Round Robin Testing in Support of IPC J-STD-709
Combustion Sample Preparation Methods for Ion Chromatography Analysis of Br and Cl

Javier A. Falcon[†], Walter Flom[†], Thomas Newton[‡]
[†]Intel Corporation, Chandler, Arizona
[‡]IPC, Chicago, Illinois

Abstract
This paper will present the results of a round robin study of sample combustion followed by ion chromatography (CIC) to measure the concentration of bromine and chlorine in electronic materials. The study involved ten volunteer testing labs, each analyzing four donated polymeric samples. Its primary objective was to gauge the within-lab and lab-to-lab reproducibility of the IC results obtained using the oxygen bomb and furnace sample combustion methods. The accuracy of sample combustion method was also investigated. Statistical analysis shows the within-lab reproducibility was better for the furnace method while the lab-to-lab reproducibility was better for the oxygen bomb method. In addition, both methods showed good agreement in the results of samples with concentrations around the 1000 ppm threshold. However, neither method proved accurate for very high concentrations of bromine and chlorine. These findings led to a group of recommendation for the analysis of Br and Cl using CIC.

Introduction
In early 2008, during the development of J-STD-709 "Limits for Bromine and Chlorine in Flame Retardants and Polyvinyl Chloride in Low-Halogen Electronic Products" IPC began investigating possible analytical methods for the measurement of bromine and chlorine in electronic products by kicking off a small informal working group tasked with looking at available methods.

This working group came to the conclusion that the best option for measuring total chlorine and bromine in the wide variety of materials present in electronic products would be sample combustion followed by ion chromatography (IC). Specifically, the group decided to focus on the British Standard BS EN 14582:2007 published by BSI[1]. This method is similar to the U.S. EPA method 5050[2] and together these two methods form the basis of most oxygen bomb combustion sample preparation methods available.

Apart from the oxygen bomb combustion method, group discussions also highlighted interest in the furnace combustion method. Although this method has been available for some time[3] it has recently generated renewed interest with the release of a new instrument and a new ASTM standard[4].

With these interests in mind the group decided to perform a round robin analysis with volunteer testing organizations and sample donors. The main focus of the round robin was to determine the within and across lab reproducibility of the oxygen bomb combustion method for the donated samples. If sufficient testing organizations volunteered, a comparison with the furnace combustion method would also be conducted.

In the end this round robin consisted of 10 different labs analyzing four different samples. Six labs prepared samples using the oxygen bomb combustion, two labs prepared samples using the furnace combustion method and two labs analyzed the samples using both methods. The focus of the statistical analysis remained on the reproducibility within and across labs.

Data Collection and Processing
Test Design
This round robin consisted of 10 different labs spread across various geographies analyzing four different samples donated by two organizations. Labs were requested to combust and analyze each sample in triplicate. Six labs prepared samples for IC analysis using the oxygen bomb combustion method, two labs prepared samples using the furnace combustion method and two labs used both methods of sample preparation.

Volunteer Testing Organizations
Four different organizations volunteered to participate in the round robin testing and one was sponsored.

The oxygen bomb combustion method was performed by:
- Innovatech Labs

- Environmental Monitoring & Technologies, Inc.
- SGS Group, Consumer Testing Services

The furnace combustion method was performed by:
- COSA Instrument Corp.
- SGS Group, Consumer Testing Services
- Sumika Chemical Analysis Service, Ltd. – Sponsored by DIC Corporation

Note: some organizations volunteered multiple labs.

Sample Preparation and Test Methods
For sample preparation volunteer labs agreed to use either the oxygen bomb or furnace combustion methods (two labs agreed to analyze samples using both methods) following BS EN 14582:2007 or ASTM D7359-08. Labs were not required to report the intricate details of sample preparation (eg. sample grinding details) other than which combustion method was used.

Similarly, for the analysis of the combustate, volunteer labs agreed to use ion chromatography as the analysis method but there was no requirement to report calibration check runs, blank checks or similar details.

The test methods used in this round robin measure the total concentration of Br and Cl. These methods cannot differentiate between covalently bound or ionic Br and Cl.

Donated Samples
Samples B and C are Polyphenylene Sulfide (PPS) donated by DIC Corporation of Japan. PPS is an engineering thermoplastic commonly used in connectors and housings of electronic devices. PPS does not have brominated flame retardants (BFRs) or chlorinated flame retardants (CFRs) added to it. The Br and Cl content is residual material used during polymer synthesis.

Samples A and D are epoxy resin materials whose donor chose not to be identified. Both materials use the same epoxy resin base with the major difference being that Sample D contains intentionally added BFRs. Sample D is used in electrical laminate applications and contains 20% by weight Br (on a solid resin basis). Because of the known concentration of Br, Sample D was selected as a 'standard' that could be used for accuracy analysis. Table 1 shows the details of each sample along with the approximate concentration of Br and Cl in each. The written instructions sent to each lab along with the samples are provided in **Appendix A.**

Table 1. Overview of donated samples.

Label	Name	Br (ppm)	Cl (ppm)
A	Epoxy Resin	NA	NA
B	PPS	NA	~1,500
C	Halogen Free PPS	NA	~700
D	Brominated Epoxy Resin	200,000	~1,300

Data Processing
Individual labs submitted their analysis results directly to us via email using a previously provided Excel data sheet. Labs were assigned unique identification numbers to prevent tracing of results to individual labs. The raw data reported by each lab along with the reporting Excel data sheet are provided in **Appendix B.**

Data Review and Outlier Detection
The results for each sample were plotted against analysis lab and sample preparation method to check for the presence of outliers or inconsistencies. Figures 1 & 2 show the plots for Br and Cl respectively. The data is also provided in table format in **Appendix C.**

A review of the graphs in Figure 1 reveal compelling evidence for the removal of certain data points prior to analysis:

- Samples B and C contained relatively low amounts of Br. In fact, for these two samples the majority of labs did not report actual values for the Br concentration but instead reported less than (<) values.
- Lab 8 chose not to analyze Sample D with the furnace combustion sample preparation method due to it's high Br concentration.
- It can be argued that the results from Lab 2 for Samples A and D show an unusual amount of within-lab variation. These possible outliers cannot be correlated to order of sample run. In addition, Lab 2 did not provide comments in their analysis report indicating any unusual occurrences during the analysis.

A similar review of the graphs in Figure 2 lead to the following findings:
- As stated above, Lab 8 chose not to analyze Sample D with the furnace combustion sample preparation method.
- Once again the results from Lab 2 appear to show an unusual amount of within-lab variation, this time for Samples B and D. As before, the possible outliers cannot be correlated to order of sample run. Again, Lab 2 did not provide comments in their analysis report indicating any unusual occurrences during the analysis. In addition, the results for Samples A and C appear to be outside the range of the other labs.

Another point to note is that both Lab 4 and Lab 9 reported the exact same value for each run (meaning 0 standard deviation for the triplicate analysis) of a few samples. Specifically, Lab 4 reported the exact same value for the Cl concentration of Samples B and D. Lab 9 reported the exact same value for the Br concentration of Sample D and the Cl concentrations of Samples A, B and D. Although this is unusual, we decided to retain these points in the analysis.

Based on the findings above, Samples B and C were removed from the Br analysis data set. In addition, the blank values from Lab 8 were excluded from the Sample D analysis. Finally, due to the questions around the data reported, Lab 2 was completely removed from the analysis data set.

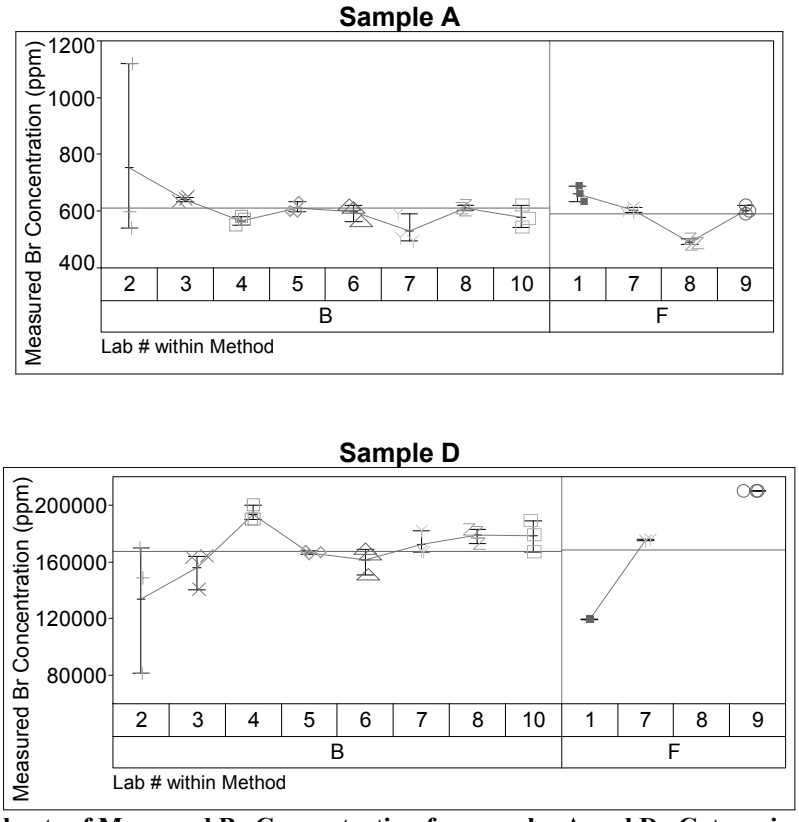


Figure 1. Variability charts of Measured Br Concentration for samples A and D. Categories 1 through 10 indicate the individual lab number. Categories B & F indicate Bomb Combustion and Furnace Combustion respectively. The solid line in all graphs indicates the grand mean across all labs for each method. NOTE: The majority of labs reported either ND (not detected) or less than (<) values for the concentration of Br in samples B & C. Therefore results were not plotted for these samples.

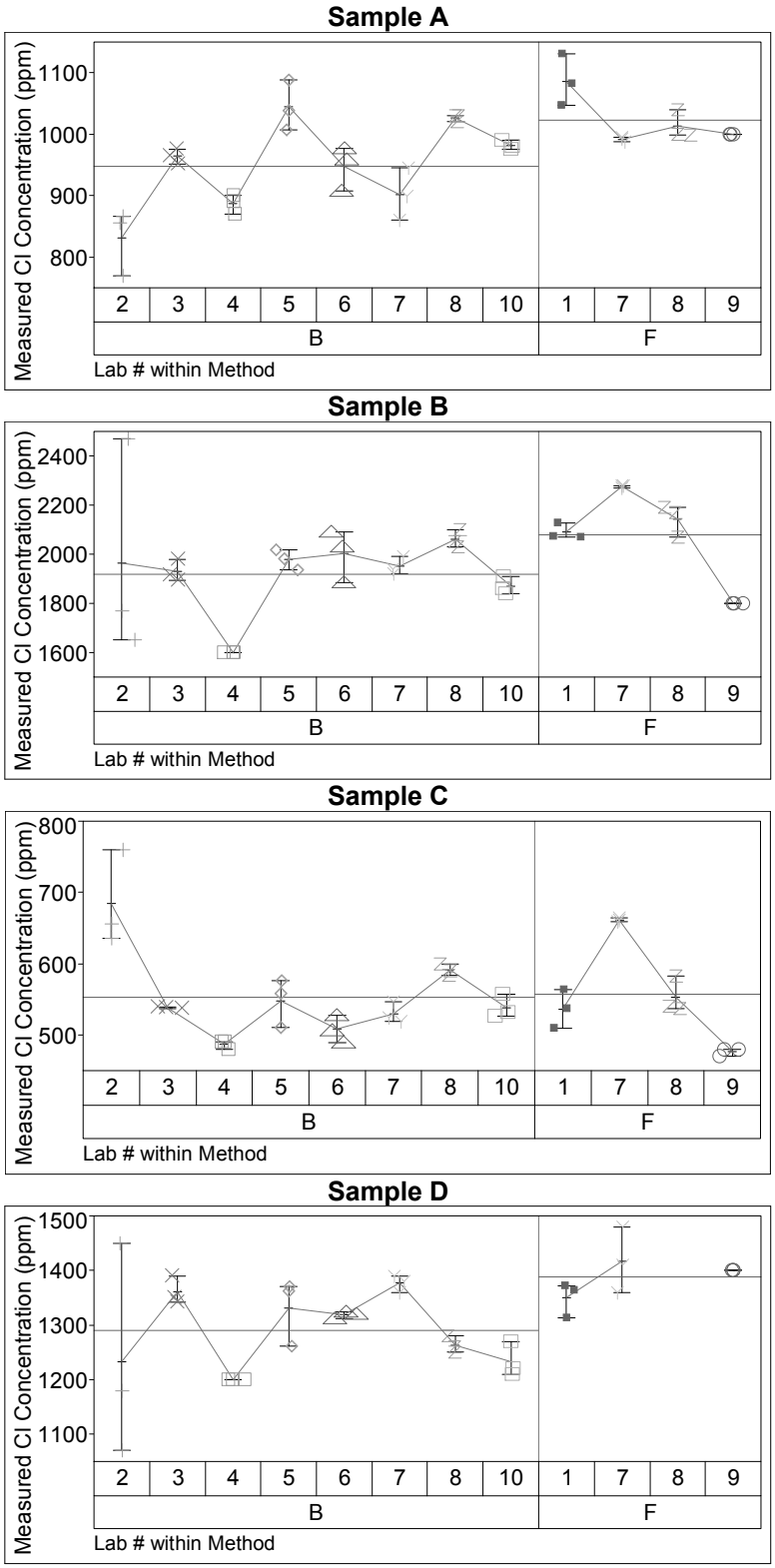


Figure 2. Variability charts of Measured Cl Concentration (ppm) for Samples A through D. Categories 1 through 10 indicate the individual lab number. Categories B & F indicate Bomb Combustion and Furnace Combustion respectively. The solid line in all graphs indicates the grand mean across all labs for each method.

Statistical Analysis Results
All statistical analysis was performed using JMP® 7.0.1 software.

All Labs Accuracy Analysis for Sample D
The results from each method across all labs were analyzed in order to asses at an aggregate level the accuracy of the concentration of Br in Sample D. Sample D was prepared specifically for this purpose with a known Br concentration of 200,000 ppm or 20 wt%.

Table 2 shows various statistics calculated for both methods such as mean, standard deviation and 95% confidence interval. The bias values shown on Table 2 were calculated using 200,000 ppm as the 'standard' value.

Table 2. Statistics calculated for the Br concentration of Sample D for each method across all labs.

Statistic	Oxygen Combustion	Furnace Combustion
Mean	172,381	168,255
Std Dev	13,962	39,576
Std Err Mean	3,046	13,192
upper 95% Mean	178,737	198,676
lower 95% Mean	166,026	137,834
N	21	9
Bias	-27,618	-31,745

If the results are grouped for all labs, neither method proved to be statistically accurate for Sample D. This result is likely caused by the relatively high concentration of Br found in the sample. In general, very high concentrations of analyte normally require significant dilution before IC analysis in order to fall within the created calibration curve. Increasing dilution can easily impact the accuracy of the finals results. In our study both Labs 3 and 9 reported a significant increase of final dilution volume for Sample D when compared to the other samples.

In addition, many manufacturers of combustion equipment warn not to combust samples with high halogen concentration[5]. As stated previously, Lab 8 chose not to analyze Sample D for this reason. Similarly, Lab 3 commented in their results "Please note that the manufacturer of our bombing vessel recommends that the halide concentrations should not exceed ca. 1000 ppm."

Although not directly related to accuracy, it is possible to make a final point regarding the general agreement of the reported values for all samples across both methods.

Lab 7 Accuracy Analysis for Sample D
Having one lab prepare Sample D with both methods provided an opportunity to compare the accuracy of each method within one entity.

Table 3. Statistics calculated for the Br concentration of sample D for each method performed by lab 7.

Statistic	Oxygen Combustion	Furnace Combustion
Mean	172,333	175,333
Std Dev	8,386	577
Std Err Mean	4,891	333
upper 95% Mean	193,166	176,767
lower 95% Mean	151,500	173,899
N	3	3
Bias	-27,667	-24,667

Table 3 shows various statistics calculated for both methods including mean, standard deviation and 95% confidence interval. The bias values shown on Table 3 were calculated using 200,000 ppm as the 'standard' value.

The Lab 7 mean for both methods are very similar although the standard deviation for the furnace method is significantly lower compared to the oxygen combustion method.

The bias observed for both methods is similar to that seen in section 4.1.1. This corroborates the idea that both methods have difficulties accurately measuring relatively high concentration of Br.

Variance Component Analysis

Variance component analysis assesses the amount of variation in a dependent variable that is associated with one or more random-effects variables. Results are typically reported in a variance components table which shows the proportion of variance attributable to each random variable. In this round robin analysis the focus was on estimating the variance within each individual lab (eg. how reproducible the results are within each lab) and the variance between labs (eg. how reproducible results are across labs). For this analysis the data was grouped by sample and method and analyzed across and within labs.

Figure 3 shows the normalized variance components computed for each sample by method/element combination. Variance components were normalized by dividing by the grand mean of each sample and method. It can be seen in Figure 3 that the within-lab reproducibility is about the same or slightly better (lower % sigma) for the furnace combustion method for both Br and Cl across all samples. However, Figure 3 also shows that the lab-to-lab reproducibility is better for the oxygen bomb combustion method for both Br and Cl across most samples (only Cl samples A and D worse).

A specific example that clearly demonstrates these trends can be seen in Figure 1 - Sample D and in the standard deviations shown on Tables 2 and 3. For the furnace combustion method the reported values for each individual lab are closely clustered together with the largest within-lab range being approximately 1,000 ppm. However, the values across labs cover a range of approximately 90,000 ppm. For the oxygen bomb method the largest within-lab range is approximately 23,000 ppm while the largest lab-to-lab range (for the mean of each lab) is approximately 40,000 ppm.

As discussed in the accuracy section some of the trends observed in the results of Sample D could be due to the high concentration of Br. However similar trends can also be seen for the Br concentration of Sample A which contains a much lower concentration of Br. In addition, similar trends are observed in two of the four Cl measurements.

One final point can be made regarding the stability of the within-lab and lab-to-lab reproducibility for the oxygen bomb combustion method for both Br and Cl. Looking at Figure 3 it is easy to see that for both Br and Cl across all samples the within-lab and lab-to-lab reproducibility remain very tightly grouped for this method. The furnace combustion method shows a similar stability for the within-lab reproducibility but the lab-to-lab reproducibility clearly varies significantly for both Br and Cl depending on the samples.

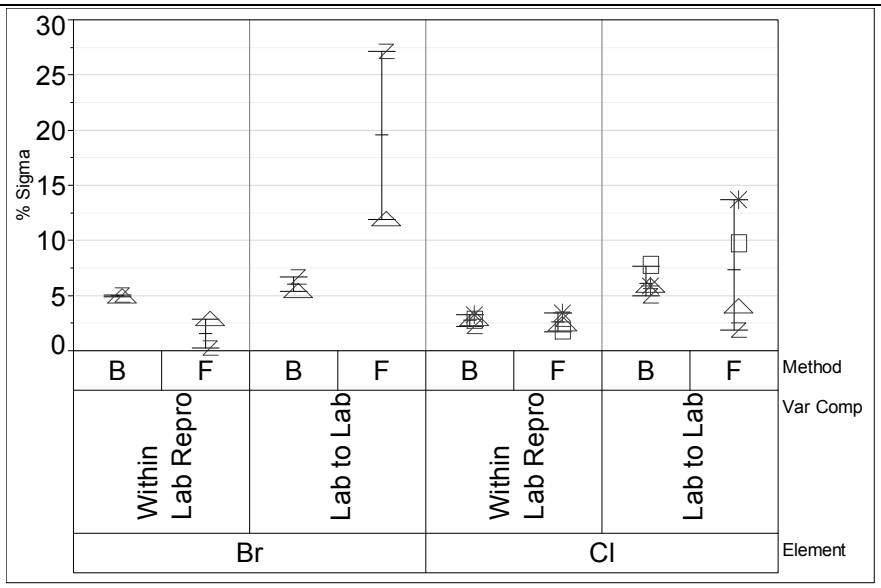


Figure 3. Normalized square root of variance components for within and across lab by element. Variance components were normalized by dividing by the grand mean of each sample & method combination. Sample A = Δ, Sample B = □, Sample C = *, Sample D = Z.

Conclusions and Recommendations

The general conclusions and recommendations reached from the statistical analysis of the reported data are given below.

- Grouping the data across all labs shows that neither method is statistically accurate for the measurement of Br concentration in sample D.
  - We recommend that neither method be used to measure the concentration of Br (and likely Cl as well) for levels above 10-15 wt%.

- With regards to the reproducibility of the results (for the samples analyzed) the furnace combustion method shows about the same or slightly less within-lab variation for Br and Cl concentrations across all samples. The oxygen bomb combustion method shows less lab-to-lab variation for Br and Cl concentration for most samples. Also, the within-lab and lab-to-lab reproducibility is quite stable for the oxygen bomb combustion method for both Br and Cl across all samples.
  - Based on these observations, and on the long standing track record of the oxygen bomb combustion method, we recommend that it be used as the standard test method for total Br and Cl.
  - The furnace combustion method does clearly offer significant advantages over the oxygen bomb combustion method. This is particularly true with respect to automation and control of the combustion process. Because of these advantages we also recommend an additional round robin effort by IPC in order to better understand this method and what it can offer.

- The concentrations of Br for sample A and of Cl for sample C are quite close for both methods.
  - This is a confirmation that both methods appear to have no issues measuring Br and Cl below the 1000 ppm threshold.
  - If the measurement of low levels of Br and Cl is a topic of interest we also recommend additional study into the limits of detection for each method by using samples with known low (100 ppm and below) concentrations.

References

1. British Standard Method BS EN 14582:2007, *Characterization of waste – Halogen and sulfur content – Oxygen combustion in closed systems and determination methods*.

2. U.S. EPA Method 5050, *Bomb Preparation Method for Solid Waste*.

3. Evans K.L and Moore C.B., *Anal. Chem*., 52 (1980) 1908.

4. ASTM Method D7359 – 08, *Standard Test Method for Fluorine, Chlorine and Sulfur in Aromatic Hydrocarbons and Their Mixtures by Oxidative Pyrohydrolytic Combustion followed by Ion Chromatography Detection (Combustion Ion Chromatography – CIC)*.

5. Parr Instrument Company sheet No. 205M, *Operating Instruction for 1108 Oxygen Combustion Bomb.*

Appendix A

A1 – Instructions provided to each lab with samples

Samples for IPC Round Robin Testing in Support of J-STD-709

This package contains the four samples to be analyzed for the current round robin test. Each package should contain four different materials labeled A through D (please see the image below).

We request that each laboratory conform to the following guidelines for sample handling, storage and analysis:

- Use your lab's standard material handling and storage procedures
    - Except for: each lab should retain enough as received resin sample to perform 2 additional combustions and IC analysis. Samples should be retained for 1 month.
- Use your lab's standard sample preparation procedures (eg grinding, sieving and combustion aid use). These details may be requested after results are provided.
- Samples should be combusted using either an O_2 combustion bomb or the furnace combustion method and analyzed by Ion Chromatography (IC). At all times follow your labs and the manufacturer's operations and safety procedures.
    - IC details (eg calibration curves) may be requested after results are provided.
- Report data using template found on page two of this document (this template is also provided in an electronic format).

NOTE: The four samples provided cover a very wide range of halogen concentrations. Some samples may contain high levels of Br and/or Cl (in excess of 10 weight %).

For questions or comments please contact:

Javier Falcon
Intel Corporation
Email: Javier.A.Falcon@Intel.com
Phone: 480-552-7911

Tom Newton
IPC
Email: ThomasNewton@ipc.org
Phone: 847-597-2849

SAMPLE A

	Lab Name & Location	Date of combustion : Date of IC analysis	Initial Sample Weight (mg)	Combustion Absorption Solution Volume (ml)	Final Dilution Sample Volume (ml)	Measured Br Concentration (ppm)	Measured Cl Concentration (ppm)
Run 1							
Run 2							
Run 3							

Comments:

SAMPLE B

	Lab Name & Location	Date of combustion : Date of IC analysis	Sample Weight (mg)	Combustion Absorption Solution Volume (ml)	Final Dilution Sample Volume (ml)	Measured Br Concentration (ppm)	Measured Cl Concentration (ppm)
Run 1							
Run 2							
Run 3							

Comments:

SAMPLE C

	Lab Name & Location	Date of combustion : Date of IC analysis	Sample Weight (mg)	Combustion Absorption Solution Volume (ml)	Final Dilution Sample Volume (ml)	Measured Br Concentration (ppm)	Measured Cl Concentration (ppm)
Run 1							
Run 2							
Run 3							

Comments:

SAMPLE D

	Lab Name & Location	Date of combustion : Date of IC analysis	Sample Weight (mg)	Combustion Absorption Solution Volume (ml)	Final Dilution Sample Volume (ml)	Measured Br Concentration (ppm)	Measured Cl Concentration (ppm)
Run 1							
Run 2							
Run 3							

Comments:

A2 – Data reporting template

Appendix B

B1 – Results reported for sample A

Lab #	Run	Method	Measured Br Concentration (ppm)	Measured Cl Concentration (ppm)
1	**1**	F	634	1047
1	**2**	F	660	1082
1	**3**	F	688	1130
3	**1**	B	641.48	975.77
3	**2**	B	634.01	951.37
3	**3**	B	648.33	964.96
2	**1**	B	599	856
2	**2**	B	1120	866
2	**3**	B	541	770
9	**1**	F	590	1000
9	**2**	F	600	1000
9	**3**	F	620	1000
7	**1**	B	507	860
7	**2**	B	495	899
7	**3**	B	591	945
7	**1**	F	604	995
7	**2**	F	596	993
7	**3**	F	612	987
5	**1**	B	600	1038
5	**2**	B	599	1007
5	**3**	B	634	1088
4	**1**	B	550	870
4	**2**	B	580	890
4	**3**	B	570	900
8	**1**	B	620	1020
8	**2**	B	611	1030
8	**3**	B	604	1030
8	**1**	F	482	999
8	**2**	F	487	1000
8	**3**	F	504	1040
6	**1**	B	620	958.8
6	**2**	B	563.5	976.8
6	**3**	B	611.4	908.1
10	**1**	B	620	980
10	**2**	B	542	990
10	**3**	B	573	975

B2 – Results reported for sample B

Lab #	Run	Method	Measured Br Concentration (ppm)	Measured Cl Concentration (ppm)
1	1	F	10.2	2128
1	2	F	10.8	2074
1	3	F	20.8	2070
3	1	B	ND	1978.59
3	2	B	ND	1913.88
3	3	B	ND	1894.41
2	1	B	38	1770
2	2	B	86.5	1650
2	3	B	40	2470
9	1	F	<10	1800
9	2	F	<10	1800
9	3	F	<10	1800
7	1	B	ND	1990
7	2	B	ND	1920
7	3	B	ND	1940
7	1	F	ND	2270
7	2	F	ND	2280
7	3	F	ND	2280
5	1	B	<50	1936
5	2	B	<50	1983
5	3	B	<50	2018
4	1	B	<50	1600
4	2	B	<50	1600
4	3	B	<50	1600
8	1	B	<50	2050
8	2	B	<50	2100
8	3	B	<50	2030
8	1	F	<50	2070
8	2	F	<50	2170
8	3	F	<50	2190
6	1	B	<50	1885
6	2	B	<50	2091
6	3	B	<50	2031.1
10	1	B	ND	1860
10	2	B	ND	1840
10	3	B	ND	1910

B3 – Results reported for sample C

Lab #	Run	Method	Measured Br Concentration (ppm)	Measured Cl Concentration (ppm)
1	1	F	ND	537
1	2	F	ND	509
1	3	F	ND	563
3	1	B	ND	537.16
3	2	B	ND	539.31
3	3	B	ND	537.60
2	1	B	32	656
2	2	B	18	636
2	3	B	<12.1	760
9	1	F	<10	480
9	2	F	<10	470
9	3	F	<10	480
7	1	B	ND	547
7	2	B	ND	519
7	3	B	ND	524
7	1	F	ND	664
7	2	F	ND	661
7	3	F	ND	659
5	1	B	<50	510
5	2	B	<50	576
5	3	B	<50	558
4	1	B	<50	490
4	2	B	<50	490
4	3	B	<50	480
8	1	B	<50	584
8	2	B	<50	590
8	3	B	<50	600
8	1	F	<50	540
8	2	F	<50	537
8	3	F	<50	583
6	1	B	<50	506.6
6	2	B	<50	527.7
6	3	B	<50	489.6
10	1	B	ND	532
10	2	B	ND	526
10	3	B	ND	557

B4 – Results reported for sample D

Lab #	Run	Method	Measured Br Concentration (ppm)	Measured Cl Concentration (ppm)
1	1	F	119892	1372
1	2	F	119231	1313
1	3	F	119173	1364
3	1	B	140212.33	1341.92
3	2	B	163841.72	1389.75
3	3	B	162969.62	1349.96
2	1	B	149,000	1450
2	2	B	170,000	1070
2	3	B	81,800	1180
9	1	F	210,000	1400
9	2	F	210,000	1400
9	3	F	210,000	1400
7	1	B	167000	1360
7	2	B	182000	1390
7	3	B	168000	1380
7	1	F	176000	1480
7	2	F	175000	1360
7	3	F	175000	1410
5	1	B	167766	1261
5	2	B	166635	1362
5	3	B	165250	1370
4	1	B	200000	1200
4	2	B	190000	1200
4	3	B	190000	1200
8	1	B	173000	1280
8	2	B	181000	1250
8	3	B	183000	1260
8	1	F	NA	NA
8	2	F	NA	NA
8	3	F	NA	NA
6	1	B	168777.9	1319.5
6	2	B	150789.4	1324.3
6	3	B	164777.8	1311.3
10	1	B	189000	1270
10	2	B	179000	1210
10	3	B	167000	1220

Appendix C

C1 – Descriptive statistics of results reported for Br concentration of samples A & D
Note: results for Br concentration of samples B & C have been omitted.

Sample A

Lab #	Method	Mean	Standard Deviation
2	B	753.3	318.9
3	B	641.3	7.2
4	B	566.7	15.3
5	B	611.0	19.9
6	B	598.3	30.4
7	B	531.0	52.3
8	B	611.7	8.0
10	B	578.3	39.3
1	F	660.7	27.0
7	F	604.0	8.0
8	F	491.0	11.5
9	F	603.3	15.3

Sample D

Lab #	Method	Mean	Standard Deviation
2	B	133600.0	46072.6
3	B	155674.6	13397.8
4	B	193333.3	5773.5
5	B	166550.3	1260.1
6	B	161448.4	9445.1
7	B	172333.3	8386.5
8	B	179000.0	5291.5
10	B	178333.3	11015.1
1	F	119432.0	399.4
7	F	175333.3	577.4
9	F	210000.0	0.0

*Note: Lab 8 did not analyze sample D

C2 – Descriptive statistics of results reported for Cl concentration of samples A, B, C & D

Sample A

Lab #	Method	Mean	Standard Deviation
2	B	830.7	52.8
3	B	964.0	12.2
4	B	886.7	15.3
5	B	1044.3	40.9
6	B	947.9	35.6
7	B	901.3	42.5
8	B	1026.7	5.8
10	B	981.7	7.6
1	F	1086.3	41.7
7	F	991.7	4.2
8	F	1013.0	23.4
9	F	1000.0	0.0

Sample B

Lab #	Method	Mean	Standard Deviation
2	B	1963.0	442.9
3	B	1929.0	44.1
4	B	1600.0	0.0
5	B	1979.0	41.1
6	B	2002.4	106.0
7	B	1950.0	36.1
8	B	2060.0	36.1
10	B	1870.0	36.1
1	F	2090.7	32.4
7	F	2276.7	5.8
8	F	2143.3	64.3
9	F	1800.0	0.0

Sample C

Lab #	Method	Mean	Standard Deviation
2	B	684.0	66.6
3	B	538.0	1.1
4	B	486.7	5.8
5	B	548.0	34.1
6	B	508.0	19.1
7	B	530.0	14.9
8	B	591.3	8.1
10	B	538.3	16.4
1	F	536.3	27.0
7	F	661.3	2.5
8	F	553.3	25.7
9	F	476.7	5.8

Sample D

Lab #	Method	Mean	Standard Deviation
2	B	1233.3	195.5
3	B	1360.5	25.6
4	B	1200.0	0.0
5	B	1331.0	60.8
6	B	1318.4	6.6
7	B	1376.7	15.3
8	B	1263.3	15.3
10	B	1233.3	32.1
1	F	1349.7	32.0
7	F	1416.7	60.3
9	F	1400.0	0.0

*Note: Lab 8 did not analyze sample D

Combustion Sample Preparation Methods for Ion Chromatography Analysis of Br and Cl

Javier A. Falcon and Walter Flom
Intel Corporation

Tom Newton
IPC

Acknowledgements
Derek Hetherington
Intel Corporation

VOLUNTEER ORGANIZATIONS

- Thanks to all the volunteer and sponsoring organizations for their support. This report would not be possible without them.
- Volunteer labs and sponsors:
  - COSA Instrument Corporation
  - DIC Corporation – Sample donor
  - Environmental Monitoring & Technologies, Inc.
  - Innovatech Labs
  - SGS Group, Consumer Testing Services
  - Sumika Chemical Analysis Service, Ltd. – Sponsored by DIC Corporation

*One sample donor requested to remain anonymous

AGENDA

- Round Robin Background
- Method Overview
  - Sample Combustion & Absorption
  - Combustion Methods
  - Ion Chromatography
- Data Collection & Processing
  - Round Robin Structure
  - Samples Analyzed
- Statistical Analysis
  - Reported Values – Sanity Check
  - Summary Statistics
  - Additional Analysis
- Summary & Recommendations

IPC J-STD-709 As Of Early 2009

- Limits for Bromine and Chlorine in Flame Retardants and Polyvinyl Chloride in "Low Halogen" Electronic Products
- This standard was trying to establish maximum limits for the halogens bromine (Br) and chlorine (Cl) when used in BFRs, CFRs and PVC in electronic components and assemblies
  - Plastic components (substrate , mold compounds, solder masks, underfill materials, etc)
  - PCB assemblies
  - Plastic in cables, connectors, sockets, and wiring
  - Mechanical plastics (enclosures, fans, etc)
  - Films, tapes, and adhesives

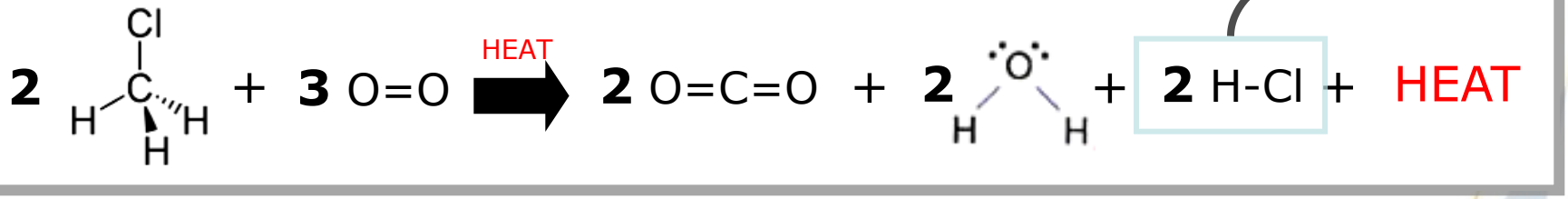
BACKGROUND

- In early 2008 IPC kicked off a small working group (WG) to investigate analytical methods that could measure total Br and Cl concentrations
- WG concluded that oxygen bomb combustion followed by ion chromatography (bCIC) was the best method available
- Following this conclusion WG decided to perform a round robin study to gauge the reproducibility of within-lab and lab-to-lab results – not meant to be a full Gauge R&R
- Finally, WG members also showed strong interest in evaluating a newer combustion method, furnace combustion (fCIC)

SAMPLE COMBUSTION

Example:

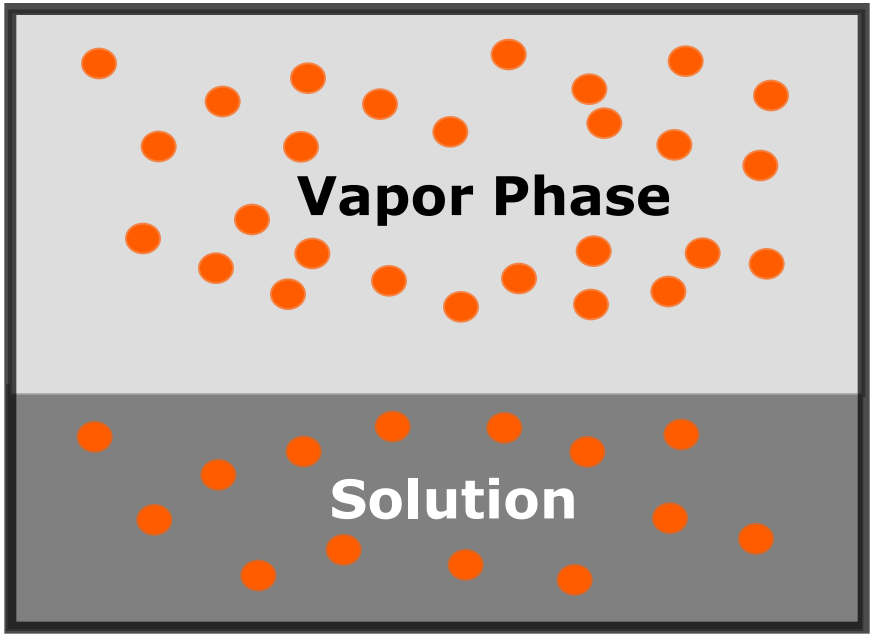
Ionic Cl



- Theoretically the combustion process breaks all covalent bonds and produces ionic species which can be measured with ion chromatography

GAS ABSORPTION

$$HCl_{(g)} + H2O_{(l)} \rightarrow H3O^{+}_{(l)} + Cl^{-}_{(aq)}$$

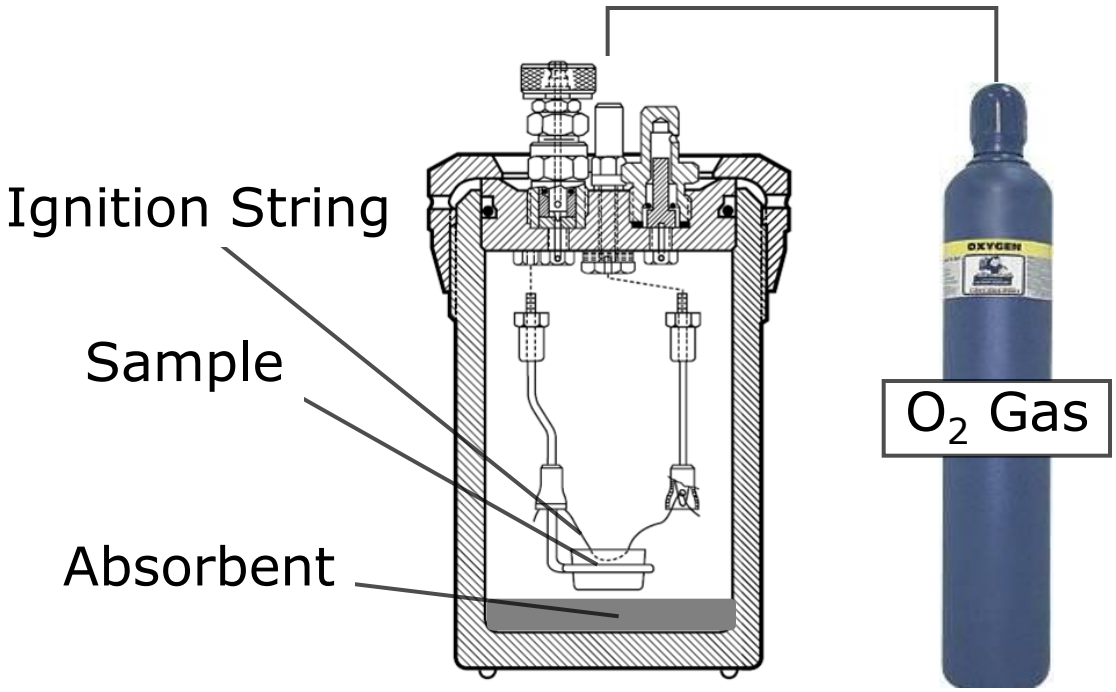


- Absorption of the combustion gases into the absorbent solution is a key for enabling IC analysis

COMBUSTION METHODS

Oxygen Bomb Combustion

O_2 bomb

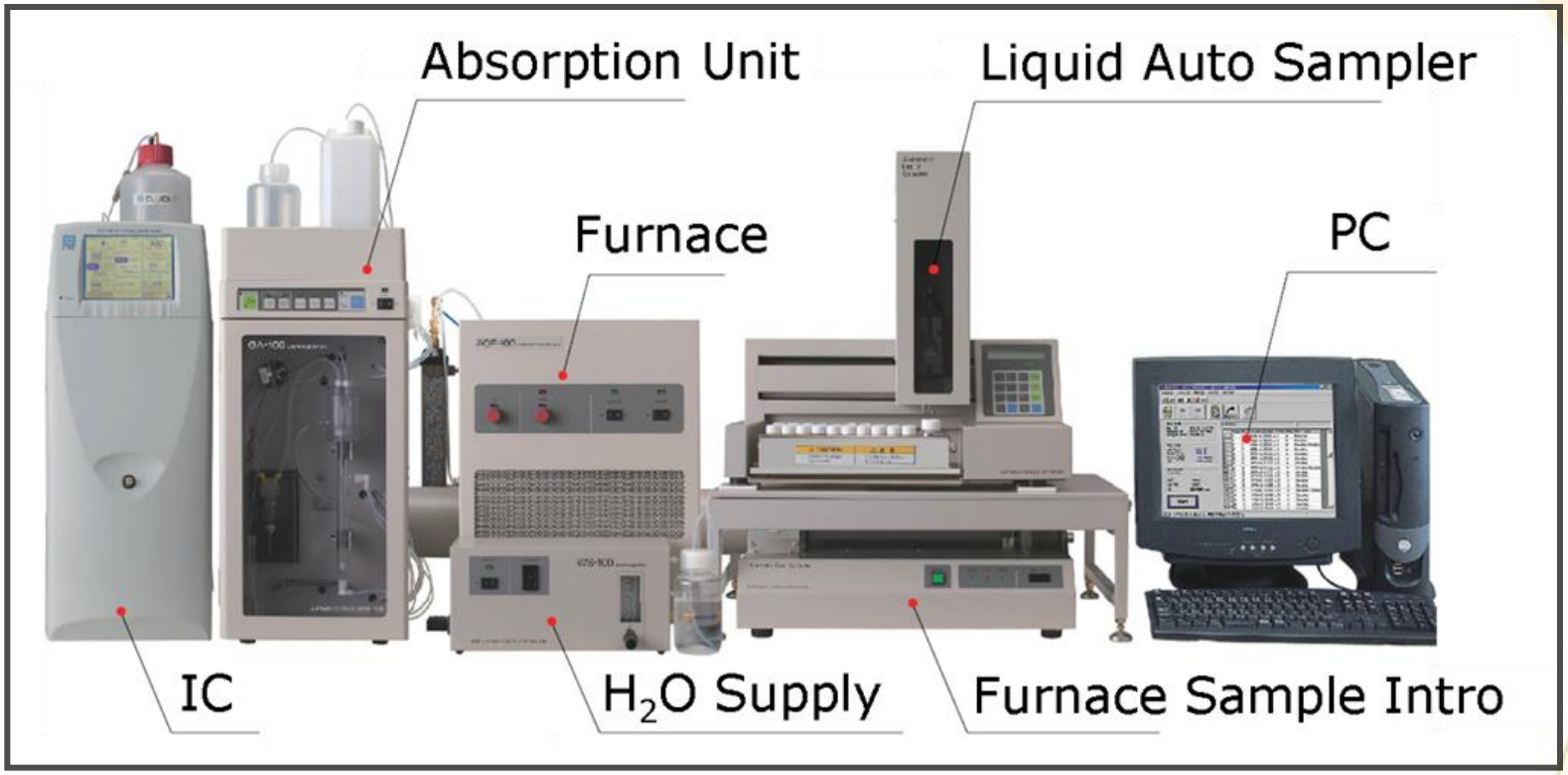


- Oxygen bomb method is time consuming and very labor intensive
- Multiple steps required to complete combustion and sample recovery before IC

http://www.parrinst.com/doc_library/members/4700_Oxygen_Bombs.pdf

COMBUSTION METHODS

Furnace Combustion

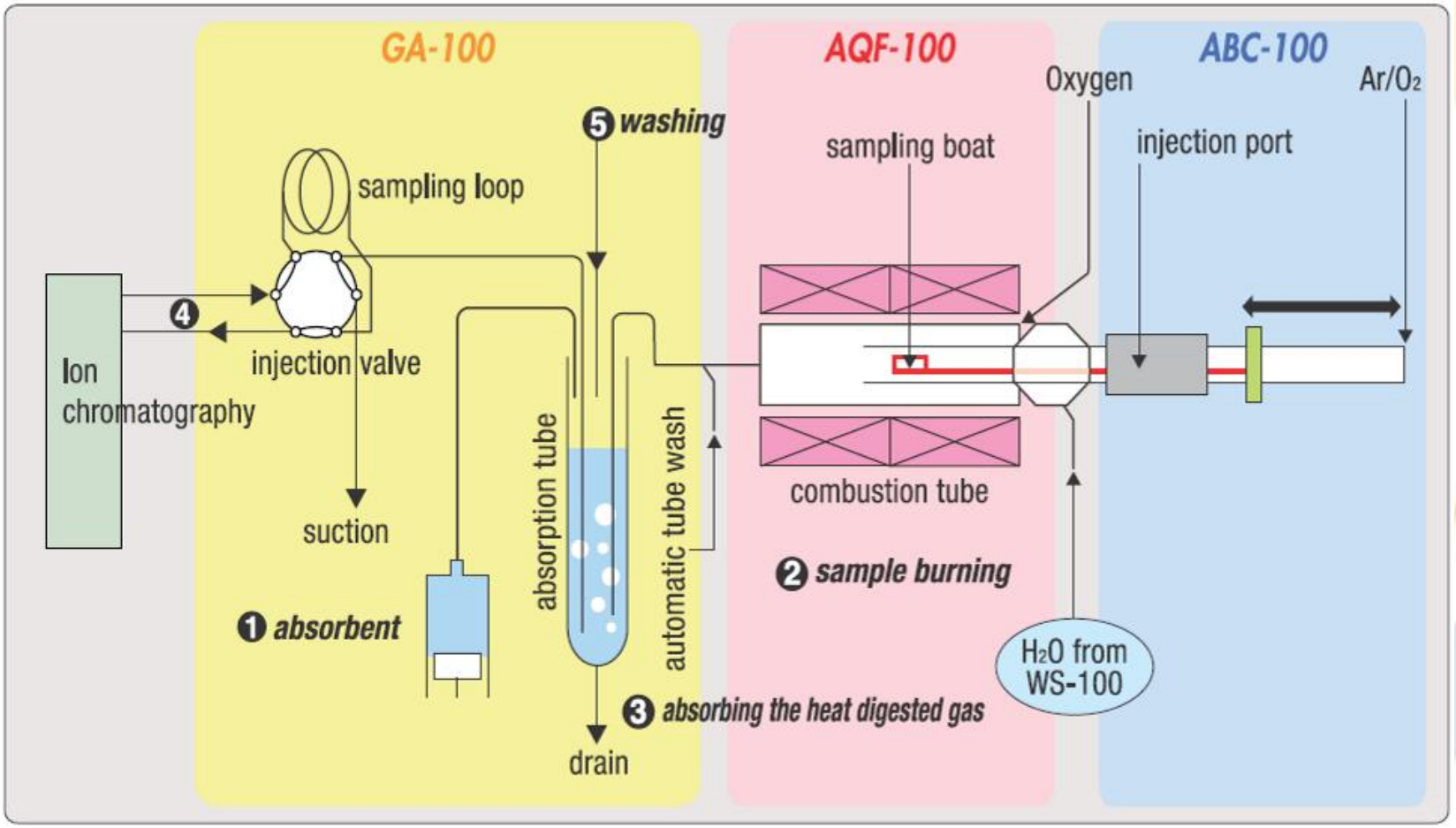


- Furnace method can be automated and simplifies sample combustion and analysis

http://www.dins.jp/dins_e/1prdcts/pdf/Cat%200807AQF1000K_em.pdf

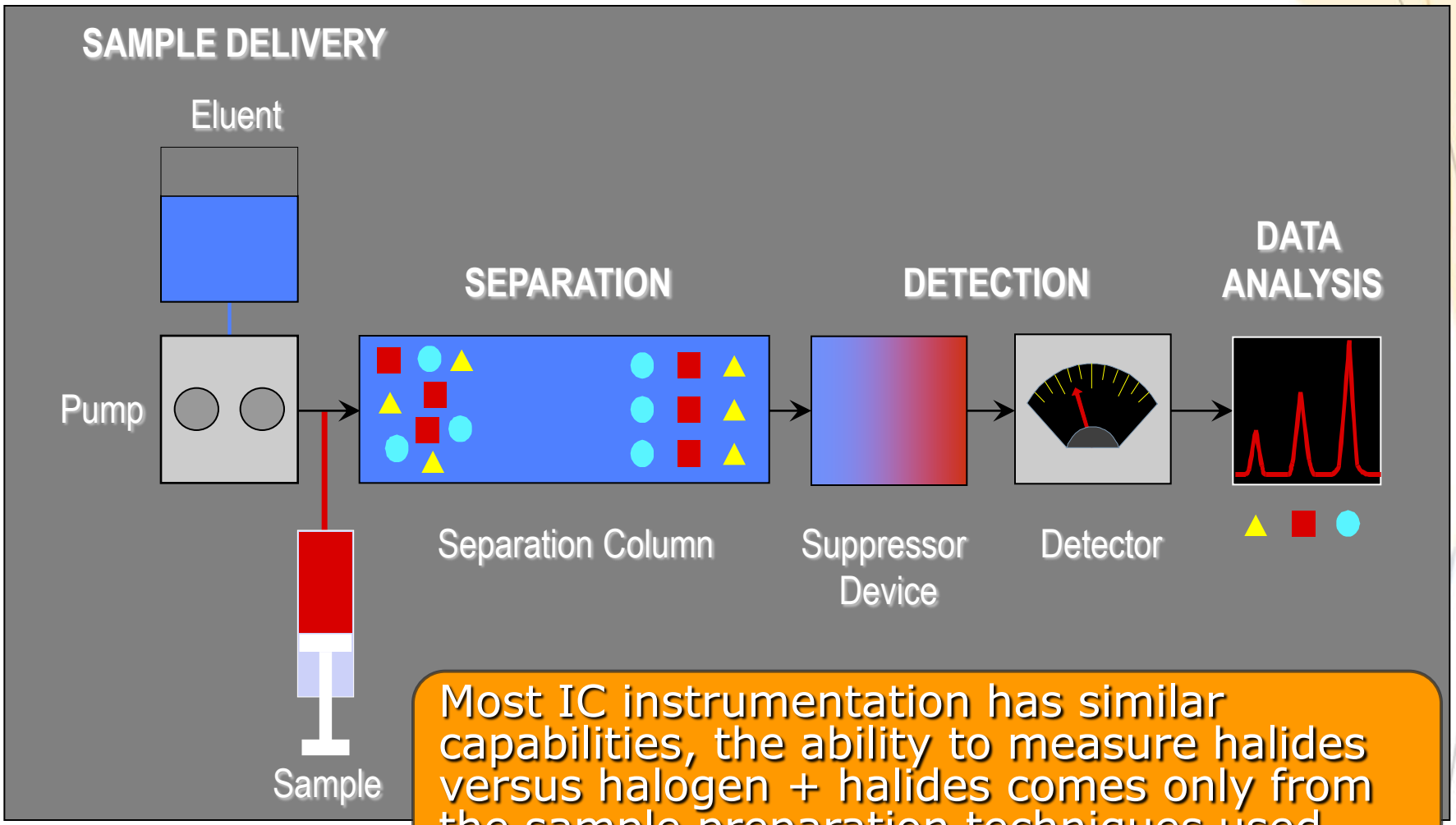
COMBUSTION METHODS

Furnace Combustion



http://www.dins.jp/dins_e/1prdcts/pdf/Cat%200807AQF1000K_em.pdf

ION CHROMATOGRAPHY



Most IC instrumentation has similar capabilities, the ability to measure halides versus halogen + halides comes only from the sample preparation techniques used.

ROUND ROBIN STRUCTURE

- Ten volunteer labs from four companies
- Four donated samples combusted and measured in triplicate
- Used two combustion methods followed by IC
  - Six labs used the oxygen bomb combustion method (US EPA 5050)
  - Two labs used the furnace combustion method (ASTM D 7359 -08)
  - Two labs used both methods
- Results reported electronically by each lab

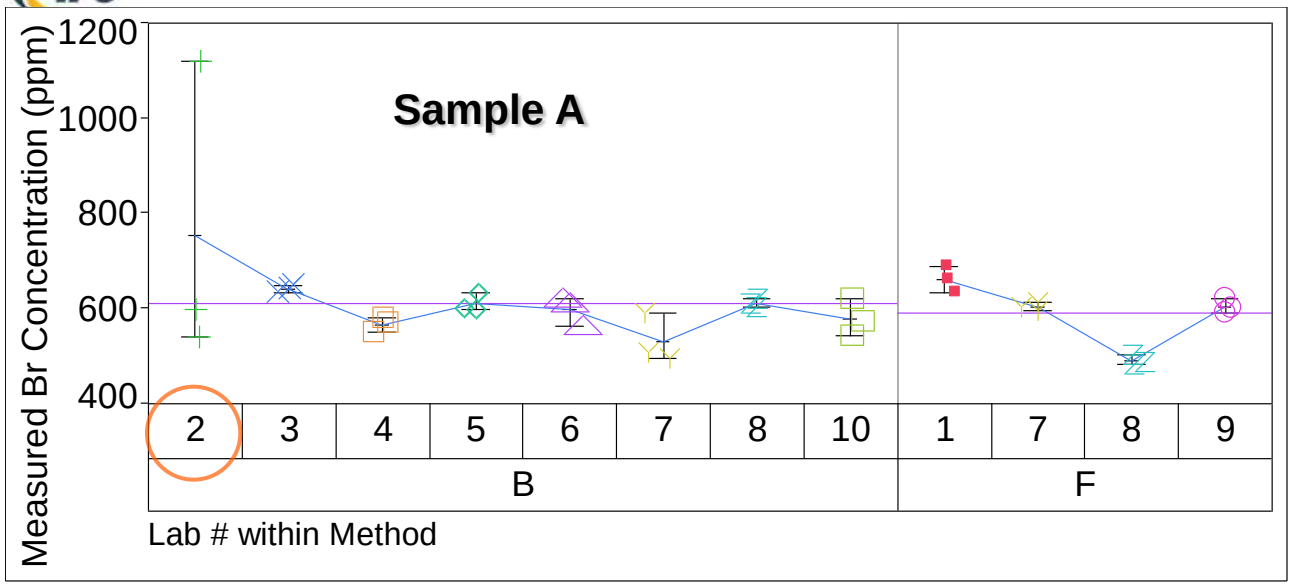
SAMPLES TESTED

Label	Name	Br (ppm)	Cl (ppm)
A	Epoxy Resin	NA	NA
B	PPS	NA	~1,500
C	Halogen Free PPS	NA	~700
D	Brominated Epoxy Resin	200,000	~1,300

- Epoxy resin samples are the base resin commonly used to make substrate and motherboard laminate cores
- Polyphenylene Sulfide (PPS) is an engineering thermoplastic commonly used in connectors and housings of electronic devices

Sample package

MEASURED [Br] VALUES

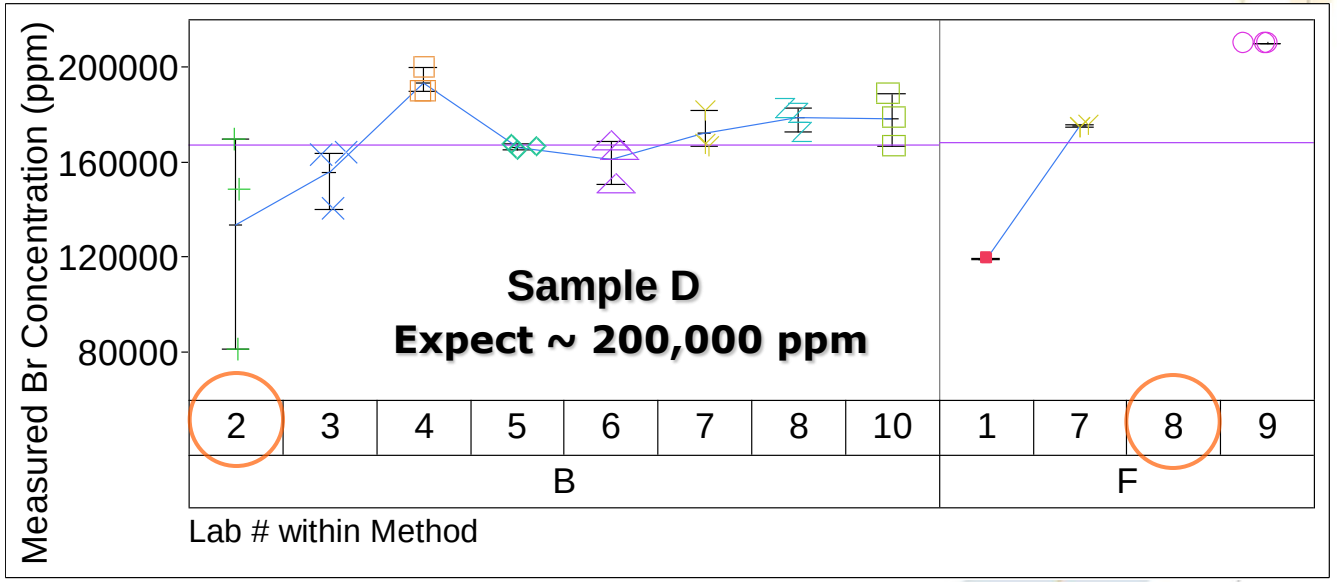


Sample A

Except for Lab #2, measured values show reasonable agreement within and across labs and methods

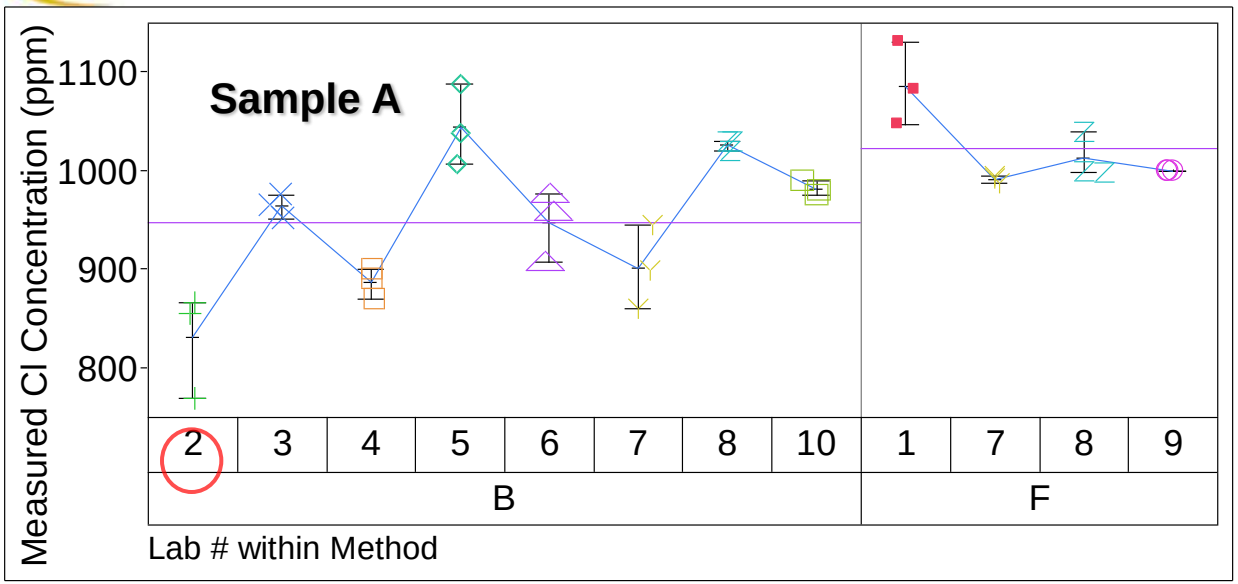
Sample D

Large variation seen across labs



NOTE: Results for samples B & C are not shown because most labs reported either ND (not detected) or less than (<) values for the Br concentration.

MEASURED [Cl] VALUES #1

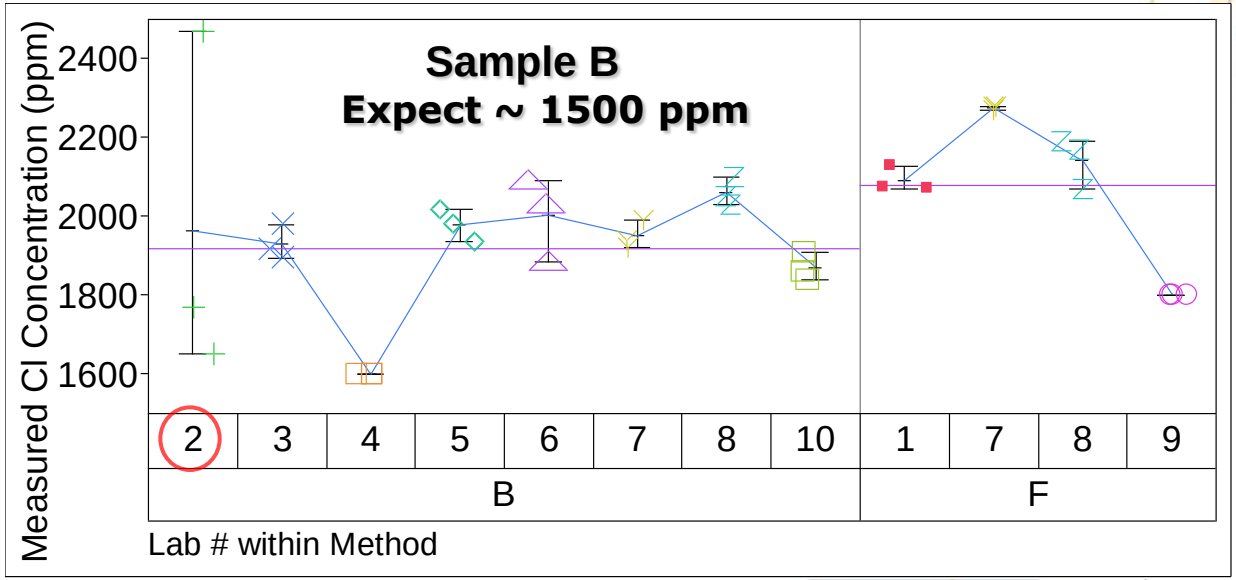


Sample A

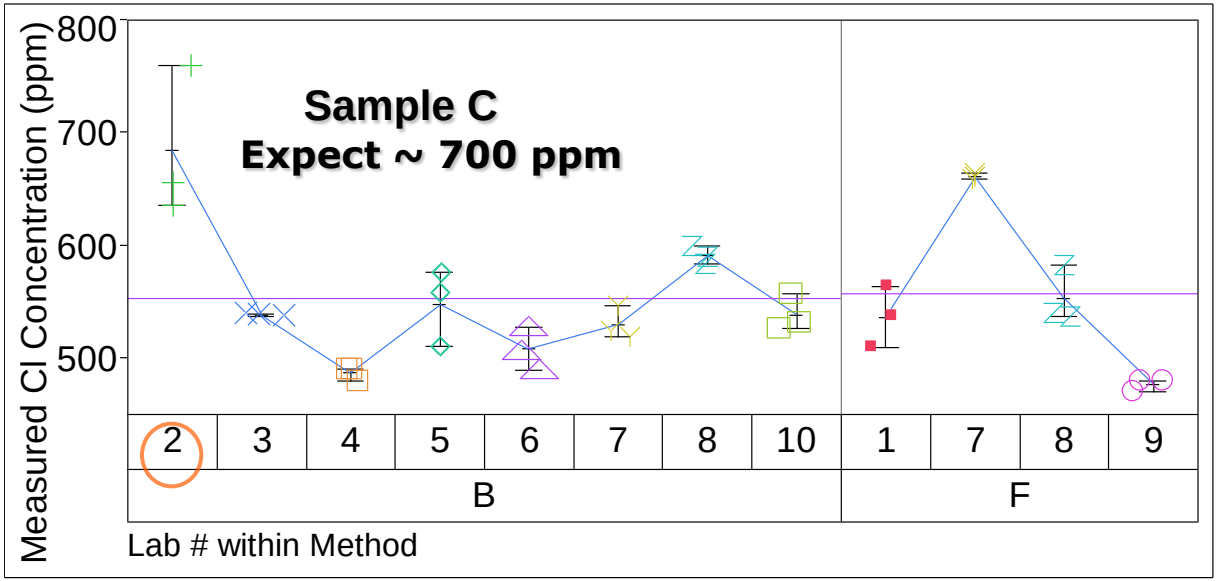
Except for Lab #2, measured values show reasonable agreement within and across labs. fCIC results are slightly higher

Sample B

Some variation seen across labs



MEASURED [Cl] VALUES #2

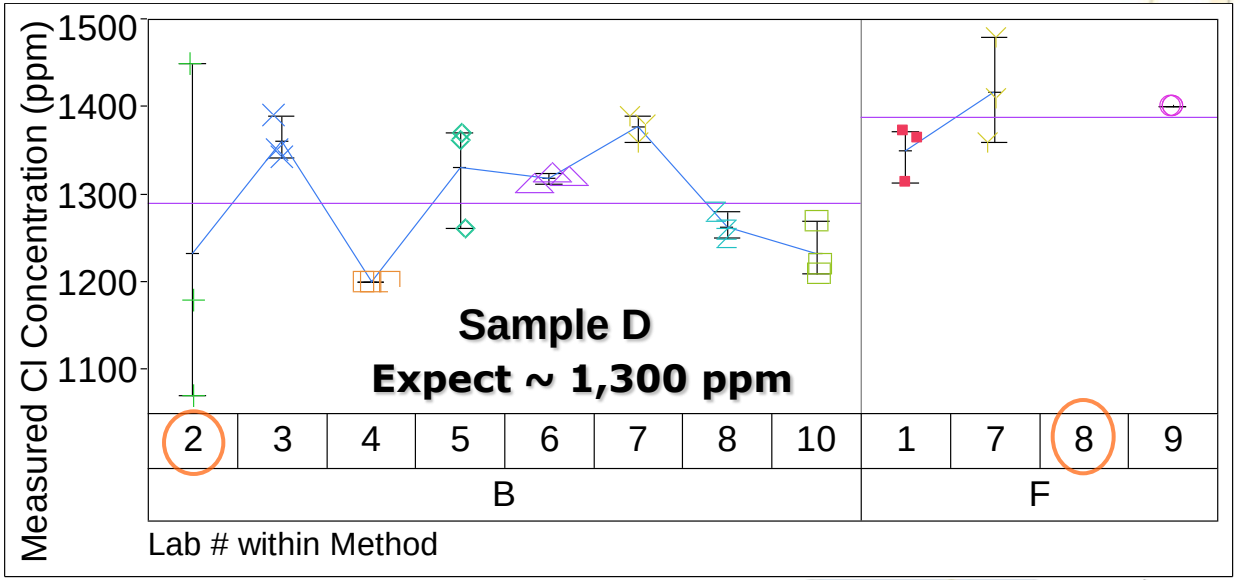


Sample C

Large variation seen across labs

Sample D

Large variation seen across labs



[Br] DESCRIPTIVE STATISTICS

Sample	Method	Overall* Mean	Overall Standard Deviation
A	B	591.2	36.0
	F	598.8	71.1
D	B	172,381	13,962
	F	168,255	39,576

- Mean values between combustion methods agree fairly well for both samples (mean delta is ~1-3%)
- For bCIC overall standard deviation is below 10% of mean value
  - fCIC shows higher values of standard deviation indicating higher variability between labs

*Both sample statistics exclude lab 2, sample D statistics exclude lab 8

[Cl] DESCRIPTIVE STATISTICS

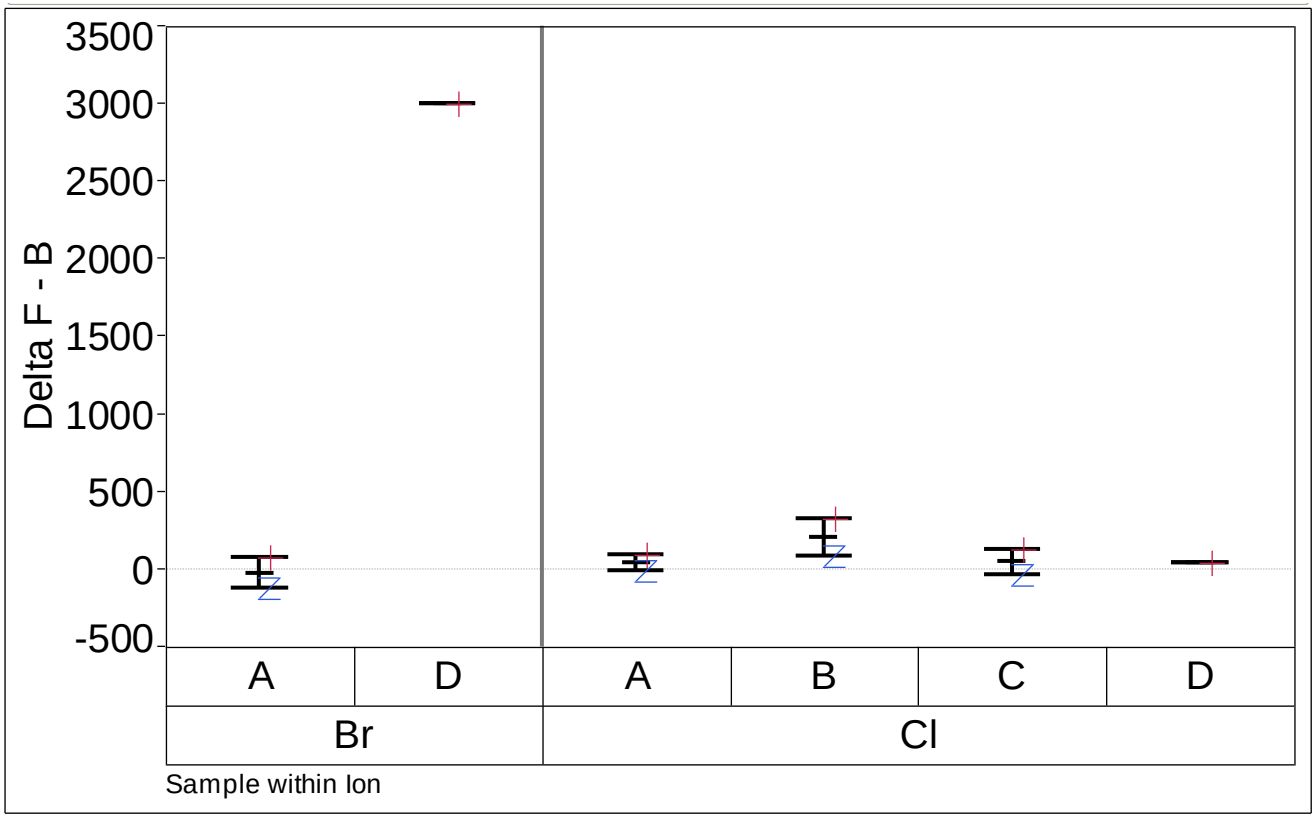
Sample	Method	Overall* Mean	Overall Standard Deviation
A	B	964.7	59.0
	F	1022.7	43.3
B	B	1912.9	150.2
	F	2077.7	201.0
C	B	534.3	32.8
	F	556.9	77.0
D	B	1297.6	66.6
	F	1388.8	34.9

F mean > B mean for all samples

- Mean values between combustion methods agree for all samples (largest delta is ~ 8%, sample B)
- Standard deviation for most samples remains below 10% of mean

*All sample statistics exclude lab 2, sample D statistics exclude lab 8

METHOD COMPARISON

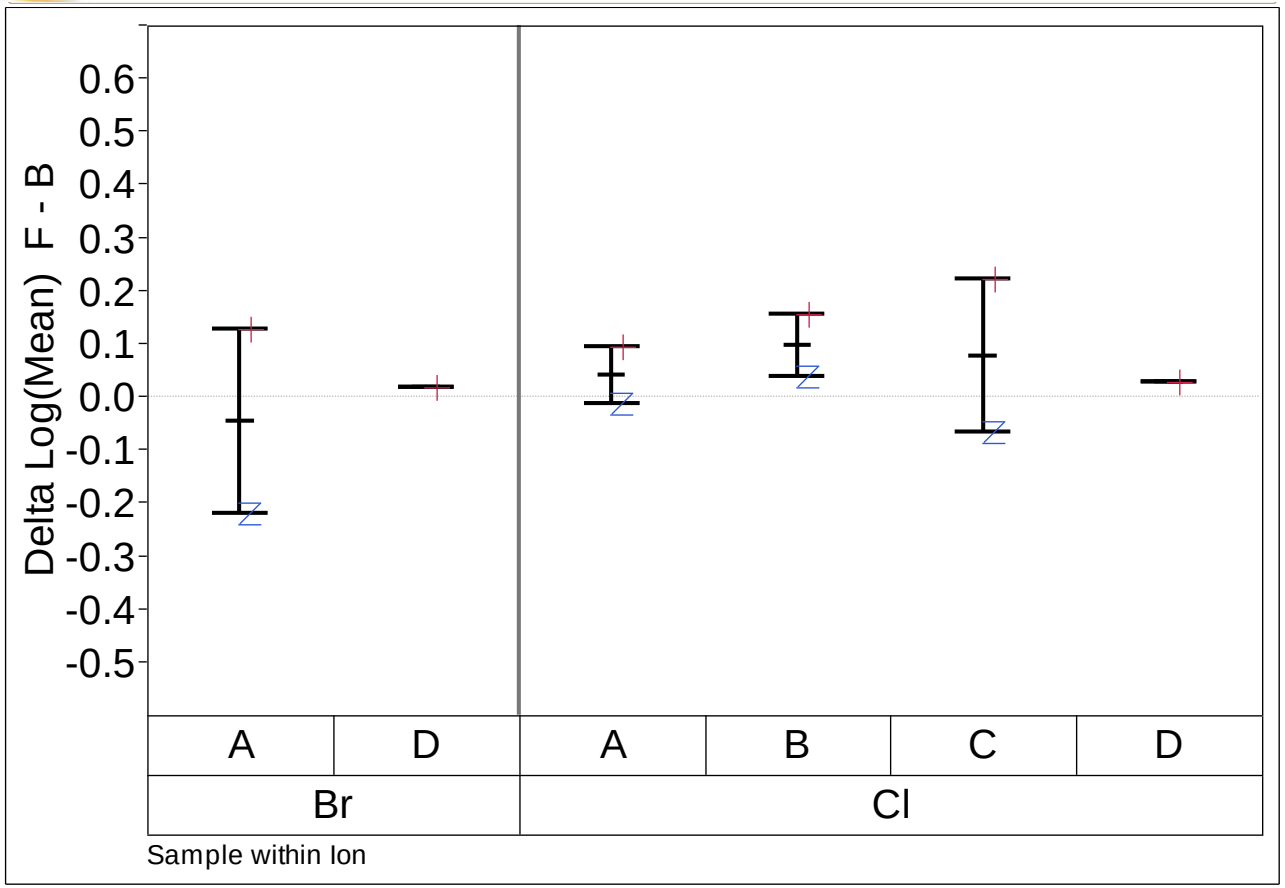


Ideally all delta values equal zero

- Calculated the delta of means between methods (F – B) for the 2 labs which used both sample preparation methods

*Data from lab 7 & 8 only

METHOD COMPARISON #2



t Test Results

Lower Confidence Limit = -0.050

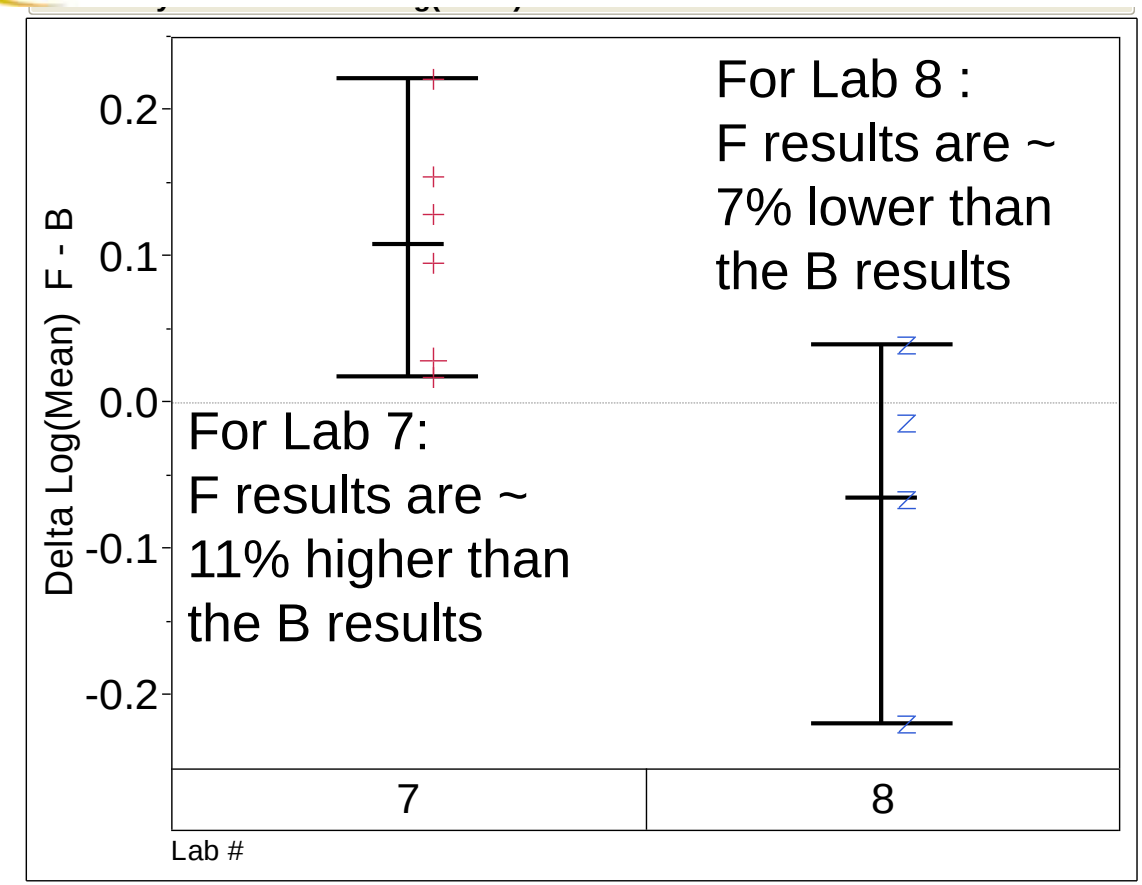
Upper Confidence Limit = 0.127

Prob > | t | = 0.315

- Use natural log to create one model for means comparison
- t Test shows that deltas are statistically equal

*Data from lab 7 & 8 only

METHOD COMPARISON #3



Clear differences observed for the two labs analyzed

- Although the mean of the deltas calculated by sample are statistically the same we must keep in mind that we are working with a very small data set

ACCURACY ANALYSIS –

Sample D Br Results All Labs

Statistic	bCIC	fCIC
Mean	172,381	168,255
Std Dev	13,962	39,576
Std Err Mean	3,046	13,192
upper 95% Mean	178,737	198,676
lower 95% Mean	166,026	137,834
N	21	9
Bias	-27,618	-31,745

Reference value of 200,000 ppm

- Across all Labs, neither method proved to be statistically accurate
- fCIC has Lab with smallest bias but also has largest group bias
- bCIC shows smallest group bias

ACCURACY ANALYSIS –

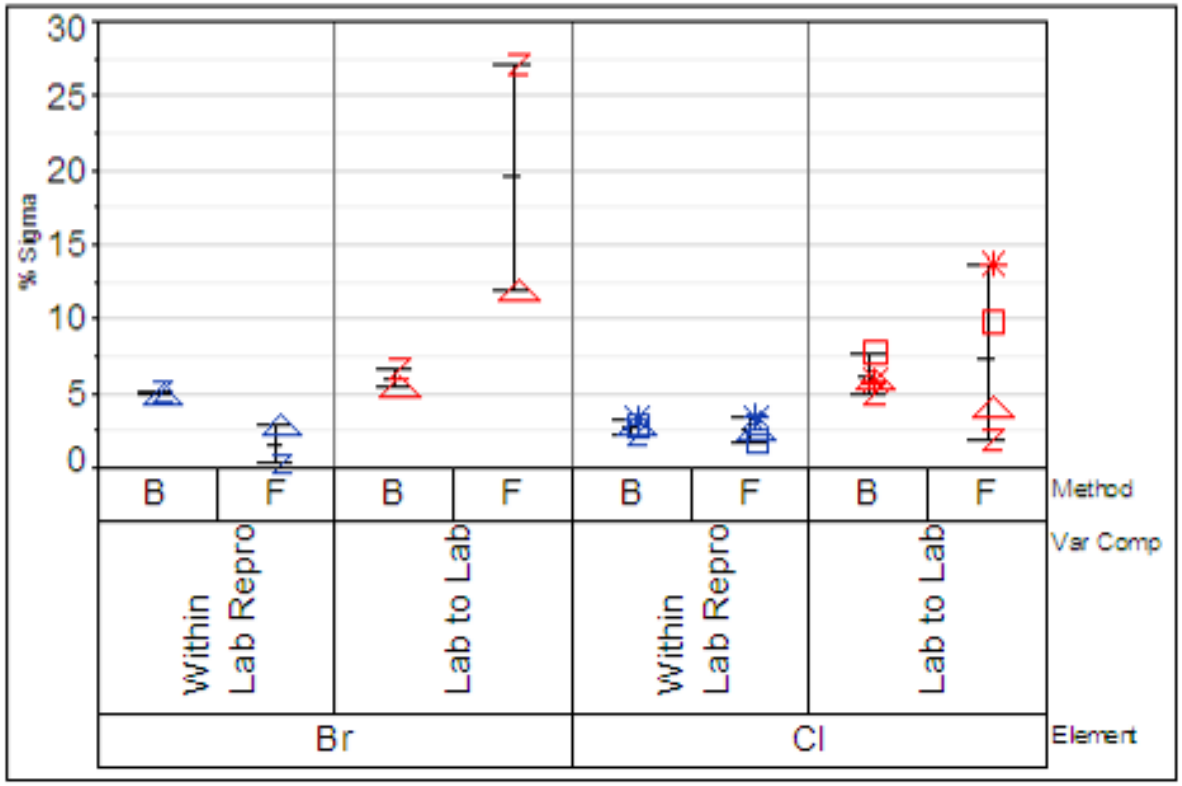
Sample D Br Results Within Lab 7

Statistic	bCIC	fCIC
Mean	172,333	175,333
Std Dev	8,386	577
Std Err Mean	4,891	333
upper 95% Mean	193,166	176,767
lower 95% Mean	151,500	173,899
N	3	3
Bias	-27,667	-24,667

Reference value of 200,000 ppm

- Within one Lab (Lab 7) the mean values are very close (< 1% delta)
- The standard deviation for fCIC is significantly lower versus bCIC
- Bias values are also very close

REPRODUCIBILITY –
Variance Components Analysis



- The within-Lab reproducibility *[blue symbols]* is slightly better for fCIC for both Br and Cl across all samples.
- The Lab-to-Lab reproducibility *[red symbols]* is better for bCIC for both Br and Cl across most samples

Sample A = Δ, Sample B = ☐, Sample C = *, Sample D = Z