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THE SINGLE DEFLECTION METHOD OF WEIGHING.

BY PAUL H. M.-P. BRINTON.

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Of the routine manipulations required in chemical analysis few are more important, and at the same time more tedious, than the operation of weighing, and any shortening of the time necessary for this would be a great help. Routine analysts usually find short cuts, but the research worker who carries though his analyses with a different end in view, and gives less thought to simplifying manipulative details, frequently wastes much time and patience in the use of the balance. The method described in this paper has been adopted after exhaustive tests as to its reliability and rapidity, and it seems only fair to offer to others the advantage of the great saving of time which this system effects, without the sacrifice of essential accuracy. The method was brought to the writer's attention a number of years ago by Dr. F. N. Guild, of the University of Arizona, who had used it for many years, but could not give the source from which it originally came. So far as can be learned, the procedure has never been described in book or journal, with the exception of a short paper by Turner.[1] It is believed that the method is almost unknown, and is used in very few laboratories. Those who have heard the method mentioned probably regard it with the same scepticism as did the writer, who refused

[1] *Chemist-Analyst*, January, 1916.

to even try it for 10 years, so unorthodox did the system appear; and so little faith did he have that any degree of accuracy was obtainable by so simple a procedure.

The method is carried out as follows: The balance is given a permanent overload on the left arm by screwing the adjusting nut on one end of the beam until when the beam and pans are released the pointer will swing out from 3 to 7 scale divisions to the right. The pan arrests must be so adjusted that there is no lateral vibration of the pans when released. Before determining the zero point the stability of the pans is assured by moving the pan-arrest button in and out a few times. The beam is then freed, and the pans are next released by a gentle, steady motion. The pointer will swing out to the right, and the turning point of this single excursion is taken as the zero point. To obtain the weight of any object it is only necessary to add weights until the pointer is caused to swing out to the same point on the ivory scale. The convenience and rapidity of the method were immediately apparent, but grave doubts were entertained as to its practicability and reliability until confidence was established by critical investigation.

Constancy of Deflection.

A Becker aluminum balance was used, and 4 sets of weighings were made, each consisting of 9 observations. The deflection readings are shown in Table I. The 4 sets were made in determining the sensibility of the balance with empty pans, and with 50 g. loads, so concordance between A and D, and between B and C, is not to be looked for. The arithmetical mean of each set has been calculated, and also the value of d/s, in which d represents the maximum deviation from the arithmetical mean in each set, and s the sensibility of the balance in scale divisions per milligram.

Table I.

										Mean.	d/s.
A.........	3.7	3.75	3.8	3.75	3.8	3.8	3.75	3.8	3.75	3.77	0.015
B.........	8.8	8.8	8.8	8.85	8.75	8.8	8.75	8.85	8.8	8.80	0.010
C.........	8.65	8.7	8.6	8.6	8.6	8.65	8.65	8.65	8.6	8.63	0.015
D.........	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.55	3.60	0.010

It will be seen that with this balance the constancy of deflection fulfils the strictest demands of accuracy, for the values of d/s indicate that the greatest error of observation in this step will probably not exceed 0.015 mg. The weighings were made by an experienced manipulator, with a splendid balance, ideally situated, and with a reading lens for observation of deflections. To give the method a more thorough trial, experiments were made with a section of 10 average students who had never handled an analytical balance (although 3 had had a course in assaying). These men were assigned to balances which cost from $35 to $75 each, selected at random in the regular student balance room. Each student made 4 sets of weighings, with 5 to 7 observations in each set. The sensibilities of the balances registered from 2.6 to 4.9 scale divisions per milligram. In Table II are recorded the values of d/s, in which d was taken as the greatest deviation from the mean in any set for each student. The number of readings by each observer was from 20 to 28.

TABLE II.

Student	1	2	3	4	5	6	7	8	9	10
d/s	0.03	0.10	0.03	0.06	0.06	0.04	0.08	0.06	0.03	0.03

From this it is seen that in the work of entirely inexperienced students, with ordinary balances, any error introduced through inconstancy of deflection will probably not exceed 0.1 mg. These students had no idea that their results were to be tabulated for publication, and it is certain that further practice in weighing would increase the accuracy of their observations.

In order to test the effect of one's prejudice in favor of making all subsequent readings in any one set agree with the estimate made in the first observation, the same 10 students were asked to read the deflection on one high grade balance. Only one student was allowed in the room at at a time, so no mental prejudice was operative. The observations extended over a period of two hours, and the deflection was determined at intervals by the writer, whose readings are shown under the asterisks in Table III. Each student made 5 to 7 observations, and in the case of only one operator did a deviation from the mean as great as 0.1 scale division occur. The sensibility of the balance was 5.0.

TABLE III.

Student	*	1	2	3	4	*	5	6	7	8	9	10	*
Deflection	3.7	3.7	3.8	3.7	3.8	3.8	3.8	3.8	3.8	3.8	3.9	3.8	3.85

From the writer's observations it seems probable that the zero point shifted a tenth of a division or so during the period, and taking this into account one must be struck by the concordance of the readings of 11 experimenters, 10 of whom were inexperienced.

For those trying the method on a very sensitive balance it is suggested that attention be paid to the effect of the currents of air, or the lengthening of the beam, caused by the heat of the hand near one pan, for it will be found that the first swing does not always accord with those which follow. This method is so rapid that irregularities are easily detected which would frequently escape observation by ordinary manipulation.

The balance case had been closed a long time, and these deflection readings were taken:

3.9 3.9 3.9 3.9 3.9 3.9

The hand was then held 15 seconds near the left pan, and as soon as the door had been closed, the following series of observations was begun:

4.0 3.95 3.9 3.9 3.9

The experiment was repeated, holding the hand near the right pan for 15 seconds, with the following results:

3.6	3.9	3.95	3.9	3.95

It is seen that with a sensitive balance a few moments must be allowed for abatement of jar and air currents, but equilibrium is soon re-established. This is not to be construed as a criticism peculiar to this particular method, for it will be understood that the same precaution is necessary with any system of weighing.

Behavior with Various Loads.

Two faults frequently found in balances, especially in those of cheaper grade, are varying sensibility under increasing load, and inequality in the lengths of the two lever arms. It is evident that both these conditions would influence the accuracy of absolute weighings by the single deflection method, but in nearly every instance in analytical work the weighing consists in comparing the weight of an empty vessel (watch glass, crucible, or dish) with that of the same vessel containing at most a few grams of sample or ignited precipitate. Manifestly, then, the error introduced by varying sensibilities, or by inequality of arms, would be negligible in nearly all cases of analytical practice. The method has been successfully used by students in calibrating weights by the method of Richards,[1] and a few hours only are required by even a beginner for the calibration of a full set of weights.

Precautions and Limitations.

The single deflection method of weighing cannot be used with those types of balances in which the beam and pan-arrests are all released by one operation, as by the turning of one milled head or lever; and it has occasionally been found that a balance of the correct general type has failed to give concordant readings in successive weighings. In nearly every instance it has been found that these balances failed to yield concordant weighings by any other method.

The pan-arrests must be clean and adjusted to the proper height. A little alcohol will remove any grease which might tend to cause sticking of the pan-arrest to the bottom of the pan.

A little experience with a particular balance will soon show one just how far the method can be trusted with that instrument. With the balance habitually used by the writer, which has an unvarying sensibility with loads up to 50 g., the method is regarded as suitable to work of the very highest accuracy. It is realized that the error of a single observation should be greater than that of the mean of 3 or 5 observations, but it may be pointed out that it is much easier to read with the highest accuracy when the swing is to one side only, and does not cross a center point.

[1] This Journal, 22, 144 (1900).

Furthermore, the chance for lapse of mental concentration and attention is greatly diminished in the single deflection method. In work of great importance the weighing can be checked by a second weighing in less time than is needed for one weighing by the conventional methods.

It is certainly not advisable to teach this method to students as their sole equipment for weighing operations, for a number of good balances on the market are of the "single release" type; but with proper emphasis on the limitations of the process the single deflection method can be given to students with great benefit. An analyst who will weigh out a 3-g. sample of steel, for determination of phosphorus, with an accuracy greater than within one mg., has little greater chance of success in the world than he who will weigh out a 0.2-g. sample of copper foil, for standardizing, with an acuracy less than within 1 mg.

TUCSON, ARIZONA.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

INTERMEDIATE AND COMPLEX IONS. V. THE SOLUBILITY PRODUCT AND ACTIVITY OF THE IONS IN BI-BIVALENT SALTS.[1]

BY WILLIAM D. HARKINS AND H. M. PAINE.

Received October 3, 1918.[2]

The first evidence which indicates that *all salts* which give, on complete ionization, 3 or more ions, ionize in steps in such a way as to give intermediate ions, was presented by Harkins[3] in 1911. The earlier idea was that intermediate ions are present in aqueous solution of some of the salts of higher types, but not in all cases. Thus Abegg and Spencer,[4] in 1905, considered that thallous oxalate gives rise to an intermediate ion, but potassium oxalate does not, while in 1911 Jellinek[5] concluded that intermediate ions are present in solutions of sodium sulfate, but not when potassium sulfate is the solute. Such salts are mercuric chloride, cadmium chloride, and lead chloride were commonly believed to give intermediate ions, but the more ordinary salts were in general supposed to ionize in one step or else to give only a negligible fraction of intermediate ions. Perhaps the strongest evidence in favor of ionization in one step

[1] This series of papers was begun by the senior author in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology and has been continued in the laboratory of the University of Chicago with the consent of Professor A. A. Noyes.

[2] Revised manuscript received April 21, 1919. The paper was completed, except for minor changes, in June, 1914.

[3] THIS JOURNAL, **33**, 1836–72 (1911); Harkins and Pearce, *Ibid.*, **37**, 2679 (1916).

[4] *Z. anorg. Chem.*, **46**, 406 (1905).

[5] *Ibid.*, **76**, 309 (1911).