THE ACTUAL ACCURACY OF CHEMICAL ANALYSIS.[1]

BY FREDERIC P. DEWEY.

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THE subject of this paper does not embrace the consideration of ways and means for the increase of analytical accuracy, or the question, what can be or should be attained in that direction. I desire simply to call attention to the degree of accuracy exhibited in actual every day practice. In estimating this, little weight will be given to the evidence afforded by the agreement of duplicate or multiple determinations by the same chemist; for I am convinced that such agreement is a delusion and a snare. Nor will special importance be attached to the agreement of two or even three analysts in special cases, or to the agreement between two methods practiced by the same analyst. I propose to compare the results obtained by several chemists, working upon the same sample and by various methods, in order to exhibit, as I have said, the actual condition of practice.

The available material for illustrating this phase of the question is unfortunately scanty; but something has been done; and I hope, by calling attention to some of the work in this line, to stimulate further work in the same direction by inducing others to prepare suitable samples and submit them to various chemists who are competent and willing to make the necessary determinations and fully describe the methods they employ.

I draw most of my illustrations from the "Transactions of the American Institute of Mining Engineers," the "Proceedings of the Association of Official Agricultural Chemists," and from personal experience.

MANGANESE IN STEEL.

In May, 1881, Mr. William Kent presented a paper to the American Institute of Mining Engineers entitled "Manganese Determinations in Steel,"[2] in which he gave twenty-four determinations of manganese, made by ten different chemists, employing two main methods, on samples from a plate of steel.

[1] Read before the Washington Section of the American Chemical Society, May 14th, 1896, and published jointly with the American Institute of Mining Engineers.

[2] Trans. A. I. M. E., 10, 101.

These results presented the remarkable range of from 1.14 to 0.303 per cent., and one chemist reported results ranging from 1.14 to 0.434 per cent.

A portion of this variation was undoubtedly due to variations in the sample, since the same sample was not used throughout by the different chemists.

Throwing out the anomalous result of 1.14 per cent. we have twenty-three determinations running from 0.619 per cent. to 0.303 per cent., with an average of 0.415 per cent. Thus showing that at that time the determination of manganese in steel, when only about four-tenths per cent. was probably present, might exhibit an extreme variation between the highest and the lowest results of about three-tenths per cent., or seventy-five per cent. of the amount of manganese present.

These results were certainly very discouraging; but if they did nothing else they served to call attention to the very unsatisfactory character of the determination of manganese in steel at that time.

I do not recall any recent symposium on the determination of manganese in this class of material, but in 1886 Capt. A. E. Hunt,[1] in giving a measure of the accuracy of the colorimetric method, speaks of a variation of 0.02 per cent. in steels containing 0.15 to one and five-tenths per cent. of manganese as "sufficiently accurate for all practical work," thus clearly intimating that the current results of analysis by other methods were at least as good. This degree of accuracy, if attained by different chemists upon the same sample, must be considered a satisfactory advance over the results reported by Mr. Kent.

Early in 1883 Mr. G. C. Stone began a series of contributions on the "Determination of Manganese in Spiegel."[2] In his first paper he reported thirteen determinations by five chemists, all working upon the same "works" sample, showing from 15.49 to 13.83 per cent., and also twenty-six determinations by ten chemists, all working upon a sample of the same spiegel, prepared with especial care jointly by Mr. Stone and one of the other chemists, showing from 14.56 to 10.36 per cent. But some of the low results were obtained by experimental methods.

[1] Trans. A. I. M. E., 15, 104.

[2] Trans. A. I. M. E., 11, 323; 12, 295 and 514.

In the fall of 1883 Mr. Stone reported twenty additional determinations by five other chemists, ranging from 14.20 to 10.76 per cent.; the extremes being reported by the same chemist when working by different methods, his favorite method giving from 13.84 to 13.65 per cent., and three low results, less than eleven per cent., being obtained by the Williams' method. In this connection Mr. Stone presented an interesting table, dividing the methods used into four classes and the results into three classes, giving respectively, below thirteen per cent., between thirteen and fourteen per cent., and above fourteen per cent.

In the spring of 1884 Mr. Stone reported twenty-seven new results, nineteen by four new chemists, and eight by one previously reported, whose new results were obtained by several methods.

We have thus seventy-three determinations by nineteen different chemists. Of these two are thrown out on account of the method used, and eleven "because the chemists were not entirely satisfied with them," leaving sixty determinations by eighteen chemists, using twelve methods.

These sixty results range from 14.47 to 12.60 per cent., and average 13.39 per cent. Leaving out eight determinations by one method which is considered to give low results, the lowest determination becomes 12.92 per cent. and the average 13.48 per cent., showing an extreme variation of 1.45 per cent. of manganese between the highest and lowest results, and showing only forty-four per cent. of the results within two-tenths per cent. of the average.

In the discussion of Mr. Stone's second paper, Mr. J. B. Mackintosh[2] presented an analysis of Mr. Stone's first forty-six results, retaining the results by the Williams' method, from which he argued that the evidence pointed to 12.956 per cent. as the true content of manganese in this spiegel. If this is the case, then there is a very decided tendency to get too high results in this class of work.

Taken as a whole, this investigation would seem to show that variations of five-tenths per cent. in the determination of manganese in this grade (ten to fifteen per cent. manganese) of

[1] Trans. A. I. M. E., 12, 300.

spiegel are to be expected, and much wider variations may be found.

PHOSPHORUS IN PIG IRON.

Early in the 80's, Messrs. Potter and Riggs, of St. Louis, Mo., sent out a sample of pig-iron for the determination of phosphorus.

This examination yielded twenty-six results, by eleven chemists, using five methods, ranging from 0.181 to 0.141 per cent., and averaging 0.160 per cent. and showing an extreme variation of 0.040 per cent. The maximum variation reported by any one chemist was 0.017 per cent., while three reported duplicates agreeing with 0.001 per cent. These results have never been published. One of the chemists discovered arsenic in the sample, which would account for some of the variation in the series. His determinations in duplicate were 0.151 and 0.152 per cent.

In February, 1882, Mr. F. E. Bachman presented a paper to the American Institute of Mining Engineers,[1] in which he reported forty-four results by eighteen chemists, using four methods, ranging from 0.165 to 0.096 per cent. and averaging 0.143 per cent. The extreme variation was 0.069 per cent. The maximum variation reported by any one chemist on straight duplicates was 0.01 per cent., and the minimum 0.0004 per cent. Experimental determinations by Mr. Bachman, using different processes, yielded variations amounting to 0.043 per cent.

At the Atlanta meeting in October, 1895, Mr. Geo. Thackray presented a paper, entitled "A Comparison of Recent Phosphorus Determinations in Steel."[2] He first gives a table of determinations of phosphorus by two chemists on eight samples ranging from 0.033 to 0.012 per cent., one chemist uniformly getting high results. One chemist found from 0.080 to 0.074 per cent., and the other 0.110 to 0.088 per cent in these steels. These results were manifestly unsatisfactory.

A second table shows results by three chemists, the buyer's, the seller's and an arbitrator. By the arbitrator's determinations these steels carried from 0.080 to 0.063 per cent. of phosphorus.

[1] Trans. A. I. M. E., 10, 322.
[2] Trans. A. I. M. E., 25, 370.

The maximum difference in any set of three results was 0.017 per cent., and the minimum 0.005 per cent.

These results were obtained in the settlement of sales. As a result of the discussion which accompanied the matter, two samples of steel were prepared and sent to various chemists. A fourth table gives thirty-six results obtained from twenty-three chemists, using twenty-nine methods on one steel, showing results averaging 0.0496 per cent., and ranging from 0.055 to 0.045 per cent., an extreme variation of only 0.010 per cent. Any individual result was practically within 0.005 per cent. of the average.

On the second sample thirty-eight results were reported averaging 0.0835 per cent., and ranging from 0.091 to 0.076 per cent., an extreme variation of 0.015 per cent.

My own results on these steels are not given, as they were not reported in time; but they add two more results by one more chemist in each case, and the results fall within the limits.

These results must be regarded as highly satisfactory, and show that here, at least, is one determination that can be made by many chemists, working in different ways, and yet with results agreeing very closely together. While it may not be necessary to determine many things as closely as phosphorus in steel, yet it would be highly satisfactory if we could do so; and this is a good standard of excellence for us to aim at.

PHOSPHORIC ACID.

As compared with the accuracy secured in the determination of phosphorus in steel, the 1894 report of the Association of Official Agricultural Chemists,[1] shows that on one sample thirty-nine determinations of insoluble phosphoric acid by eighteen chemists, working by the official method, showed results ranging from 0.45 to 0.03 per cent., with an average of 0.27 per cent., the extreme variation being 0.42 per cent., or over one and one-half times the average determination.

By another method, on the same sample, thirty-six determinations by nineteen chemists showed results varying from 0.34 to

[1] Proceedings of the Eleventh Annual Convention of the Association of Official Agricultural Chemists, August 23, 24, 25, 1894. Bulletin 43, U. S. Department of Agriculture, Division of Chemistry, p. 76.

0.04 per cent., with an average of 0.19 per cent., the extreme variation being 0.30 per cent., or over one and one-half times the average.

We have thus seventy-five determinations by nineteen chemists working by two methods, showing results ranging from 0.45 to 0.03 per cent., with an average of 0.233 per cent., the extreme variation being 0.42 per cent., or nearly twice the average determination.

On another sample thirty-three determinations by seventeen chemists working by the official method, showed results ranging from 3.85 to 2.24 per cent., with an average of 2.82 per cent., the extreme variation being 1.61 per cent., or considerably more than one-half of the average.

By another method, on the same sample, thirty-five determinations by seventeen chemists showed results ranging from 3.49 to 2.18 per cent., with an average of 2.83 per cent., the extreme variation being 1.31 per cent., or nearly one-half the average.

Summing up again, we have sixty-eight determinations by eighteen chemists working by two methods, showing results ranging from 3.85 to 2.18 per cent., with an average of 2.82 per cent., the extreme variation being 1.67 per cent.

The same report[1] shows that on one sample the results of twenty-nine determinations of citrate soluble phosphoric acid by fourteen chemists, by the direct method of Ross, varied from 2.47 to 1.04 per cent., with an average of 1.52 per cent., the extreme variation being 1.43 per cent., or nearly equal to the average of all the determinations.

On the same sample, by the official method, the results of twenty-three determinations by fourteen chemists ranged from 2.26 to 1.18 per cent., with an average of 1.46 per cent., the extreme variation being 1.08 per cent., or over two-thirds of the average determination.

Summing up, we have fifty-two determinations by fourteen chemists working by two methods, ranging from 2.47 to 1.04 per cent., and averaging 1.49 per cent., the extreme variation being 1.43 per cent., or nearly equal to the average.

[1] *Ibid.*, p. 72.

On another sample thirty-six determinations by fifteen chemists by the direct method of Ross, range from 3.29 to 1.87 per cent., with an average of 2.36 per cent., the extreme variation being 1.42 per cent., or considerably over one-half of the average determination.

On the same sample, twenty-four determinations by fifteen chemists, ranged from 3.40 to 2.08 per cent., with an average of 2.60 per cent., the extreme variation being 1.32 per cent., or a little over one-half of the average determination.

Summing up, we have sixty determinations by fifteen chemists working by two methods, ranging from 3.40 to 2.08 per cent., and averaging 2.44 per cent., the extreme variation being 1.32 per cent., or a little over one-half of the average determinations.

In the determination of the total phosphoric acid,[1] forty-five determinations, by eighteen chemists, ranged from 20.67 to 19.74 per cent., with an average of 20.09 per cent., the extreme variation being 0.93 per cent. By a volumetric method, thirty determinations, by eleven chemists, ranged from 20.60 to 19.83 per cent., with an average of 20.14 per cent., the extreme variation being 0.77 per cent. By another volumetric method, twenty-one determinations by ten chemists, ranged from 20.45 to 19.27 per cent., with an average of 19.96 per cent., the extreme variation being 1.18 per cent.

Combining these results, we have ninety-six determinations by eighteen chemists working by three methods, ranging from 20.67 to 19.27 per cent., with an average of 20.08 per cent., the extreme variation being 1.40 per cent.

Similarly, on another sample, we have 120 determinations, by twenty-two chemists, working by the same three methods, ranging from 18.15 to 16.25 per cent., with an average of 17.26 per cent., the extreme variation being 1.90.

Again, on another sample, we have ninety-six determinations by twenty-one chemists, working by the same three methods, ranging from 2.85 to 2.20 per cent., with an average of 2.50 per cent., the extreme variation being 0.65 per cent.

COPPER.

At the August meeting of the A. I. M. E., in 1882, Mr. W.

[1] *Ibid.*, pp. 81, 82, 83.

E. C. Eustis presented a paper entitled "Comparison of Various Methods of Copper Analysis."[1] For the purpose of this comparison a very complex sample was made up, containing sulphides, oxides and metallic copper, a silicate, sulphides of iron and zinc, arsenic and nickel. The paper reports forty-five determinations by seventeen chemists, using some eight methods. The results showed a wide variation, ranging from 53.34 to 43.92 per cent. and averaging 47.75 per cent. On throwing out a set of six results from one concern, all of which were more than two per cent. and two of them nearly five per cent. above the nearest other result, as being manifestly too high, and two results by one chemist and one method, which were more than two per cent. below the nearest other result, the series still ranges from 48.72 to 46.24 per cent., with an average of 47.23 per cent., and a maximum variation of 2.48 per cent., which cannot be considered very satisfactory.

The same paper reported seventeen determinations by seven chemists on borings of pig copper. These ranged from 91.07 to 98.17 per cent. and averaged 94.25 per cent. On throwing out two results that were nearly three per cent. higher than the nearest other result, and four that were over three per cent. below the nearest other result, the series ranges from 94.91 to 94.38 per cent. with an average of 94.69 per cent. The extreme variation of only 0.53 per cent. must be regarded as very good work, especially when we consider the character of the material.

At the Florida meeting in March, 1895, the results of a symposium on copper and copper matte, initiated by Dr. A. R. Ledoux, of New York City, were presented.[2] Eight chemists reported the copper in the matte, some in duplicate or more, as determined by electrolysis, as ranging from 55.17 to 54.50 per cent. and averaging 54.91 per cent. The extreme variation was only 0.67 per cent; and this must be regarded as satisfactory, and very much better than the results on Mr. Eustis' complex mixture.

Six chemists reported results by the cyanide method, ranging from 54.8 to 50.55 per cent, all but one of the results being below

[1] Trans. A. I. M. E., 11, 120.

[2] Trans. A. I. M. E., 25, 250 and 1000.

the lowest electrolytic result. These cannot be regarded as satisfactory.

A plate of copper made from melted anodes was drilled and six chemists reported the copper in the drillings, as found by the electrolytic method, as ranging from 98.46 to 97.04 per cent., and averaging 97.67 per cent. with a maximum difference of 1.42 per cent. These results are not as good as those previously reported by Mr. Eustis.

GOLD AND SILVER IN COPPER MATERIALS.

The symposium above referred to was undertaken primarily to test methods of assaying copper material for gold and silver. Fourteen chemists reported the silver by scorification assay, some entirely uncorrected, some partially corrected, and some corrected for both loss in slag and cupel and presence of copper in the silver button. The averaged results ranged from 135.38 to 122.88 ounces per ton and averaged 128.86 ounces per ton; the extreme variation being 12.5 ounces per ton, or nine and seven-tenths per cent. of the average.

Nine chemists reported ten results by combined wet and scorification methods, a few of them corrected for slag and cupel absorption. The averaged results ranged from 130.68 to 123.03 and averaged 127.25 ounces per ton. The extreme variation was seven and six-tenths ounces per ton, or 5.97 per cent. of the average determination.

One chemist reported 123.6 ounces per ton by crucible method.

Another reported 126.2 ounces per ton by combined wet and crucible method, corrected for slag and cupel.

Summing up, we have twenty-six results by twenty chemists working by two main methods, but both of them modified in various ways, and two methods, each by a single chemist, varying from 135.38 to 122.88 and averaging 127.94 ounces per ton. The extreme variation was 12.5 ounces per ton, or 9.77 per cent. of the average determination.

In the case of the silver assay of the copper borings, nine chemists reported by the scorification method, with and without corrections. The averaged results varied from 164.35 to 154.40, and averaged 159.36 ounces per ton. The extreme variation was 9.95 ounces per ton, or 6.24 per cent. of the average.

Fifteen chemists reported sixteen results by combined wet and scorification methods, with and without corrections. The averaged results varied from 161.40 to 148.50 and averaged 156.48 ounces per ton. The extreme variation was 13.9 ounces per ton, or 8.88 per cent. of the average. A single chemist reported 161.35 ounces per ton by combined wet and crucible process, corrected for slag and cupel.

Summing up, we have twenty-six determinations by twenty chemists working by three methods, ranging from 164.35 to 148.5 and averaging 157.67 ounces per ton. The extreme variation was 15.85 ounces per ton, or 10.05 per cent. of the average determination.

Twenty chemists working by the four methods reported twenty-six results on the gold in the matte varying from 2.41 to 1.85 and averaging 2.245 ounces per ton. The extreme variation was 0.56 ounce per ton, or 24.94 per cent. of the average.

On the gold in the copper borings twenty chemists working by two main methods, each one variously modified, and the combined wet and crucible method by a single chemist, reported twenty-six results varying from 0.501 to 0.205 and averaging 0.307 ounce per ton. The extreme variation was 0.296 ounce per ton, or 96.4 per cent. of the average determination.

POTASH.

In the determination of potash the 1894 report of the Association of Official Agricultural Chemists[1] gives six determinations of potassium chloride by six chemists by one method, ranging from 97.79 to 99.32 per cent. with an average of 98.56 per cent, the extreme variation being 1.53 per cent. By another method on the same sample seven determinations by seven chemists range from 97.21 to 98.86 per cent., averaging 98.16 per cent. Combining these results we have thirteen results by seven chemists, by two methods, ranging from 97.21 to 99.32 per cent. and averaging 98.35 per cent., the extreme variation being 2.11 per cent.

This report contains also a table of results on soil analyses[2] which I quote entire.

1 page 22.
2 page 41.

Table of Averages.

Soil Sample No. 2.

	Provisional method.					Hilgard method.				
	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.
		Per cent.	Per cent.	Per cent.			Per cent.	Per cent.	Per cent.	
Insoluble matter	14	76·874	77·733	76·19	2	12	76·619	77·910	75·380	3·3
K_2O	13	0·405	0·510	0·27	59	11	0·431	0·670	0·250	98
CaO	13	0·460	0·605	0·360	53	10	0·538	0·680	0·390	54
MgO	11	0·425	0·589	0·360	54	9	0·425	0·627	0·320	72
Fe_2O_3	9	3·504	4·260	2·955	37	7	4·347	6·400	3·300	70
Al_2O_3	9	6·613	7·500	6·240	19	7	6·285	6·828	4·460	38
P_2O_5	16	0·496	0·600	0·410	38	12	0·510	0·660	0·430	45
Fe_2O_3, Al_2O_3, and P_2O_5	12	10·754	11·400	10·220	11	10	11·071	12·100	10·550	14
N	7	0·276	0·290	0·262	10	..	.....	.....	.....	....
P_2O_5, Goss method	5	0·467	0·493	0·425	15	..	.....	.....	.....	....

Soil Sample No. 3.

	Provisional method.					Hilgard method.				
	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.
		Per cent.	Per cent.	Per cent.			Per cent.	Per cent.	Per cent.	
Insoluble matter	11	80·520	81·255	79·980	1·6	10	80·448	82·010	79·47	3·1
K_2O	10	0·422	0·500	0·305	46	9	0·396	0·630	0·240	98
CaO	9	0·372	0·425	0·300	33	8	0·411	0·600	0·275	79
MgO	8	0·381	0·524	0·270	67	7	0·369	0·490	0·265	61
Fe_2O_3	6	3·251	4·330	2·310	62	5	3·746	4·870	3·025	49
Al_2O_3	6	6·191	7·440	5·670	29	5	5·770	6·164	5·050	19
P_2O_5	11	0·418	0·555	0·350	49	9	0·429	0·560	0·309	59
Fe_2O_3, Al_2O_3, and P_2O_5	8	9·927	10·350	9·440	9	7	10·091	10·590	9·550	10
N	6	0·190	0·224	0·175	26	..	.....	.....	.....	....
P_2O_5, Goss method	4	0·369	0·390	0·354	10	..	.....	.....	.....	....