

SOME FREQUENTLY-NEGLECTED ERRORS OF ANALYSIS.

BY H. DROOP RICHMOND.

IN many commercial laboratories it is the practice for several experimenters to weigh on one balance and with one set of weights; and in more than one that I have known the weights are left on the pans when the weighings are finished, and the weight-box is left open. In laboratories where such is the practice, the standardizing of weights, and the daily adjustment of the balance to its zero point are also neglected.

I had occasion once to use a set of weights that had been used continually for some years in a busy laboratory, in which the standardizing of the weights was considered superfluous, and took the opportunity of comparing them to see to what extent errors might arise from this cause. The results were :

Nominal Weight.	Real Weight.	Nominal Weight.	Real Weight.
10'	Taken as Standard	·5	·4982
10"	9·9997	·2	·1993
5	4·9990	·1'	·0971
2	1·9991	·1"	·0982
1'	·9987	·05	·0485
1"	·9989	·02	·0191
1'''	1·0008	·01'	·0092
		·01"	·0089

As an example of the error which may occur, I quote the analysis of a commercial sulphate of copper. This is an actual example obtained with other weights; I have supposed, for purposes of illustration, that the above weights were used :

Tare of watch glass	4·3370	
Watch glass and sample	5·3387	Supposing 1''' had been added the real weight is
			1·0017	1·0025
Tare of Platinum	13·0032	
Platinum and Copper	13·2373	Supposing ·2, ·02, and ·01' had been added the real weight is
			·2341	·2317
Percentage: Cu	23·37	...
CuSO ₄ ·5OH ₂	91·83	...
				...
			Apparent.	Real.
			23·37	23·11
			91·83	90·82

I have here chosen a striking case for purposes of illustration, but it is one that may occur in many laboratories, and may lie in opposite directions with different analysts; this possibly is a partial explanation of the differences between chemists in commercial analysis. I have found that two or three hours is sufficient for the comparison of a set of weights, and would recommend Gauss' method of reversal (*cf. Miller, Phil. Trans., 1856, iii.*) as the most useful method of determining them.

In the majority of balances that I have used the zero point has varied with the load; thus in a long-beam Oertling I found :

Load in each Pan.	Zero Point in Milligrammes.
none	0·0
1 gramme.	+ 0·3
2 "	+ 0·6
5 "	+ 1·0
10 "	+ 1·2
20 "	+ 1·7
50 "	+ 3·6

By the ordinary method of weighing there would be ·03 per cent. difference in the apparent value of a 1 gramme weight, according as it were weighed with no other load or with a load of 50 grammes. This would be of no practical importance in ordinary work, but it illustrates the absurdity of stating results to the third place of decimals per cent., which I have seen on commercial certificates of analysis.

Neglect of correction of weighings to a vacuum is invariably practised in commercial analysis, yet it may affect the fourth place of decimals in density determinations of strong sulphuric acid, and may cause errors of nearly 0·1 per cent. in normal solutions, if barium sulphate, or silver chloride, or bromide be weighed.

That graduated instruments are frequently incorrect is universally known, but in many laboratories they are used as sold without being checked.

It is a less well-known fact, though a committee of the British Association has reported on this, that blowing out pipettes is less accurate than simply allowing them to drain, and then touching the end of the pipette against the side of the vessel in which it has been allowed to drain. It must also be remembered that a pipette which delivers 10 c.c. of water will not deliver the same volume of sulphuric acid or milk or of any fluid of differing viscosity; two 10-c.c. pipettes, each correct for water, may not deliver the same volume of sulphuric acid, and errors in oil analysis by the Maumené method may thus arise.

Turning to the errors of standard solutions, the expansion by heat is a cause of error; thus, with normal sulphuric acid, calling the value 15° 100, the following values at various temperatures are found:

Temperature.	Value.
10°	100·12
15°	100·00
20°	99·85
25°	99·69
30°	99·52

As the extremes in the table may be taken to represent the temperatures attained in a laboratory in summer and winter, it follows that a difference of 0·6 per cent. may be due to the neglect of expansion of a standard solution.

Another error in alkalimetric titrations may occur from the standardization of baryta solution on normal sulphuric acid; I have already referred to this (ANALYST xvi., 166), but as since then Richards has redetermined the atomic weight of barium, I have corrected my figures for this.

Thus the standard acid used contained 5.08° per cent. of H_2SO_4 (using 137.5 as the atomic weight of barium and correcting the weighings to a vacuum standard) instead of 5.104 per cent. The percentage deduced from Pickering's tables was found to be, on fully correcting the density determinations, 5.093 per cent., the corrected densities being

at	$\frac{1}{4^\circ}$	1.00381
and	$\frac{20^\circ}{4^\circ}$	1.03218.

The following determinations of strength of the baryta solution were found at 25° :

14.14 c.c. gave	.1705	grs. BaSO_4	=	.1041	Normal
39.48 " "	.4790	" "	=	.1039	"
29.48 " "	.3588	" "	=	.1042	"
Titrated with $\frac{N}{10}$ Hydrochloric Acid			=	.1040	"
Titrated with Oxalic Acid			=	.1042	"
Mean1041	"

Titrated with the Sulphuric Acid referred to above it was

				.10301	Normal
				.10315	"
Mean10308	"

It is seen that titration with sulphuric acid shows the baryta solution to be 1 per cent weaker than it really is, and this is no doubt due to the carrying down of barium hydroxide by the barium sulphate.

I may mention also that a standard silver solution has the same property, and that in Mohr's method of chlorine estimation, the value of the silver solution as estimated from the silver contained differs from that obtained by titrating pure sodium chloride by fully 1 per cent. (see ANALYST, xiv., 229). The work of Stas has explained this. The influence of carbon dioxide in solutions of acid has been lately discussed.

With one more fact which is not widely recognised, I bring this somewhat rambling paper to a close, Platinum is permeable at a red-heat by the reducing gases of a Bunsen flame, and precipitates such as copper oxide and manganese dioxide may be somewhat reduced, and the copper oxide may contain less oxygen than CuO , and the manganese may be weighed as a lower oxide than Mn_3O_4 . This may be avoided by the use of the muffle.

DISCUSSION.

Mr. Hehner thought the society would feel obliged to Mr. Richmond for calling attention to facts with which all analysts were supposed to be acquainted. It was highly desirable to test weights occasionally.

Dr. Walter J. Sykes mentioned that properly graduated instruments could be obtained from some firms on the Continent at prices a little higher than those charged for the ordinary ones in England.

Mr. Arthur Ling said it was desirable that the measuring-vessels used for volumetric analysis by one observer, or in any given laboratory, should be verified by means of one set of weights, because sets of weights often differed in standard. With regard to the measurement of liquids by pipettes, one of the best plans was that advocated in Thorpe's Dictionary, viz., to allow the contents of the instrument to drain, and then touch the surface of the liquid once with the point. The most accurate pipettes, however, were probably those having two marks, one above and the other below the bulb.

Dr. Morgan said that the error in regard to weights was very much reduced if one operator followed his work right through with one set of weights. It was not desirable to have sets of weights by various makers in a laboratory.

Mr. Hehner said that he had never found a serious error in the calibration of pipettes. Standard solutions were mostly exceedingly dilute, compared with the strong sulphuric acid to which Mr. Richmond referred. No doubt for very accurate work, where it was necessary to reduce weights to vacuum value, it was advisable to check everything, but, for ordinary work, errors due to weights which had become a little worn were more or less compensated by other errors. He did not wish to be understood to say that, in his opinion, it was desirable to use very highly-worn weights, but it must be within the experience of most chemists that good weights which had become black and tarnished, when tested were found to be still accurate.

Mr. Richmond said that he wished to draw attention to the importance of accuracy in detail; an analyst who took the small precautions of standardizing weights, etc., would undoubtedly furnish to his clients more reliable results than if he left such things to chance.

The following papers were also read: "The Analysis of Waters for Minute Quantities of Poisonous Metals," by E. Russell Budden; "Note on the Analysis of Phosphor Tin," by Frank L. Teed, Ph.D.; "Note on Lemon and Orange Peel," by E. G. Clayton. The publication of these is unavoidably held over.
