Appendix D

Balance Protocol for Gravimetric Determination of Sample Weights using a Precision Balance

BP-A1

California Environmental Protection Agency

Air Resources Board

Balance Protocol for Gravimetric Determination of Sample Weight Using a Precision Analytical Balance

BP-A1

NOTE: This is a new Test Protocol. For clarity the proposed text is shown in normal type.

Adoption Date: [To be determined]

Table of Contents

1. SCOPE AND APPLICATION

This Protocol summarizes a set of procedures and tolerances for weighing objects in the range of 0 to 1000g with a resolution of 0.001 g. This protocol only addresses balance operations, it does not address project requirements for equilibration, sample hold time limits, sample collection etc.

2. SUMMARY OF METHOD

The balance is zeroed and calibrated using procedures defined herein. Object weight determinations are conducted along with control object weight determinations, zero checks, calibration checks, sensitivity checks, and replicate weightings in a defined sequence designed to control and quantitatively characterize precision and accuracy.

3. DEFINITIONS

N/A.

4. INTERFERENCES

Object weights can be affected by temperature and relative humidity of their environment, air currents, static electricity, gain and loss of water vapor, gain or loss of and loss of volatile compounds directly from the sample or from contaminants such as finger prints, marker ink, and adhesive tape.

Contamination, transfer of material to or from the samples, is controlled by conducting operations inside a clean area dedicated to the purpose and having a filtered laminar air flow where possible; by wearing gloves while handling all samples and related balance equipment; by using forceps to handle small objects, and by keeping the balance and all related equipment inside the clean area.

Air currents are controlled by conducting weighing operations inside a closed chamber or glove box and by allowing the substrates to reach temperature and relative humidity equilibrium. The chamber is maintained at 40% relative humidity and 25 $^{\circ}$C by a continuous humidity and temperature control system. The temperature and RH conditions are recorded at least once per weighing sessions. Equilibration times for samples that are particularly sensitive to humidity or to loss of semi-volatiles species are specified by project requirements.

Static electric charges on the walls of the balance and the weighed objects, including samples, controls, and calibration weights, can significantly affect balance readings. Static is avoided by the operator ground himself and test objects as described in the balance manual.

5. PERSONNEL HEALTH AND SAFETY

N/A

6. EQUIPMENT AND SUPPLIES

- Filtered, temperature and humidity controlled weighing chamber.
- Precision Balance
- Plastic forceps
- Nylon fabric gloves.
- Working calibration weights: ANSI Class 2, 1000g and 500 g
- Working sensitivity weight: 50 mg
- Reference objects: references are one or more objects that are typical of the objects to be weighed during a project, but that are stored permanently inside the balance glove box. Reference objects are labeled Test1, Test2, Test3, etc.

7. REAGENTS AND STANDARDS

N/A

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

N/A. See relevant project requirements and SOPs.

9. QUALITY CONTROL

Data quality is controlled by specifying frequencies and tolerances for Zero, Calibration, Linearity, and Sensitivity checks. If checks do not meet tolerance criteria, then samples must be re-weighed. In addition, the procedures specify frequencies for Control Object Checks.

Data quality is quantitatively characterized using Zero Check, Calibration Check, and Control Check data. These data are summarized monthly in statistics and QC charts.

See Section 11 for procedures, frequencies, and tolerances.

10. CALIBRATION AND STANDARDIZATION

The absolute accuracy of the balance is established by calibration against an ANSI Class 2, stainless steel working weight: 1000.000 g +/- 0.0025 g. Linearity is established checking the midpoint against an ANSI Class 2 stainless steel working weight: 500.000 +/- 0.0012 g. Sensitivity is established using and ANSI Class 2 stainless steel or aluminum working weight: 50 mg. Precision is checked by periodically checking zero, calibration, and reference object weights.

See Section 11 for procedure.

11. PROCEDURE

11.1 Overview of Weighing Sequence

Weighing a series of substrates consists of performing the following procedures in sequence, while observing the procedures for handling and the procedures for reading the balance:

1. Initial Adjustment
2. Weigh 8 samples
3. Zero Check
4. Weigh 8 samples
5. Zero Check
6. Weigh 8 samples
7. Calibration Check
8. Return to step 2.
9. If less than 24 cans are weighed, perform a final Calibration Check at the end of weighing.

This sequence is interrupted and samples are reweighed if QC check tolerances are not met. Each of these procedures along with procedures for handling and reading the balance are described below. The QC tolerances referred to in these procedures are listed in Table 1. The QC codes described in these procedures are summarized in Table 2. The data are recorded in the Precision Balance Data Log, a sample is shown in Table 3.

11.2 Handling

1. Never touch samples, weights, balance pans, etc. with bare hands. Wear powder free gloves to handle the weights, controls, and samples.

11.3 Reading the Balance

1. Close the door. Wait for the balance stabilization light to come on, and note the reading.

2. Watch the balance reading for 30 sec (use a clock). If the reading has not changed by more than 0.001 g from the reading noted in step 1, then record the reading observed at the end of the 30 sec period.
3. If the reading has drifted more than 0.001 g note the new balance reading and go to step 2.
4. If the balance reading is flickering back and forth between two consecutive values choose the value that is displayed more often than the other.
5. If the balance reading is flickering equally back and forth between two consecutive values choose the higher value.

11.4 Initial Adjustment

1. Empty the sample pan Close the door. Select Range 1000 g
2. Wait for a stable reading
3. Record the reading with QC code IZC (initial zero check)
4. Press the Tare button
5. Record the reading in the logbook with QC code IZA (initial zero adjust)
6. Place the 1000 g working calibration weight on the balance pan
7. Wait for a stable reading.
8. Record the reading with QC code ICC (initial cal check)
9. Press the Calibrate button
10. Record the reading with QC code ICA (initial cal adjust)
11. Remove the calibration weight.
12. Wait for a stable reading.
13. Record the reading with QC code IZC.
14. If the zero reading exceeds +/- 0.002 g, go to step 4.
15. Place the 500 g calibration weight on the balance pan
16. After a stable reading, record the reading with QC code C500. Do not adjust the balance.
17. Add the 0.050 g weight to 500 g weight on the balance pan.
18. After a stable reading, record the reading with QC code C0.05. Do not adjust the balance.
19. Weigh reference object TEST1, record reading with QC code T1.
20. Weigh the reference object TEST2, TEST3, etc. that is similar in weight to the samples that you will be weighing. Record with QC code T2, T3, etc.

11.5 Zero Check

1. Empty the sample pan. Close the door.
2. Wait for a stable reading
3. Record the reading with QC code ZC

4. If the ZC reading is less than or equal to the zero adjustment tolerance shown in Table 1, return to weighing and do not adjust the zero.

   If the ZC reading exceeded the zero adjustment tolerance, proceed with steps 5 through 7.
5. Press the Tare button
6. Record the reading in the logbook with QC code ZA.
7. If the ZC reading exceeded the zero re-weigh tolerance, change the QC code recorded in step 3 from ZC to FZC. Then enter a QC code of FZ into the QC code column of all samples weights obtained after the last valid zero check. Re-weigh all of those samples, recording new data in new rows of the logbook.

11.6 Calibration Check

1. First, follow procedures for Zero Check. If the ZC was within tolerance, tare the balance anyway (i.e. follow steps 5 and 6 of the Zero Check method)
2. Place the 1000 g working calibration weight on the sample pan, wait for a stable reading.
3. Record the reading with QC code C1000
4. If the C1000 reading is less than or equal to the calibration adjustment tolerances, skip steps 5 through 8 and proceed to step 9. Do not adjust the calibration.
5. If the C100 reading exceeded the calibration adjust tolerance, press the Calibrate button.
6. Record the reading in the logbook with QC code CA
7. Perform a Zero Check (follow the Zero Check method)
8. If the C1000 reading exceeded the calibration re-weigh tolerance, change the code recorded in step 3 from C1000 to FC1000. Enter FC into the QC column for all sample weights obtained after the last valid calibration check. Re-weigh all of those samples, recording new data in new rows of the logbook.

11.7 Replicate Weighing Check

1. This protocol does not include reweigh samples to obtain replicates. The projects for which this protocol is intended already include procedures multiple weightings of each sample.

Table 1. QC Tolerances and Frequencies for Balance Protocol A1

Reading tolerance:
0.001 g, stable for 30 sec

Adjustment Tolerances:

Zero:	- 0.003	to	+0.003 g.
Calibration:	999.997	to	1000.003 g
Controls:	none		
Replicates:	none		

Re-weigh Tolerances:

Zero:	- 0.005	to	+0.005 g.
Calibration:	999.995	to	1000.005 g
Controls:	none		
Replicates:	none		

Reference Objects:
Test 1 – A reference object weighing about 400 g
Test 2 – A refernce object weighing about 200 g
Test 3 – A reference object weighin about 700 g.

QC Frequencies:

Zero Checks:	once per 8 samples
Calibration Checks:	once per 24 samples
Repeat weighings:	none (test method includes replicate determinations)
Control objects:	once per weighing session

Table 2. QC Codes For Balance Protocol A1

IZC	Initial Zero Check
IZA	Initial Zero Adjust
ICC	Initial Calibration Check
ICA	Initial Calibration Adjust
ZC	Zero Check
ZA	Zero Adjust
CC	Calibration Check
CA	Calibration Adjust
R	Replicate Filter Weighing
FZ	Sample Failed Zero Check
FC	Sample Failed Calibration Check
T1	Test Object 1: empty can of automotive refrigerant
T2	Test Object 2:
T3	Test Object 3:

12. DATA ANALYSIS AND CALCULATIONS

For Zero Checks, let Z equal the recorded Zero Check value. For control checks let T1, T2, etc. equal the recorded value for control object Test 1, Test 2, etc. For Calibration Checks, let C1000 equal C1000 reading minus 1000, M = C500 – 500, S = .C.050 – C500 - .050. For Replicate Checks, let D equal the loss that occurred between the first and second measurements. In summary:

T1 = T1
T2 = T2
T3 = T3
Z = ZC - 0
C = C1000 - 1000
M = C500 – 500
G = C.050 – C500 - .050

Tabulate the mean and standard deviation for each of the following: Z, C, M, G. T1, T2, T3. Depending on the number of operators using the balance and the number of protocols in use, analyze the data by subcategories to determine the effects of balance operator and protocol. Each of these standard deviations, S_Z, S_C, etc. is an estimate of the precision of single weight measurement.

For Z, C, M, and G, check the mean value for statistical difference from 0. If the means are statistically different than zero, troubleshooting to eliminate bias may be called for. For Z, C, M, G, T1, T2, T3, check that the standard deviations are all comparable. If there are systematic differences, then troubleshooting to eliminate the problem may be called for.

Note that the precision of a weight *gain*, involves two weight determinations, and therefore is larger than S by a factor of sqrt(2). On the other hand replicates weighings improves the precision of the determinations by a factor of sqrt(N). If N= 2, i.e. duplicates, then the factors cancel each other.

To estimate the overall uncertainty in a weight determination, a conservative estimate might be to combine the imprecision contributed by the zero with the imprecision contributed by the calibration.

$$U_{.} = \text{sqrt}(S_Z^2 + S_C^2)$$

The uncertainty in a weight *gain* from N replicates is then given by:

$$U_{gain.} = \text{sqrt}(2) * \text{sqrt}(S_Z^2 + S_C^2) / \text{Sqrt}(N)$$

But due to the balance adjustment and reweigh tolerances, we expect S_Z to approximately equal S_C, to approximately equal S_M, etc. tolerances, so that the equation above becomes:

$$U_{gain.} = 2 * S / \text{Sqrt}(N)$$

Where S is any individual standard deviation; or better, a pooled standard deviation.

13. METHOD PERFORMANCE

The data necessary to characterize the accuracy and precision of this method are still being collected. The method is used primarily to weigh objects before and after a period of soaking to determine weight loss by subtraction. Given the reweigh tolerances, we expect the that the precision of weight gain determinations will be on the order of 0.006 g at the 1-sigma level. Bias in the weight gain determination, due to inaccuracy of the calibration weight and to fixed non-linearity of the balance response is on the order 0.005% of the gain.

14. POLLUTION PREVENTION

When discharging half the can contents during can preparation, do not vent the contents to f the small can to the atmosphere. Use an automotive recovery machine to transfer small can contest to a recovery cylinder.

15. WASTE MANAGEMENT

Return full and half full cans to the place of purchase for a refund of the purchase deposit. Dispose of the contents of the recycle cylinder through a service that consolidates waste for shipment to EPA certified facilities for reclaiming or destruction.

16. REFERENCES

Precision Balance Instruction Manual. Company, City, State

Table 3. Precision Balance Data Log

						QC	Can	Can	Recorded	
Rec #	**Date**	**Time**	**Proj.**	**Prot.**	**Tech.**	**Code**	**Type**	**ID#**	**grams**	**Comment**
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										
11										
12										
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