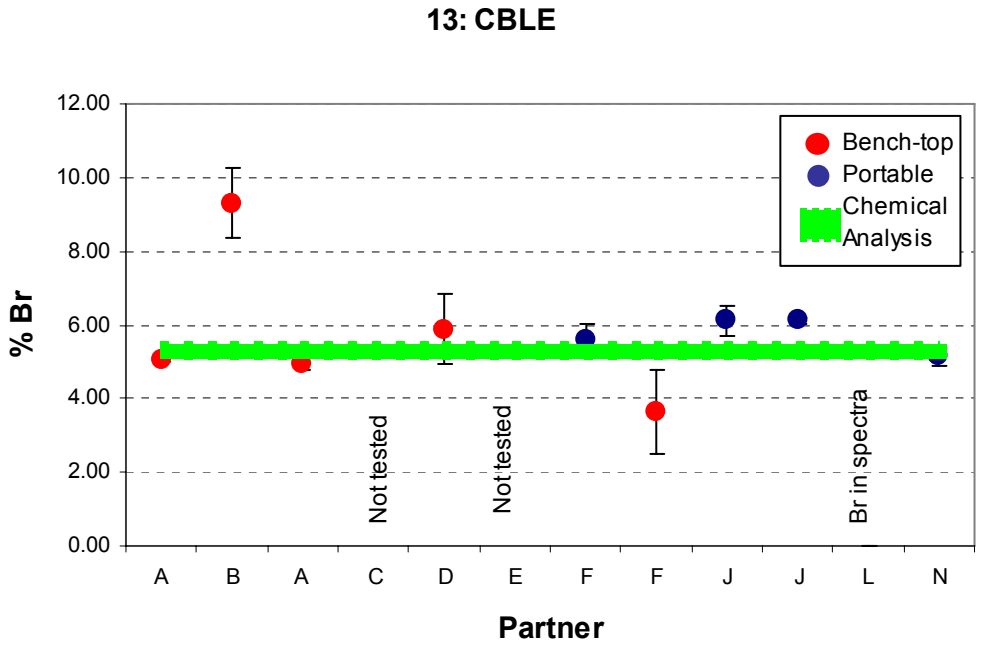

Figure 41: Results on CBLE sample for Br (wt%) for PIN/SiLi detector systems

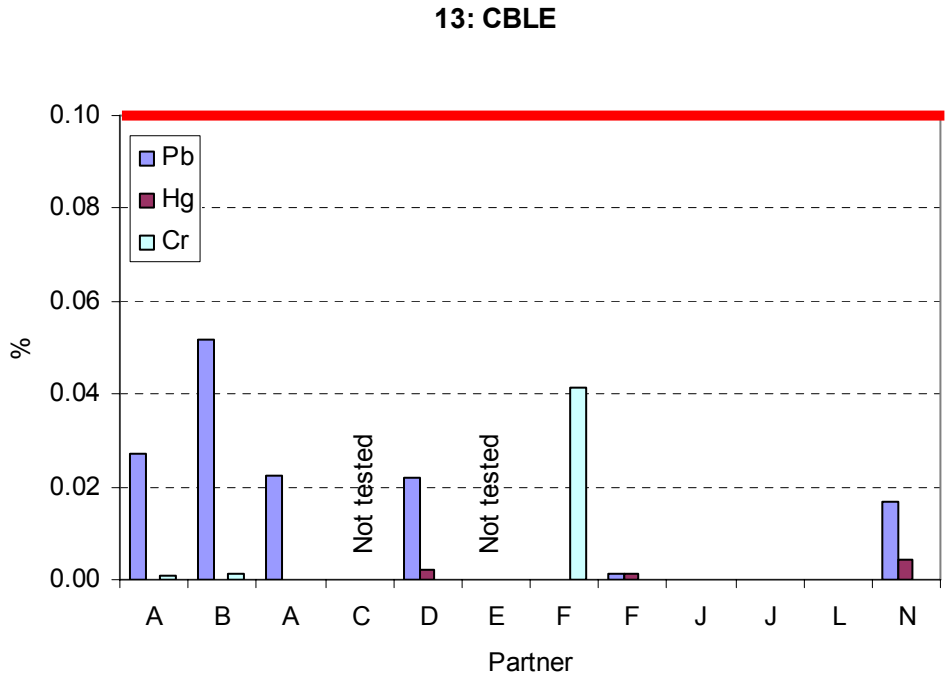

Figure 42: Results on CBLE sample for Pb, Hg, and Cr (wt%) for PIN/SiLi detector systems

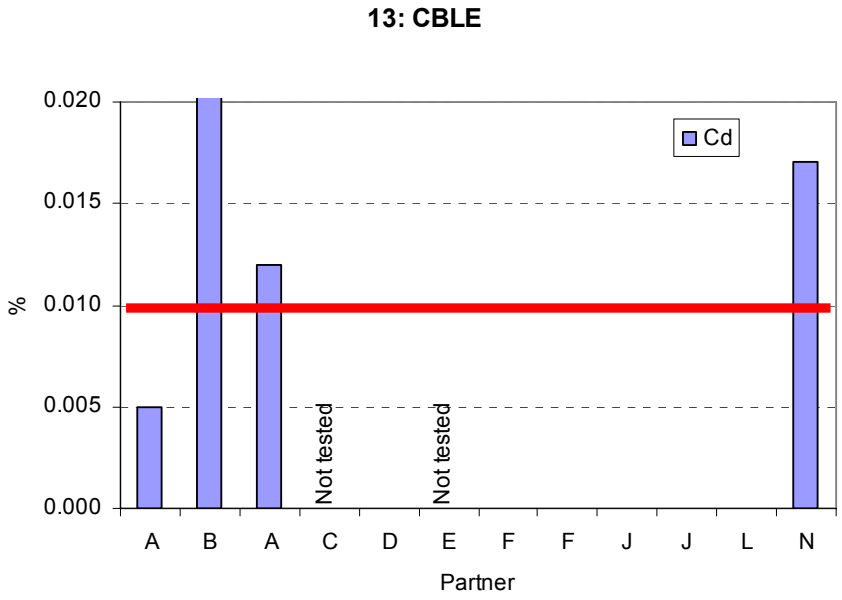

Figure 43: Results on CBLE sample for Cd (wt%) for PIN/SiLi detector systems

3.12 SAMPLE 14 (MMC)

Sample 14 (MMC) was a blue, brominated non-PVC connector housing and is shown in Figure 44.

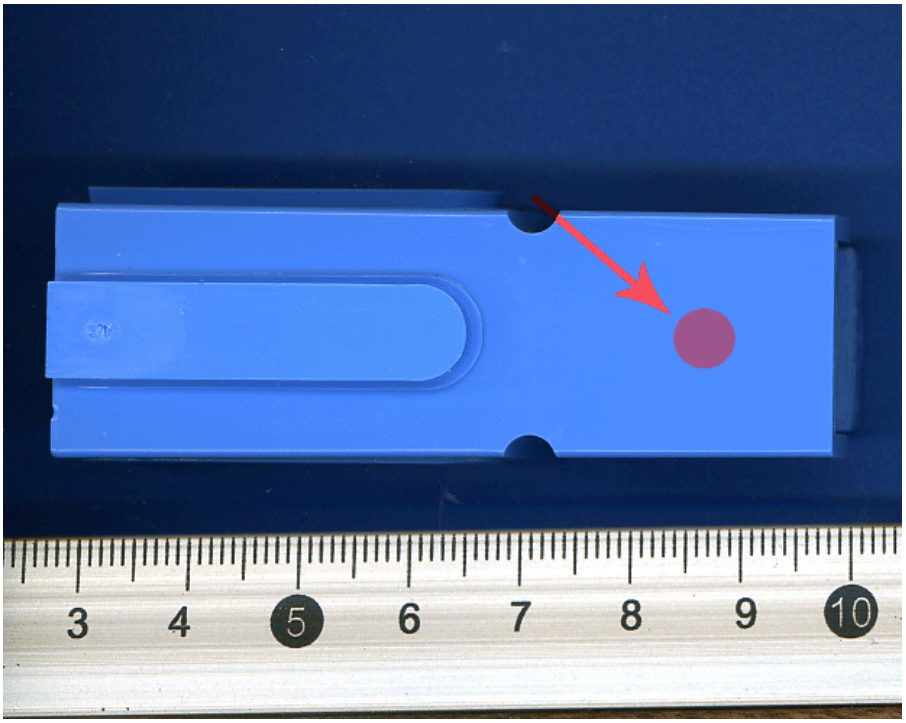

Figure 44: Sample 14 (MMC)

3.12.1 MMC Chemical Analysis Results

MMC	Bromine %	Cadmium%	Mercury %	Lead %	Chromium %
	1.30	<0.001	<0.001	0.007	<0.001
	1.30	<0.001	<0.001	0.004	<0.001
				0.009	
Average	**1.30**	**<0.001**	**<0.001**	**0.007**	**<0.001**

3.12.2 MMC Proportional Counter Results

For all three proportional counter based instruments, a bromine peak was present in the spectra recorded.. One system (GT) gave an automatically calculated average bromine content of 0.857% (not speciated). This was lower than the average chemical analysis result (1.3%). No other RoHS restricted contaminants were noted.

3.12.3 MMC PIN/SiLi Results

The results for PIN/SiLi detector systems are shown in Figures 44 to 46 and indicate the sample was RoHS compliant for mercury, lead and cadmium. However, one system (NZ) falsely recorded high levels for chromium (>0.1%), and another (LX) high levels for lead (0.096%) – see Figure 45.

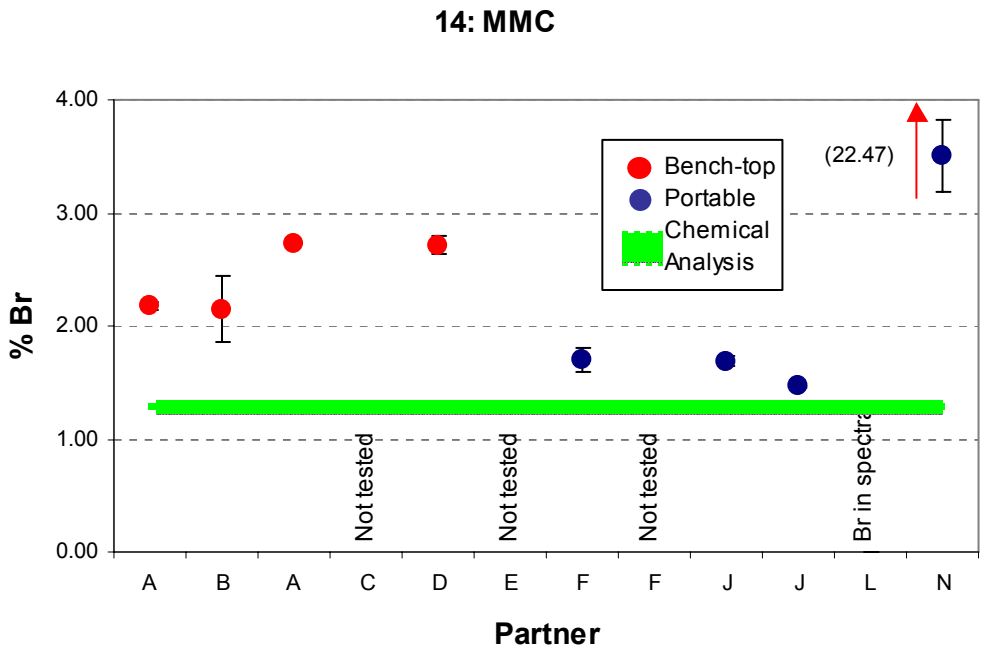

Figure 45: Results on MMC sample for Br (wt%) for PIN/SiLi detector systems

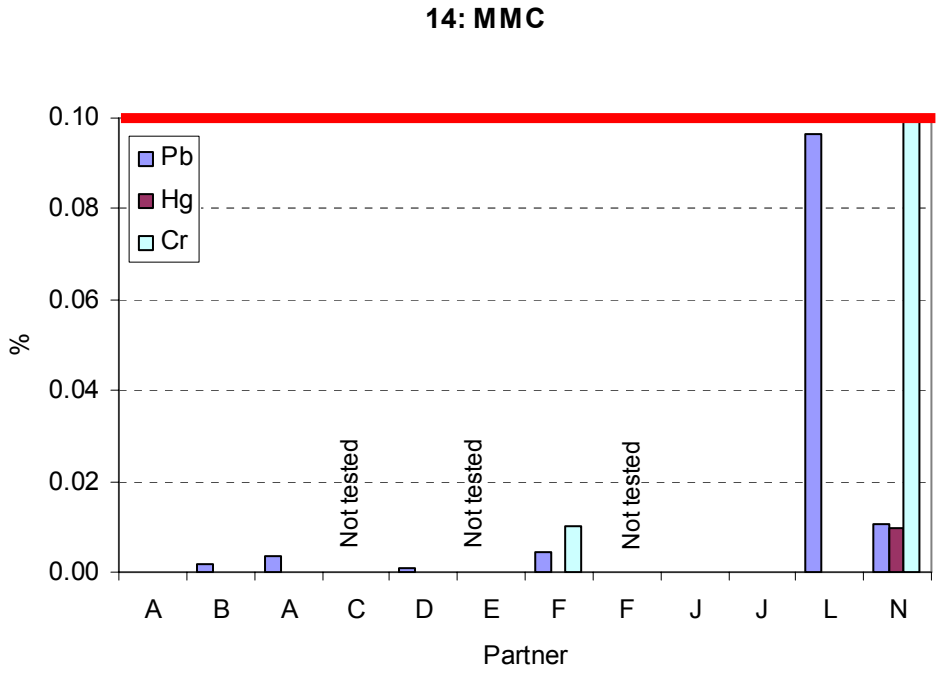

Figure 46: Results on MMC sample for Pb, Hg, and Cr (wt%) for PIN/SiLi detector systems

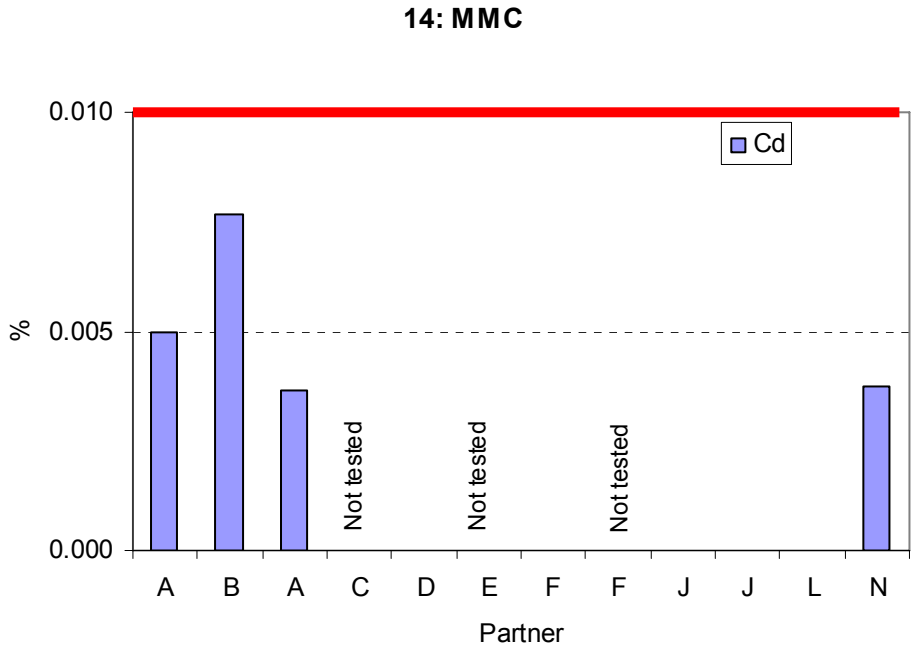

Figure 47: Results on MMC sample for Cd (wt%) for PIN/SiLi detector systems

4 DISCUSSION OF XRF ANALYSIS OF PLASTIC COMPONENTS

It is important to note that a direct comparison between XRF results and chemical analysis results above is difficult. The XRF results are taken at a particular point on the sample. The chemical analysis is undertaken on a grind of the whole sample and therefore should be considered an average for the sample as a whole. Any segregation within the plastic may therefore result in the two techniques giving different results. Furthermore, chemical analysis requires a minimum sample size, whereas the XRF technique is capable of analysing much smaller sample sizes.

In choosing plastic samples for the evaluation, a very wide range of typical electronics components were evaluated before the final selection was made. It was noted in this sorting procedure, that RoHS non-compliant components did not typically contain lead, mercury, bromine or chromium at levels around the RoHS limit of 1000ppm. Indeed, typical values for non-compliant components were above 0.25% (2500ppm) or less than 0.05% (500ppm).

The bench-top and portable XRF systems based on PIN or SiLi detectors showed themselves to be efficient at distinguishing between non-compliant (typically 2500+ppm) and compliant components (typically <500ppm). Of the eight typical non-RoHS compliant electronic components tested, all twelve PIN/SiLi systems achieved 100% identification of non-compliance. Of the three typical RoHS compliant components tested, the twelve PIN/SiLi systems achieved 100% identification of compliant components for lead and mercury. Three typical components containing bromine or chromium were correctly identified as containing these elements and requiring alternative tests for speciation. ***For levels of Pb, Hg, Br or Cr between 500ppm and 2000ppm, additional techniques are recommended.***

On tests of twelve components using PIN/SiLi systems, only two false detects for Cr at around 1000ppm were registered. In the case of cadmium, bench-top and portable XRF systems proved efficient at distinguishing non-compliant systems above 1000ppm cadmium. Below this figure additional techniques may be required. In tests of ten components not containing cadmium, seven false detects for cadmium (all at 260ppm or below), were registered.

Proportional counter based systems, although not specifically designed to test for RoHS compliance in plastics, are capable of registering the presence of RoHS-restricted elements when they are at typical levels found in plastics (>3%). Below this level, their ability to find the elements has to be questioned. Even for higher contamination levels, proportional counter based systems were not capable of giving quantitative results. ***It is recommended that proportional counter systems should not be used for RoHS compliance measurements.***

Presentation of the samples is important. In the case of the NET/NETAS comparison (see Section 3.5), it can clearly be seen that, if the plastic is tested whilst still attached to its accompanying cable, the lead level detected may “suppressed” by the material within the strain relief. In this instance, the lower results were still non-compliant, but should this example have been closer to the RoHS limit, this suppression could have caused the sample to appear compliant. ***Where measured contaminant levels are close to the RoHS limit, it is recommended that the plastic be tested in isolation***.

5 RESULTS FOR SOLDERS AND SOLDERED JOINTS

Summary results are given graphically in the Sections below. The summaries are averages of three instrument readings except where stated. For the purposes of averaging, where a system returned a “not detected” result, it was equated to 0.

5.1 SAMPLES 15 TO 22 (PB1 TO 8)

Samples 15 to 22 were lead-contaminated tin samples with varyious levels of contamination, as presented in Figure 48.

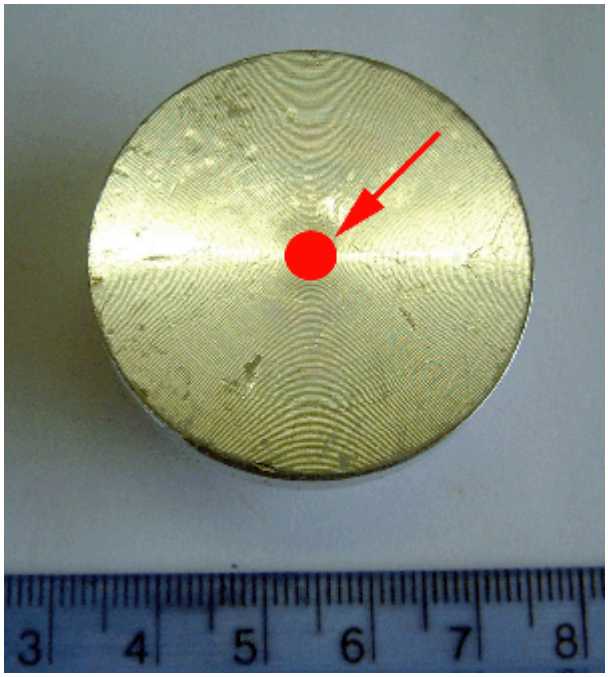

Figure 48: Example of samples 15 to 22 (Pb1 to Pb8)

5.1.1 Pb1 to Pb8 Chemical Analysis Results

Pb1	**Lead %**	**Cadmium%**
	0.0048	Not tested
	0.0048	Not tested
Average	***0.005***	
Pb2	**Lead %**	**Cadmium%**
	0.0107	<0.0001
	0.0107	
Average	***0.011***	***<0.0001***
Pb3	**Lead %**	**Cadmium%**
	0.0263	Not tested
	0.0265	Not tested
Average	***0.026***	
Pb4	**Lead %**	**Cadmium%**
	0.0491	Not tested
	0.0485	Not tested
Average	***0.049***	
Pb5	**Lead %**	**Cadmium%**
	0.1000	Not tested
	0.0960	Not tested
Average	***0.098***	
Pb6	**Lead %**	**Cadmium%**
	0.1892	<0.0001
	0.1936	
Average	***0.191***	***<0.0001***
Pb7	**Lead %**	**Cadmium%**
	1.0277	<0.0001
	1.0327	
Average	***1.030***	***<0.0001***
Pb8	**Lead %**	**Cadmium%**
	1.9438	Not tested
	1.8978	Not tested
Average	***1.921***	

5.1.2 Pb1 to Pb8 Proportional Counter Results

None of the three proportional counter based instruments were able to detect any lead in samples Pb1 to Pb4 (i.e lead below 0.05%). For Pb5 (0.1% Pb), only two systems detected the lead (GT & MY) with only one system (MY) indicating levels that were above the RoHS limit i.e. RoHS non-compliant. For Pb6 to Pb8, all three systems registered the presence of lead at levels in excess of the RoHS limits. The results for sample Pb5 to Pb8 are shown in Figures 48 to 49.

These systems were not used to test for cadmium.

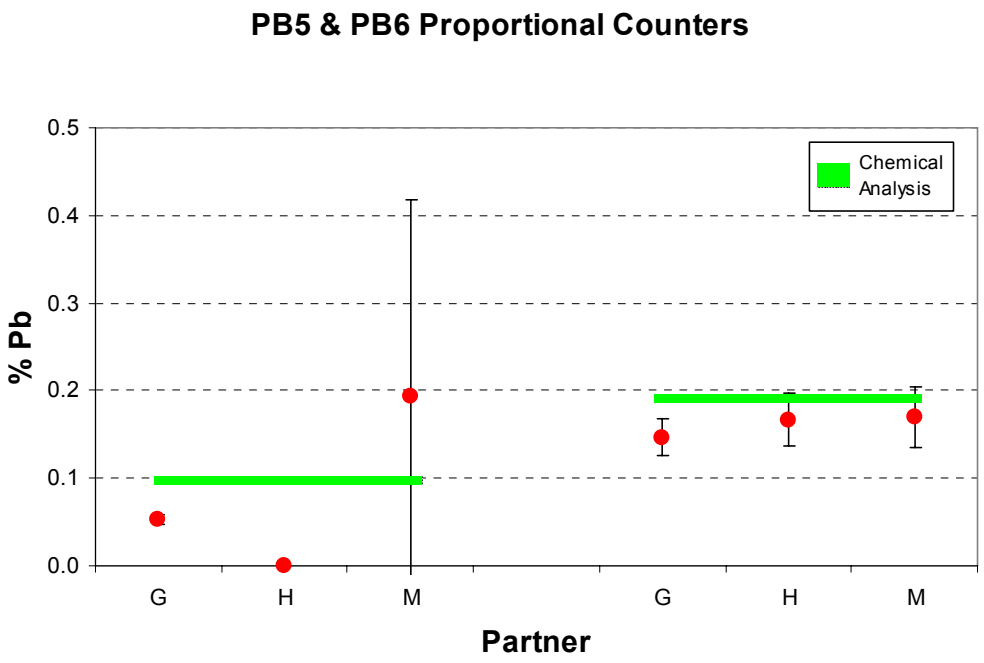

Figure 49: Proportional counter results (wt%) for Pb5 (left) and Pb6 (right)

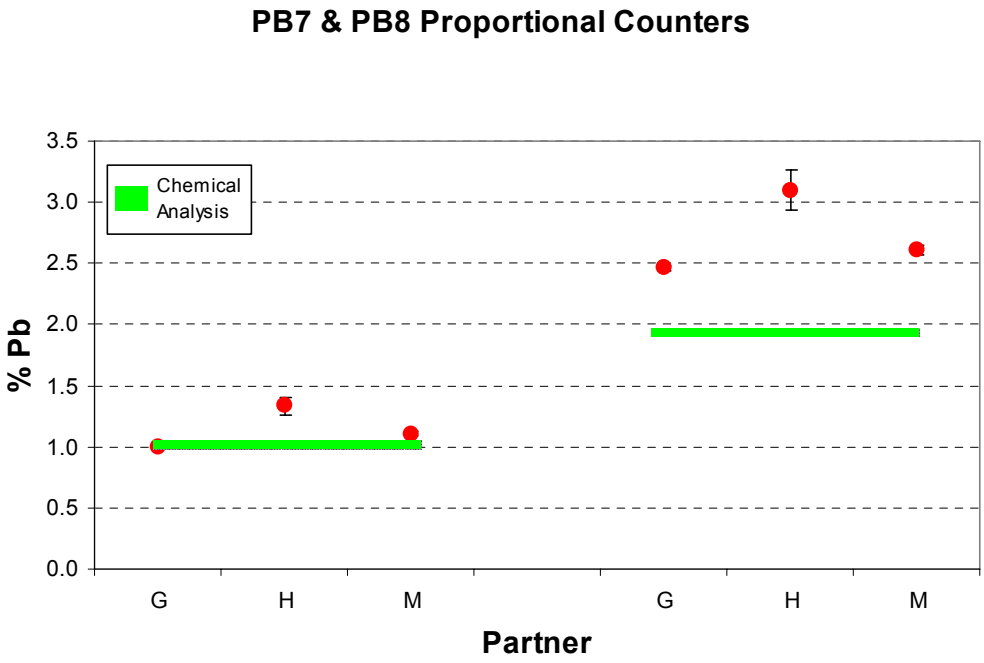

Figure 50: Proportional counter results (wt%) for Pb7 (left) and Pb8 (right)

5.1.3 Pb1 PIN/SiLi Results

The results for PIN/SiLi detector systems for sample Pb1 are presented in Figure 51. All the bench top systems tested recorded the presence of small quantities of lead. Three portable systems did not detect lead, while the fourth (NZ) recorded a high level of lead (0.037%), but not sufficient for RoHS non-compliance.

Only one system (CQ) indicated the non-compliant presence of cadmium.

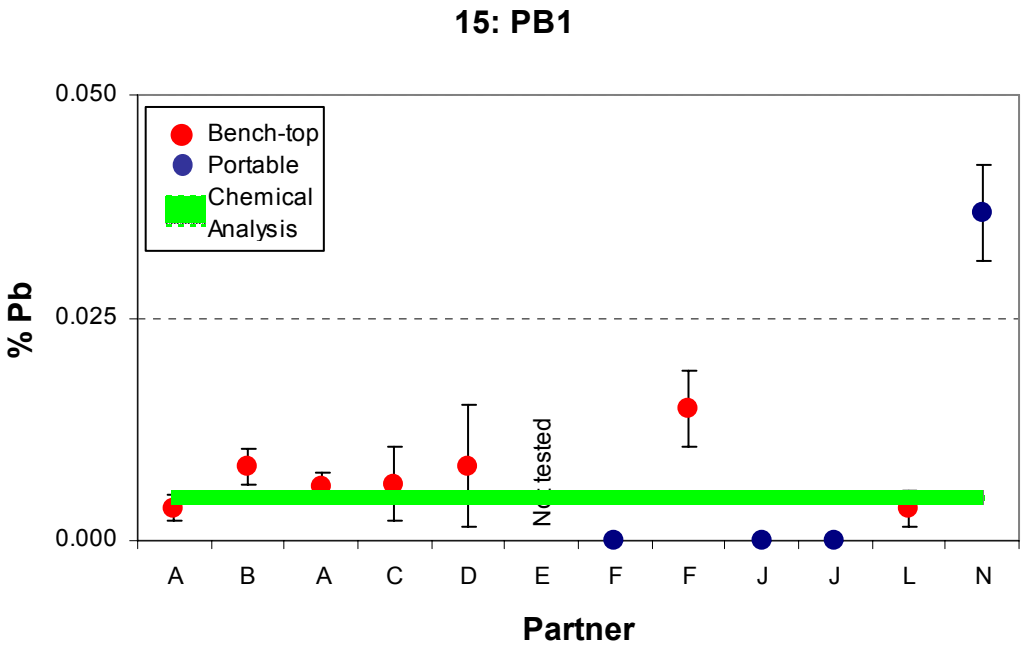

Figure 51: Results for Pb1 sample for Pb (wt%) for PIN/SiLi detector systems

5.1.4 Pb2 PIN/SiLi Results

The results for PIN/SiLi detector systems for sample Pb2 are presented in Figure 52. All the bench top systems tested recorded the presence of lead. Three portable systems did not detect the lead, while the fourth (NZ) recorded a high lead level (0.033%), similar to the level in sample Pb1, but not sufficient for RoHS non-compliance. Two systems (AP & CQ) falsely indicated the non-compliant presence of cadmium, shown in Figure 53.

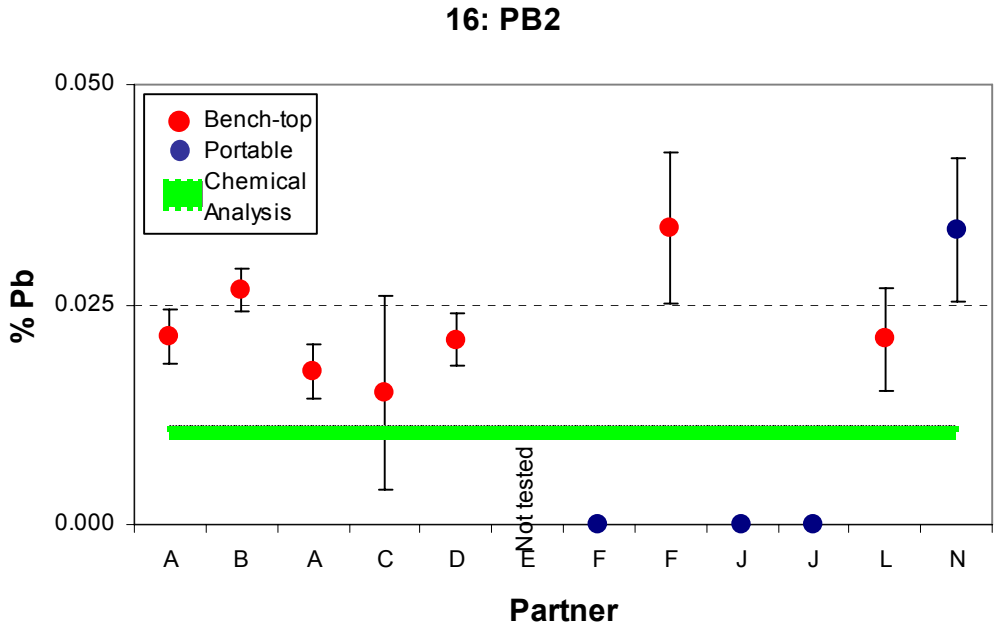

Figure 52: Results on Pb2 sample for Pb (wt%) for PIN/SiLi detector systems

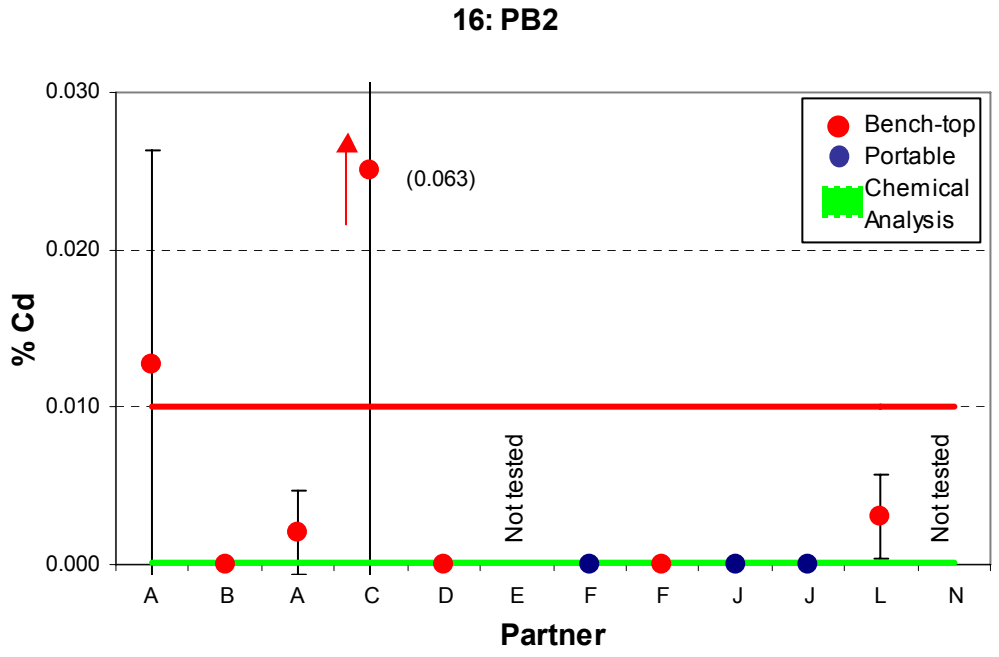

Figure 53: Results on Pb2 sample for Cd (wt%) for PIN/SiLi detector systems

5.1.5 Pb3 PIN/SiLi Results

The results for PIN/SiLi detector systems for sample Pb3 are presented in Figure 54. All the bench top systems tested detected the presence of lead. However, one portable system (FR) did not detect the presence of lead.

Only one system (CQ) indicated the presence of cadmium

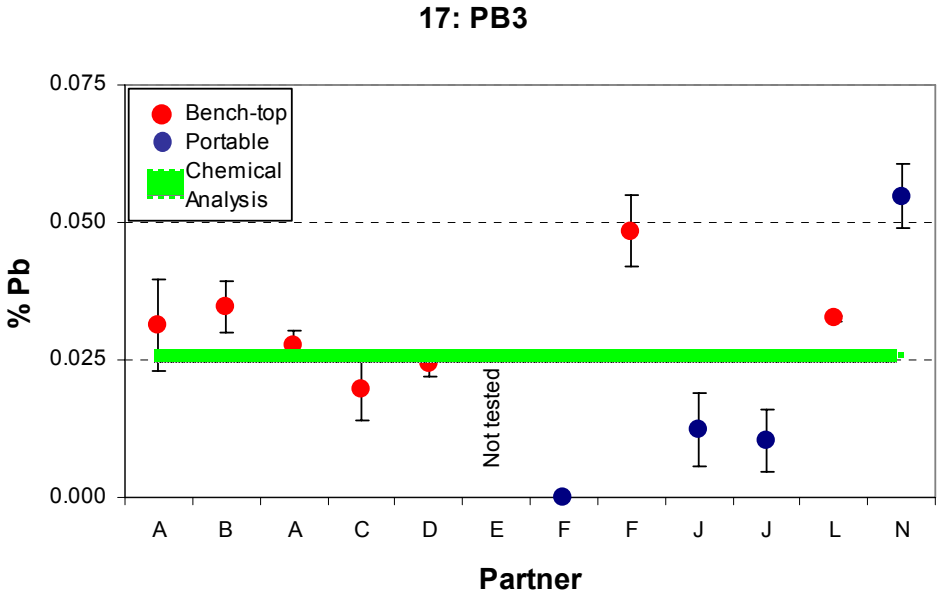

Figure 54: Results on Pb3 sample for Pb (wt%) for PIN/SiLi detector systems

5.1.6 Pb4 PIN/SiLi Results

The results for PIN/SiLi detector systems for sample Pb4 are given in Figure 55. One bench top system (EQ) did not detect the presence of lead.

Only one system (CQ) indicated the non-compliant presence of cadmium.

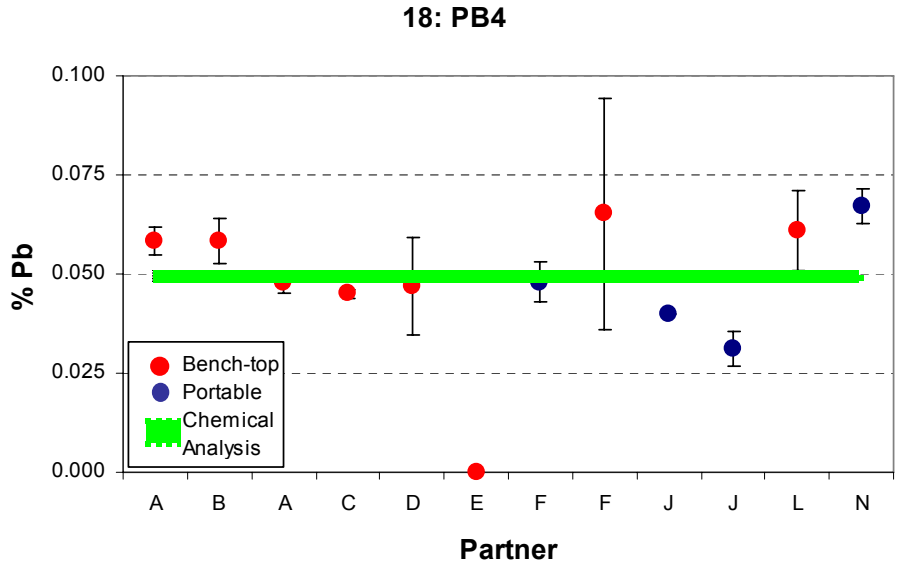

Figure 55: Results on Pb4 sample for Pb (wt%) for PIN/SiLi detector systems

5.1.7 Pb5 PIN/SiLi Results

The results for PIN/SiLi detector systems for sample Pb5 are given in Figure 56. All the systems indicated the sample was RoHS non-compliant for lead (>0.1% Pb) - or was within 10% of the RoHS limit - except one (EQ).

Only one system (CQ) indicated the non-compliant presence of cadmium.

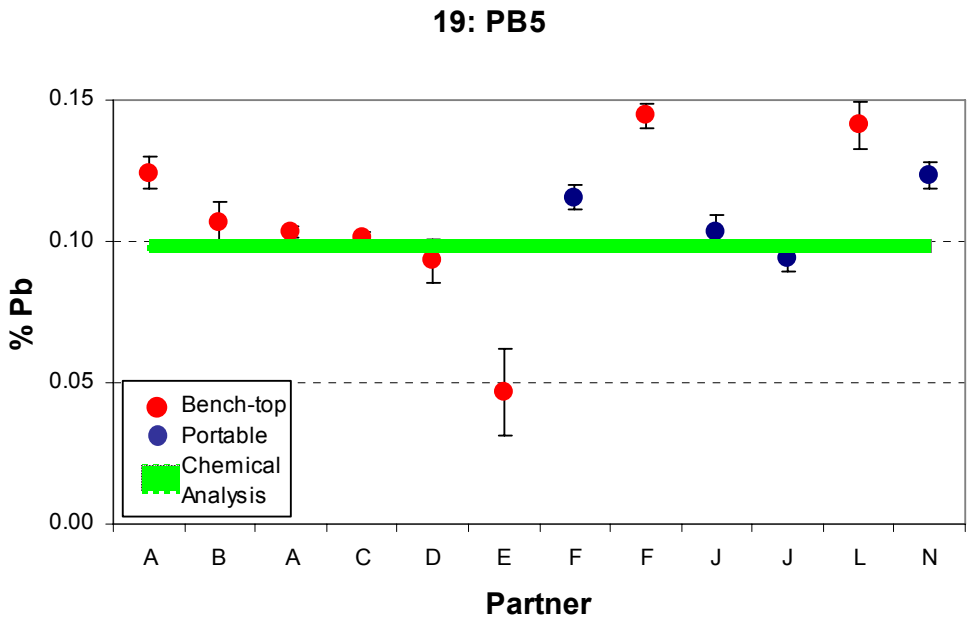

Figure 56: Results on Pb5 sample for Pb (wt%) for PIN/SiLi detector systems

5.1.8 Pb6 PIN/SiLi Results

The results for PIN/SiLi detector systems for sample Pb6 are presented in Figure 57. All the systems indicated that the sample was RoHS non-compliant for lead (>0.1% Pb). Two systems (CQ & JW) falsely indicated the presence of cadmium as indicated in Figure 58.

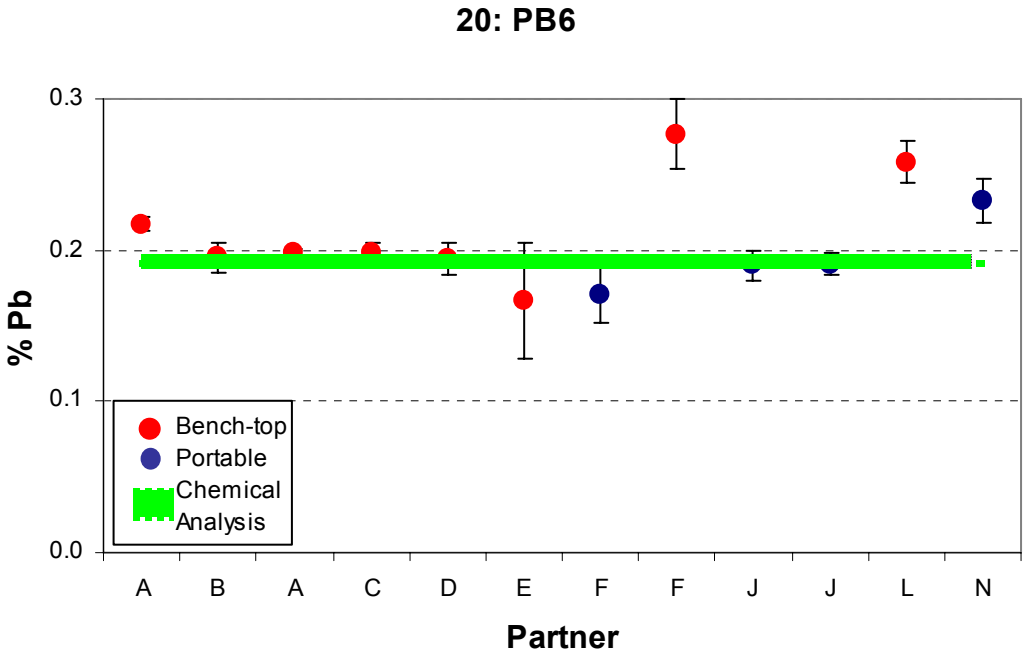

Figure 57: Results on Pb6 sample for Pb (wt%) for PIN/SiLi detector systems

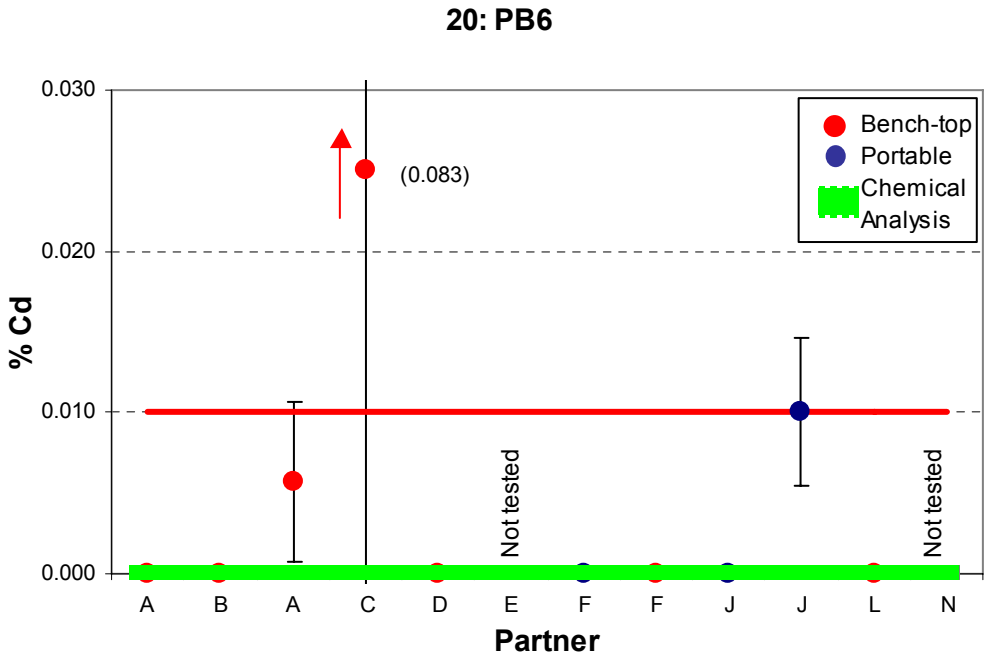

Figure 58: Results on Pb6 sample for Cd (wt%) for PIN/SiLi detector systems

5.1.9 Pb7 PIN/SiLi Results

The results for PIN/SiLi detector systems for sample Pb7 are summarised in Figure 59. All the systems indicated the sample was RoHS non-compliant for lead (>0.1% Pb). Three

systems (BP, CQ & DQ) falsely indicated the non-compliant presence of cadmium as indicated in Figure 60.

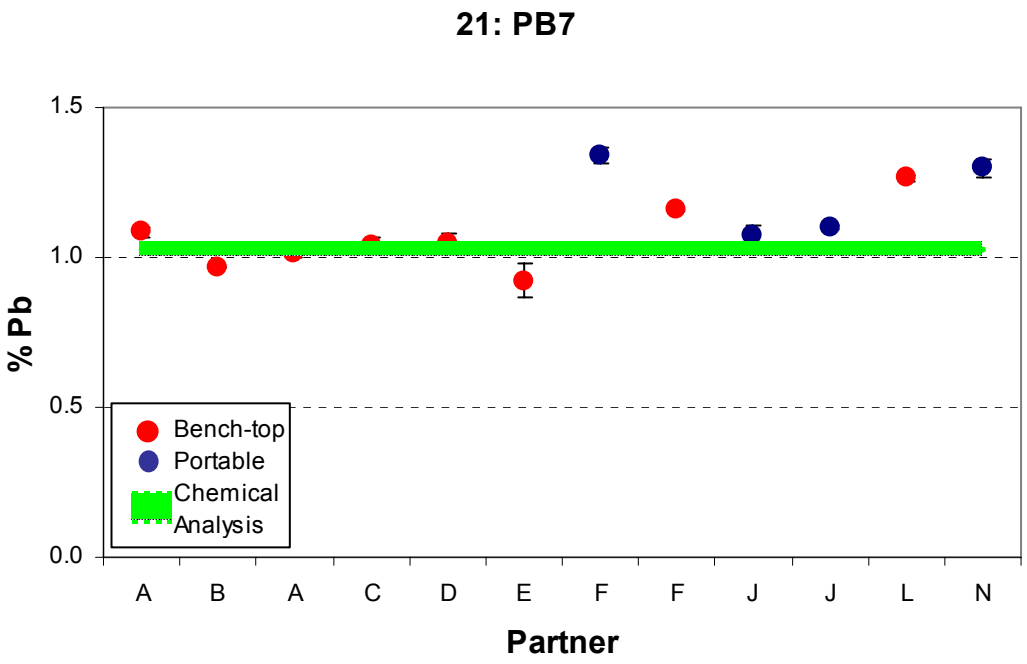

Figure 59: Results on Pb7 sample for Pb (wt%) for PIN/SiLi detector systems

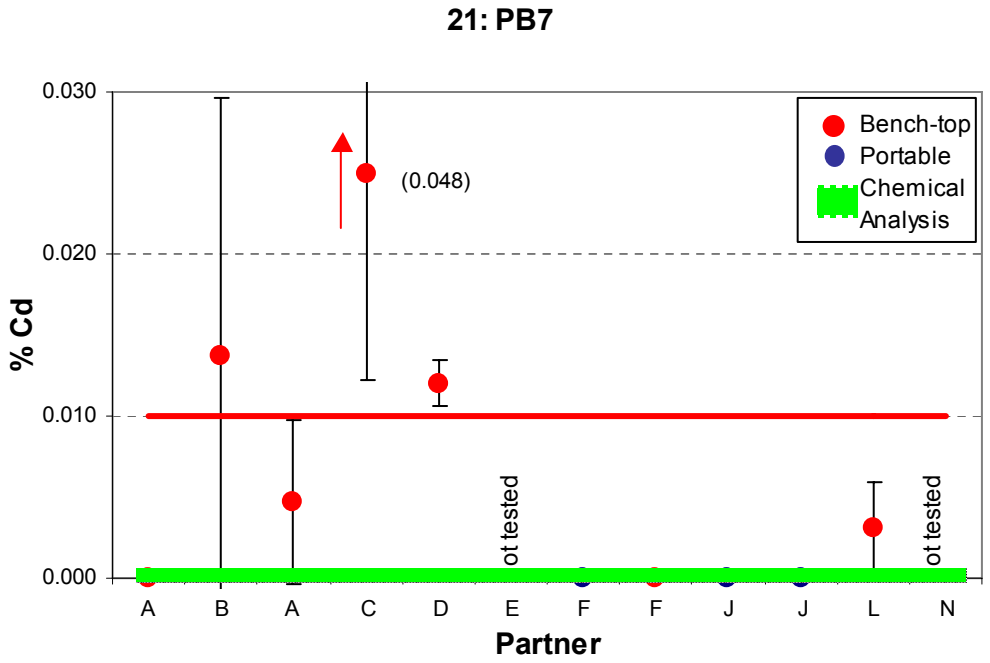

Figure 60: Results on Pb7 sample for Cd (wt%) for PIN/SiLi detector systems

5.1.10 Pb8 PIN/SiLi Results

The results for PIN/SiLi detector systems for sample Pb8 are shown in Figure 61. All the systems indicated that the sample was RoHS non-compliant for lead (>0.1% Pb).

Only one system (CQ) indicated the non-compliant presence of cadmium.

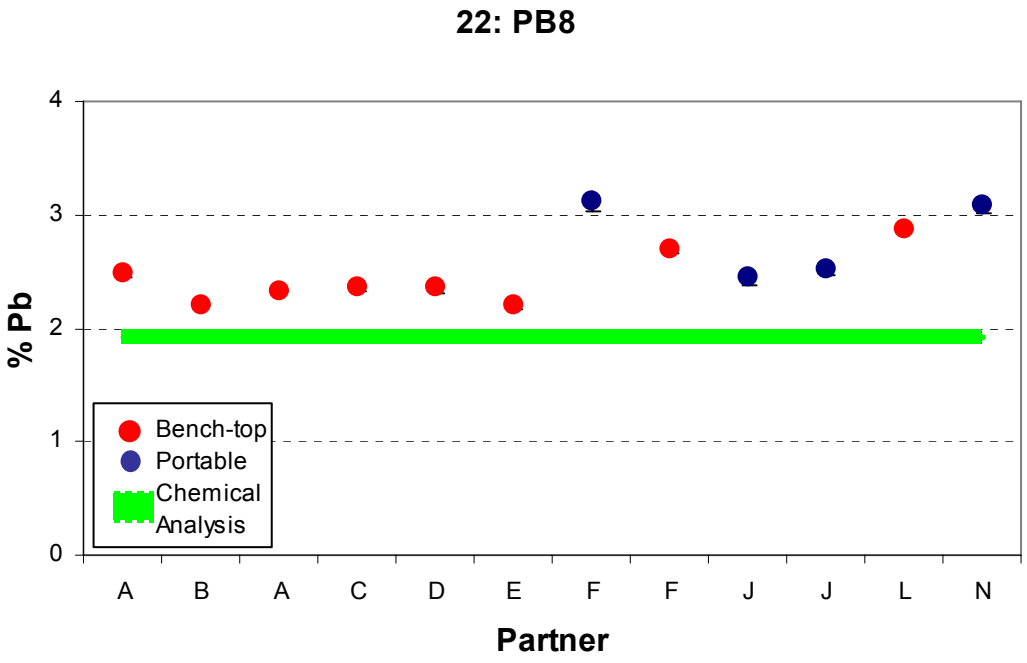

Figure 61: Results on Pb8 sample for Pb (wt%) for PIN/SiLi detector systems

5.2 SAMPLES 23 TO 27 (NPL1 TO 5)

Samples 23 to 27 were lead-contaminated SAC solder joints (as shown in Figure 62) with various levels of contamination. The samples were created by soldering SOIC components, having various levels of lead in tin plating, to an otherwise lead-free system (SAC paste, ENIG PCB).

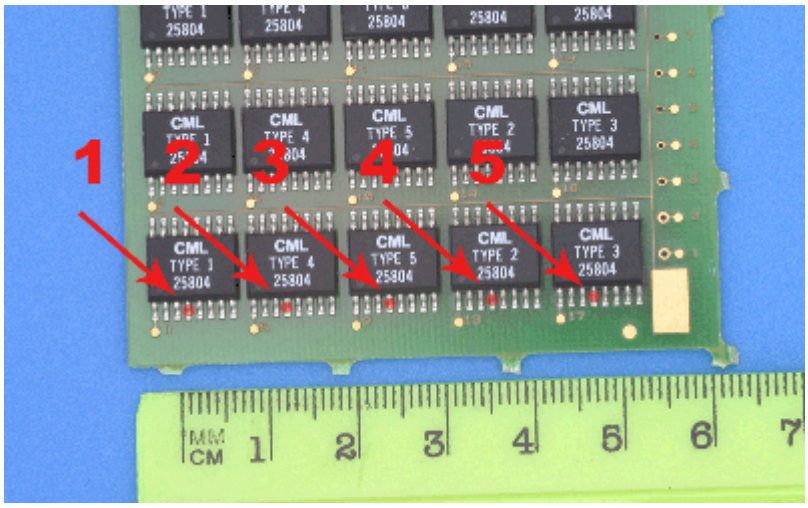

Figure 62: Sample 23 to 27 (NPL1 to NPL5)

5.2.1 NPL1 to NPL5 EDX Analysis Results

The results of the EDX area analysis of the samples are summarised in Table 4. The joint volumes were insufficient to enable reliable chemical analyses. Cadmium was not detected for any of these samples using EDX i.e. any cadmium present was at less than 0.1%.

Table 4: EDX Pb analysis on samples NPL1 to NPL5

Sample		Average
NPL1	0.0	0.0
NPL2	1.9	2.7
	2.8	
	2.0	
	4.3	
NPL3	11.3	10.8
	10.5	
	10.6	
NPL4	20.6	19.0
	20.3	
	18.1	
	16.9	
NPL5	17.7	16.8
	17.4	
	16.4	
	15.8	

5.2.2 Samples NPL1 to NPL5 Proportional Counter Results

Only two proportional counter based instruments completed the test matrix. One system (GT) performed well but the other system was less accurate, always recording much higher lead levels than those indicated from EDX measurements or those from system GT. Indeed, for sample NPL1 (no lead) system MY indicated a level of 8% Pb. Apart from the NPL1 sample, the two systems correctly identified the remaining joints as being non-compliant for lead. No tests were undertaken for the presence of cadmium using these systems. The results are summarised in Figure 63.

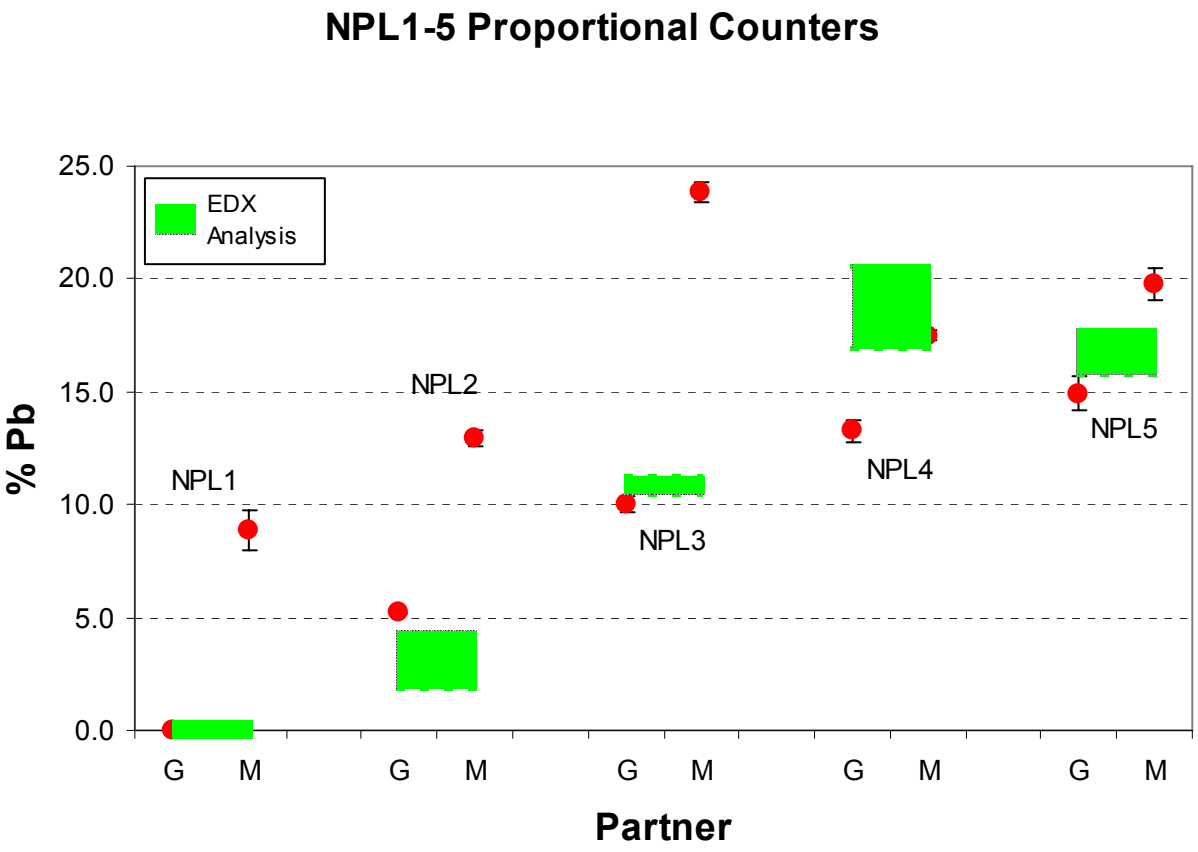

Figure 63: Results on NPL1 to NPL5 samples for Pb (wt%) for proportional counter detector systems

5.2.3 NPL1 PIN/SiLi Results

The results for PIN/SiLi detector systems for sample NPL1 are presented in Figure 64. Seven of the twelve systems indicated the presence of small quantities of lead, but not sufficient to indicate RoHS non-compliance of the joint for lead.

Two systems (AQ and FS) out of eight tested, indicated the non-compliant presence of cadmium.

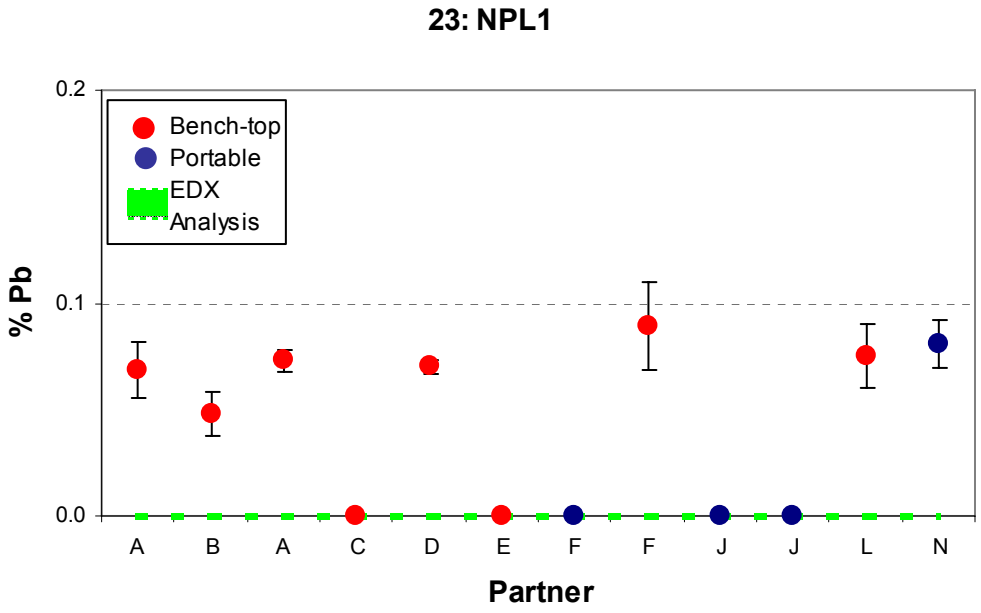

Figure 64: Results on NPL1 sample for Pb (wt%) for PIN/SiLi detector systems

5.2.4 NPL2 PIN/SiLi Results

The results for PIN/SiLi detector systems for sample NPL2 are summarised in Figure 65. Although the bench-top systems all indicated the presence of significant (non-compliant) levels of lead in the joint, only one of the portable systems (JV) indicated that lead was present in the joint, at a non-compliant lead level detected at 0.156%.

One system (AQ) indicated the non-compliant presence of cadmium. Four systems were not used to test for cadmium.

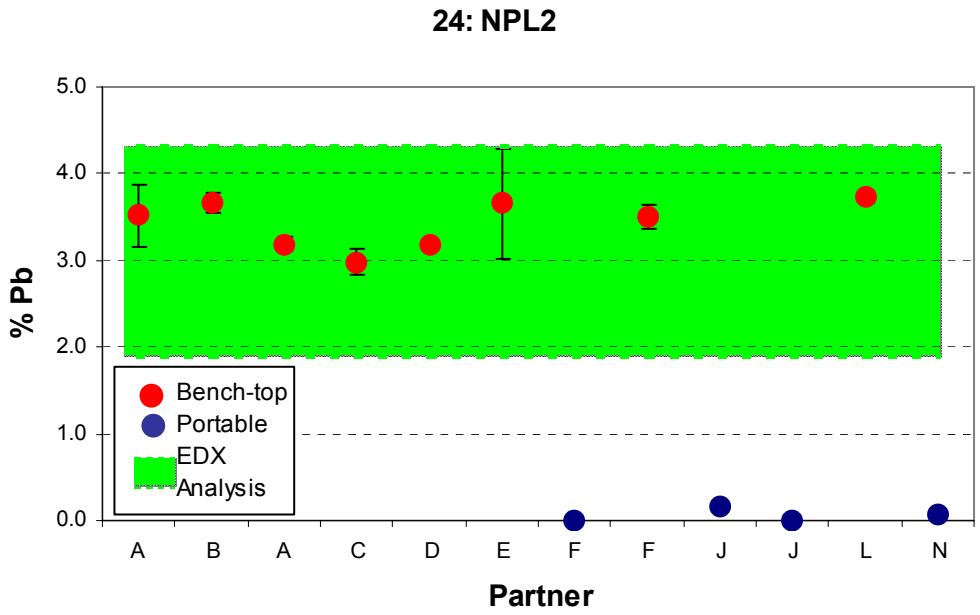

Figure 65: Results on NPL2 sample for Pb (wt%) for PIN/SiLi detector systems

5.2.5 NPL3 PIN/SiLi Results

The results for PIN/SiLi detector systems for sample NPL3 are presented in Figure 66. The bench-top systems all indicated the presence of significant levels of lead above 7% in the joint. However, whilst three of the portable systems (FR, JV & NZ) indicated that the joint was non-compliant for lead, the levels recorded were very low (0.157% to 0.655%).

One system (AQ) indicated the non-compliant presence of cadmium. Four systems were not used to test for cadmium.

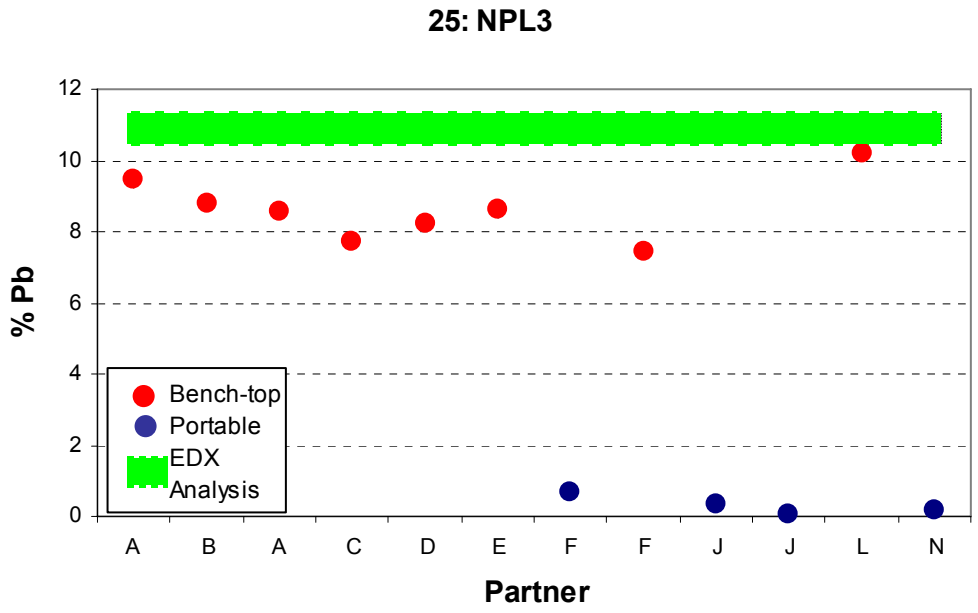

Figure 66: Results on NPL3 sample for Pb (wt%) for PIN/SiLi detector systems

5.2.6 NPL4 PIN/SiLi Results

The results for PIN/SiLi detector systems on sample NPL4 are presented in Figure 67. The bench-top systems all indicated the presence of significant (non-compliant) levels of lead above 11% in the joint. In addition, three of the portable systems (FR, JV & NZ) indicated that the joint was non-compliant with very low lead levels recorded (0.166% to 3.038% Pb).

One system (AQ) indicated the non-compliant presence of cadmium. Four systems were not used to test for cadmium.

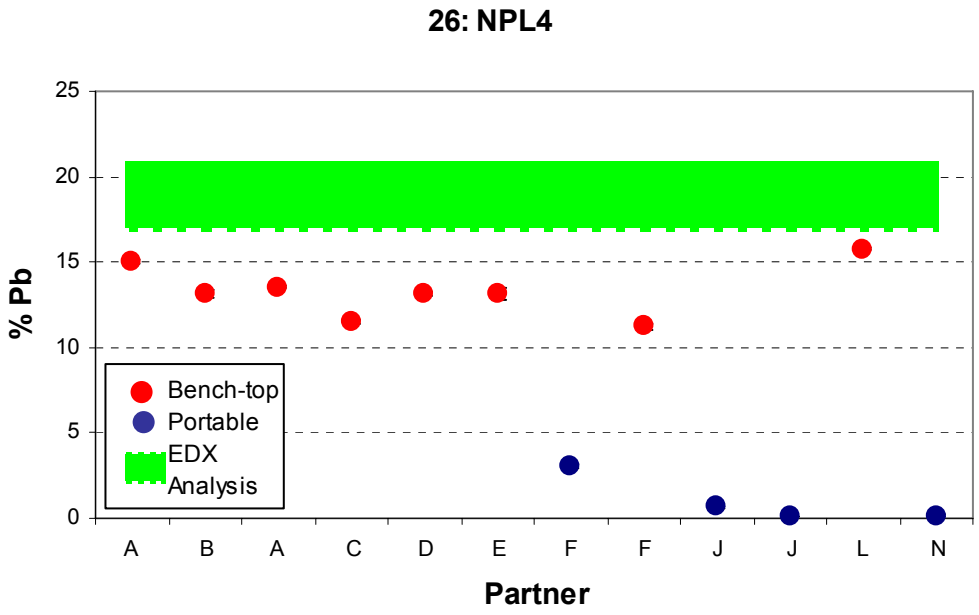

Figure 67: Results on NPL4 sample for Pb (wt%) for PIN/SiLi detector systems

5.2.7 NPL5 PIN/SiLi Results

The results for PIN/SiLi detector systems for sample NPL5 are summarised in Figure 67. The bench-top systems again all indicated the presence of significant levels of lead above 11% in the joint. In addition, three of the portable systems (FR, JV & NZ) indicated that the joint was non-compliant with very low lead levels detected (0.498% to 2.454% Pb).

One system (AQ) indicated the non-compliant presence of cadmium. Four systems were not used to test for cadmium.

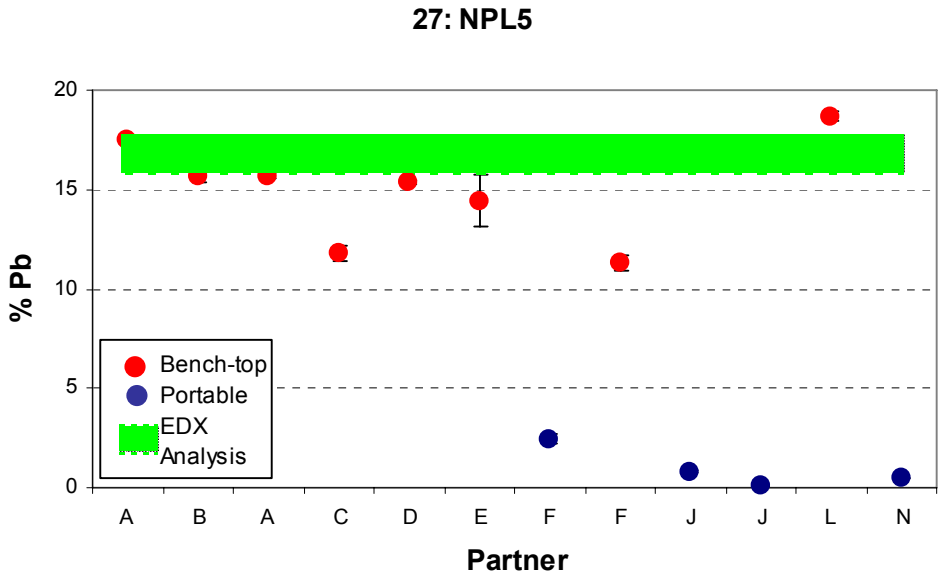

Figure 68: Results on NPL5 sample for Pb (wt%) for PIN/SiLi detector systems

5.3 SAMPLES 31 AND 32 (BGA1 AND BGA2)

Samples 31 and 32 were assembled BGAs as illustrated in Figure 62. The BGA1 sample was created by soldering a eutectic SnPb component to an ENIG-finished PCB using SnPbAg solder paste. This resulted in soldered BGA joints containing ~35 to 40% Pb. The BGA2 sample was created by soldering a lead-free SnAgCu component to an ENIG-finished PCB using SnPbAg solder paste. This resulted in soldered BGA joints containing ~ 10% Pb. The joints were tested from the top of the component through the component body. In addition, some systems were used in attempts to test the joints from the underside through the PCB.

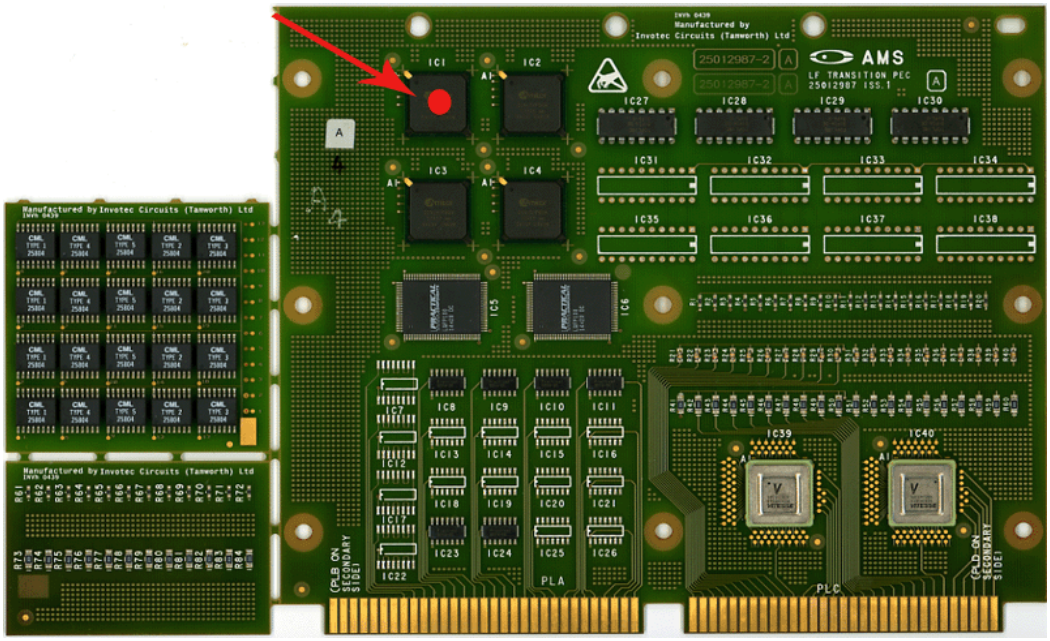

Figure 69: Samples 31 and 32 (BGA1 and BGA2)

5.3.1 BGA1 Results

This sample was tested using ten PIN/SiLi and proportional counter systems. Two systems recorded low levels of lead (JV at 0.011% and JW at 0.005%) well below the 0.1% limit. The spectra for one system (FR) indicated the presence of lead but it was not possible to quantify the amount. Only one system (NZ) indicated non-compliant lead levels at 1.98%, significantly lower than the actual content of 35+% Pb.

5.3.2 BGA2 Results

This sample was tested using eight PIN/SiLi and proportional counter systems. Only one system (NZ) indicated the presence of lead with a non-compliance level of 0.32%, significantly lower than the actual content of 10% Pb.

5.4 SAMPLE 35 (R60L)

Sample 35 was an assembled R1206 chip resistor as shown in Figure 62. The sample was created by soldering a tin-terminated component to an ENIG-finished PCB using SnAgCu solder paste. This resulted in a lead-free solder joint. Area analysis using EDX confirmed there was no lead (<0.1% Pb) present. However, the component had a passivation layer over the resistive element that did contain lead (see similar component RES tested as sample 10 below - Section 7.1), and hence the participants were asked to test the soldered joint for the presence of lead.

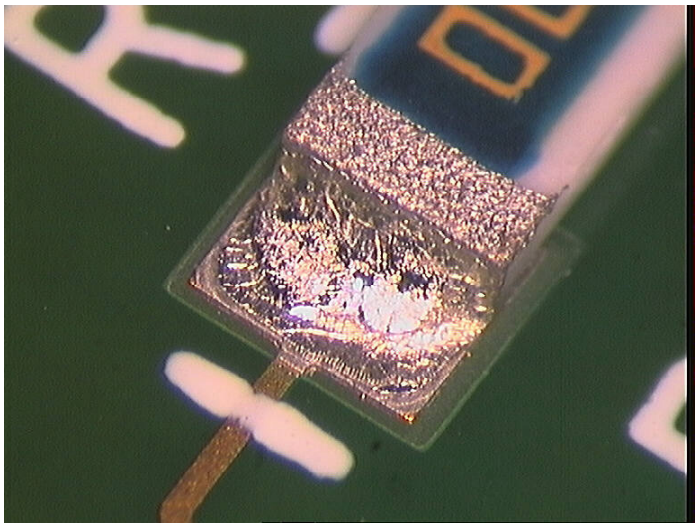

Figure 70: Sample 35 (R60L)

5.4.1 R60L Results

Eleven systems, including one proportional counter system, were used to test this sample, and the results are shown in Figure 71. Eight of the systems indicated the presence of lead at low levels, with five of them (DQ, FR, JW, LX and NZ) indicating the joint was non-compliant (with levels of 0.11% to 0.75% Pb).

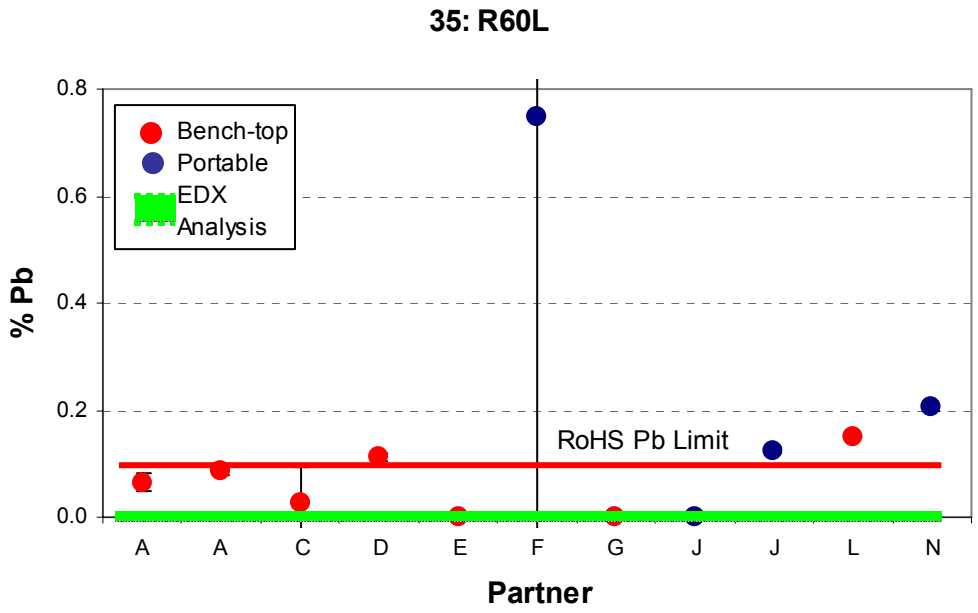

Figure 71: Results on R60L sample for Pb (wt%)

6 DISCUSSION FOR SOLDERS AND SOLDERED JOINTS

As discussed in Section 0, it is important to understand that a direct comparison between XRF results and chemical analysis is difficult. The XRF results are taken from a particular point on the sample, whilst the chemical analysis is undertaken on a grind of a larger sample and therefore should be considered more of an average for the sample as a whole. Any segregation within an alloy, therefore, may result in the two techniques giving apparently conflicting results. It should be remembered that whilst chemical analysis requires a minimum sample size, the XRF technique can be used to examine much smaller samples,

6.1 BULK ALLOY ANALYSIS

For larger samples, large spot sizes can be an advantage. Sampling over a larger area can reduce the effects of segregation within the sample and give a more meaningful value for the analysis. For the bulk alloy samples, PIN/SiLi based XRF systems demonstrated their ability to detect lead levels down to around 500ppm Pb. Some systems achieved good repeatability at 50ppm Pb. Not only did all the systems achieve 100% successful identification of 2000ppm Pb in the tin, but when the lead level was reduced to 1000ppm lead, eleven of the twelve systems indicated either non-compliance for lead, or a level within 10% of the RoHS limit. Thus all PIN or SiLi detector based systems proved suitable for screening bulk solder samples for RoHS compliance for lead, detecting the presence of lead at or above 2000ppm. For lead levels between 500ppm and 2000ppm, additional techniques are recommended if more accurate elemental analysis is required. These detection levels are more than sufficient for distinguishing tin whisker mitigation levels of above 4% Pb.

The situation regarding false detection levels for cadmium in Sn/Pb matrixes need to be addressed. Although ten PIN/SiLi systems completed full matrix analysis for cadmium, 50%

of the systems (AP, BP, CQ (7 times), DQ and JW) gave false detections of cadmium. Two systems were not used in the tests for cadmium.

All the proportional counter based systems proved capable of measuring lead in bulk solder samples at 0.2% or above. Only one system was able to detect lead down to 0.1%. None of the systems was able to detect levels below 0.1% Pb. Although this response would be adequate for tin whisker mitigation purposes, in which lead levels at or above 4% are required, clearly for RoHS compliance, some proportional counter based systems should not be used for RoHS screening.

6.2 SOIC SOLDER JOINT ANALYSIS

For the much smaller surface mount solder joints, the measurement window size (or spot size) is an issue. For accurate determination of the lead content, samples need to fill the measurement window. The spot size for portable systems in this study tended to be at least 3mm diameter. With the toe of the SOIC solder joints tested in NPL1 to NPL5 being approximately 0.65mm x 1mm, the joint only fills around 8% of the measurement window. Solder joints by their nature, tend to be thinner samples and the signal from other materials beneath the solder joint may modify the lead values. Another complication is that the joint areas measured were not of constant thickness due to the shape of the fillet. Although, one of the portable systems did fail the NPL2 sample (~3%Pb) for non-compliance, the measured values were still very low at around 0.16%Pb. Similarly for the NPL3 sample with lead at around 11%, three portable systems correctly indicated non-compliance but gave measured lead levels of 0.18 to 0.66%. Thus, for ***distinguishing samples containing high lead levels (40+%), the majority of the handheld systems would prove adequate***, but most systems would not detect non-compliant joints where the lead levels were below 3%. Such systems may be suitable for measuring joints by a destructive route, if sufficient joints were removed from the assembly and collected together to fill the measurement window.

The bench top systems, with their generally smaller spot sizes (0.1 to 2mm diameter), were able to identify non-compliant joints, with the eight systems tested being successful on every occasion.

Measurements for cadmium were completed for eight systems (portable and bench top), and six false detections out of forty measurements were registered on two systems (AQ (5 times) and FS). All measured values were less than 0.1% Cd.

The performance of the three proportional counter based systems was variable. Only two systems were used to undertake a full set of measurements. Whilst one system (GT) performed well recoding acceptable levels for lead in the joints, the other system gave high lead levels of 8% for the lead-free sample NPL1.

6.3 RESISTOR JOINT ANALYSIS

Spot size also played a part in the analysis of the R1206 solder joint in sample R60L. The R1206 joint in this sample was approximately 3 x 2 mm, filling around 85% of the typical measurement window of a handheld system (if 3mm in diameter). Although no lead (<0.1%) was present in the joint, six systems failed the sample for non-compliance for lead (i.e. having lead values >0.1% - values of 0.11 to 0.75% Pb). The majority of these systems had larger spot sizes and consequently the measurement window extended beyond the joint area

and included part of the top of the component and PCB base as shown in Figure 72. The signal therefore included some contribution from the resistor, which contained lead in a passivation layer of the resistive element. Thus false RoHS non-compliances for lead were generated. However, none of the recorded lead levels were above 1% and therefore would not affect their use for tin whisker mitigation applications.

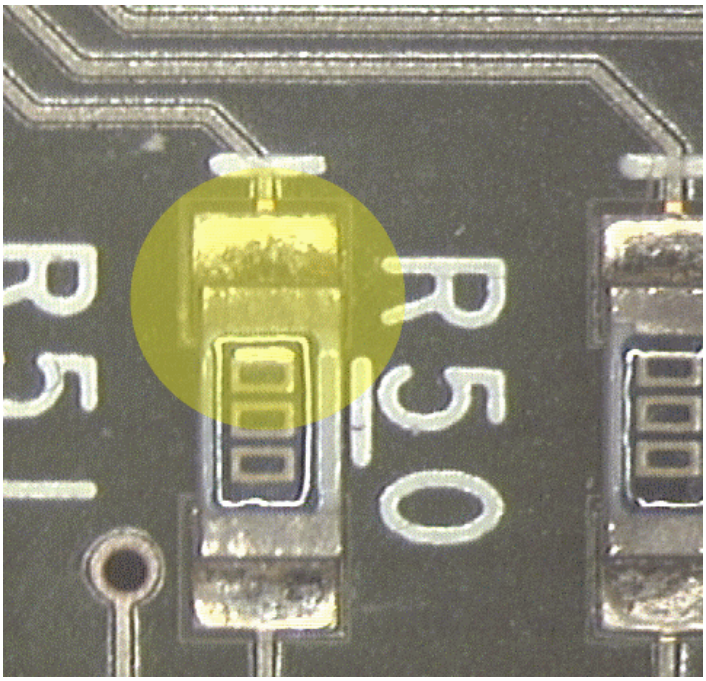

Figure 72: Image of R1206 chip resistor with 3mm diameter measurement area superimposed.

6.4 BGA JOINT ANALYSIS

Two samples (BGA1 and BGA2) were studied to determine whether the XRF systems could be used to obtain a measurement of the lead content of assembled BGA balls (approximately 40% and 10%), when examined through the top of the BGA. This type of measurement is of interest to allow non-destructive testing of completed assemblies, as may be required on product imported into the EU. Only one system (NZ) was capable of obtaining a lead signal sufficient to indicate that both samples were non-compliant. However, it should be noted that the measured values from this system were significantly below the actual sample values (1.98% for the 40% Pb sample, and 0.32% for the 10% Pb sample). Thus, if the level of any lead contamination levels were low, none of the systems could be relied upon to determine RoHS compliance. Similarly false negatives may be generated in tin whisker mitigation applications.

7 RESULTS FOR OTHER ELECTRONIC COMPONENTS

Summary results are presented graphically in the Sections below. The summaries show averages of three instrument readings except where stated. For the purposes of averaging, where a system returned a “not detected” result, it was equated to 0.

7.1 SAMPLE 10 (RES)

Sample 10 was a lead-free R1206 0Ω chip resistor (see Figure 72). This component, similar to the component used in sample 35 above, had a passivation layer over the resistive element that contained lead. The results of an EDX analysis of the resistive element area are provided in Table 5. EDX analysis of the resistor termination indicated that none of the RoHS restricted materials were present at levels greater than 0.1%. The participants were asked to test the resistor termination with the element towards the detector.

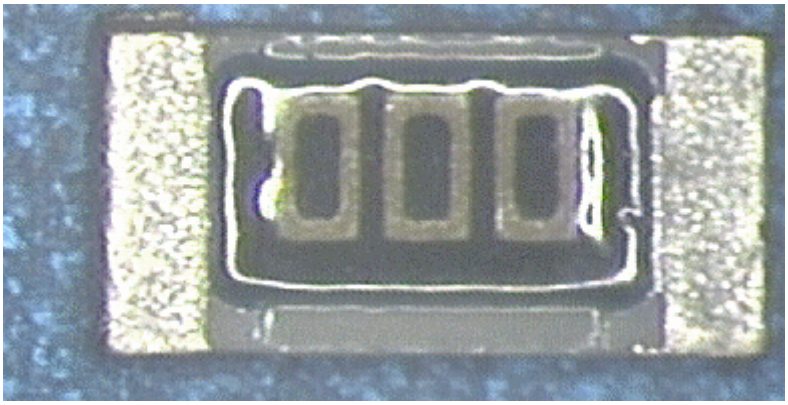

Figure 73: Sample 10 (RES)

Table 5: EDX analysis of RES resistive element area

	EDX Analysis Termination
Pb	40.2
Al	19.3
Co	5.5
Ti	28.3
Cr	6.9

7.1.1 RES Results

All fifteen systems tested (including three proportional counter systems) detected lead above the RoHS limit of 0.1%. However, the levels recorded varied between 0.136% and 30% (see Figure 73).

Four systems of nine evaluated detected low levels of cadmium, with two systems (DQ and FS) indicating the termination was non-compliant with levels of >0.01% Cd (0.321% and

0.042%). Four systems of seven (FR, FS, JV and JW) evaluated recorded levels of chromium of >0.1% (values ranged from 0.25 to 1.41%).

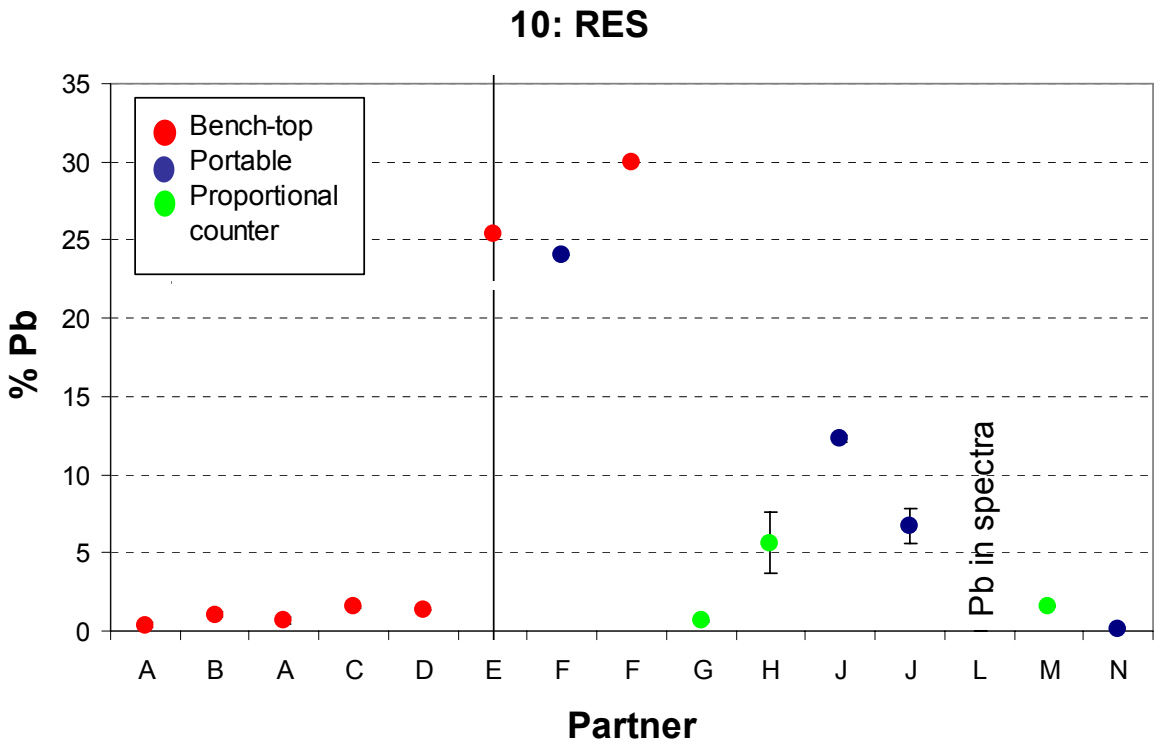

Figure 74: Results on RES sample for Pb (wt%)

7.2 SAMPLES 28 AND 29 (REL1 AND REL2)

Samples 28 and 29 were reels of chip resistors as shown in Figure 75. REL1 contained SnPb-terminated resistors with 11% Pb in the component finish. REL2 was a reel of lead-free resistors, similar to sample 10 RES above (i.e. no lead in the termination, but lead present in the passivation). The participants were asked to analyse the resistor termination whilst still in the tape by examining from the side of the reel. These samples were tested to determine if components needed to be removed from the tape to enable an accurate assessment of the lead content of the termination.

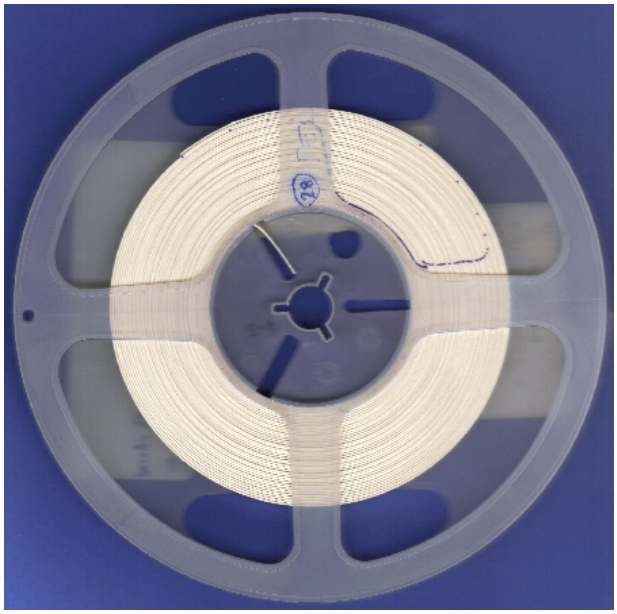

Figure 75: Samples 28 and 29 (REL1 and REL2)

7.2.1 REL1 Results

Six of the eleven systems (AQ, CQ, DQ, HU, JV and MY) that were used to evaluate this sample (including three proportional counter systems) indicated that the level of lead (>0.1%) was such as to mark the sample as RoHS non-compliant for lead. The levels detected ranged from 0.119% to 33% (see Figure 75), although only one system (HU) recorded a value well in excess of the known termination content of 11%.

7.2.2 REL2 Results

Four of the nine systems (CQ, DQ, HU and NZ) that were used to test this sample (including two proportional counter systems) indicated that the sample was RoHS non-compliant for lead, or recorded lead peaks in the relevant spectra. The levels detected varied fro 0.425% to

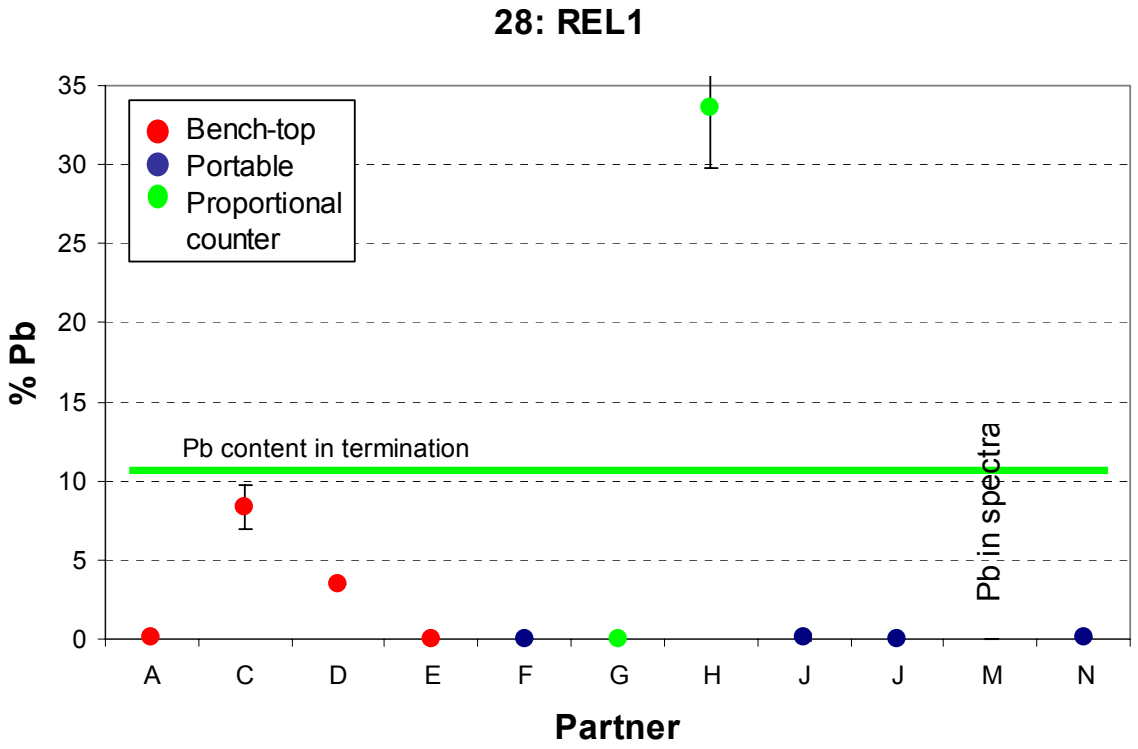

Figure 76: Results on REL1 sample for Pb (wt%)

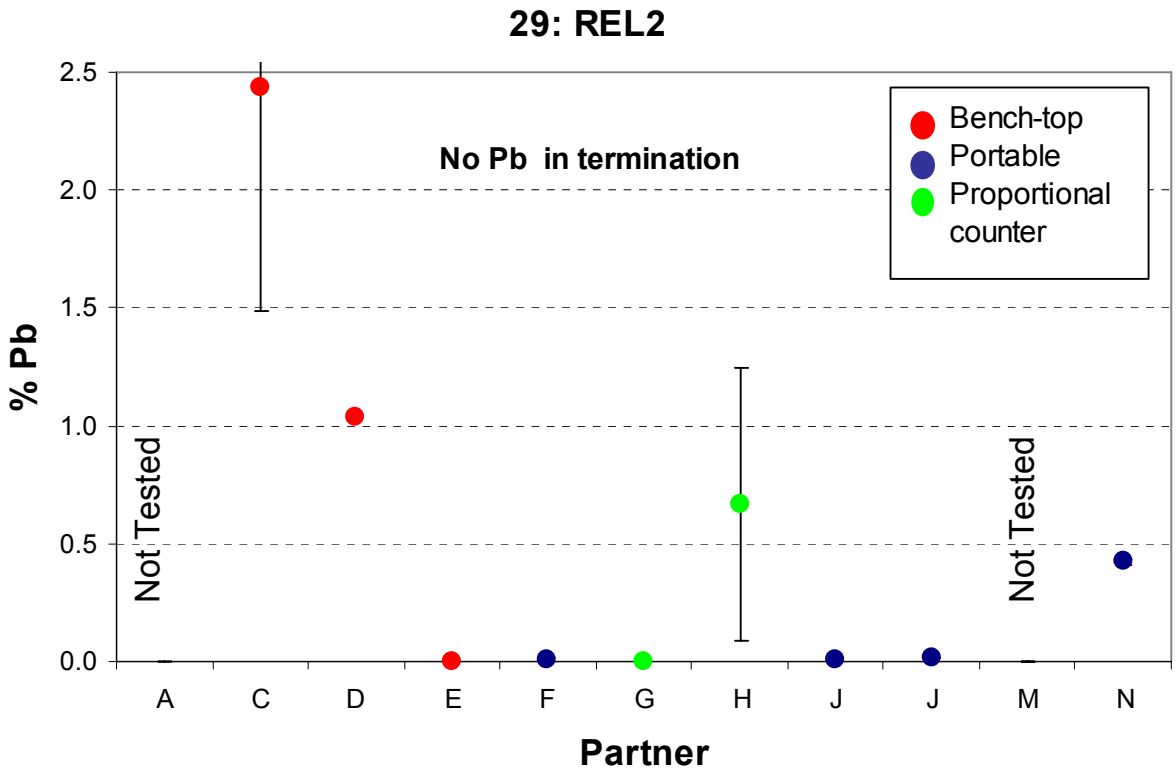

Figure 77: Results on REL2 sample for Pb (wt%)

7.3 SAMPLES 32 AND 32A (STCK AND STCK1)

Samples 32 and 32A were sticks or tubes of SOIC components as illustrated in Figure 78. STCK contained SnPb-terminated SOICs with 36% Pb in the component finish. STCK1 was a tube of lead-free SOICs. The participants were asked to analyse the SOIC terminations whilst still in the tubes. These samples were tested to determine if components needed to be removed from tubes/sticks for an accurate assessment of the lead content of the termination.

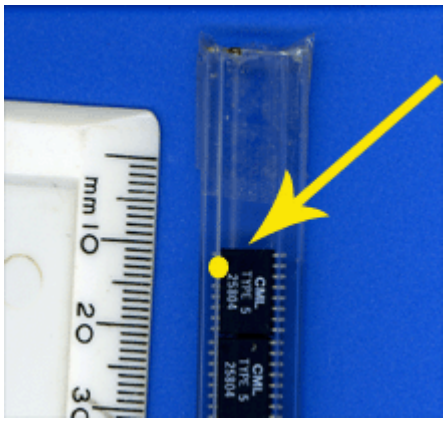

Figure 78: Samples 32 and 32A (STCK and STCK1)

7.3.1 STCK Results

Eight systems out of twelve tested including three proportional counter systems (AP, AQ, CQ, DQ, EQ, GT, HU and MY), recorded lead peaks in the relevant spectra, or indicated that sample STCK was RoHS non-compliant (>0.1% Pb). However, the measured lead levels were very low (1.52% to 20.7%) in view of the known lead content of the termination (36% Pb). It should be noted that three of these systems (DQ, EQ and FR) also indicated that sample STCK1 was RoHS non-compliant for lead, even though it was nominally lead-free. The results are shown in Figure 79.

7.3.2 STCK1 Results

Four systems out of ten evaluated (including two proportional counter systems) incorrectly recorded lead peaks in the spectra, or indicated the sample was RoHS non-compliant for lead (DQ, EQ, FR and HU, values ranged 0.1% to 7.0%),. The results are presented in Figure 80.

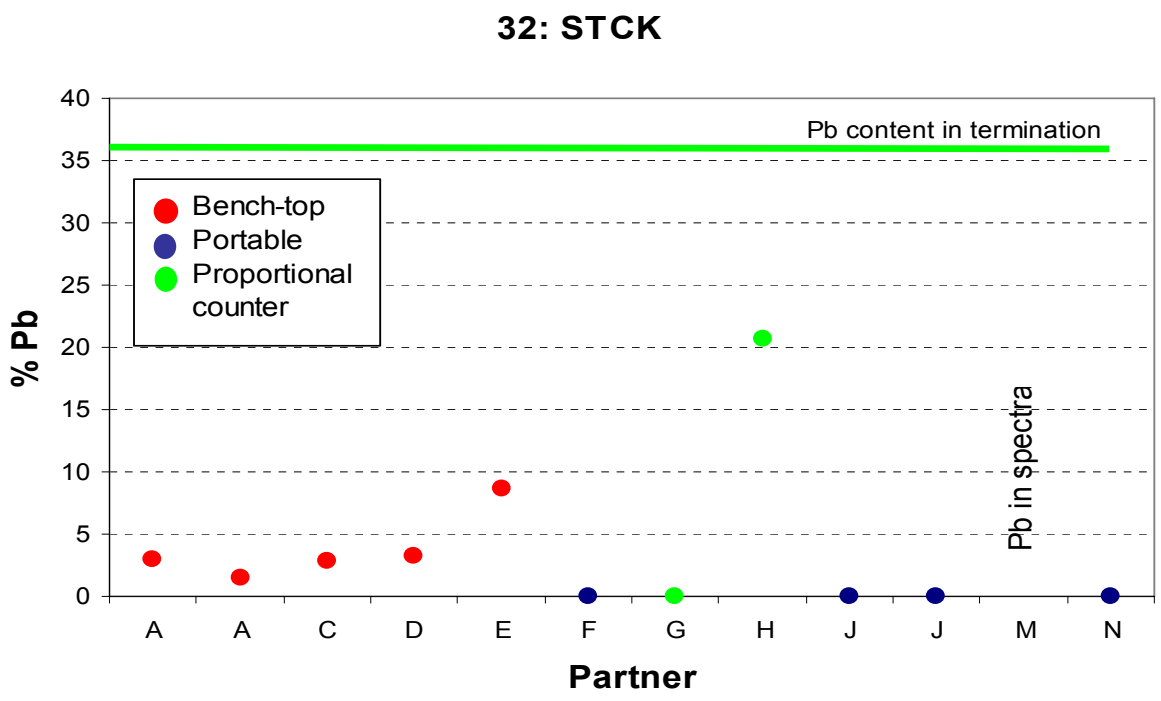

Figure 79: Results on STCK sample for Pb (wt%)

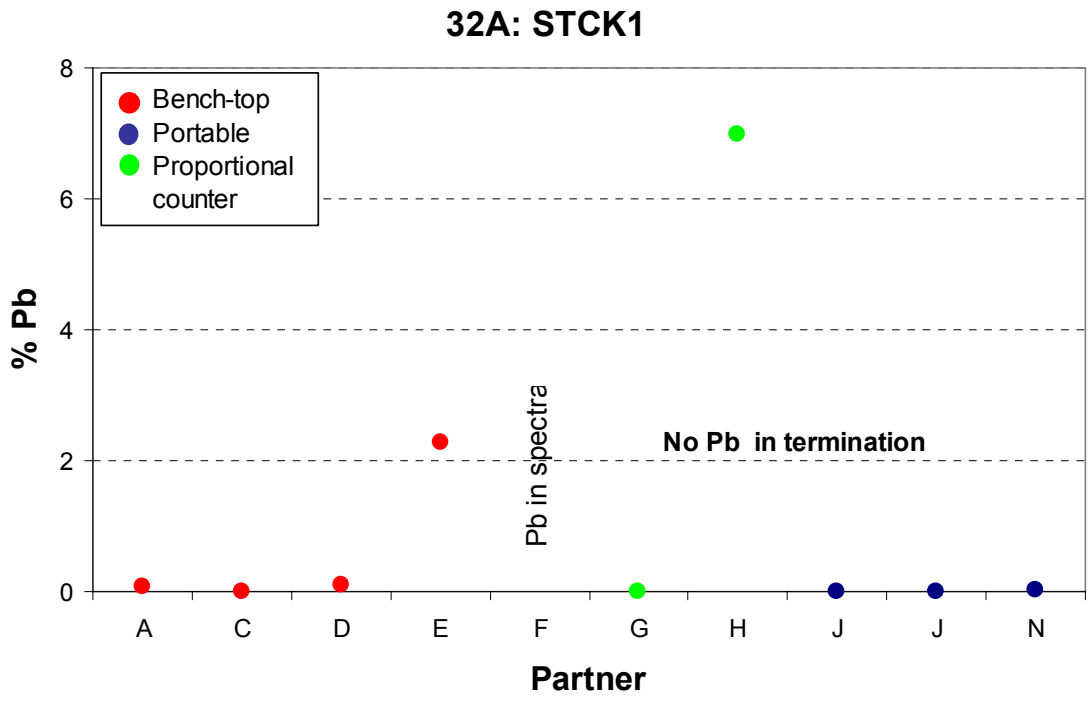

Figure 80: Results on STCK1 sample for Pb (wt%)

7.4 SAMPLES 33, 34 AND 35 (PSTE1, PSTE2 AND PSTE3)

Samples 33 to 35 were tubs of solder paste. PSTE1 (sample 33) comprised a Sn62 solder paste containing 35.6% Pb. PSTE2 (sample 34) was a SAC solder paste contaminated with 0.96% Pb. The final paste (PSTE3, sample 35) was a SAC paste which was shown to contain 0.04% Pb. The participants were asked to examine the pastes whilst still in the tub, with the tub inverted (so that the paste in the bottom of the tub was closest to the detector, as shown in Figure 81). These samples were tested to determine if a paste sample needed to be removed from its container for accurate assessment of the lead content of the termination.

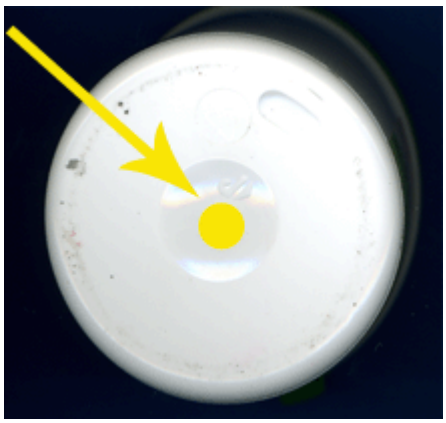

Figure 81: Samples 33 to 35 (PSTE1, PSTE2 and PSTE3)

7.4.1 PSTE1 Results

All ten of the systems evaluated (including one proportional counter system), recorded lead peaks in the relevant spectra, or indicated rgwe sample was RoHS non-compliant for lead (AP, AQ, CQ, DQ, EQ, FR, GT, JV, JW and NZ; values ranged from 1.01% to 45.9%). Three of these systems (AP, CQ and GT) also indicated the presence of lead (>0.1%) in the nominally lead-free PSTE3 sample. The results are summarised in Figure 82.

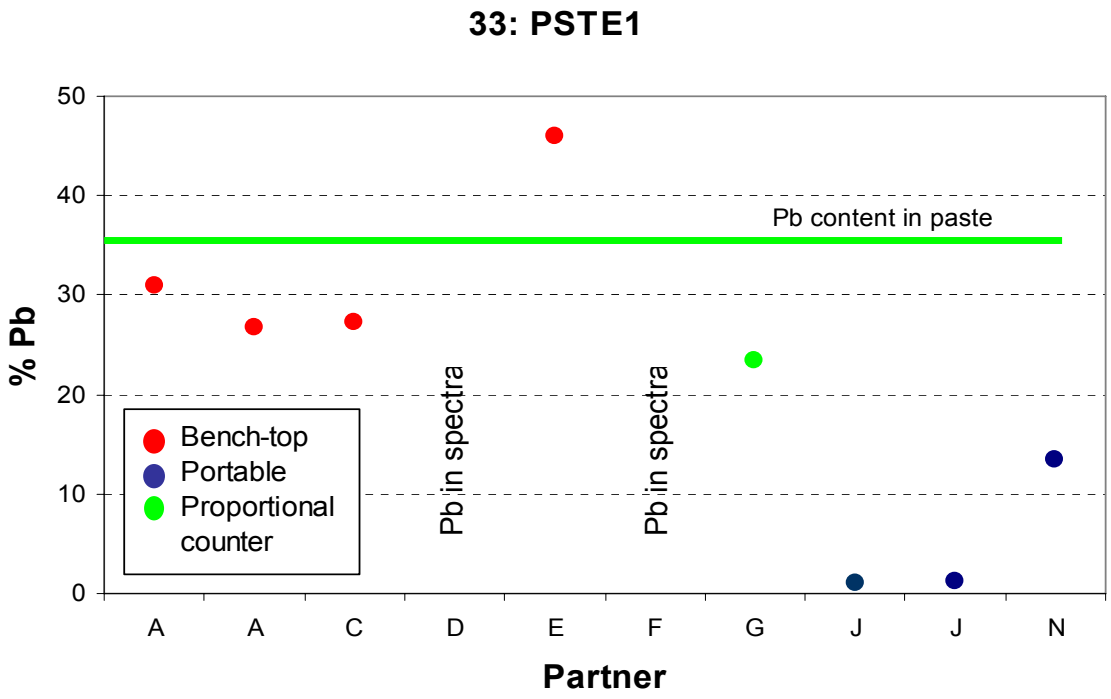

Figure 82: Results on PSTE1 sample for Pb (wt%)

7.4.2 PSTE2 Results

Five of the ten systems evaluated (including one proportional counter system), indicated the sample was RoHS non-compliant for lead (>0.1% Pb - AP, AQ, CQ, GT and NZ – see Figure 82), although the levels of lead recorded were significantly lower than the actual value (0.2% to 1.2%). Three of these systems (AP, CQ and GT) also indicated the presence of lead (>0.1%) in the lead-free PSTE3 sample (see Figure 83). Three other systems indicated the presence of lead (FR, JV and JW) but at levels <0.1% Pb.

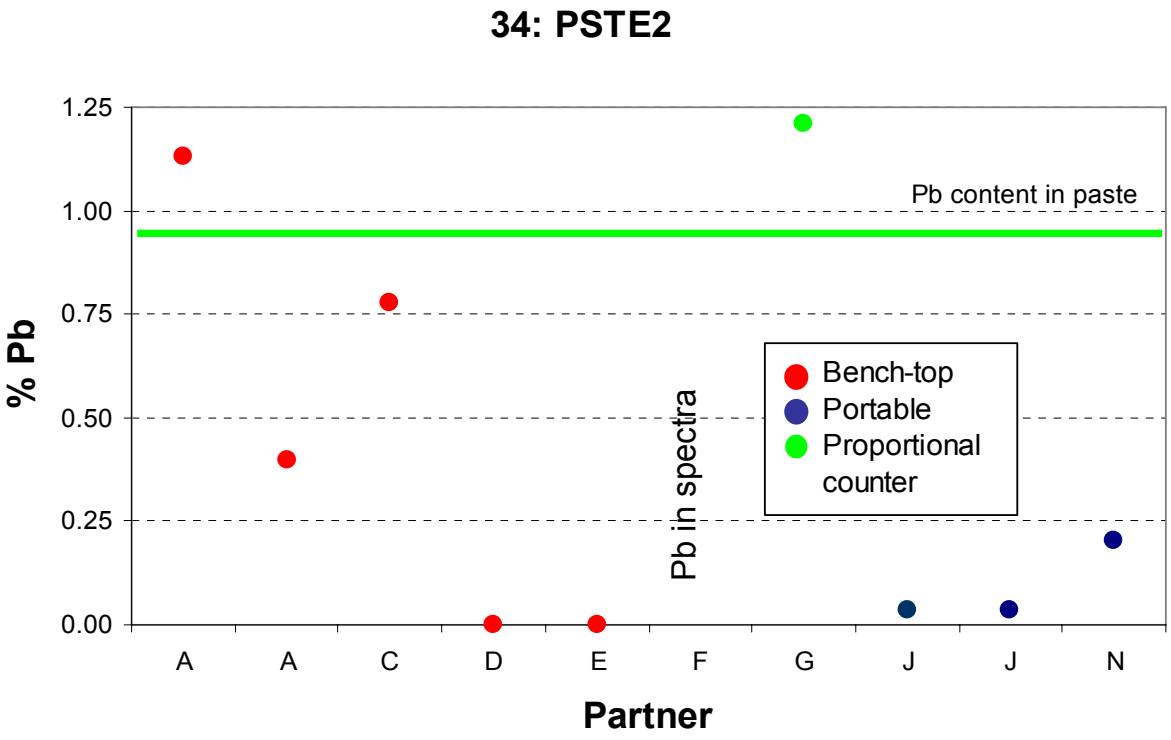

Figure 83: Results on PSTE2 sample for Pb (wt%)

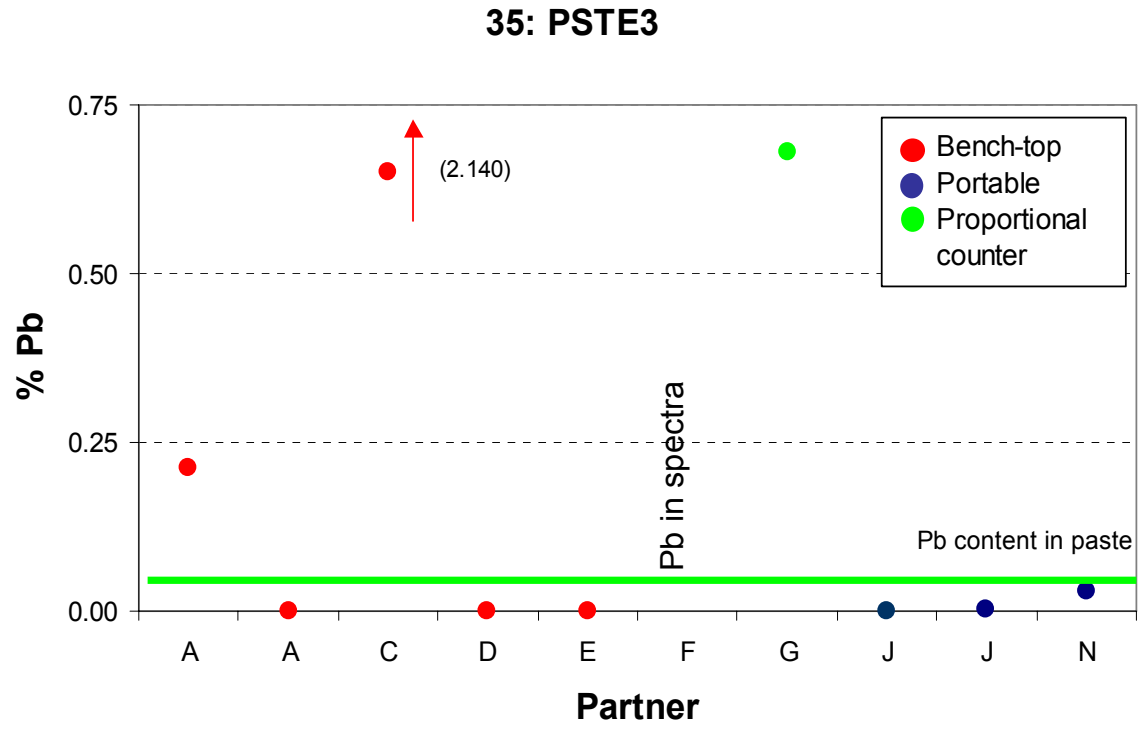

Figure 84: Results on PSTE3 sample for Pb (wt%)

7.4.3 PSTE3 Results

Three of the ten systems evaluated (including one proportional counter system), indicated the sample was RoHS non-compliant for lead (>0.1% Pb - AP, CQ and GT; values from 0.2% to 2.1% – see Figure 83).

7.5 SAMPLE 11 (SCRW)

Sample 11 was a chromium-passivated zinc-plated screw, as shown in Figure 85. Tests for CrVI were inconclusive. This sample was tested to determine if the chromium of the coating could be assessed using the XRF technique.

Figure 85: Samples 11, SCRW

7.5.1 SCRW Results

Fourteen systems were evaluated (including three proportional counter systems) for this sample. Eleven of the systems recorded chromium in the spectra or indicated that the sample was RoHS non-compliant containing greater than 0.1% Cr (AP, BP, AQ, CQ, DQ, EQ, FR, JV, JW, LX and NZ; values ranged from 0.77% to 1.8% Cr) – see Figure 86.

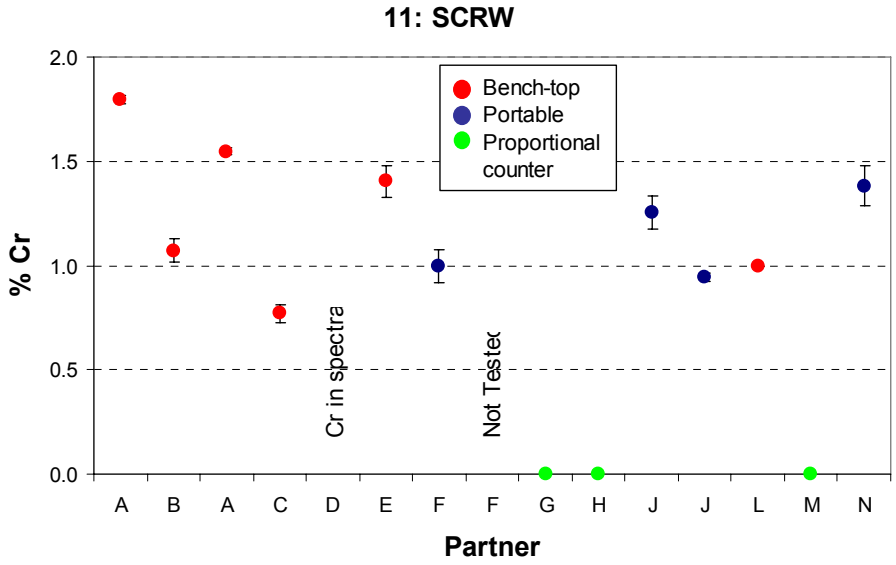

Figure 86: Results on SCRW sample for Cr (wt%)

7.6 SAMPLE 36 (POST)

Sample 36 was a threaded brass spacer with a tin-plated finish (as shown in Figure 87). The coating was lead-free but the brass underneath contained lead as an aid to machining. Under the RoHS legislation, up to 4% Pb is permissible in copper alloys. This sample was tested to determine if the lead content of the tin coating could be accurately assessed.

Figure 87: Samples 36, POST

7.6.1 POST Results

The results of the EDX analysis of the coating indicated that there was <0.1% Pb in the component plating. However, twelve of the fourteen systems tested, including three proportional counter systems, recorded lead peaks in the spectra, or indicated the sample was RoHS non-compliant (>0.1%) for lead (AP, BP, AQ, DQ, EQ, FR, HU, JV, JW, LX, MY and NZ; values ranged from 0.18% to 3.7%). One of the systems (GT) also indicated the presence of lead (>0.1%). The results are summarised in Figure 88.

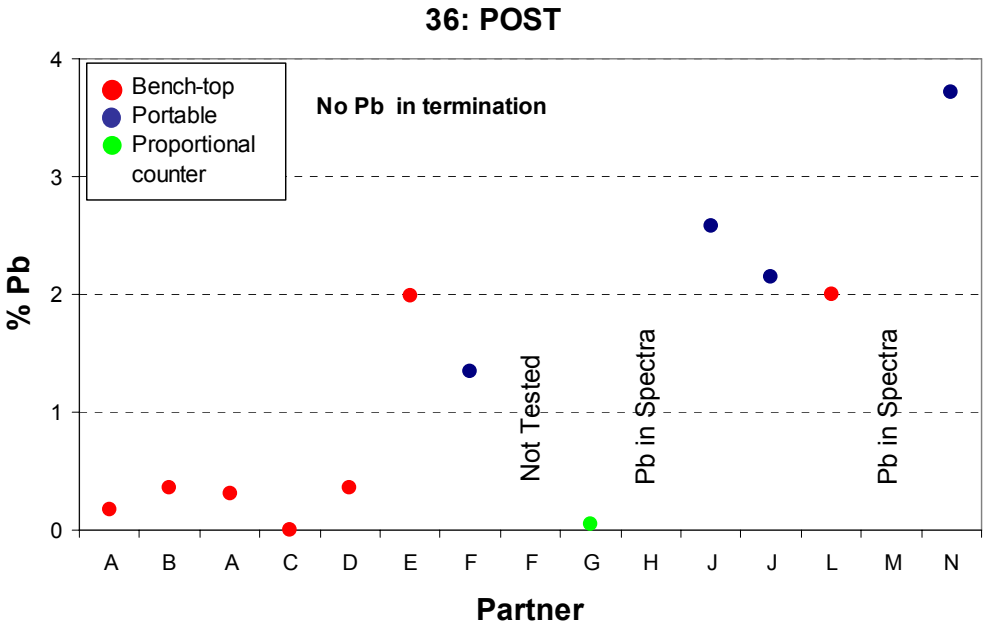

Figure 88: Results on POST sample for Pb (wt%)

8 DISCUSSION FOR OTHER ELECTRONIC COMPONENTS

8.1 COMPONENTS IN PACKAGING

At goods-inwards inspection, there are distinct advantages in being able to test components/materials without removing them from their secondary packaging (tapes, reels, sticks etc.). This may avoid deterioration of the material after opening, as in the case of solder pastes, or prevent wastage as in the case of components in reels. Handling damage in removing components from sticks can also be avoided.

Two samples (REL1 and REL2) were used to study the possibility of testing chip resistors in their reels. REL1 was a typical SnPb-terminated resistor (11%Pb). For **RoHS compliance** evaluation, when tested in the reel, five of the eleven XRF systems tested (including one proportional counter based system) did not record a sufficiently high lead level for the resistors to be correctly assessed as RoHS non-compliant for lead. Of the remaining systems, four recorded significantly lower lead being present than was actually the case. One proportional counter based system recorded significantly higher (34%) lead content, and the remaining system (proportional counter based) did not quantify the amount of lead present. In terms of **tin whisker mitigation**, eight of the ten systems giving quantitative results failed to show that the resistors contained greater than 4% Pb in the termination and thus suitable for tin whisker mitigation. ***Thus for both RoHS and tin whisker mitigation inspection, removal of the components from the reel would be required***.

The REL2 sample was similar to the RES sample but the component terminations were lead-free (<0.1% Pb) although lead was present in the passivation of the resistive element. Only nine systems completed the analysis for these samples, of which four indicated the resistors were not RoHS compliant containing only 0.43 to 2.4% Pb. Thus for RoHS inspection, removal of the components from the reel would again be required. Furthermore, in terms of tin whisker mitigation, none of the systems tested indicated that the resistors were suitable (i.e. having above 4% Pb), but as a number of the recorded values were significantly higher than the actual lead levels, removal of the components from the reel is still recommended.

Two samples of SOIC components in sticks or tubes were also tested. STCK contained SnPb-terminated components with 36% Pb. Four of the ten quantitative systems did not record a sufficiently high lead level for the resistors to be correctly assessed as RoHS non-compliant for lead. All four of these systems were portable, and thus had larger spot sizes. As with the SOIC solder joints (Section 6 above), the measurement windows of these systems were relatively large compared to the component termination size, and thus the lead signal monitored was diluted by surrounding materials. The other systems, with generally smaller measurement windows, did not record accurate lead levels in the terminations, giving values between 1.5 and 21% Pb. Although these components are clearly suitable for tin whisker mitigation, only two of the ten quantitative systems indicted that the lead levels were above the 4% required. Thus, ***for both RoHS and tin whisker mitigation inspection, removal of the components from the stick or tube would be required***. For systems with larger measurement windows, several components may need to be collected together to fill the measurement window with terminations for accurate analysis.

For the STCK1 sample, which was RoHS compliant (<0.1%Pb), four of the ten systems tested indicated that lead was present above 0.1%, or recorded lead peaks in the spectra, giving a false RoHS non-compliance. One proportional counter based system indicated a false compliance for tin whisker mitigation. These results, combined with the results for the STCK sample indicate that ***for both RoHS and tin whisker mitigation inspection, removal of the components from the stick or tube is recommended***.

8.2 SOLDER PASTE IN POTS

Three samples of solder pastes in pots or tubs were provided for testing by the various systems. PSTE1 was a standard Sn62 solder paste containing approximately 36% Pb. All ten systems evaluated correctly indicated the paste was not RoHS compliant for lead, or contained lead in the relevant spectra. But the measured values were, with one exception, below the true value (in two cases as low as 1%). For these two examples, the paste would have been falsely identified as not being suitable for tin whisker mitigation applications.

For PSTE2 with a lower lead level (~1%), four of the ten systems did not correctly identify the paste as RoHS non-compliant. However, all the XRF systems correctly indicated non-suitability for tin whisker mitigation applications. When lead was present in the paste at only a very low level (PSTE3, 0.040% Pb), three systems falsely indicated the paste was RoHS non-compliant for lead. Again all the systems correctly indicated the non-suitability of this paste for tin whisker mitigation applications.

Due to the the degree in uncertainty with the solder paste measurements, ***it is recommended that a paste sample sufficient to fill the measurement window of the test instrument, should be removed from the pot for testing.***

8.3 OTHER COMPONENTS

The RES sample was the same type of component as used in R60L and REL2, i.e. the component termination was lead-free but lead was present in the passivation of the resistive element. Of the twelve systems evaluated, when the component was tested with the resistive element towards the detector, all indicated the component was not RoHS compliant for lead or recorded lead peaks in the relevant spectra. The lead levels varied between 0.14 and 30%. The higher levels of lead recorded were generally associated with those systems that used a larger measurement area. Clearly, the lead in the passivation was providing the lead signal being recorded by the instruments. Two systems also incorrectly indicated the terminations contained non-compliant levels of cadmium (DQ and FS). In addition, four systems indicated the presence of chromium. This is not speciated and was present in the component marking, not in the termination. In terms of tin whisker mitigation, five systems incorrectly indicated that the lead levels in the termination were above 4%. Generally, it is advised that ***when testing chip resistor component terminations for RoHS compliance or tin whisker mitigation, the resistor should be tested from the reverse side with the resistive element facing away from the instrument detector***.

The POST sample was an example of a component with more than one layer of metal present. In this case the component was RoHS compliant because although the surface coating was tin, the under laying metal was brass containing lead, but at less than the permitted 4% level. However, when tested twelve out of fourteen systems incorrectly indicated the component was RoHS non-compliant or recorded lead peaks in the spectra. For

tin whisker mitigation, although none of the systems indicated more than 4% Pb, one (NZ) came close (3.7%) and two (JV and JW) indicated over 2% Pb. The results indicate that ***operators need a sound understanding of the materials involved in the construction of the samples in order to ensure meaningful analyses are generated***.

The final sample needing discussion is the chromium-passivated zinc-coated screw. The tests proved inconclusive for CrVI but chromium was clearly present on the surface. The amounts of chromium recorded by the various quantitative instruments ranged between 0.77 and 1.8%. Whilst all these values are above the 0.1% RoHS limit, there is a question over their interpretation, in particular, what constitutes the measured volume, and hence the percentage of chromium present – passsivation, coating, whole screw etc? Clearly these XRF systems are quite capable of indicating the presence of chromium, but due to lack of speciation, not able to determine RoHS compliance.

The three proportional counter systems did not detect the presence of chromium.

9 CONCLUSIONS & RECOMMENDATIONS

The purpose of this study was to investigate the suitability of using of XRF systems for screening electronics parts in two applications; RoHS compliance and tin whisker mitigation. In total, fifteen systems were tested with a range of forty typical electronics components and assemblies. Eleven different systems were evaluated at twelve different sites. Systems based on PIN, SiLi and proportional counter detectors were included. Eleven systems were bench top instruments and four were portable. Forty different samples were included in the study, ranging from contaminated plastic components through bulk solder alloys to solder joints and solder-terminated components.

In identifying possible samples for the project, it was found that typical non-compliant electronics components do not contain Pb, Hg, Br or Cr at levels around the 1000ppm RoHS limit. Rather, contamination levels of these elements were generally significantly higher than 1000 ppm.

- XRF systems using PIN or SiLi detectors proved generally efficient at distinguishing between RoHS non-compliant components (typically 2000+ppm contamination) and compliant components (typically <500ppm). For contamination levels between 500ppm and 2000ppm, additional techniques are recommended if accurate elemental analysis is required, although as already indicated, components falling within these limits are considered to be rare.
- Of the eight typical plastic electronics components tested containing lead, cadmium or mercury, all twelve PIN/SiLi systems achieved 100% identification of non-compliant components.
- For three typical plastic RoHS compliant components tested, all twelve PIN/SiLi systems achieved 100% identification of compliance for lead and mercury. Three typical plastic components containing bromine or chromium were correctly identified as containing these elements, and requiring alternative tests for speciation.
- For bulk solder samples, PIN/SiLi based XRF systems proved excellent for measuring lead levels down ~500ppm Pb, and some systems achieved good repeatability at 50ppm Pb. All systems achieved 100% identification of non-compliance for lead contamination at 2000ppm Pb in tin. At 1000ppm lead in tin, eleven of twelve systems indicated RoHS non-compliance for lead (or within 10% of RoHS limit).

- In determination of the cadmium content of samples, XRF systems using PIN or SiLi detectors proved excellent at distinguishing non-compliant systems above 1000ppm Cd. However, below this level, additional techniques may be required. The lower RoHS limit for cadmium of 100ppm did generate some incorrect detections for this element. In the case of plastic components, four systems incorrectly recorded the presence of cadmium. In the case of bulk solder samples, 50% of the systems gave at least one false detection for cadmium. For plastic components, only two incorrect detections for chromium at around 1000ppm were registered.
- Proportional counter based systems were capable of registering the presence of RoHS-banned elements when they are at typical levels found in plastics (>3%) but below this level, their ability to detect the elements was uncertain. Even at the higher contamination levels, proportional counter based systems were not capable of giving quantitative results.
- For tin whisker mitigation in solder samples, where lead levels in excess of 4% are required, all the systems are capable of detecting/measuring the lead content, providing the sample size is large enough to fill the measurement window. Indeed, all systems proved capable of determining lead levels of 1% and above in solder.
- Some care should be taken in utilising these instruments in certain circumstances. When unfamiliar components are being assessed, instrument operators require a sound understanding of the materials involved in the test structure to avoid any incorrect indications of RoHS non-compliance, and/or allow meaningful interpretation of the data. For example, incorrect indications of suitability tin whisker mitigation can be obtained from components that have lead in a base material (that is itself RoHS exempt), beneath a lead-free metallisation.
- Ideally samples should be segregated to provide single materials for testing, particularly if initial measurements from a complete sample indicate the presence of any RoHS restricted substances, or the presence of lead in tin whisker mitigation testing. Measurement areas should be chosen to ensure test samples fill the detection window or multiple samples should be collected in a suitable container to achieve the same effect.
- Samples should be removed from tape/tubes/tubs for accurate analysis. If segregation is suspected in plastic or solder samples, multiple sampling over a range of areas of the sample is recommended. Larger measurement areas are generally better for avoiding inaccurate results associated with segregation.
- Determination of lead levels in assembled area array joints has been shown to be difficult. For accurate determination of lead levels, destructive testing involving BGA removal and testing of the exposed joints is recommended. If the XRF equipment to be used has a measurement area greater than the size of the joint to be tested, removal of a number of joints from the assembly, and collecting them together to fill the measurement window, may be necessary.
- For measurements on alloys used in assembly, testing of reflowed solder on unused component lands or test points could be used for alloy determination. Such measurements would be eased and improved if specific test pads and corresponding stencil apertures were added (at the design stage) to available space or onto break-off areas. .

In conclusion, XRF systems offer a viable method of screening for RoHS compliance (References 4 to 7) and tin whisker mitigation (Reference 8). Compared to chemical analysis, these systems offer lower unit cost, lower running costs and faster results. Smaller sample sizes are also possible. However, the use of these systems does require at least a semi-skilled

operator, who has a sound understanding of the principles of equipment theory and likely composition of materials involved in component and assembly manufacture.

10 ACKNOWLEDGEMENTS

The work was carried out as part of a project in the Materials Processing Metrology Programme of the UK Department of Innovation, Universities & Skills. We gratefully acknowledge the support and co-operation of the following companies without whose help this project would not have been possible.

Alcatel Alenia Space Italia
EADS Astrium
Fischer Instrumentation (GB) Ltd.
MBDA (UK) Ltd
Oxford Instruments Analytical
Research in Motion
RMD Instruments
Roentgenanalytik
Rolls Royce Marine
RS Components Ltd
Thermo Fisher Scientific Niton Analysers
Tin Technology

Grateful acknowledgement is also due to Ian Axford and Paul Norris of LGC, and David Clack of Tin Technology for advice, chemical analysis and the details of processes used.

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