A Review of Halogen/Halide-Free Test Methods and Classifications for Soldering Materials in the Electronics Industry

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Abstract
Over the last few years, there has been an increase in the evaluation and use of halogen-free soldering materials. In addition, there has been increased scrutiny into the level of halogens and refinement of the definition and testing of halogen-free soldering materials. The challenge has been that there has been no common standard across the industry in terms of halogen-free definitions and the corresponding test methods to determine these. This has created confusion in the industry as to what end users want and what soldering materials suppliers can actually provide. This paper will review the status of both halogen-free and halide-free in terms of definitions, test methods and the limitations and accuracy of test methods used to determine if a soldering material is halogen/halide-free or not. For halogen-free and halide-free definitions, the paper will review the different industry standards which are currently available and those being drafted, and it will discuss any similarities and differences. It will also cover the origins of some of the definitions mentioned in the standards. The paper will include a review of the accuracy and limitations of several test methods and preparation techniques for halogen and halide determination.

Introduction
In the electronics industry, there is a significant push toward halogen-free products. This movement is due to legislation from various countries, and public outcry from well publicized negative third world recycling practices, as well as non-government organizations (NGOs) testing and publishing information on electronic devices regarding their content of various potentially hazardous materials. Halogen-free products are also being mandated by certain OEMs as a means to lessen potential chemical effects on the environment.

In electronics assemblies, halogens can be found in the plastics for cables and housings, board laminate materials, components, and soldering fluxes and pastes. In solder pastes and fluxes, the halogenated compounds are used as activators that remove oxides to promote solder wetting. Eliminating the halogenated compounds can have a significant negative effect on the board assembly process. Process assembly challenges are not the only issues electronics assemblers face as they become halogen-free. The use of proper test methodologies to determine that the soldering products are actually halogen-free is currently not well defined as there are a variety of test methods and standards in the industry.

Halide content has been measured either qualitatively or quantitatively with halide testing being specified for more than fifty years with standards such as the United States Federal Specification QQ-S-571 standard [1] followed by MIL-F-14256 [2] and IPC-SF-818[3] standards and currently in standards such as IPC J-STD-004[4]. The specifications have listed requirements for the halide content of flux-containing soldering materials.

The terms halogen and halide have caused confusion in the electronics industry with definitions to try and clear up the confusion provided by standards such as JEITA ET-7304[5] and IPC-J-STD-004[4]. The term halogen refers to all halogen family elements and halogen compounds including those which are present in nature. The JEITA ET-7304 standard [5] specifically targets the halogen families of chlorine (Cl), bromine (Br) and Fluorine (F) used as the activators for soldering materials. The term halide is defined as the halide ion or halide salt compound having an ionic character (e.g. Cl^-, Br^-, F^-).

Covalently bonded halogens do not disassociate in water, and therefore the chloride, bromide and fluoride are still attached (covalently bound) to other species (typically organic), and will not be detected by techniques such as ion chromatography or titration. Ionically bonded halogens do disassociate in water into the negatively charged halide ion (Cl^-, Br^-, F^-, etc.) and the positively charged species (H^+, Na^+ etc.). Test methods used to look for ionic species, such as ion chromatography, will only detect halides.

A better understanding of the test methods, what they are capable of detecting in terms of halides and halogens, and how they relate to the various halogen-free definitions and standards is required. A variety of these test methods and standards will be discussed in the following sections as well as some test preparation techniques.

Halogen-free definition and standards
A variety of halogen-free definitions and standards have been developed in the electronics industry based on PCB laminates, components and soldering materials. The developed standards for PCB Laminates include IEC 61249-2-21[6], JPCA-ES-01[7] and IPC-4101[8]. All three standards indicate less than 900ppm Cl (<0.09wt %), less than 900ppm Br (<0.09wt %) and less than 1500ppm total Cl and Br (<0.15wt % Cl + Br).

The developed standards for components include JEDEC JEP709 standard [9]. This standard indicates that a solid state device must meet the following requirements to be defined as low halogen in terms of less than 1000ppm Br (from BFR[Brominated flame retardants] sources), less than 1000ppm Cl (from CFR[Chlorinated flame retardants], PVC[Polyvinyl Chloride] and PVC co-polymers sources). For the PCB laminates used in components the Cl and Br limits would follow the guideline in IEC 61249-2 standard [6].

The developed standards for soldering materials include JEITA ET-7034[5] and IPC J-STD-004[4]. The JEITA ET-7034 standard [5] states halogen content less than 1000ppm Cl, less than 1000ppm Br and less than 1000ppm F. An updated draft of the JEITA standard, JEITA ET-7034A [10], also includes Iodine (I) with a value of less than 1000ppm. In contrast, the IPC J-STD-004[4] document does not currently have a requirement for halogen content. J-STD-004 standard [4] only specifies a halide content less than 500 ppm total halide. The amendment to J-STD-004[4] currently being added does include optional testing for halogen content and is leaning towards the 900ppm Cl, 900ppm Br and 1500ppm total halogen content suggested requirements.

Test Methods used to determine Halide / Halogen Content
The test methods used to analyze for halides and halogens are outlined in the following section.

Silver Chromate Paper Test for Bromide and Chloride (Halide)

The Silver Chromate paper test method based on IPC J-STD-004[4] and IPC TM-650 2.3.33[11] is a qualitative test in which a sample of flux is applied to Silver Chromate Paper and allowed to remain on it for one minute. If the paper changes color then it indicates the presence of Chloride or Bromide. This test only identifies the halogen in the ionic form (halide) and is prone to false positives from chemicals such as amines, cyanides, and isocyanates. It also provides no indication as to the total halogen present.

Fluoride Spot Test for Fluoride (Halide)

The fluoride spot test method based on IPC J-STD-004[4] and IPC-TM-650 2.3.35.1[12] is a qualitative test and is designed to determine the presence (if any) of fluoride(s) in the soldering flux by visual examination after placement of a drop of liquid test flux in a zirconium - alizarin purple lake. This method only detects the presence of the fluoride ion.

Although the following test methods, titration and ion chromatography, which are discussed in the next section are used to measure ionic halide, they may be used following oxygen combustion to determine total halogen content.

Titration Method for Chloride, Bromide and Fluoride (Halide)

These are quantitative tests that assess the chloride and bromide (IPC-TM-650 2.3.35[13]) and fluoride (IPC-TM-650 2.3.35.2[14]) present in a flux expressed as Chloride equivalents. A flux or flux extract is titrated to its endpoint using the appropriate IPC test methods. The test methods are an improvement over Silver Chromate paper test and fluoride spot test methods in that it provides a value for how much halide is present. However, this test method detects only halides and not total halogens unless an oxygen combustion method is used to prepare the sample prior to titration. Additionally, there are a wide variety of organic chemicals that can falsely be identified as halides.

Ion Chromatography for Chloride, Bromide, Fluoride and Iodide (Halide)

This is a quantitative test method (IPC J-STD-004 [4] and IPC-TM-650 2.3.28[15]) for Chloride, Bromide, Fluoride and Iodide that can identify the total quantity of halides present in a flux. Based on the retention time in the ion exchange column, a chromatogram is developed and peaks are identified as various ions based on previously developed standards. This test method allows a quantification of how much halide ions are present and which particular halide is present. The challenge with ion chromatography testing by itself is that it only identifies the ionic halide species and the covalently bonded halogen are not detected again, unless the sample has been prepared using an oxygen combustion method prior to Ion

Chromatography testing. In addition, there are chemicals that have similar retention times to Cl^- and Br^- which can result in non-halides being misidentified as a halide.

There is a growing practice of running ion chromatography on reflowed flux residue in terms of sample preparation before Ion Chromatography testing. There are two reasons that people typically utilize this type of method. First, they are examining the flux residues remaining on the PCB for any species that may lead to an increased occurrence of corrosion or dendrite growth from halide ions that do not volatilize. Secondly, any covalently bound halogens contained in the flux may disassociate during the reflow process and then the subsequent extraction and chromatography testing will detect these dissociated halogens as well as the halides that do not volatilize. However, if all of the covalently bound halogens are not disassociated, then the amount of halogens will be underreported.

The IPC J-STD-004 standard [4] mentions in Appendix B-10 that the IPC-TM-650 2.3.28 test method[15] is intended for the detection of ionic halides only and is not be confused with total halogen content determination [ionic halide plus non-ionic (covalent) halogen]. Total halogen content should be tested by oxygen bomb combustion testing using a test method such as EN14582 standard [16] followed by Ion Chromatography testing which is mentioned in the next section.

Oxygen Bomb Combustion Testing followed by Ion Chromatography testing (Halogen)

The use of Oxygen bomb combustion followed by ion chromatography testing is growing in popularity in the electronics industry. The oxygen bomb test method involves subjecting a sample of flux or solder paste to an oxygen bomb combustion in which all of the organic materials are burnt off at very high temperature. This process breaks the covalent bonds for all halogens. The remaining ash consists of the ionic halides and other inorganic materials. The dissolved ash is then run through ion chromatography to determine the total halide content of a material even if it originally contained covalently bonded halogens. Since most halide restrictions are based on the finished circuit board assembly, there has been a discussion on whether the oxygen bomb combustion test followed by Ion Chromatography test should be run on the reflowed flux residue rather than the unreflowed flux.

To determine the halogen content of the flux residue, one could begin by testing the flux or the flux portion of a solder paste through TGA (Thermo-Gravimetric Analysis) equipment using a simulated reflow profile. This will provide an approximate value for the amount of flux residue remaining after reflow. Then, after testing the raw flux through oxygen bomb combustion followed by Ion Chromatography testing, a simple conversion could be done using the safe assumption that no halogen present will volatilize. For example, if the oxygen bomb combustion followed by Ion Chromatography test results show 450 ppm of Chloride present and the TGA results shows that the flux volatilizes 50% during reflow, it would be determined that there will be 900 ppm Cl- in the flux residue. Table 1 shows a hypothetical example of the halogen content variation based on different reporting values for the solder paste, flux and reflowed flux residue.

Table 1: Halogen content variation based on different reporting values for the solder paste, flux and reflowed flux residue.

Halogen content variation based on reporting			
	Mass (g)	Mass of Halogen (g)	Halogen Content (in ppm)
Solder Paste (100g flux and 900g solder metal)	1000	0.045	45
Flux (base material)	100	0.045	450
Flux Residue (50% of 100g) (as 50% of the flux volatilized during reflow)	50	0.045	900

In a study run by Jensen et al. [17] using oxygen bomb combustion testing followed by Ion Chromatography testing, they found the bromide concentration of the raw flux was lower than the reflowed sample. Many companies running the halogen content test are currently using raw flux for testing, as this seems to be the easiest to implement. It is important that those interpreting the results understand that there will likely be a higher ppm level in the flux residue due to the decreased mass of the tested sample. Results of the study are reported in Tables 2 and 3[17].

Table 2: Solder Paste Extracted by Centrifuge, Prepared with Oxygen Bomb and Analyzed via Ion Chromatography[17]. Oxygen Bomb Combustion Test Method: EPA SW-846 5050/9056 / SW5050[18]

Anions by Ion Chromatography	Result/ mg/kg	Reporting Limit/ mg/kg	Weight/ g
Bromide	1210	72	0.000607
Chloride	<162	162	<0.000081
Fluoride	<72	72	<0.000036
Iodide	<700	700	<0.00035

Table 3: Solder Paste Reflowed at 240°C, Prepared with Oxygen Bomb and Analyzed via Ion Chromatography[17]. Oxygen Bomb Combustion Test Method: EPA SW-846 5050/9056 / SW5050[18]

Anions by Ion Chromatography	Result/ mg/kg	Reporting Limit/ mg/kg	Weight/ g
Bromide	2110	55.7	0.00105
Chloride	<125	125	<0.0000625
Fluoride	<55.7	55.7	<0.0000278
Iodide	<700	700	<0.00035

The oxygen bomb combustion test procedure mentioned in EN 14582 standard [16] indicates that methods such as Ion Chromatography can be used for the determination of halides after oxygen bomb combustion testing. There are various other oxygen bomb combustion test methods which can be used in addition to EN 14582[16], including EPA SW-846 5050/9056 [18] and JPCA ES-01-2003[7] standards. JEITA ET-7304 standard [5] mentions that any of these three oxygen bomb combustion test methods can be used. Most laboratories typically use EN 14582 standard [16] which appears to gaining in popularity.

Results and Discussion

Halogen-free Definitions and Standards

For the definition of halogen-free for PCB Laminates when the IEC 61249-2-21 standard [6] was being developed, there were discussions about the ability of the test methods to repeatability detect low Chlorine and Bromine levels in PCB laminates using the semi-open flask test method which was the method used to detect Bromine and Chlorine in PCB laminates.

In some cases, a lower level of Chlorine and Bromine (200-300ppm) was being pushed for by certain groups. Because of the difficulty in repeatability detecting these low levels of Chlorine and Bromine, certain other groups were pushing for a 1500ppm to 2000ppm range.

As a compromise, the maximum level of both Chlorine and Bromine agreed upon in IEC 61249-2-21 standard [6] as was already indicated in previous sections, was less than 900ppm Chlorine and less than 900ppm Bromine for a halogen-free PCB laminate with a total value of Chlorine and Bromine not to exceed 1,500ppm.

This halogen-free definition was also used for halogen-free PCB Laminates included in JPCA-ES-01[7] and IPC-4101[8] standards. As already mentioned, the test method used for detection of Bromine and Chlorine in PCB laminates was the semi-open flask method. It has been found that this method of detection is not as accurate as the Oxygen bomb combustion test methods and there are discussions to consider the inclusion of the use of the Oxygen bomb test method for laminates in IPC 4101 standard [8].

For the definition of halogen-free soldering materials, the JEITA ET-7304 standard [5] discussed whether the value of 900ppm should be used for both Chlorine and Bromine as is used for copper clad PCB laminate materials or if the 1000ppm limit mentioned in the European Union RoHS legislation for the two brominated flame retardants PBDE (Polybrominated Diphenyl Ethers) and PBB (Polybrominated Biphenyls) should be used. The JEITA ET-7034 standards group decided that a difference of 100ppm was not significant either technically or environmentally, so the 1000ppm limit should be adopted for Bromide and Chloride. The committee who wrote the JEITA ET-7304 standard [5] are alsoo looking to add Iodine (I) into their standard in addition to Chlorine, Bromine and Fluorine [10].

For IPC J-STD-004 standard [4], when quantitative requirements were placed on halide content, a product was deemed halide-free if the halide content measured was less than 0.05wt% or 500ppm. The 500ppm definition most likely came from the typical detection limit for halides at that time and the fact that raw materials containing trace halide naturally, typically fell below this limit.

The reasons why the IEC 61249-2-21 [6], JEITA ET-7034 [5], and IPC J-STD-004 [4] standards were not in line with each other included different times of standard publication, different materials involved, and different reasons as to why the determinations were being run (I.e. environmental safety concerns versus determination of flux activity level).

Halogen testing data

In order to understand halogen-free material testing detection methods, published data relating to halogen-free testing was reviewed. The JEITA ET-7304 standard [5] has data which included:

- Ion Chromatography testing of raw flux (unsoldered) versus flux residue(reflowed)
- Preparation using three combustion methods (quartz tube, oxygen flask, and oxygen bomb) at various temperatures and times

Ion Chromatography Only, Raw Flux versus Flux Residue Testing: The JEITA ET-7304 standard [5] study compared raw flux with reflowed flux residue. Three samples were tested with five replicates each. Based on the information provided, it was assumed that the samples were either simply diluted versus reflowed and diluted and the chloride concentration was determined via ion chromatography. The samples were not prepared using an oxygen bomb combustion method. The analysis showed that the chloride concentration of the reflowed samples was less than that of the raw flux. Data is presented in Table 4.

Table 4: Cl^- concentration measured on raw flux and reflowed flux residue using Ion Chromatography only (not Oxygen bomb combustion then Ion Chromatography) [5]

Sample No.		**1st**	**2nd**	**3rd**	**4th**	**5th**	**Average**	**%RD**
Test 1	-	13.1	12.7	12.4	11.3	11.3	12.2	6.6
Test 2	-	273	273	270	268	274	272	1.1
Test 3	-	1170	1190	1170	1200	1170	1180	1.4
Test 1	Residue after reflow	16.6	11.7	13.9	15.0	16.6	14.8	13.9
Test 2	Residue after reflow	44.8	33.9	32.6	34.2	32.7	35.6	14.5
Test 3	Residue after reflow	78.1	73.2	78.2	79.0	80.4	77.8	3.5

Various paste and flux suppliers have completed specific analyses to try and address concerns that they have with halogen determination. There is still some debate as to whether the worst case ppm halogen in the unreflowed sample should be reported or that of the flux after reflow should be used. The after reflow value more closely describes the amount of halogen that would be present on a soldered assembly.

Comparison of Different Combustion Methods: Another study that was performed which indicated in the JEITA ET-7304 standard [5] was a comparison of three common combustion methods, quartz tube, open flask and oxygen bomb with varying combustion temperatures and times. The data presented was assumed to be performed in a single laboratory. The sample tested was a soldering flux. A statistical analysis of the data showed that 95% of the Cl results, regardless of combustion method chosen fell in the range of 340ppm $\pm$ 22ppm. The Br results showed a slightly larger range at a 95% confidence interval (307ppm $\pm$ 39ppm). The oxygen bomb combustion method had the tightest range of results, as shown in Tables 5 and 6, so was the most repeatable of the test methods evaluated from the study.

Table 5: A comparison of three common combustion methods using various combustion temperatures and times on the measured Cl and Br values for soldering flux[5].

Number	Combustion Method	Amount of sample mg	Combustion temperature °C	Combustion time S	Conditions	Cl (mg/kg = mass ppm)	Br (mg/kg = mass ppm)
1	Quartz tube	5	1000	300	Combustion tube 1	333	301
2	Quartz tube	10	900	300	Combustion tube 2	327	295
3	Quartz tube	10	1000	120	Combustion tube 3	355	335
4	Quartz tube	10	1000	300	Combustion tube 4	345	322
5	Quartz tube	10	1000	600	Combustion tube 5	355	341
6	Quartz tube	10	1100	300	Combustion tube 6	332	305
7	Quartz tube	20	1000	300	Combustion tube 7	348	329
8	Oxygen flask	10	No Setting	Time allowed to stand: 20mins	Flask 1	347	295
9	Oxygen flask	20		Time allowed to stand: 20mins	Flask 2	351	275
10	Oxygen flask	40		Time allowed to stand: 20mins	Flask 3	334	305
11	Oxygen bomb	100	No Setting	Time allowed to stand: 20mins	Bomb 1	320	283
12	Oxygen bomb	200		Time allowed to stand: 20mins	Bomb 2	342	305
13	Oxygen bomb	400		Time allowed to stand: 20mins	Bomb 3	334	306

Table 6: Average of the test result analysis values showing better repeatability for the oxygen bomb versus the quartz tube or oxygen flask test methods [5]

Combustion method	Average or Standard Deviation	Cl (mg/kg = ppm)	Br (mg/kg = ppm)
Quartz tube	Average	344.4	317.7
Oxygen flask	Average	335.0	286.0
Oxygen bomb	Average	338.0	305.5
Quartz tube	Standard deviation	11.1	18.8
Oxygen flask	Standard deviation	15.5	11.8
Oxygen bomb	Standard deviation	5.7	0.7

As the JEITA test standard results [5] were from a single laboratory, one of the major points of concern for those who are required to report halogen content would be the potential lack of repeatability between laboratories reportedly using the same test methodology. Toleno et al. [19] reported findings of their lab-to-lab comparative analysis. Based on the adhesive material tested, halogens were not intentionally added, but it was known that there are halogens naturally present in the material. The samples of the same lot batch of material were sent to three different labs for analysis to determine the amount of halogens present. As can be seen in Table 7, two laboratories using the same method obtained very different results, whereas two laboratories using two different methods obtained results within experimental error of one another. Therefore, not only is the test method important, but also the sample preparation and halide ion detection methodology used.

Table 7: Halide testing of an adhesive material from three test laboratories showing differences in test results[19].

	Method Utilized	Chlorine (ppm)	Bromine (ppm)	Fluorine (ppm)
Lab 1	EN14582 (Oxygen bomb) [16]	ND	ND	ND
Lab 2	EN14582 (Oxygen bomb) [16]	748	ND	2010
Lab 3	IEC612249-2-21 (Combustion flask) [6]	606	ND	1460

In another study by Seelig et al. [20] data was presented from a global round robin study of six laboratories using the EN 14582 [16] oxygen bomb combustion test method. A paste was prepared with 13,000ppm bromine (NC-A sample) and a control paste prepared with 0ppm bromine (NC-B sample). The pastes were oxygen bomb combusted and analyzed via Ion Chromatography.

Comparative data from the six laboratories is shown in Table 8. Laboratory 3 data shows a variation in reported Bromine value for the NC-A paste sample compared with the other five laboratory results. In Table 9, the results for Laboratory 3 were omitted showing a relatively close set of Bromine data results for NC-A sample paste for the five laboratories.

These findings are very useful, but a study of results for solder pastes that were closer to the halide-free pass/fail limit of 900ppm Br and 900ppm Cl would be more beneficial in determining the probability of false failures being reported. It would also be beneficial to know the accuracy limit, reproducibility (inter-laboratory and laboratory-to-laboratory) and uncertainty limits surrounding the acceptance levels of 900ppm Br and 900ppm Cl and total Br and Cl of 1500ppm.

Table 8: Solder paste bromine test data from six different test laboratories using the EN 14582 [16] oxygen bomb combustion test method for two no-clean solder pastes [20].

	NC-A Sample (13,000ppm Bromine)	**NC-B Sample (0ppm Bromine)**
Lab 1	11,700	0
Lab 2	10,906	0
Lab 3	7,627	73
Lab 4	12,700	0
Lab 5	10,000	0
Lab 6	10,993	0
Mean	10,654	12
Standard Deviation	1,735	30

Table 9: Solder paste bromine test data from six different test laboratories using the EN 14582 [16] oxygen bomb combustion test method for two no-clean solder paste with the outlier Laboratory 3 test data removed [20].

	NC-A Sample (13,000ppm Bromine)	**NC-B Sample (0ppm Bromine)**
Lab 1	11,700	0
Lab 2	10,906	0
Lab 4	12,700	0
Lab 5	10,000	0
Lab 6	10,993	0
Mean (Lab 3 removed)	11,260	0
Standard Deviation (Lab 3 removed)	1,006	0

Based on this data review, an industry-wide gage repeatability and reproducibility study is needed prior to establishing preferred halide test methodology and halogen-free pass/fail test limits.

Conclusions

In terms of trends for halogen-free definitions and standards, most of the standards for components, boards and materials use either 900ppm or 1000ppm Br or Cl as the definition for halogen-free. Many OEMs use the 900ppm Br, 900 ppm Cl and 1500ppm total Br + Cl criteria in specifying halogen-free products. This is close to the restriction requirements for substances such as PBDE (Polybrominated Diphenyl Ethers) and PBB (Polybrominated Biphenyls) and lead mentioned in the European Union RoHS legislation which indicates less than 1000 ppm.

The differences between halogen-free definitions have varied based on different dates of standard publication from around the world as well as different amounts of data available in the determination of halogen-free. As the halogen-free definitions varied, the test methods by which to measure these halogens have also varied. There has been a movement to use Oxygen bomb combustion testing followed by Ion Chromatography analysis. Based on the data reviewed, there have been variations seen in test results for halogens in soldering materials based on laboratory to laboratory test differences.

Future Work

Future work would include conducting round robin testing to address inter-laboratory test variation. Testing would take place using raw and reflowed flux samples. The samples would be prepared for analysis using the EN14582 oxygen bomb test method [15] as this would appear to be the most repeatable. The proposed round robin testing would include samples which were halogen-free as well as samples containing 900ppm Chloride and 900ppm Bromide. At least one of the halogen containing compounds could be run multiple times at each laboratory over several days to determine test method reproducibility. The main focus of this study would be to determine the source of any inter-laboratory variability and how to resolve these discrepancies.

As already indicated, work should be done to standardize the halogen-free definitions between IEC, JEITA and IPC standards. Also, the determination of halogen content using the oxygen bomb combustion test method followed by ion chromatography testing on different soldering, board and component materials would be of benefit.

Acknowledgements

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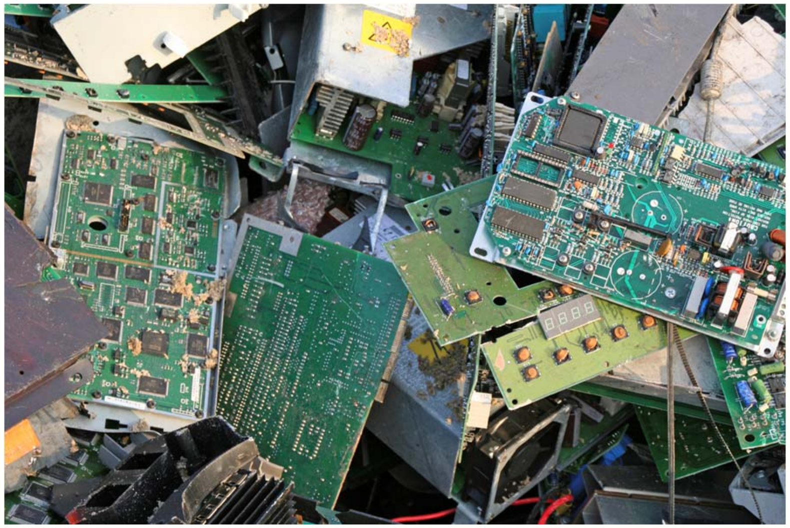
Why the Push for Halogen-Free Electronics?

- Legislation from Various Countries
  - Dangerous recycling practices (burning of boards with dioxins emitted)
  - Lessen potential environmental effects



Possible Sources of Halogens in Electronics

- Plastics for Cables and Housings
- Board Laminate Materials
- Components
- Soldering Fluxes and Pastes
- Underfills, Surface Mount Adhesives, Conformal Coatings, and other adhesives

Halogens in Soldering Materials

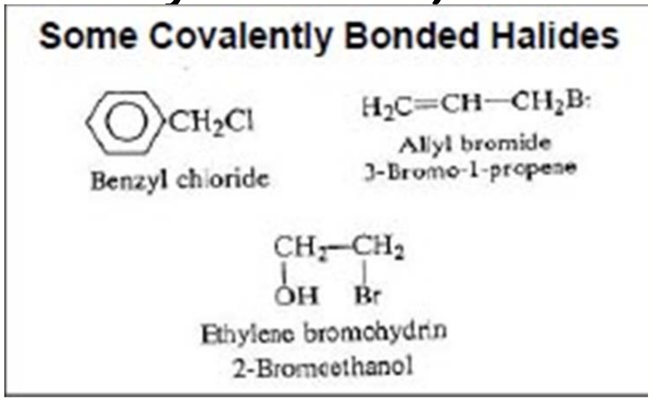
- Why are Halogens Used?
  - Halogenated compounds in solder pastes and fluxes are used as activators that remove oxides to promote solder wetting.

Halogen-free and Halide-free terms

- The terms Halogen and Halide have caused confusion in the electronics industry
- Halogen refers to all halogen family elements (Cl, Br, F, I, As) and halogen compounds including those which are present in nature.
- Halide is defined as halide ion or halide salt compound having an ionic character (e.g. Cl^-, Br^-, F^-).

Halogen and Halide terms (cont.)

- Covalently bonded halogens do not disassociate into ionic charged species, so the chloride, bromide and fluoride are still attached (covalently bound) to other species (typically organic).



- Ionically bonded halogens (Halides) do disassociate into negatively charged halide ions (Cl^-, Br^-, F^-, etc.) and positively charged species (H^+, Na^+ etc.).

Halogen-free definitions and standards (PCBs)

- Standards for PCB Laminates include IEC 61249-2-21, Japan JPCA-ES-01 and IPC-4101.
- All three standards indicate:
  - less than 900ppm Cl (<0.09 wt%)
  - less than 900ppm Br (<0.09 wt%)
  - less than 1500ppm total Cl + Br (<0.15 wt% Cl + Br)

Low Halogen definitions and standards (Components)

JEDEC JEP709 standard low halogen definition:

- less than 1000ppm Br (from BFR[Brominated flame retardants] sources)
- less than 1000ppm Cl (from CFR[Chlorinated flame retardants], PVC[Polyvinyl Chloride] and PVC co-polymers sources)

- For the PCB laminates used in components the Cl and Br limits follow IEC 61249-2 standard (<900 ppm Br, <900ppm Cl, <1500ppm Br +Cl).

Halogen-free definitions and standards (Soldering Materials) [JEITA ET-7034]

- JEITA ET-7034 standard states:
  - less than 1000ppm Cl
  - less than 1000ppm Br
  - less than 1000ppm F.

Updated draft of this Japan standard, JEITA ET-7034A, also includes Iodine (I) with:

– less than 1000ppm I.

Halide-free definitions and standards (Soldering Materials) [IPC J-STD-004]

- IPC J-STD-004 standard does not currently have a requirement for halogen content limit.
- IPC J-STD-004 standard for a halide-free soldering material is:
  - less than 500 ppm total halide.

An amendment to J-STD-004 currently being discussed does include optional testing for halogen content for:

- Less than 900ppm Cl
- Less than 900ppm Br
- Less than 1500ppm total Cl + Br.

Test Methods used to determine Halide Content

- Qualitative halide tests
  - Silver Chromate Paper Test for Bromide and Chloride
  - Fluoride Spot Test for Fluoride
- Quantitative halide tests
  - Titration Method for Chloride, Bromide and Fluoride
  - Ion Chromatography for Chloride, Bromide, Fluoride and Iodide

Titration Method for Chloride, Bromide and Fluoride

- Quantitative test assessing chloride and bromide and fluoride present in flux expressed as Chloride equivalents.
- Flux or flux extract titrated to its endpoint using appropriate test methods.
- Test methods are improvement over Silver Chromate paper and Fluoride spot methods as they provide a value for halide present.
- Test method detects only halides and not total halogens unless an oxygen combustion method is used to prepare sample prior to titration.
- Wide variety of organic chemicals can falsely be identified as halides.

Ion Chromatography for Chloride, Bromide, Fluoride and Iodide

- Quantitative test method for Chloride, Bromide, Fluoride and Iodide to identify total quantity of halides present in a flux.
- Only identifies ionic halide species and the covalently bonded halogen are not detected unless sample is prepared using oxygen combustion method prior to Ion Chromatography testing.
- Some chemicals which are

non-halides can being misidentified

as a halide during the test.

Preparation Techniques to determine Halogen Content

- In order to detect halogens, Oxygen Bomb Combustion is used as a preparation technique to dissociate all the halogens into halides

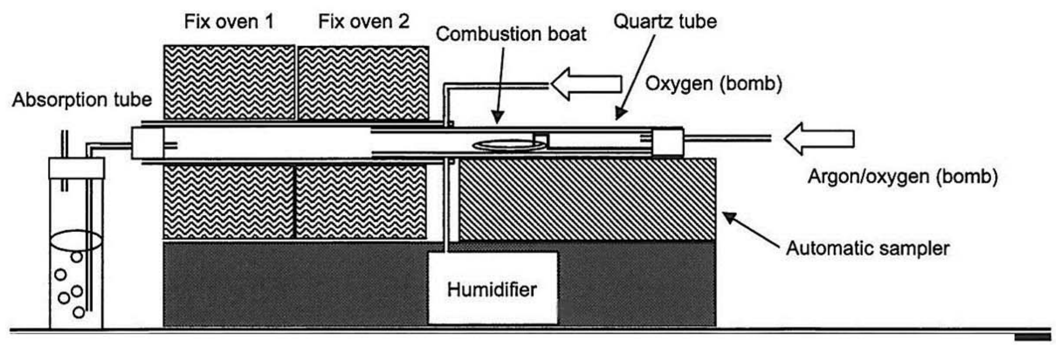
- After Oxygen Bomb Combustion, Titration or Ion Chromatography can be used

Oxygen Bomb Combustion Testing followed by Ion Chromatography testing to determine Halogen content

- This test growing in popularity in electronics industry.
- Involves subjecting sample flux or solder paste to oxygen bomb combustion where all organic materials are burnt off at very high temperature.
- Process breaks covalent bonds for all halogens with remaining ash consisting of ionic halides and other inorganic materials.
- Dissolved ash is then run through ion chromatography to determine total halide content.
- EN14582 method is most common standard in use

Three Types of Oxygen Combustion Preparation Technique

- Quartz tube



- Oxygen or combustion flask

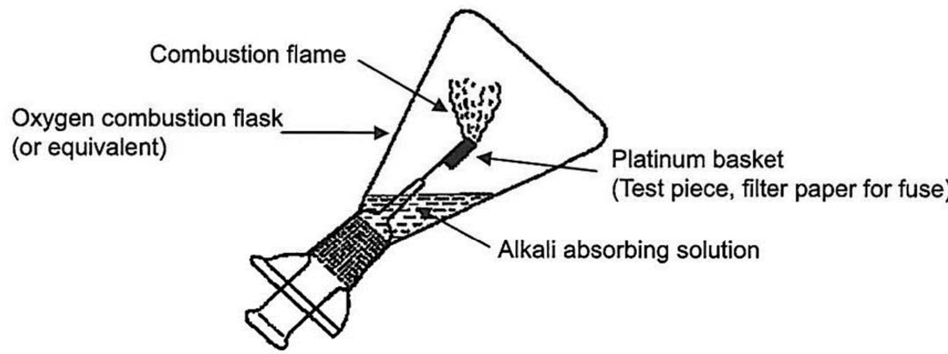


Figure A.3 – Example of sample combustion

- Oxygen bomb

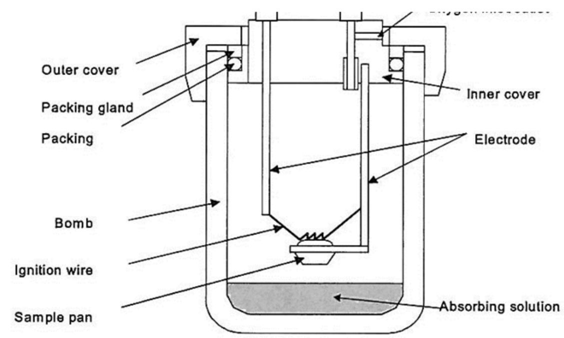


Figure C.1 – The oxygen bomb equipment

Ref: JEITA ET-7034 standard

Analysis of test result data for oxygen bomb versus quartz tube or oxygen/combustion flask test methods[JEITA ET-7034 standard]

Combustion method	Average or Standard Deviation	Cl (mg/kg = ppm)	Br (mg/kg = ppm)
Quartz tube	Average	344.4	317.7
Oxygen flask	Average	335.0	286.0
Oxygen bomb	Average	338.0	305.5
Quartz tube	Standard deviation	11.1	18.8
Oxygen flask	Standard deviation	15.5	11.8
Oxygen bomb	Standard deviation	5.7	0.7

Repeatibility of Oxygen Bomb test method is better than other methods evaluated (Oxygen/Combustion flask and Quartz tube)

Halogen content variation based on different reporting values for solder paste, flux and reflowed flux residue using Oxygen bomb

Halogen content variation based on reporting			
	Mass (g)	Mass of Halogen (g)	Halogen Content (in ppm)
Solder Paste (100g flux and 900g solder metal)	1000	0.045	45
Flux (base material)	100	0.045	450
Flux Residue (50% of 100g) (as 50% of the flux volatilized during reflow)	50	0.045	900

Solder sample type used will give a different reporting value which can lead to misinterpretation of halogen content

Bromine Content Analysis with Oxygen Bomb Combustion with Ion Chromatography for raw flux (top) versus reflowed solder paste (bottom)- Jensen et al. (Indium)

Anions by Ion Chromatography	Result/ mg/kg	Reporting Limit/ mg/kg	Weight/ g
Bromide	1210	72	0.000607
Chloride	<162	162	<0.000081
Fluoride	<72	72	<0.000036
Iodide	<700	700	<0.00035

Anions by Ion Chromatography	Result/ mg/kg	Reporting Limit/ mg/kg	Weight/ g
Bromide	2110	55.7	0.00105
Chloride	<125	125	<0.0000625
Fluoride	<55.7	55.7	<0.0000278
Iodide	<700	700	<0.00035

Important to understand that there will likely be a higher ppm level in reflowed flux residue versus raw flux due to decreased mass of tested sample used for flux residue

Halogen testing of an adhesive material with an amount of naturally occurring Cl and F from 3 test labs showing differences in test results measured by Ion Chromatography (Toleno et al.- Henkel)

	Method Utilized	Chlorine (ppm)	Bromine (ppm)	Fluorine (ppm)
Lab 1	EN14582 (Oxygen bomb) [16]	ND	ND	ND
Lab 2	EN14582 (Oxygen bomb) [16]	748	ND	2010
Lab 3	IEC612249-2-21 (Combustion flask) [6]	606	ND	1460

Lab. 1 test results are not consistent with Lab. 2 and 3
Lab. 1 used same test method as Lab. 2 (Oxygen Bomb sample preparation) and a different method than Lab. 3 (Combustion/Oxygen flask same preparation)

Solder paste bromine test data from six test labs. using oxygen bomb combustion with Ion Chromatography for two no-clean solder pastes [Seelig et al. - AIM].

	NC-A Sample (13,000ppm Bromine)	NC-B Sample (0ppm Bromine)
Lab 1	11,700	0
Lab 2	10,906	0
Lab 3	7,627	73
Lab 4	12,700	0
Lab 5	10,000	0
Lab 6	10,993	0
Mean	10,654	12
Standard Deviation	1,735	30

Lab. 3 test results are not consistent with other labs

Used EN14582 standard.

Solder paste bromine test data from six test labs. using oxygen bomb combustion with Ion Chromatography for two no-clean solder pastes (Lab. 3 data removed) [Seelig et al. - AIM].

	NC-A Sample (13,000ppm Bromine)	NC-B Sample (0ppm Bromine)
Lab 1	11,700	0
Lab 2	10,906	0
Lab 4	12,700	0
Lab 5	10,000	0
Lab 6	10,993	0
Mean (Lab 3 removed)	11,260	0
Standard Deviation (Lab 3 removed)	1,006	0

Conclusions

- For halogen-free definitions and standards, most of the standards for components, boards and materials use either 900ppm or 1000ppm Br or Cl as the definition for halogen-free.
- Many OEMs use the 900ppm Br, 900 ppm Cl and 1500ppm total Br + Cl criteria in specifying halogen-free products.
- This is close to restriction requirements for PBDE (Polybrominated Diphenyl Ethers), PBB (Polybrominated Biphenyls) and lead mentioned in EU RoHS legislation of less than 1000 ppm.

Conclusions (Cont.)

- Halogen-free definitions have varied based on different dates of standard publication and different amounts of data available to determine halogen-free.
- As halogen-free definitions varied, the test methods to measure these halogens have also varied.
- Movement to use Oxygen bomb combustion testing followed by Ion Chromatography analysis based on improved results versus other test methods.
- Based on data reviewed, there are still variations seen in test results for halogens in soldering materials based on lab. to lab. test differences using Oxygen bomb combustion followed by Ion Chromatography.

Future Work

- Need to conduct round robin testing to address inter-laboratory test variation using Oxygen bomb followed by Ion Chromatography.
- Testing would need to take place using raw and reflowed flux samples prepared for analysis using the EN14582 oxygen bomb test method.
- Proposed round robin testing would include samples which were halogen-free as well as samples containing 900ppm Chloride and 900ppm Bromide.
- At least one of the halogen containing compounds could be run multiple times at each lab. over several days to determine test method reproducibility.

Future Work (Cont.)

- The main focus of this study would be to determine the source of any inter-laboratory variability and how to resolve these discrepancies.
- As already indicated, work should be done to standardize the halogen-free definitions between IEC, JEITA and IPC standards.
- Also, the determination of halogen content using the oxygen bomb combustion test method followed by ion chromatography testing on different soldering, board and component materials would be of benefit.

Acknowledgements

- The authors would like to thank the various persons involved in developing the data and standards discussed in this paper.

- Appendix

Silver Chromate Paper Test

- Qualitative test with sample of flux applied to Silver Chromate Paper and allowed to remain on it for 1 minute.
- If the paper changes color then presence of Chloride or Bromide.
- Test only identifies the halogen in the ionic form (halide) and prone to false positives from chemicals such as amines, cyanides, and isocyanates.
- Also provides no indication as to the total halogen present.

Fluoride Spot Test

- Qualitative test to determine the presenceof fluoride(s) in soldering flux by visual examination after placement of a drop of flux in zirconium - alizarin purple lake.
- Method only detects the presence of the fluoride ion.