

Air Buoyancy Correction in High-Accuracy Weighing on Analytical Balances

Randall M. Schoonover* and Frank E. Jones

National Bureau of Standards, Washington, D.C. 20234

In the context of the calculation and application of air buoyancy corrections in weighing, the calibration of single-pan direct-reading analytical balances is treated in detail. The resulting equations are applied to the calibration of syringes and to the weighing of granular or powdered materials or liquids in weighing bottles.

In the development of techniques to optimally apply Karl Fischer reagent titration to the determination of water (I) it has been necessary to meticulously calculate and apply air buoyancy corrections in the several weighing operations involved. Since treatment of air buoyancy in weighing involves proper use of and, particularly, calibration of analytical balances, we present here the definitive, fairly detailed yet concise description of weighing on analytical balances which did not heretofore exist in the chemical literature.

THE ANALYTICAL BALANCE

The work reported here is directed toward the use and calibration of the single-pan direct-reading analytical balance. In this type of balance the load on the pan is balanced by weights which are built into the balance and which are manipulated through external controls and by a functional characteristic of the balance which has been adjusted to approximately indicate in mass units the remaining weight beyond the least of the built-in weights. The nominal values of the built-in weights are indicated as dial readings or other direct readout, and the remaining weight is indicated on a ground glass screen or displayed electronically; we shall refer to these indications as "dial" and "screen" indications, respectively. Modern top-loading electronic balances which use force transducers do not have built-in weights. The electronic readout can be treated as a screen indication.

Calibration of Built-in Weights. The built-in weights are usually accurately adjusted by the manufacturer to one of the "apparent mass" scales. The "apparent mass" of an object is the mass which, under specified ambient conditions (20 °C and air density of 0.0012 g cm⁻³), exerts the same force on a balance as the same mass of a reference material of specified hypothetical density. The hypothetical densities corresponding to the two apparent mass scales in current use are 8.0 g cm⁻³ and 8.3909 g cm⁻³. It is necessary to convert from the apparent mass to the approximate true mass of the built-in weights by using the equation

$$B = I \left[\frac{1 - (0.0012/\rho_I)}{1 - (0.0012/\rho_B)} \right] = IQ \quad (1)$$

where B is the approximate true mass of the built-in weight, I is the mass of the hypothetical reference material (i.e., the dial reading), ρ_B is the density of the built-in weight, and ρ_I is the hypothetical density (2). The values of ρ_B and ρ_I are supplied by the manufacturer. Values of Q are listed in Table I.

The value of B calculated by use of eq 1 may differ from the true mass value of the built-in weight, although it might be sufficiently close to the true mass value for the particular measurement which the analyst wishes to make. For more

Table I. Examples of Values of Q , $[1 - (0.0012/\rho_I)]/[1 - 0.0012/\rho_B]$

ρ_B , g cm ⁻³	Q	
	$\rho_I = 8.0$ g cm ⁻³	$\rho_I = 8.3909$ g cm ⁻³
7.76	1.000 004 6	1.000 011 6
7.80	1.000 003 8	1.000 010 8
7.90	1.000 001 9	1.000 008 9
8.00	1.000 000 0	1.000 007 0

accurate measurements it is necessary to calibrate the built-in weights using standard weights. The built-in weights are used in combination in the operation of balance, therefore it is necessary only to calibrate the individual weights and add the results to arrive at the values for the calibrations.

In the calibration of a built-in weight, a standard weight of mass S (from a set of standard weights covering the mass range of built-in weights) approximating the mass, D_i and ρ_{L_0} , = $\Sigma_0 - \Sigma_i$, of the built-in weight and a small weight of mass Δ approximately one-fourth of the range of the screen are used on the balance pan to generate the following mass balance equations:

$$L_0 \left(1 - \frac{\rho_a}{\rho_{L_0}} \right) = \Sigma_0 \left(1 - \frac{\rho_a}{\rho_B} \right) - O_1 K_C \quad (2)$$

$$L_0 \left(1 - \frac{\rho_a}{\rho_{L_0}} \right) = S \left(1 - \frac{\rho_a}{\rho_S} \right) + \Sigma_i \left(1 - \frac{\rho_a}{\rho_B} \right) - O_2 K_C \quad (3)$$

$$L_0 \left(1 - \frac{\rho_a}{\rho_{L_0}} \right) = S \left(1 - \frac{\rho_a}{\rho_S} \right) + \Sigma_i \left(1 - \frac{\rho_a}{\rho_B} \right) + \Delta \left(1 - \frac{\rho_a}{\rho_\Delta} \right) - O_3 K_C \quad (4)$$

$$L_0 \left(1 - \frac{\rho_a}{\rho_{L_0}} \right) = \Sigma_0 \left(1 - \frac{\rho_a}{\rho_B} \right) + \Delta \left(1 - \frac{\rho_a}{\rho_\Delta} \right) - O_4 K_C \quad (5)$$

where L_0 is the balance tare, Σ_0 is the mass of all of the built-in weights, Σ_i is the sum of the mass of all the built-in weights less the mass of the weight removed for calibration, the O_s are screen observations, K_C is a factor which calibrates the screen over about one-fourth of the range, ρ_a is the density of air, and ρ_{L_0} , ρ_S , ρ_B , and ρ_Δ are the densities of the tare, standard, built-in, and small weight, respectively. Σ_0 corresponds to the unloaded pan dial reading of zero and the difference, $\Sigma_0 - \Sigma_i$, corresponds to the dial reading when the standard weight is on the balance pan. The density of air is calculated from measurements of pressure, temperature, and humidity by using an air density equation in ref 3. The screen reading of the unloaded pan, O_1 , must be near zero. From this set of mass balance equations

$$D_i = \left[S \left(1 - \rho_a/\rho_S \right) - \frac{(O_2 + O_3 - O_1 - O_4)K_C}{2} \right] / (1 - \rho_a/\rho_B) \quad (6)$$

and

$$K_C = \frac{\Delta(1 - \rho_a/\rho_\Delta)}{(O_3 - O_2)} \quad (7)$$

This sequence of measurements is repeated for each dial reading which represents a discrete weight; the remaining dial readings correspond to combinations of the discrete weights and are readily assigned mass value by summing the appropriate mass values.

Calibration of the Screen. It is also necessary to calibrate that part of the balance indication that does not relate to the built-in weights, i.e., the "screen" indication. We distinguish between the calibration of a small part of the screen to arrive at K_C in the preceding section and the calibration of the entire screen for use in normal weighing on the balance. It is convenient to determine a single calibration factor, K_S , to be applied to the entire screen. However, for greatest accuracy the lack of linearity of the screen indication must be taken into account. One can determine the nonlinearity by observing the change in screen indication with the application of standard weights at various points in the range of the screen. If the nonlinearity is of consequence to the user, a series of such observations can be fitted to an empirical formula that can be applied in subsequent use of the balance. This procedure is discussed in greater detail in ref 4. In the present paper we shall be concerned with the determination of K_S .

Determination of K_S . The screen can be calibrated in the same manner as was set forth for the calibration of built-in weights. First the balance is zeroed and then one places on the balance pan a standard weight of mass equal to the nominal screen full-scale indication and observes the screen indication. K_S is equal to the ratio of the true mass of the standard weight less the buoyant effect to the screen indication. The value of K_S can also be determined by calibrating the screen using the least increment of the built-in weights. This is accomplished by placing sufficient mass ("tare" on the balance pan to bring the screen indication to near full-scale at a particular dial setting, D_1 . The screen indication, O_1 , is noted and the dial setting is increased by one least increment to D_2 , and the new screen indication, O_2 is noted. K_S is then calculated to be

$$K_S = \frac{(D_2 - D_1)_t(1 - \rho_a/\rho_B)}{(O_1 - O_2)} \quad (8)$$

where $(D_2 - D_1)_t$ is the mass difference corresponding to the two dial settings, calculated with either eq 1 or eq 6.

AIR BUOYANCY

A quantity of material being weighed on an analytical balance experiences a supporting buoyant force equal to the product of the mass of air it displaces and the acceleration due to gravity. The mass of air displaced is equal to the product of the density of air and the volume of the displaced air. Similarly, the built-in weights experience a supporting buoyant force. The relationship between the mass of the material, A , and the mass of the corresponding built-in weights, B , taking into account the buoyant forces, is

$$A = B \frac{[1 - (\rho_a/\rho_B)]}{[1 - (\rho_a/\rho_A)]} \quad (9)$$

where ρ_A and ρ_B are the densities of the material and the built-in weights, respectively. Eliminating B from the right-hand side

$$\frac{B - A}{B} = 1 - \frac{[1 - (\rho_a/\rho_B)]}{[1 - (\rho_a/\rho_A)]} \quad (10)$$

A plot of eq 10 is a convenient form in which to display the buoyancy effect. In Figure 1, the relative magnitude of the buoyancy effect, $(B - A)/B$, is plotted against the density of

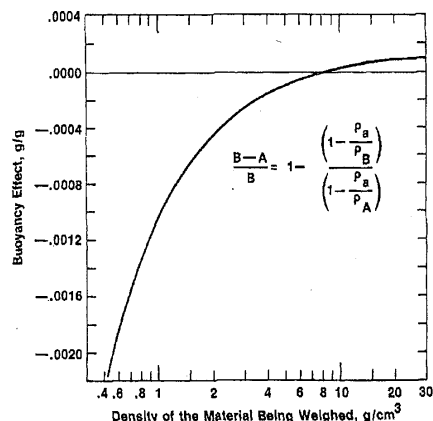


Figure 1. Plot of the relative magnitude of the buoyancy effect, $(B - A)/B$, against the density of the material being weighed, ρ_A , for $\rho_a = 0.0012 \text{ g cm}^{-3}$ and $\rho_B = 8.0 \text{ g cm}^{-3}$.

Table II. Typical Calculations

(1) Calculation of Approximate True Mass, B , for a 10-g Built-in Weight, Using eq 1

$$I = 10 \text{ g}; \rho_1 = 8.39 \text{ g/cm}^3; \rho_B = 7.78 \text{ g/cm}^3$$

$$B = 10 \left[\frac{1 - (0.0012/8.39)}{1 - (0.0012/7.78)} \right] = 10.000112 \text{ g}$$

(2) Calculation of True Mass, D_1 , for the Same 10-g Built-in Weight, Using eq 6

$$S = 10.0000550 \text{ g}; \rho_a = 0.001172 \text{ g/cm}^3; \rho_S = 7.90 \text{ g/cm}^3;$$

$$O_s = 0004 \text{ div}; O_2 = 1998 \text{ div}; O_1 = 0005 \text{ div}; O_4 =$$

$$1998 \text{ div}; K_C = 0.000010 \text{ g/div}; \rho_B = 7.78 \text{ g/cm}^3$$

$$D_1 = [10.0000550[1 - (0.001172/7.90)] - (4 + 1998 - 5$$

$$- 1998)(0.000010)/2]/[1 - (0.001172/7.78)]$$

$$D_1 = 10.000088 \text{ g}$$

(3) Determination of K_S by Built-in Weight, Using eq 8

$$(D_2 - D_1)_t = (D_2 - D_1)Q = 0.1 \times 1.0000112 \text{ g}; \rho_a =$$

$$0.001172 \text{ g/cm}^3; \rho_B = 7.78 \text{ g/cm}^3; O_1 = 9988$$

$$\text{div}; O_2 = 0002 \text{ div}$$

$$K_S = \frac{(0.1 \times 1.0000112)[1 - (0.001172/7.78)]}{(9988 - 2)} =$$

$$0.000010 \text{ g/div}$$

(4) Determination of the Mass, M_U , of TiO_2 Powder, Using eq 14

$$D_F - D_E = (92.5 - 72.3)(1.0000112) \text{ g}; \rho_a = 0.001173$$

$$\text{g/cm}^3; \rho_o = 7.78 \text{ g/cm}^3; O_4 = 2083 \text{ div}; O_2 = 4399 \text{ div};$$

$$K_S = 0.000010 \text{ g/div}; \rho_U = 4.60 \text{ g/cm}^3$$

$$M_U = [(92.5 - 72.3)(1.0000112)[1 - (0.001173/7.78)] +$$

$$(2083 - 4399)(0.000010)]/[1 - (0.001173/4.60)]$$

$$M_U = 20.179169 \text{ g}$$

the material being weighed. The curve crosses the axis of abscissas at the density of the built-in weights.

Buoyancy Applied to Weighing of Syringes. The volume of a liquid (such as a mixture of methanol and water in the Karl Fischer titration determination of water (1)) dispensed from a syringe is determined from a calibration of the syringe. The syringe is calibrated (5) by filling with water to a particular graduation on the barrel, weighing the syringe before and after dispensing the water (in both cases the syringe is open to the atmosphere), and inferring the volume from the mass and density of the water dispensed. In ref 5 it was demonstrated that the volume of water contained at the 0.500 graduation on a 1-mL-capacity syringe can be determined with a precision (standard deviation of the mean for 15 measurements) of 1.2 parts in 10000. The buoyancy effect calculated by using eq 10 is 1.05 parts in 1000; therefore, for this example, it is necessary to include the buoyancy effect in the calculation

of syringe volume, or of the mass of water contained.

The mass balance equation for the weighing of the empty syringe is

$$S[1 - (\rho_a/\rho_S)] = D_E[1 - (\rho_a/\rho_D)] + (O_2 - O_1)K_S \quad (11)$$

where S and ρ_S are the mass and density, respectively, of the syringe, D_E and ρ_D are the mass and density, respectively, of the combination of built-in weights O_2 and O_1 are the screen indications with and without the syringe on the balance pan, and K_S is the calibration factor for the screen. O_1 is usually adjusted to zero. The mass balance equation for the weighing of the syringe containing a mass M_w of water is

$$S[1 - (\rho_a'/\rho_S)] + M_w[1 - (\rho_a'/\rho_w)] = D_F[1 - (\rho_a'/\rho_D)] + (O_4 - O_3)K_S \quad (12)$$

where D_F is the mass of the combination of built-in weights, ρ_w is density of the water inferred from the temperature of the water (θ), ρ_a' is the density of air at the time of the weighing, and O_4 and O_3 are the screen indications with and without the syringe on the balance pan. If the two weighings are done sufficiently close in time that the air density does not change, $\rho_a = \rho_a'$. If we set O_1 and O_3 equal to zero, the mass of water, M_w , in the syringe is

$$M_w = \frac{(D_F - D_E)[1 - (\rho_a/\rho_D)] + (O_4 - O_2)K_S}{[1 - (\rho_a/\rho_w)]} \quad (13)$$

Buoyancy Applied to Weighing in Weighing Bottles.

For the determination of the mass, M_U , of a solid material (granular, powder, etc.) or a liquid by weighing in a weighing bottle an equation similar to eq 13 applies

$$M_U = \frac{(D_F - D_E)[1 - (\rho_a/\rho_D)] + (O_4 - O_2)K_S}{[1 - (\rho_a/\rho_U)]} \quad (14)$$

where ρ_U is density of the material. The density of a granular material or a powder can be determined by using a gas pycnometer.

Typical calculations using equations in this paper are given in Table II.

ACKNOWLEDGMENT

The authors thank R. S. Davis for suggesting Figure 1.

LITERATURE CITED

- (1) Jones, F. E., unpublished results.
- (2) Pontius, P. E. *NBS Monogr. (U.S.)* 1974, No. 133, 15.
- (3) Jones, F. E. *J. Res. Natl. Bur. Stand. (U.S.)* 1978, 83, 419.
- (4) Bowman, H. A.; Schoonover, R. M. *J. Res. Natl. Bur. Stand., Sect. C* 1987, 71, 179.
- (5) Jones, F. E. *Anal. Chem.* 1980, 52, 384.
- (6) Wagenbreth, H.; Blanke, W. *PTB-Mitt.* 1971, S. 412.

RECEIVED for review October 28, 1980. Accepted February 19, 1981.

CORRESPONDENCE

Ion-Selective Electrodes Based on an Ionic Polymer

Sir: Plasticizers are required in polymer membrane ion-selective electrodes (PMISEs) in order to increase ionic mobility in the polymeric membrane. The work of Oesch and Simon (1) indicates that the loss of plasticizer and/or electroactive species from the solvent polymeric membrane phase into the sample solution determines the lifetime of PMISEs based on neutral ligands. While this study dealt only with neutral ligands, it is safe to conclude that loss of ligand or plasticizer from the membrane is a factor controlling the lifetime for any type of PMISE. The work of Cutler et al. with surfactant-sensitive PMISEs based on charged ligands (2) attests to the generality of this mechanism for electrode demise and also allows generalization of Oesch and Simon's statement that "serious limitations as to lifetime have to be expected in certain applications" of PMISEs.

Since the polymer membrane used in electrodes of this type are essentially water insoluble, covalent attachment of the electroactive species to the polymer would be an attractive solution to the ligand leaching problem. It should be noted that PMISEs based on ion-exchange resins (3), which were investigated a number of years ago, are an example of ion-selective electrodes (ISE) of this type. The selectivities of the ion exchange resin based electrodes were, however, too low for practical analytical applications. Recent attempts to prepare ISEs by covalent attachment of selective ligands to polymers (2, 4, 5) have not resulted in longer-lived electrodes because the polymers used have required plasticizing. Hence, demise of the electrode via leaching of the plasticizer remains a problem. The pH-sensitive polymer film electrode of

Heineman (6) is an interesting exception since the polymer employed apparently does not require plasticizer.

It is well-known that ionic clusters are formed in ionic polymers containing a sufficient quantity of covalently attached ionic groups (7). These ionic clusters contain the polymer-attached ion, its counterion, and water of hydration as well as some of the polymer chain material (7). Recent studies of DuPont's Nafion polymers have yielded much information about the physical characteristics of these ionic clusters (8-10). In a model developed by Gierke (9) the ionic clusters (about 40 Å in diameter) are randomly distributed throughout the backbone tetrafluoroethylene (TFE) polymer and are connected by small (about 10 Å in diameter) channels. Yeager and Kipling (10) present data indicating that ions may diffuse from cluster to cluster via these small channels. Hence, in ionic polymers containing ionic clusters, a mechanism for ionic transport without plasticizing the polymer apparently exists. PMISEs based on these polymers should, therefore, have essentially infinite lifetimes since no leachable membrane components are required. These considerations prompted us to investigate the response characteristics of PMISEs based on Nafion membranes. Preliminary results of this investigation are reported here.

EXPERIMENTAL SECTION

Nafion Pretreatment and Electrode Preparation. The Nafion polymers are a family of perfluorosulfonate cation-exchange polymers developed by DuPont, having the basic structural formula shown below. The Nafion polymer used in this study