TechNotes

Bulletin No. 100

Precision and Accuracy – Assessing your Calorimeter

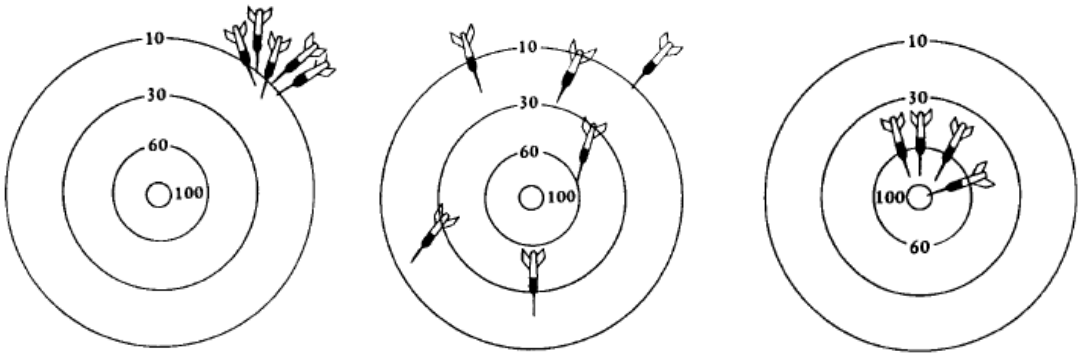
How to determine the range of acceptable results for your calorimeter.

Standard methods specify parameters by which calorimetry results are evaluated. These methods often employ terms such as repeatability and reproducibility.

- Repeatability – The maximum acceptable difference between duplicate determinations on the same reference sample in the same laboratory by the same operator using the same equipment.
- Reproducibility – The maximum acceptable difference between the mean of duplicate determinations carried out in two different laboratories on the same reference sample.

These terms are related to precision and accuracy.

- Precision - A measure of how closely analytical results can be duplicated. Replicate samples (prepared identically from the same sample) are analyzed in order to establish the precision of a measurement.
- Accuracy – A measure of how close to a true or accepted value a measurement lies.

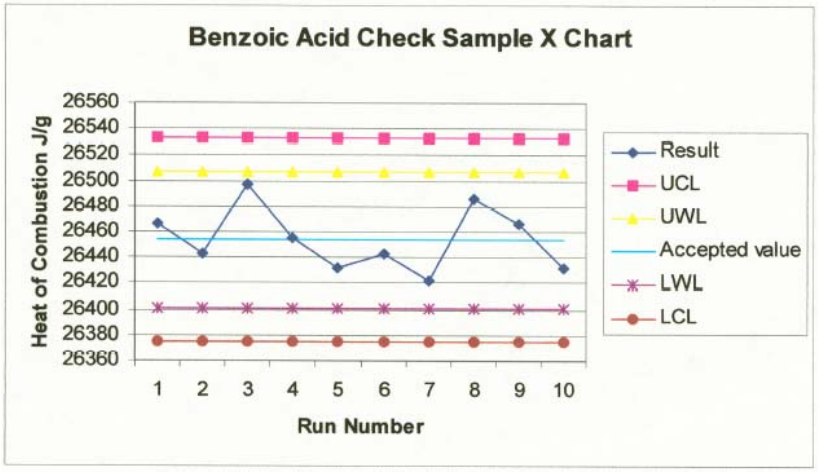


Precise but not accurate ***Accurate but not precise*** ***Precise and accurate***

Some instruments, by design, are able to provide data with greater precision than others. Instruments may be classified based on their expected performance and this classification is used to define limits by which data can be assessed. Since results are expected to scatter with a normal distribution within established limits, systematic trends or patterns in the data plots may be an early warning of problems.

A control chart is a graphical way to interpret test data. In its simplest form, a selected reference sample is measured periodically and the results are plotted sequentially on a graph.

Example of X Chart for Check sample Runs



Limits for acceptable values are defined and if the data stays within the limits, this is accepted as evidence that the precision of the measurement remains in control. The monitored precision measurement and the accuracy of the measurement of the standard may be transferred, by inference, to the measurement of samples made by the system while it is in a state of control.

Control charts, including the factors for calculating control limits are discussed more thoroughly elsewhere. The ASTM, Manual on Presentation of Data and Control Chart Analysis[1] is an excellent source of information. The central line is either the known value for the test sample (e.g., certified value), or the mean of 10 sets of independent measurements. Control limits are then calculated according to the following relationships:

UCL	Mean or accepted value $+\frac{3*sigma}{\sqrt{N}}$
UWL	Mean or accepted value $+\frac{2*sigma}{\sqrt{N}}$
Central Line value X(bar)	Mean of the 10 most recent measurements or the accepted
LWL	Mean or accepted value $-\frac{2*sigma}{\sqrt{N}}$
LCL	Mean or accepted value $-\frac{3*sigma}{\sqrt{N}}$

The Upper Warning Limit (UWL) to the Lower Warning Limit (LWL) defines an area in which 95% of the plotted points are expected to lie. The Upper Control Limit (UCL) to the Lower Control Limit (LCL) defines the area in which almost all (99.7%) of the plotted points are expected to lie when the system is in a state of statistical control. It should be clear that when 5% of the points (one in twenty) lie outside of the warning limits or when values fall outside of the control limits, the system is behaving unexpectedly and corrective actions, and even rejection of data, may be required.

For the above limits, N represents the number of repetitive measurements of the reference sample, the mean of which is plotted on an Xbar chart. For an X chart (single measurement of the reference sample) N=1. The standard deviation of the measurement process is sigma. In this instance, sigma is taken as 0.10% of the mean of the ten most recent measurements or 0.10% of the accepted value if tests are being performed using a reference material, for example, benzoic acid, run as an unknown.

In relation to calorimetry, sigma is used as the classification of the instrument of choice. Parr Calorimeters are classified as follows:

Parr Calorimeter Model	Sigma or Instrument Class
6400 Automatic Isoperibol Calorimeter	0.10%
6300 Automatic Isoperibol Calorimeter	0.10%
6200 Isoperibol Calorimeter	0.10%
6100 Compensated Jacket Calorimeter	0.20%
1341 Plain Jacket Calorimeter	0.30%
6725 Semi-micro Calorimeter	0.40%

Using Control Charts to Assess Calorimeters

Calculating relative standard deviation (RSD) is one method for determining the precision of the results obtained from a calorimeter. The standard deviation is a statistic used as a measure of the dispersion or variation in a data set.

$$RSD = \frac{Std.Dev.}{Mean} \times 100\% = \frac{\sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}}}{\bar{x}} \times 100\%$$

For example:

N	EE Value
1	2406
2	2410
3	2408
4	2406
5	2402
Average $\bar{x}$	2406
Standard Deviation $\sqrt{\frac{\sum(x_i - \bar{x})^2}{N-1}}$	2.829
RSD $\frac{Std.Dev.}{Mean} \times 100\%$	0.12%

The calculated RSD can be plotted in an Xchart and used to monitor the operation of the calorimeter. The Upper Control Limit will differ based on N, or in this application, the number of samples analyzed, the Confidence Level (CL) chosen and the precision class of the instrument. Parr utilizes a CL of 99.7% (3 sigma) for all calorimeters. Tables 2, 3, 4, and 5 illustrate important selected control limits for calorimeter operation when benzoic acid is used as a test sample.

By examining Tables 2 – 5, we can see that if 5 samples of a standard material are analyzed using a 0.10% classification of instrument, an RSD of up to 0.20% is allowed. If 15 samples are analyzed using the same instrument, an RSD of up to 0.15% is acceptable.

Alternatively, if 5 samples of a standard material are analyzed using a 0.20% classification of instrument, an RSD of up to 0.39% is allowed. If 15 samples are analyzed using the same instrument, an RSD of up to 0.31% is acceptable.

We can now determine the expected accuracy of one known sample using Tables 2 – 5 in relation to Parr Calorimeters.

Parr Calorimeter Model	Sigma or Instrument Class	Expected Accuracy (Benzoic Acid, 1.0g)
6400 Automatic Isoperibol Calorimeter	0.10%	11373 ± 34 Btu/lb
6300 Automatic Isoperibol Calorimeter	0.10%	11373 ± 34 Btu/lb
6200 Isoperibol Calorimeter	0.10%	11373 ± 34 Btu/lb
6100 Compensated Jacket Calorimeter	0.20%	11373 ± 68 Btu/lb
1341 Plain Jacket Calorimeter	0.30%	11373 ± 102 Btu/lb
6725 Semi-micro Calorimeter	0.40%	11373 ± 137 Btu/lb

Example 1:

A customer has purchased a new 0.10% class calorimeter and anxiously analyzes 5 samples of benzoic acid pellets. They are dismayed to obtain results that yield an RSD value of 0.17%. They quickly analyze 5 more samples for a total of 10 results and still, their RSD for the data is 0.15%! Are they correct in assuming that they have purchased a poor calorimeter?

No. The classification of the instrument, 0.10%, is the value of sigma that is used to determine the range of acceptable results, and is not the UCL of the data. As they have purchased a 0.10% class instrument, we can examine Table 2 to determine an acceptable UCL for the results. The maximum acceptable RSD for 5 samples of a known standard is 0.20%. The user obtained an RSD of 0.17%, less than the 0.20% UCL, and definitely acceptable. After analyzing 10 samples, the user obtained an RSD of 0.15%, less than the 0.17% UCL and again, acceptable.

Example 2:

The repeatability specification for a standard bomb calorimetric method is 50 Btu/lb at the 95% confidence level. In order to relate this specification to an RSD we need to use the range chart. Therefore, from Table 1 we know that the UCL multiplier for two observations, at a confidence level of 2 sigma (95%), is 2.834.

$$50 = 2.834\sigma$$
$$\sigma = \frac{50}{2.834}$$
$$\sigma = 17.64 Btu/lb$$

If the mean value of the sample tests is 10000 Btu/lb, then the maximum acceptable relative standard deviation (RSD) between two runs will be:

$$RSD = 100\frac{17.64}{10000}$$
$$RSD = 0.18\%$$

Example 3:

An instrument test specification for bomb calorimeters states that 15 consecutive tests should have a range no greater than 50 Btu/lb, 99% of the time, when benzoic acid is the test sample (Hc = 11373 Btu/lb). What RSD could this instrument be reasonably expected to achieve using benzoic acid?

The UCL on the range control chart for n=15 (3 sigma or 99%) from Table 1 is 5.740.

$$\sigma = \frac{50}{5.740}$$
$$\sigma = 8.711$$
$$RSD = 100\frac{8.711}{11373}$$
$$RSD = 0.077\%$$

Example 4:

Five consecutive energy equivalent results are obtained from a 0.1% RSD classification calorimeter providing an RSD of 0.1694%. How can we determine if the instrument is performing as expected?

n	Btu/lb
1	2382.9365
2	2374.1442
3	2379.5344
4	2380.1503
5	2384.7292
Ave.	2380.3007

Since n=5, the control chart (Table 2) provides the upper limit of the RSD or 0.1964%. The result obtained was 0.1694% which is less than 0.1964% telling us that the instrument precision is acceptable.

Example 5:

ACME Labs uses benzoic acid every 10th test to analyze the performance of their instrument. They have an internal procedure which defines that the result must not deviate by more than 50 Btu/lb from the accepted value of 11373 Btu/lb. Is this a reasonable expectation for their 0.20% classification calorimeter?

If we look at Table 3 where n=1, we see that an acceptable range for this sample (a known value), on a 0.20% calorimeter is ±68.2 Btu/lb. The calorimeter is not designed to offer the level of accuracy ACME is requiring.

However, if ACME were to purchase a 0.10% classification calorimeter, their 50 Btu/lb specification would fall within expectations. As is shown in Table 2, a 0.10% classification calorimeter should provide results on a benzoic acid sample that do not deviate by more than 34.1 Btu/lb from 11373 Btu/lb.

Example 6:

Vendor X and Vendor Y offer calorimeters for sale. Vendor X claims that their instrument precision is 0.088% whereas Vendor Y states that their instrument provides 0.10% precision. Once questioned, the vendors provided their confidence levels; Vendor X uses a 95% confidence level and Vendor Y uses a 99% Confidence Level. In this example, the actual precision of both instruments is identical; however, Vendor X is willing to accept that one in 20 tests will be outliers (5%) while Vendor Y will only accept one outlying test in 100 runs (1%). Identical instrument performance can yield different specifications depending on how aggressive the instrument manufacturer chooses to be with the specification.

Table 1 – Range Control Chart

The range, R, of a sample, n, is the difference between the largest observation and the smallest observation. For sample of size n, the factors needed to calculate the multipliers for the upper control limit (UCL) for a range control chart are shown in the following table. If an upper allowable limit is known with an associated confidence level (usually 95 or 99%), then the population standard deviation can be derived or calculated.

UCL (upper control limit, 3 sigma or 99%) = [tabulated value for n observations (3 sigma)]*sigma
UCL (upper control limit, 2 sigma or 95%) = [tabulated value for n observations (2 sigma)]*sigma

n	Range UCL multiplier (3 sigma)	Range UCL multiplier (2 sigma)
1		
2	3.687	2.834
3	4.357	3.469
4	4.699	3.819
5	4.918	4.054
6	5.078	4.230
7	5.203	4.370
8	5.307	4.487
9	5.394	4.586
10	5.469	4.672
11	5.534	4.747
12	5.592	4.814
13	5.646	4.876
14	5.696	4.933
15	5.740	4.984
16	5.782	5.032
17	5.820	5.076
18	5.857	5.118
19	5.888	5.155
20	5.922	5.193
21	5.950	5.226
22	5.979	5.259
23	6.006	5.290
24	6.031	5.319
25	6.055	5.347

Table 2 – Calorimeter Control Limits when Benzoic Acid is Used as a Test Sample

Accepted Heat of Combustion taken as 11373 Btu/lb
Instrument precision 0.10%
Control limits are based on 99% confidence (3 sigma) values
Values are in Btu/lb

Numbers of Observations in a Group	UCL for the Range (High - Low) Within the Group	UCL for the RSD Within the Group	Maximum Permissible Deviation of the Group Mean From the Accepted Value or Grand Mean
1			34.1
2	41.9	0.26%	24.1
3	49.6	0.23%	19.7
4	53.4	0.21%	17.1
5	55.9	0.20%	15.3
6	57.8	0.19%	13.9
7	59.2	0.18%	12.9
8	60.4	0.18%	12.1
9	61.3	0.17%	11.4
10	62.2	0.17%	10.8
11	62.9	0.16%	10.3
12	63.6	0.16%	9.8
13	64.2	0.16%	9.5
14	64.8	0.16%	9.1
15	65.3	0.15%	8.8
16	65.8	0.15%	8.5
17	66.2	0.15%	8.3
18	66.6	0.15%	8.0
19	67.0	0.15%	7.8
20	67.4	0.15%	7.6
21	67.7	0.15%	7.4
22	68.0	0.14%	7.3
23	68.3	0.14%	7.1
24	68.6	0.14%	7.0
25	68.9	0.14%	6.8

Table 3 – Calorimeter Control Limits when Benzoic Acid is Used as a Test Sample

Accepted Heat of Combustion taken as 11373 Btu/lb
Instrument precision 0.20%
Control limits based on 99% confidence (3 sigma) values
Values are in Btu/lb

Numbers of Observations in a Group	UCL for the Range (High - Low) Within the Group	UCL for the RSD Within the Group	Maximum Permissible Deviation of the Group Mean From the Accepted Value or Grand Mean
1			68.2
2	83.9	0.52%	48.3
3	99.1	0.46%	39.4
4	106.9	0.42%	34.1
5	111.9	0.39%	30.5
6	115.5	0.37%	27.9
7	118.3	0.36%	25.8
8	120.7	0.35%	24.1
9	122.7	0.34%	22.7
10	124.4	0.33%	21.6
11	125.9	0.33%	20.6
12	127.2	0.32%	19.7
13	128.4	0.32%	18.9
14	129.6	0.31%	18.2
15	130.6	0.31%	17.6
16	131.5	0.31%	17.1
17	132.4	0.30%	16.6
18	133.2	0.30%	16.1
19	133.9	0.30%	15.7
20	134.7	0.29%	15.3
21	135.3	0.29%	14.9
22	136.0	0.29%	14.5
23	136.6	0.29%	14.2
24	137.2	0.29%	13.9
25	137.7	0.28%	13.6

Table 4 – Calorimeter Control Limits when Benzoic Acid is Used as a Test Sample

Accepted Heat of Combustion taken as 26454 J/g
Instrument precision 0.10%
Control limits based on 99% confidence (3 sigma) values
Values are in J/g

Numbers of Observations in a Group	UCL for the Range (High - Low) Within the Group	UCL for the RSD Within the Group	Maximum Permissible Deviation of the Group Mean From the Accepted Value or Grand Mean
1			79.3
2	97.5	0.26%	56.1
3	115.2	0.23%	45.8
4	124.2	0.21%	39.7
5	130.0	0.20%	35.5
6	134.2	0.19%	32.4
7	137.5	0.18%	30.0
8	140.3	0.18%	28.0
9	142.6	0.17%	26.4
10	144.6	0.17%	25.1
11	146.3	0.16%	23.9
12	147.8	0.16%	22.9
13	149.2	0.16%	22.0
14	150.6	0.16%	21.2
15	151.7	0.15%	20.5
16	152.8	0.15%	19.8
17	153.8	0.15%	19.2
18	154.8	0.15%	18.7
19	155.6	0.15%	18.2
20	156.5	0.15%	17.7
21	157.3	0.15%	17.3
22	158.0	0.14%	16.9
23	158.8	0.14%	16.5
24	159.4	0.14%	16.2
25	160.1	0.14%	15.9

Table 5 – Calorimeter Control Limits when Benzoic Acid is Used as a Test Sample

Accepted Heat of Combustion taken as 26454 J/g
Instrument precision 0.20%
Control limits based on 99% confidence (3 sigma) values
Values are in J/g

Numbers of Observations in a Group	UCL for the Range (High - Low) Within the Group	UCL for the RSD Within the Group	Maximum Permissible Deviation of the Group Mean From the Accepted Value or Grand Mean
1			158.6
2	194.9	0.52%	112.1
3	230.3	0.46%	91.6
4	248.4	0.42%	79.3
5	260.0	0.39%	70.9
6	268.5	0.37%	64.7
7	275.1	0.36%	59.9
8	280.6	0.35%	56.1
9	285.2	0.34%	52.9
10	289.1	0.33%	50.2
11	292.6	0.33%	47.8
12	295.6	0.32%	45.8
13	298.5	0.32%	44.0
14	301.1	0.31%	42.4
15	303.5	0.31%	41.0
16	305.7	0.31%	39.7
17	307.7	0.30%	38.5
18	309.6	0.30%	37.4
19	311.3	0.30%	36.4
20	313.1	0.29%	35.5
21	314.6	0.29%	34.6
22	316.1	0.29%	33.8
23	317.5	0.29%	33.1
24	318.8	0.29%	32.4
25	320.1	0.28%	31.7

Table 6 – Calorimeter Control Limits when Benzoic Acid is Used as a Test Sample

Accepted Heat of Combustion taken as 6318.4 Cal/g
Instrument precision 0.10%
Control limits based on 99% confidence (3 sigma) values
Values are in Cal/g

Numbers of Observations in a Group	UCL for the Range (High - Low) Within the Group	UCL for the RSD Within the Group	Maximum Permissible Deviation of the Group Mean From the Accepted Value or Grand Mean
1			19.0
2	23.3	0.26%	13.4
3	27.5	0.23%	10.9
4	29.7	0.21%	9.5
5	31.1	0.20%	8.5
6	32.1	0.19%	7.7
7	32.9	0.18%	7.2
8	33.5	0.18%	6.7
9	34.1	0.17%	6.3
10	34.6	0.17%	6.0
11	35.0	0.16%	5.7
12	35.3	0.16%	5.5
13	35.7	0.16%	5.3
14	36.0	0.16%	5.1
15	36.3	0.15%	4.9
16	36.5	0.15%	4.7
17	36.8	0.15%	4.6
18	37.0	0.15%	4.5
19	37.2	0.15%	4.3
20	37.4	0.15%	4.2
21	37.6	0.15%	4.1
22	37.8	0.14%	4.0
23	37.9	0.14%	4.0
24	38.1	0.14%	3.9
25	38.3	0.14%	3.8

Table 7 – Calorimeter Control Limits when Benzoic Acid is Used as a Test Sample

Accepted Heat of Combustion taken as 6318.4 Cal/g
Instrument precision 0.20%
Control limits based on 99% confidence (3 sigma) values
Values are in Cal/g

Numbers of Observations in a Group	UCL for the Range (High - Low) Within the Group	UCL for the RSD Within the Group	Maximum Permissible Deviation of the Group Mean From the Accepted Value or Grand Mean
1			37.9
2	46.6	0.52%	26.8
3	55.1	0.46%	21.9
4	59.4	0.42%	19.0
5	62.1	0.39%	17.0
6	64.2	0.37%	15.5
7	65.7	0.36%	14.3
8	67.1	0.35%	13.4
9	68.2	0.34%	12.6
10	69.1	0.33%	12.0
11	69.9	0.33%	11.4
12	70.7	0.32%	10.9
13	71.3	0.32%	10.5
14	72.0	0.31%	10.1
15	72.5	0.31%	9.8
16	73.1	0.31%	9.5
17	73.5	0.30%	9.2
18	74.0	0.30%	8.9
19	74.4	0.30%	8.7
20	74.8	0.29%	8.5
21	75.2	0.29%	8.3
22	75.6	0.29%	8.1
23	75.9	0.29%	7.9
24	76.2	0.29%	7.7
25	76.5	0.28%	7.6

For more information on how precision statements relate to 6000 Series Calorimeters, contact Technical Service at parr@parrinst.com

[1]ASTM Committee E-11 on Quality and Statistics. Manual on Presentation of Data and Control Chart Analysis. 6th ed. Philadelphia: ASTM, 1992.