Summary

Titration of iodine with thiosulfate in a dil. acid solution gives results 0.1 to 0.3% higher and more concordant than the results of titration in a neutral solution.

The presence of air affects the titration of iodine with thiosulfate when the acidity of the solution is equivalent to 0.3 *M* hydrochloric acid or greater, causing too much thiosulfate to be required.

An apparent excess of oxidizing action of dichromate is caused by the titration of the iodine in a solution of too high an acid concentration. This can be corrected by exclusion of air, but more easily by dilution to such a hydrogen-ion concentration that the presence of air will not interfere.

Chromates can be determined within 0.1% by the iodide method under the proper conditions.

Potassium dichromate as a standard for thiosulfate solutions agrees with pure iodine within 0.1% but gives a slightly lower value. Errors in the iodine standardization leading to such a difference seem about as probable as errors in the dichromate standardization.

A standard permanganate solution is unreliable as a standard for thiosulfate solutions.

Newport, Rhode Island

[Contribution from the Philadelphia Works of E. I. du Pont de Nemours and Co.]

THE EFFECT OF VARIATION IN WEIGHT OF THE RIDERS AND PLUMMETS OF THE WESTPHAL BALANCE UPON THE ACCURACY OF SPECIFIC-GRAVITY DETERMINATIONS

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The Westphal balance is largely used in the oil and heavy chemical industries because of the rapidity and ease with which specific-gravity determinations can be made. It is sometimes used to check the accuracy of hydrometers. Obviously for this purpose it is necessary that accurate results be obtained with the instrument, since a variation of ± 0.005 from the true specific gravity in the indicated density of the standardizing liquid will lead to an error in an hydrometer reading ranging from $\pm 2.0°$ to $\pm 0.2°$ Bé. from the true reading, the maximum error being attained when the standardizing liquid has a low specific gravity, (0.60–0.61). The accuracy of specific-gravity determinations with the Westphal balance is dependent upon the exact interrelation of the plummet displacement P, the weight of the index weight W, the weight of the first decimal rider R_1, and the weights of the second, third and fourth decimal riders R_2, R_3, and R_4. It has been found with instruments at present in use that this interrelation is not exact, and that weight variations in the riders and weights enumerated, which render this multiple relationship inexact, will cause plus or minus errors, often of considerable magnitude, in specific-gravity determinations.

When the weights of W and R_1 agree exactly with the weight of water displaced by the plummet at 15°, and R_2, R_3, and R_4 are exactly 0.1, 0.01 and 0.001, respectively, of the weight of R_1, no corrections are necessary, as the balance will indicate the true specific gravity of the liquid tested. The riders, weights and plummets of any two balances are not interchangeable, and it is probably this fact together with careless handling of the riders which is the source of variation in weights of the riders of any specific system.

The unit upon which all instrumental dimensions and effective weights of the perfect Westphal balance are based is 5. This applies also to Mohr and Sartorius specific-gravity balances. The beam should have an effective length of exactly 10 cm., divided from the knife-edge to the point of suspension of the plummet into 10 divisions spaced 1 cm. apart. The plummet should weigh exactly 10 g. in air and displace 5 g. of water at 15°. The suspension bob of the plummet, to which the upper end of the platinum suspension wire is attached, should weigh 5 g. The index weight and R_1 should weigh exactly 5 g., and R_2, R_3, and R_4, 0.5000, 0.0500, and 0.0050 g., respectively. The index weight is used only for liquids heavier than water and is always suspended from the hook at the end of the beam. In order to ascertain the magnitude of variation in weight among plummets and riders, several plummets and riders were weighed with standardized weights, with the results stated below. The displacement of the plummets was ascertained in distilled water at 15°, and the plummet thermometers were compared with a standard thermometer ranging from +9° to +21°.

PLUMMETS

No.	Weight in air G.	Displacement (G. of H_2O at 15°)	Sp. Gr.	Thermom. Corr. ° C.	Variation from 5 Mg.
1	9.7062	4.9993	1.9415	+2.3	−0.7
2	9.3219	5.0013	1.8638	+0.2	+1.3
3	10.0229	5.0021	2.0037	+0.6	+2.1

WEIGHTS AND RIDERS

W	4.9711	4.9796	5.0026	5.0037	−28.9 to + 0.37
R_1	4.9884	4.9890	5.0066	5.0067	−11.6 to + 6.7
R_2	0.4985	0.4988	0.4990	0.5020	− 1.5 to + 2.0
R_3	0.0503				
R_4	0.0049				

It can be assumed that the ordinary variation for a plummet from 5

g. displacement will be ± 3 mg., while for W and R_1 the variation may range from —30 to +10 mg. The weight of R_2 may vary from 0.5000 g. by ± 2 mg. Small variations from 0.0500 and 0.0050 g. in R_3 and R_4, provided they do not exceed ± 0.2 mg., have a negligible effect on the accuracy of the specific-gravity determination, and may ordinarily be disregarded. As the plummet displaces 5.0000 g. of water at 15°, it is obvious that a variation of ± 1 mg. from 5.0000, 0.5000, 0.0500 or 0.0050 g. in a rider will cause an error in a density determination varying from ± 0.00002 to 0.00018, dependent upon the position of the rider on the beam of the balance. A variation of ± 1 mg. in weight of W, from the plummet displacement of 5.0000 g., will cause a constant error of ± 0.0002 in all determinations.

Magnitude of the Error Involved by Variation in Weight of Plummets and Riders

To ascertain the effect which ordinary variation in weight of the various balance riders, plummet displacement, and the index weight, has upon the specific gravity, the balance readings for various combinations of riders, weights and plummets were compared with the true density of liquids lighter and heavier than water, and the results tabulated in Table I.

TABLE I

P.	W.	R_1	R_2	Sp. Gr.	Bal. Read.	Error	Corr.	Eq.
4.9993	..	5.0067	0.5020	0.9375	0.9360	−0.0015	+0.0015	1
4.9993	..	5.0067	0.4985	0.9376	0.9362	−0.0013	+0.0012	2
5.0021	..	4.9884	0.5020	0.9375	0.9398	+0.0023	−0.0023	3
5.0021	..	4.9884	0.4985	0.9375	0.9401	+0.0026	−0.0025	4
4.9993	5.0037	5.0067	0.5020	1.8437	1.8414	−0.0023	+0.0023	5
4.9993	5.0037	5.0067	0.4985	1.8437	1.8417	−0.0020	+0.0019	6
4.9993	5.0037	4.9884	0.5020	1.8437	1.8443	+0.0006	−0.0006	7
4.9993	5.0037	4.9884	0.4985	1.8437	1.8446	+0.0009	−0.0009	8
5.0021	4.9711	5.0067	0.5020	1.8437	1.8489	+0.0052	−0.0053	9
5.0021	4.9711	5.0067	0.4985	1.8437	1.8492	+0.0055	−0.0056	10
5.0021	4.9711	4.9884	0.5020	1.8437	1.8519	+0.0082	−0.0082	11
5.0021	4.9711	4.9884	0.4985	1.8437	1.8522	+0.0085	−0.0085	12

In all determinations R_3 = 0.0503 g; R_4 = 0.0049 g.

The error in specific gravity due to ordinary variation in the weight of the riders and plummets may, therefore, vary from —0.0015 to +0.0085. As the thermometers of all the plummets tested were found inaccurate, a further error is introduced into the density determination unless a thermometer correction is applied. If the specific gravity is determined at the indicated temperature with a plummet thermometer which varies $\pm 2°$ from the true temperature, the resultant balance reading will indicate a specific gravity which may vary by ± 0.0006 from the true density of the liquid at 15°, when used with fatty oils, and by ± 0.0010 when used with liquids of high specific gravity, such as 93% sulfuric acid.

The Correction of Observed Balance Readings

The elimination from the specific gravity determination of errors due to variation in weight of the riders and plummets may be accomplished either by adjusting the various weights and riders or by applying a correction to the indicated balance readings. Mechanical adjustment of the system is troublesome when variations in weight of the components are less than ± 5.0 mg., and breakage of a plummet may necessitate an entire readjustment. The application of a correction to the observed balance readings is more satisfactory and gives accurate results. The following equations were derived for the computation of the correction to be applied to any indicated balance reading, and are based upon consideration of the error produced in a specific-gravity determination by a variation of ± 1 mg. in weight of any of the riders of a specific system from the exact multiple relationship they must possess to give accurate results, and the magnitude of this error as affected by the position of the rider on the balance beam. They satisfy the conditions for *all possible variations* among plummets, index weights and riders. In these equations, C is the correction to be added to or subtracted from the indicated specific gravity; P, the weight of water at 15°, displaced by the plummet, in mg.; W, the weight of the index weight in mg.; R, the weight of the first decimal rider in mg.; R_2, the second decimal rider; R_3, the third decimal rider; R_4, the fourth decimal rider; D_1, the position of R_1 on the balance beam; D_2, the position of R_2, D_3, the position of R_3 and D_4, the position of R_4.

For Liquids Lighter than Water

When	$C/0.00002$ equals	
$R_1>P,\ R_2>0.1P$	$+\ [D_1(R_1 - P) + D_2(R_2 - 0.1P]$	(1)
$R_1>P,\ R_2<0.1P$	$+\ [D_1(R_1 - P) - D_2(0.1P - R_2)]$	(2)
$R_1<P,\ R_2>0.1P$	$-\ [D_1(P - R_1) - D_2(R_2 - 0.1P)]$	(3)
$R_1<P,\ R_2<0.1P$	$-\ [D_1(P - R_1) + D_2(0.1P - R_2)]$	(4)

For Liquids Heavier than Water

$W>P,\ R_1>P,\ R_2>0.1P$	$+\ [10(W - P) + D_1(R_1 - P) + D_2(R_2 - 0.1P)]$	(5)
$W>P,\ R_1>P,\ R_2<0.1P$	$+\ [10(W - P) + D_1(R_1 - P) - D_2(0.1P - R_2)]$	(6)
$W>P,\ R_1<P,\ R_2>0.1P$	$+\ [10(W - P) - D_1(P - R_1) + D_2(R_2 - 0.1P)]$	(7)
$W>P,\ R_1<P,\ R_2<0.1P$	$+\ [10(W - P) - D_1(P - R_1) - D_2(0.1P - R_2)]$	(8)
$W<P,\ R_1>P,\ R_2>0.1P$	$-\ [10(P - W) - D_1(R_1 - P) - D_2(R_2 - 0.1P)]$	(9)
$W<P,\ R_1>P,\ R_2<0.1P$	$-\ [10(P - W) - D_1(R_1 - P) + D_2(0.1P - R_2)]$	(10)
$W<P,\ R_1<P,\ R_2>0.1P$	$-\ [10(P - W) + D_1(P - R_1) - D_2(R_2 - 0.1P)]$	(11)
$W<P,\ R_1<P,\ R_2<0.1P$	$-\ [10(P - W) + D_1(P - R_1) + D_2(0.1P - R_2)]$	(12)

The maximum errors in a determination result when the variation in weight of the components of any specific system satisfy the conditions of Equations 1, 4, 5, or 12. When the weights of R_3 and R_4 vary more than ± 0.2 mg. from 0.01 P and 0.001 P, it becomes necessary to add additional terms to the correction equations which take the form $+D_3(R_3 - 0.01P)$ or $-D_3(0.01P - R_3)$ and $+D_4(R_4 - 0.001P)$, or $-D_4(0.001P - R_4)$ as R_3

and R_4 are heavier or lighter in weight than 0.01P and 0.001P, respectively.

Assuming $(P - W) = 6.2$ mg., $(P - R) = 5.1$ mg., $(R_1 - 0.1P) = 2.3$ mg., $(0.01P - R_3) = 0.5$ mg., and $(R_4 - 0.001P) = 0.3$ mg. Equations 3 and 11 apply to this particular system and the correction for an indicated density of 0.9555 will be

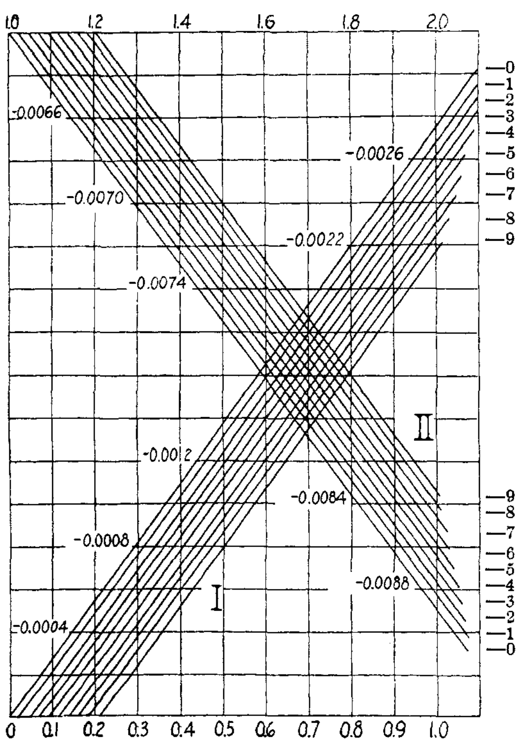
$$C = -0.00002[9(5.1) - 5(2.3) + 5(0.5) - 5(0.3)] = -0.00002(48.4 - 13) = -0.000708.$$

For an indicated density of 1.6555, the correction will be

$$C = -0.00002[10(6.2) + 6(5.1) - 5(2.3) + 5(0.5) - 5(0.3)] = -0.00002(95.1 - 13) = -0.00164.$$

The values in Table I under "Corr." were computed using Equations 1 to 12 and exactly compensate the error caused by variation in weight of the components of the various systems.

In using these equations to determine the necessary corrections to be applied for any specific combination of riders and weights, the exact displacement of the plummet in water at 15°, and the weights of W, R_1, R_2, R_3, and R_4 must be carefully ascertained so that the proper equations for computing the corrections may be selected. Two correction equations are necessary; one for liquids lighter than water and the other for liquids heavier than water. When the proper equations have been selected, the corrections to be applied are computed for densities of 0.30, 0.31, 0.32, ... 0.39, and for 0.90, 0.91, 0.92. . . . 0.99. Curves are then plotted using densities as abscissas and the computed corrections as ordinates (Fig. 1). Straight lines are drawn through the points ($C_{.30}$, 0.30) and ($C_{.90}$, 0.90), ($C_{.31}$, 0.31) and ($C_{.91}$, 0.91). . . . ($C_{.39}$, 0.39) and ($C_{.99}$, 0.99). Ten parallel lines will be obtained, which are given D_2 numbers from 0 to 9. For liquids heavier than water, the corrections are similarly computed for densities of 1.30. . . . 1.39 and 1.90. . . . 1.99 and the correction curves obtained as before (Fig. 2). Figs. 1



and 2 are computed for the systems in Table I, the components of which satisfy the conditions of Equations 3 and 11. In obtaining a correction for any indicated specific gravity from the graphs the correction is the ordinate of the point located by the intersection of the abscissa corresponding to the first two decimals in the indicated specific gravity, with the D_2 curve corresponding to D_2 in the indicated specific gravity. For an indicated specific gravity of 0.9357, obtained with the weights and riders composing the specific system to which Figs. 1 and 2 apply, the abscissa 0.93 (Fig. 1) intersects the D_2 curve numbered 3 at a point, the ordinate of which is —0.00236. This is the correction which must be applied to the indicated balance reading to obtain the true specific gravity, 0.9333, of the liquid. For an indicated specific gravity of 1.8486, the abscissa 1.84 (Fig. 2) intersects the D_2 curve numbered 4 at a point having as its ordinate the correction —0.00825. The true specific gravity of the liquid will then be 1.8404.

Summary

Accurate specific gravity determinations with the Westphal balance are possible only when the weight of water displaced by the plummet at 15°, and the weights of the riders possess an exact multiple relationship among themselves. Variations in weight of the riders which disturb this relationship produce errors, often of considerable magnitude, in specific-gravity determinations. Inaccurate plummet thermometers are also a source of error. The magnitude of ordinary variation in weight of riders and plummets has been ascertained, and equations have been derived for computing the correction which must be applied to any indicated balance reading in order to obtain the true specific gravity of liquids lighter or heavier than water. Application of the corrections for any specific system of riders to indicated balance readings is facilitated by the construction and use of correction graphs.

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