A Simple Gravimetric Method to Determine Barometer Corrections

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Presented here is a gravimetric method to calibrate barometers. The difference in forces exerted on the pan of a balance is observed for two well characterized artifacts of nearly equal masses but different volumes. During the weighing, air temperature and relative humidity are measured; the ambient pressure is then calculated from an air density equation. A barometer correction is derived and then compared to an independent value based on a standard barometer. The data indicate that pressure can be calculated with an uncertainty (1 S.D.) of not more than 400 ppm at one atmosphere.

Key words: Air density; air density equation; barometer calibration; barometric pressure; displacement volume; gravimetric method; mass artifacts; weighing.

1. Introduction

Many laboratories have modern commercial balances capable of near state-of-the-art weighing precision. Some laboratories, however, are not equipped to perform the necessary calibration of their instruments for measuring temperature, pressure and relative humidity, and hence systematic errors in the mass value assignment result.

Simple reliable instruments for measuring temperature and relative humidity are portable and can be sent elsewhere for calibration. This is not, however, generally true of the frequently-encountered aneroid and Fortin type barometers where accuracy to a few tenths of a millimeter of mercury is desirable. These instruments are best calibrated in place by pressure-defining instruments such as a standard mercury barometer or a dead-weight piston gage.

Presented here is a simple gravimetric method for a calibration of the barometer in the user's laboratory that does not require pressure equipment. Two well-characterized weights of grossly different displacement volumes are used to measure the air density directly by mass comparison on the balance [1];[1] in addition, the *ambient temperature and relative humidity must be measured*. From these data, using an air density equation [2], ambient pressure can be calculated and compared to the barometer reading made at the time of weighing. The barometer correction is derived from the barometer reading and the calculated pressure.

Although the gravimetric determination of pressure is unusual the gravimetric method to determine air density was demonstrated by Baxter [3] in 1921. Recent absolute determinations of air density [1, 4] have shown that air density calculations based on the gas laws are accurate to 4×10^{-4}. The data presented here result from mass comparisons [5] at two differing altitudes using a recent formulation [2] for the density of air in the buoyancy correction. Analysis of the data presented here suggests that a barometer correction made by the gravimetric method is accurate to 0.3 mm Hg (40 Pa) or better.

2. The Method

Given two artifact masses, A and B, with displacement volumes V_A and V_B, respectively, the indicated difference, I, when compared on a balance is

$$I = A - B + \varrho(V_B - V_A) \qquad (1)$$

where ϱ is the density of air at the time of measurement.

In this work, I results from a single double substitution weighing[2] using a five-observation format.

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[2]

$$I = \frac{(0_1 - 0_2 - 0_3 + 0_4)\Delta}{(0_3 - 0_2 + 0_4 - 0_5)}$$

The balance observations 0_1 through 0_5 correspond to five loads placed on the balance pan, from which I is calculated. The five loads are weight A, weight B, plus weight Δ, $A + \Delta$ and A. The sensitivity weight, Δ, calibrates the balance response in mass units and is chosen to be larger than $A - B$. The buoyant effect on Δ is negligible with respect to the measurement precision and has been omitted.

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[1] Figures in brackets indicate literature references at the end of this paper.

Air density variations may cause I to be undesirably large for a given balance. Such occurrences are accommodated by adding small trimming weights of known mass and volume to either A or B or both. Therefore, a more general expression for I is desirable and given as

$$I = A - B + \delta_1 - \delta_2 + \varrho(V_B - V_A + V_2 - V_1) \qquad (2)$$

where δ_1 and δ_2 are the small trimming weights and V_1 and V_2 are their respective volumes. The above weights are assumed to be at the ambient air temperature; if the volumes have been determined at some other temperature a correction for thermal expansion[3] must be applied.

Rewriting eq (2) in terms of the air density at the time of weighing, we have

$$\varrho = \frac{B - A + \delta_2 - \delta_1 + I}{V_B - V_A + V_2 - V_1} \qquad (3)$$

We can now insert the gravimetrically derived value of ϱ into an air density equation and formulate an expression for the ambient pressure, P.

Equation (43) of [2], a restricted version of the general air density formulation, was manipulated to accommodate a variation in ambient conditions and to accommodate pocket calculator computation.[4] The resultant expression for the pressure during the time of weighing is

$$P = \frac{\varrho T Z}{0.0034836} + 0.0037960 \, U e_S \qquad (4)$$

where ϱ is the gravimetric value given by eq (3).

In the above equations, T is air temperature in kelvins, U is percent relative humidity, P is barometric pressure in pascals, e_S is the saturation vapor pressure of water, Z is the compressibility factor for moist air; ϱ and ϱ' are in kg m^{-3}.

For convenience, the equation for e_S as given in [2] is reproduced here.

$$e_S = 1.7526 \times 10^{11} \varepsilon^{(-5315.56/T)}$$

ε is the base of natural logarithms. References for e_S in tabular form are given in [2].

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[3] If the volume of a weight is given at temperature t_R then the volume at any temperature t is computed from the formula $V_t = V_{tR}[1 + 3\alpha(t - t_R)]$. It is assumed that the thermal coefficient of expansion, α, is known. The use of 3α for the coefficient of cubical expansion also assumes that the material is isotropic.

[4] The modified air density formula is

$$\varrho' = \frac{0.0034836}{TZ}(P - 0.0037960 U e_S).$$

ϱ has been primed to indicate a calculated value of air density as opposed to the gravimetric value.

The sole change made to eq (43) was to put the compressibility term, Z, explicitly in the formula as a variable. Doing so improves the accuracy at laboratories whose elevation and ambient conditions differ from those applicable to the NBS. The remaining restriction, the assumed CO_2 level, still applies. As a convenience to the reader, a table of Z values from [2] is reproduced in appendix II of this report.

In summary, if one weighs two artifacts of nearly equal mass but with a large volume difference and records the ambient temperature, relative humidity and masses and displacement volumes of the trimming weights, if required, ambient pressure can be calculated and a barometer correction derived.

3. Artifacts and Instrumentation

The temperature and relative humidity were respectively measured with a mercury-in-glass thermometer and an electric hygrometer. The calibration and accuracy of these devices, as well as the certification of masses and volumes of the artifacts and trimming weights are adequately described in [5]. However, to aid in performing this method of barometer calibration, additional details concerning the artifacts and trimming weights are given in appendix I of this report.

4. Test Data

The artifacts, the masses of which are designated A and B in eq (1), correspond to a ring-shaped weight and a hermetically-sealed hollow cylindrical weight of significantly larger volume. There are two such pairs of weights, referred to as Pair 1 and Pair 2. The weights of Pair 1 are referred to as R_1 and H_1 and of Pair 2 as R_2 and H_2, where R designates the ring weight and H the hollow weight for each pair.

The weighings were performed at NBS Washington, 150 m elevation, and at the Sandia Laboratory in Albuquerque, N.M. located at 1600 m elevation. In some instances the laboratory temperature was controlled whereas the pressure was always free to vary with the prevailing weather conditions. A time period of several months elapsed from the first to the last measurement. For each day of measurement the artifact pairs were weighed only once, however both pairs were not always weighed on the same day. In all there were 22 artifact weighings with one being discarded as an obvious outlier.

The measurements of each day began and usually ended with an independent calibration of the aneroid barometer in use by comparison with a standard mercury barometer. Two aneroid barometers were required to accommodate the pressure range encountered between 150 and 1600 m elevation with sufficient resolution and reproducibility; however,

the same standard mercury barometer was used throughout the measurements to define pressure.

5. Results

The data as summarized in table 1 are segregated into two groups by altitude and the corresponding aneroid barometer. The column of gravimetrically derived values for

air density indicates the magnitude and the daily variations encountered at each location. For convenience to the reader all pressures are given in both pascals (Pa) and millimeters of mercury (mm Hg). The aneroid barometer scales are graduated in mm Hg and their corrections are likewise given. The insert at the bottom of table I is a complete data set for run 22.

The mean correction, $\overline{X}$, and the estimate of the standard

TABLE 1. *These data summarize twenty-two aneroid barometer calibrations achieved by the gravimetric method. Also given are the results of an independent comparison with a standard mercury barometer.*

			Air Density (Gravimetric) ϱ	Pressure (Gravimetric) P_1		Pressure (Standard Barometer) P_2		$P_2 - P_1$	Aneroid Correction by Gravimetric Method	Aneroid Correction by Standard Barometer	
Run	Day	Pair									
			1600 METERS ELEVATION ANEROID #1 (Sandia Laboratory, Albuquerque, N.M.)								
			kg/m³	Pa	mm Hg	Pa	mm Hg	mm Hg	mm Hg	mm Hg	
1		1	0.9801	83128	623.51	83053	622.95	−0.56	1.07		
2	1	2	0.9795	83095	623.26	83053	622.95	−0.31	1.02	0.73	0.69
3	. . . .								. . .	. . . .	
4	2	1	0.9814	83267	624.55	83282	624.67	0.12	0.57	0.70	0.69
5		1	0.9872	83745	628.14	83692	627.74	−0.40	1.12		
6	3	2	0.9854	83614	627.16	83622	627.22	0.06	0.64	0.73	0.62
7		1	0.9923	84181	631.41	84204	631.58	0.17	0.53		
8	4	2	0.9918	84130	631.03	84137	631.08	0.05	0.63	0.78	omitted
								$\overline{X} = -0.12$	$\overline{X} = 0.80$	$\overline{X} = 0.71$	
								S.D.$_x$ = 0.29	S.D.$_x$ = 0.26	S.D.$_x$ = 0.05	
								S.D.$_{\overline{x}}$ = 0.11	S.D.$_{\overline{x}}$ = 0.10	S.D.$_{\overline{x}}$ = 0.02	
			150 METERS ELEVATION ANEROID #2 (N.B.S. Laboratory, Gaithersburg, MD.)								
9		1	1.1760	100301	752.32	100261	752.02	−0.30	−0.14		
10	5	2	1.1746	100211	751.64	100229	751.78	0.14	−0.58	−0.44	−0.43
11		2	1.1775	100377	752.89	100308	752.37	−0.52	0.13		
12	6	1	1.1705	100040	750.36	100028	750.27	−0.09	−0.30	−0.40	−0.38
13		1	1.1697	100041	750.37	100066	750.56	0.19	−0.95		
14	7	2	1.1687	100009	750.13	100048	750.42	0.29	−0.73	−0.41	−0.46
15		1	1.1736	100383	752.93	100401	753.07	0.14	−0.53		
16	8	2	1.1716	100207	751.67	100228	751.77	0.16	−0.55	−0.38	−0.40
17	9	2	1.1955	101210	759.14	101202	759.08	−0.06	−0.30	−0.32	−0.39
18	10	2	1.1940	101032	757.80	101061	758.02	0.22	−0.60	−0.38	−0.37
19	11	2	1.2049	101911	764.40	101892	764.25	−0.15	−0.16	−0.31	omitted
20	12	2	1.1889	101380	760.41	101330	760.04	−0.37	0.03	−0.43	−0.23
21	13	2	1.1358	97017	727.68	97077	728.14	0.46	−0.78	−0.32	omitted
22	14	2	1.1601	98916	741.93	98917	741.94	0.01	−0.47	−0.41	−0.50
								$\overline{X} = 0.01$	$\overline{X} = -0.42$	$\overline{X} = -0.39$	
								S.D.$_x$ = 0.27	S.D.$_x$ = 0.31	S.D.$_x$ = 0.06	
								S.D.$_{\overline{x}}$ = 0.07	S.D.$_{\overline{x}}$ = 0.08	S.D.$_{\overline{x}}$ = 0.01	

Complete Data Set Run #22

$I = -0.004237$ g	$V_B = 337.71691$ cm³ @ 23.13 °C
$\delta_1 = 0.019999$ g	$T = 296.28$ K
$\delta_2 = 0.259974$ g	$U = 26.6$ percent
$V_1 = 0.00741$ cm³	Aneroid Barometer Observation = 741.94 mm Hg
$V_2 = 0.01877$ cm³	$Z = 0.99964$
$A = R_2 = 999.994442$ g	$e_S = 2831$ Pa
$B = H_2 = 1000.003844$ g	$\varrho = 0.0011601$ g/cm³ ᵃ = 1.1601 kg/m³
$V_A = 126.41067$ cm³ @ 23.13 °C	$P_2 = 98917$ Pa = 741.94 mm Hg

ᵃ kg/m³ are required for use in eq (2).

deviation of the mean, S.D.$_{\bar{x}}$, are given for the gravimetrically-derived aneroid barometer corrections and those assigned by calibration with the standard barometer. Also given, for both methods of calibration, is the estimate of the standard deviation for a single observation, S.D.$_{-x}$. Similar estimates are given for the gravimetrically derived pressure, P_1, and that assigned by the standard barometer, P_2.

One would expect the difference between P_1 and P_2 to be near zero. It is not surprising to find the difference in mean values $(P_2 - P_1)$ smaller at the lower elevation site as weighing conditions were somewhat better than those of the higher elevation where air currents and vibration were detrimental. This contention is supported by the pooled estimates of balance standard deviation, 60 μg for the higher laboratory and 40 μg for the lower one. Futhermore, the corrections assigned to the aneroid barometers by the standard barometer at both locations do not significantly differ in precision and therefore make the same error contribution at both locales, leaving only errors associated with the weighing procedure to account for the difference. However, the non-zero difference is well within 1 S.D. for the gravimetric method and is not statistically significant.

The above discussion holds true for the resultant aneroid barometer corrections.

The barometric pressure (760 mm Hg) as indicated by the standard barometer is estimated to be in error by 1 part in 30000, 0.025 mm Hg, and is dominated by reading error that is random in nature. The scale readings of the aneroid barometers are estimated to have an uncertainty of 1/10 of a division, 0.02 mm Hg. In addition, atmospheric pressure variations that occur between calibrations expose the inherent non-reproducibility of the aneroid barometer. The resultant errors are decreased by the number of repeated calibrations and are reflected by S.D.$_{\bar{x}}$ for the aneroid calibrations based on the standard barometer. The random uncertainty of the mean correction, $\overline{X}$, for the aneroid barometer as derived by comparison with the standard barometer, is taken to be S.D.$_{\bar{x}}$.

Uncertainty in the barometric pressure as determined gravimetrically arises from errors in the characterization of mass and volume of the artifacts, weighing errors (including the lack of thermal equilibrium) and errors associated with the parameters in the equation for barometric pressure. Again, random errors dominate and the inconsequential known systematic errors have been omitted here.

A relative uncertainty of 290 ppm, at the level of 1 S.D., is assigned to the gravimetrically determined air density and is combined, by the method of root sum squares, with 210 ppm uncertainty (at 1 S.D.) resulting from the equation for pressure. The resultant estimated uncertainty in the gravimetrically determined pressure is 360 ppm. For barometric pressures near 760 mm Hg this amounts to 0.27 mm Hg and to 0.23 mm Hg for pressures near 630 mm Hg.

6. Conclusions

The relative uncertainty (at 1 S.D.) in the aneroid barometer correction has been shown to be 360 ppm. This uncertainty will be propagated directly to barometric pressure determined by the instruments in combination with the random reading uncertainty of 0.02 mm Hg. The latter is usually diminished by making repeated observations of pressure during the weighing operation.

It is suggested that the gravimetric barometer calibration will adequately serve the needs of many laboratories for measurements such as precision weighing, within the limits discussed here.[5] Of course, the calibration should be performed several times and preferably on different days with significant variation in ambient pressure.

The artifacts used in this work have characteristics nearly as close to ideal as good practice allows. Experience [5] indicates that the hermetically-sealed hollow weight made from stainless steel can be replaced with a cylinder made from an aluminum alloy. Furthermore, in the author's opinion, the ring weight of nearly equal surface area could be fabricated from brass tubing, with the added benefit of having a thermal conductivity similar to that of aluminum.

This latter property may be of importance although it has not been investigated here. Similar reflective properties could be achieved by gold plating both artifacts. Under no circumstances should the aluminum weight be anodized, as anodized surfaces may become electrically charged and cause serious weighing errors.

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7. References

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[5] The resultant barometer calibration is not traceable to the N.B.S. pressure standards.

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8. Appendix I

8.1 Equipment

Fabrication of the artifacts is directed toward optimizing the difference in displacement volume between them and to adjust their masses close to 1 kg, a precision balance capacity available to most laboratories. There are other practical aspects that also must be considered, however, such as the volume measurement, fabrication techniques and surface-dependent effects related to the lack of thermal equilibrium [5] during the weighing procedure.

The artifacts used here [5] were designed to minimize surface dependent effects and to have a nominal mass of 1 kg with densities of about 2.7 g cm^{-3} for one and 7.8 g cm^{-3} for the other, and nearly equal surface areas and finish. The surface area of the less dense weight is minimized in the usual manner by designing a cylinder of equal height and diameter. Since both artifacts are of the same material, stainless steel, the low density weight is a sealed hollow cylinder of substantial wall thickness and the other is in the shape of a tube. One is tempted, by the physical principles, to fabricate the hollow cylinder of an even lower density material; however, doing so unnecessarily complicates the hydrostatic weighing for the determination of volume by approaching hydrostatic fluid density i.e. the positive buoyancy point. In addition, the wall thickness of the cylinder may not be substantial, resulting in unnecessary fragility and perhaps compressibility.

Although it is the difference in mass between the artifacts that is of interest here, derivation of mass is by assignment using well-known intercomparison techniques with standards of mass [5]. This method has many statistical advantages over a simple difference measurement. A mass of 1 kg is a convenience to both the mass assignment and the hydrostatic weighing procedures used to determine the displacement volume.

8.2 Trimming Weights

The trimming weights are commercially available and are made from sheets of known alloys. This permits the use of a handbook value for their densities in computing displacement volume. It is a routine matter to assign mass values accurate to a few micrograms in the range of 500 mg to 1 mg. The amount of trimming weights used in the barometer calibration is small provided the artifacts are adjusted close to each other and to the nominal value of the mass standard. Failure to meet these criteria may require measuring the volume of the trimming weights in place of a simple estimate based on alloy density.

9. Appendix II

TABLE 2. Compressibility factor, Z, for CO_2-free air

Temperature (Celsius)	Pressure (pascals)	Pressure (mm Hg)	Relative Humidity in Percent				
			0	25	50	75	100
19.0	70000	525.0	.99973	.99972	.99971	.99968	.99966
	75000	562.5	.99972	.99970	.99969	.99967	.99964
	80000	600.0	.99970	.99968	.99967	.99965	.99963
	85000	637.6	.99968	.99967	.99965	.99963	.99961
	90000	675.1	.99966	.99965	.99963	.99961	.99959
	95000	712.6	.99964	.99963	.99961	.99960	.99957
	100000	750.1	.99962	.99961	.99959	.99958	.99956
	101325	760.0	.99962	.99960	.99959	.99957	.99955
	105000	787.6	.99960	.99959	.99958	.99956	.99954
	110000	825.1	.99958	.99957	.99956	.99954	.99952
20.0	70000	525.0	.99974	.99973	.99971	.99969	.99966
	75000	562.5	.99972	.99971	.99969	.99967	.99964
	80000	600.0	.99970	.99969	.99967	.99965	.99963
	85000	637.6	.99969	.99967	.99966	.99964	.99961
	90000	675.1	.99967	.99666	.99964	.99962	.99960
	95000	712.6	.99965	.99964	.99962	.99960	.99958
	100000	750.1	.99963	.99962	.99960	.99958	.99956
	101325	760.0	.99963	.99961	.99960	.99958	.99956
	105000	787.6	.99961	.99960	.99958	.99957	.99954
	110000	825.1	.99959	.99958	.99957	.99955	.99953
21.0	70000	525.0	.99975	.99973	.99971	.99969	.99966
	75000	562.5	.99973	.99972	.99970	.99967	.99964
	80000	600.0	.99971	.99970	.99968	.99966	.99963
	85000	637.6	.99969	.99968	.99966	.99964	.99961
	90000	675.1	.99968	.99966	.99965	.99962	.99960
	95000	712.6	.99966	.99965	.99963	.99961	.99958
	100000	750.1	.99964	.99963	.99961	.99959	.99956
	101325	760.0	.99964	.99962	.99961	.99959	.99956
	105000	787.6	.99962	.99961	.99959	.99957	.99955
	110000	825.1	.99960	.99959	.99958	.99956	.99953
22.0	70000	525.0	.99975	.99974	.99972	.99969	.99966
	75000	562.5	.99974	.99972	.99970	.99968	.99964
	80000	600.0	.99972	.99971	.99969	.99966	.99963
	85000	637.6	.99970	.99969	.99967	.99964	.99961
	90000	675.1	.99968	.99967	.99965	.99963	.99960
	95000	712.6	.99967	.99965	.99963	.99961	.99958
	100000	750.1	.99965	.99964	.99962	.99960	.99957
	101325	760.0	.99965	.99963	.99961	.99959	.99956
	105000	787.6	.99963	.99962	.99960	.99958	.99955
	110000	825.1	.99962	.99960	.99958	.99956	.99954
23.0	70000	525.0	.99976	.99975	.99972	.99969	.99966
	75000	562.5	.99974	.99973	.99971	.99968	.99964
	80000	600.0	.99973	.99971	.99969	.99966	.99963
	85000	637.6	.99971	.99969	.99967	.99965	.99962
	90000	675.1	.99969	.99968	.99966	.99963	.99960
	95000	712.6	.99968	.99966	.99964	.99962	.99959
	100000	750.1	.99966	.99965	.99962	.99960	.99957
	101325	760.0	.99965	.99964	.99962	.99960	.99957
	105000	787.6	.99964	.99963	.99961	.99958	.99956
	110000	825.1	.99963	.99961	.99959	.99957	.99954
24.0	70000	525.0	.99977	.99975	.99973	.99969	.99965
	75000	562.5	.99975	.99973	.99971	.99968	.99964
	80000	600.0	.99973	.99972	.99970	.99967	.99963
	85000	637.6	.99972	.99970	.99968	.99965	.99962
	90000	675.1	.99970	.99969	.99966	.99964	.99960
	95000	712.6	.99968	.99967	.99965	.99962	.99959
	100000	750.1	.99967	.99965	.99963	.99961	.99957
	101325	760.0	.99966	.99965	.99963	.99960	.99957
	105000	787.6	.99965	.99964	.99962	.99959	.99956
	110000	825.1	.99964	.99962	.99960	.99957	.99954
25.0	70000	525.0	.99977	.99976	.99973	.99970	.99965
	75000	562.5	.99976	.99974	.99971	.99968	.99964
	80000	600.0	.99974	.99973	.99970	.99967	.99963
	85000	637.6	.99973	.99971	.99968	.99965	.99962
	90000	675.1	.99971	.99969	.99967	.99964	.99960
	95000	712.6	.99969	.99968	.99965	.99962	.99959
	100000	750.1	.99968	.99966	.99964	.99961	.99958
	101325	760.0	.99967	.99966	.99963	.99961	.99957
	105000	787.6	.99966	.99964	.99962	.99960	.99956
	110000	825.1	.99965	.99963	.99961	.99958	.99955
26.0	70000	525.0	.99978	.99976	.99973	.99970	.99965
	75000	562.5	.99976	.99975	.99972	.99968	.99964
	80000	600.0	.99975	.99973	.99970	.99967	.99963
	85000	637.6	.99973	.99971	.99969	.99966	.99961
	90000	675.1	.99972	.99970	.99967	.99964	.99960
	95000	712.6	.99970	.99968	.99966	.99963	.99959
	100000	750.1	.99969	.99967	.99964	.99961	.99958
	101325	760.0	.99968	.99966	.99964	.99961	.99957
	105000	787.6	.99967	.99965	.99963	.99960	.99956
	110000	825.1	.99966	.99964	.99961	.99959	.99955