the most part negative, owing to conversion into nitrates. Nitrification begins the second week, reaches its maximum during the third week, then decreases; that is, it is periodic. The total change is greatest during the first week, and decreases to the fourth, after which it is somewhat irregular.

(7) Since a large part of the nitrogen rendered available is in the form of ammonia, it is probable that ammonia plays a greater part in plant nutrition than is commonly assumed to be the case.

(8) Ammonia is probably of less value than nitrates for most cultivated plants, and the nitrification power of soils is of importance.

(9) Determination of the relative amounts of nitric and ammonia nitrogen produced from them should be of value in comparing different organic materials.

[CONTRIBUTION FROM THE COMMITTEE ON UNIFORMITY IN TECHNICAL ANALYSIS. II.]

COOPERATIVE ANALYSIS OF AN ARGILLACEOUS LIMESTONE.

Received December 30, 1905.

INTRODUCTION.

THE present contribution deals with the results obtained in an effort of the committee to secure information of the nature indicated in the second paragraph of the list of its aims as published in this Journal **26,** 1652. In other words, to endeavor to ascertain if a part of the blame for the notorious inability of different analysts to report closely agreeing results when analyzing the same materials is to be placed upon the instructors in analytical chemistry in our higher institutions of learning. The subject is, of course, a difficult one to handle, but it was hoped that by a frank invitation to coöperate a sufficient number of public-spirited instructors, earnestly desirous of improving a plainly serious situation, might be secured to afford some positive indication one way or the other.

To this end a circular letter was addressed on Jan. 1, 1905, to the heads of the chemical departments in nearly 100 universities, colleges, polytechnics and mining schools throughout this country and Canada. It was proposed to send to all who might be willing to have an analysis or analyses made by their instructors or advanced students a portion of a carefully prepared, large sample of argillaceous limestone, with a view to testing the skill of the instructors as analysts and their ability to impart skill to those in their charge. About 70 replies were received, only two of which were refusals to coöperate. Many of the letters received were extremely favorable to the purpose of the committee, and some pledged the writers to faithful coöperation.

About the middle of February samples were sent to all who had expressed a willingness to coöperate, accompanied by a second circular letter specifying the nature of the analysis desired. This "should be of such a character as to illustrate the methods used in your institution for teaching general quantitative analysis without technical application......" and "should be fairly representative of careful work." It was asked that all of the following data should be furnished, if possible: SiO_2, Al_2O_3, total iron as Fe_2O_3, TiO_2, P_2O_5, CaO, MgO, K_2O, Na_2O, H_2O both below and above 100°, CO_2, and total sulphur reported as S. The last might be reported as both S and SO_3, if found to exist in the sulphide and sulphate condition. The carbon of any organic matter that might be present should be reported as carbon, though this determination was not insisted on. Because of the impossibility of determining ferrous iron with any approach to accuracy in presence of organic matter, it was directed that this constituent should only be reported in case carbonaceous matter and sulphides were absent. And because the iron might exist in the two states of oxidation as well as in the sulphide state, and their distinct determination be probably impossible, it was thought best to ask that all be reported as Fe_2O_3, even though it was probable that most of it existed in the ferrous condition as carbonate, a very common condition in limestones. It was fully understood that the values reported for water above 100° would include that due to oxidation of the hydrogen of any carbonaceous matter that might be present, and not solely that from the silicates, but this was of no moment, since it was the ability to determine water correctly that was in question and not the distribution of this water among the mineral constituents of the sample. It will be seen that the determination of some of these points would offer a slight field for the qualitative determinative skill of the analysts.

It may be said here that these directions were but indifferently observed by many of those who sent in reports. By some they were totally disregarded, with the result, for instance, that, only sulphate sulphur being looked for and little or none found, sulphur was reported to be absent, whereas it was present in some quantity in its usual sulphide form. Again, there is reason to believe that in some instances the total was reported as SO_3, without any attempt having been made to determine its actual condition. Still again, many made no mention of titanium or phosphorus yet reported figures for alumina which included one or both of those elements as TiO_2 and P_2O_5. In another case the work of students without previous experience in quantitative work was reported. And lastly, technical methods were occasionally reported, showing disregard of the directions or else an implication that none but technical methods were taught in the institution.

THE SAMPLE.

The sample of limestone was prepared and furnished by Mr. H. A. Schaffer, of the Northampton Portland Cement Company, Stockertown, Pa., to whom the thanks of the committee are cordially rendered. It weighed about 200 pounds and was expected to wholly pass a 200-mesh sieve, but mechanical difficulties did not allow of this degree of fineness being reached by quite all of the powder. It was found that about 94 per cent. passed the sieve. The remainder differed somewhat in composition from that which passed through, as shown by comparing the following determinations with the corresponding ones of the bulk analysis at the head of the table below: SiO_2, 17.48; Al_2O_3, etc., 7.84; CaO, 38.54; MgO, 2.12 (incl. Mn and a trace CaO). It is considered in the highest degree improbable, however, that any detectable amount of segregation could happen during transport or storage of such fine material, whereby variations in the small samples might arise.

In order to learn if the sample was homogeneous throughout, six small lots were taken at intervals from top to bottom of the barrel and silica was determined in each by the chairman of the committee, this being a determination susceptible of very great accuracy when properly carried out. The results were 18.09, 18.10, 18.10, 18.05, 18.11, 18.14, thus showing complete homogeneity.

THE STANDARD ANALYSES.

Careful analyses to serve as standards of comparison were made by the chairman of the committee in the laboratory of the U. S. Geological Survey and by Dr. C. E. Waters at the Standards Bureau. The results, given at the head of the table below, are in each case the mean of closely agreeing determinations. The two analyses are sufficiently alike to serve satisfactorily the purpose for which they were made. Not much needs to be said regarding the methods used by the two analysts. They were in the main those laid down in Bulletin 176 of the Geological Survey. The ratio of silica to carbonate minerals is such that strong ignition would not give a product wholly soluble in hydrochloric acid, an observation made by some of the other analysts also, hence fusion with a small amount of sodium carbonate was resorted to in order to afford complete solubility in hydrochloric acid. Manganese was determined by the colorimetric method with ammonium persulphate and a silver salt. The carbon of carbonaceous matter was determined at the Standards Bureau by oxidation with chromic acid, and at the Survey by combustion in an air current after extraction of the carbonates by dilute hydrochloric acid and filtering on asbestos. The CO_2 evolved was in both cases weighed. It may be that this method is open to the objection that some of the carbonaceous matter may have been volatilized by the preliminary acid treatment. It is, however, certain that any loss from this cause is insignificant. In any case the values reported are not too high. The analyst of the Standards Bureau determined strontia and ignition loss and also noticed the evolution, on heating, of a small amount of ammonium salts. The Survey analyst made no effort to discover other components than those called for by the circular letter above referred to, but he did determine ignition loss, since this was done by most of the technical analysts. For the general correctness of the standard analyses, the ignition losses shown in them bear very strong evidence. This loss should cover $(CO_2+C+\text{all } H_2O)$ — (the gain by oxidation of FeS_2 to Fe_2O_3 and SO_3 + the gain of all the rest of the iron from FeO to Fe_2O_3), for it is safe to assume that all iron not pyritic in this case is in the ferrous state. At the temperature employed by the Survey analyst, all the sulphur is retained as sulphate by the lime, the carbonate is completely decomposed, and there is no loss of alkali.

On this basis the calculated loss in his analysis should have been 32.26 per cent. Duplicate tests on 1 gram and 0.5 gram respectively gave 32.25 and 32.23 per cent. For his method, see this Journal, **25,** 1198 and 1199. Similar computation for the analysis from the Bureau of Standards shows a calculated loss of 32.43 against one of 32.30 found. The difference in the two calculated losses is just equal to the difference in the respective CO_2 percentages.

THE COOPERATIVE ANALYSES.

Of the sixty-eight educators who expressed willingness to aid by furnishing analyses if possible, only a small proportion have reported at the date of completion of this report, or twenty-five in all. Many excused themselves for reasons of a varied character, and sixteen have not been heard from, notwithstanding a third circular letter calling attention to the neglect. A few hoped still to be able to report and may yet do so. The returns are therefore too limited in number to afford safe grounds for final general conclusions, except in a few particulars. It does not seem wise, however, to defer issuing this report, especially since a large number of chemists in technical work who applied for samples of the limestone are naturally desirous of comparing the standard analyses with their own. It is to be said regarding the collegiate analyses that they are from thoroughly representative institutions covering the United States from the extreme east to the Pacific coast and from the northern boundary to the Mexican line. Canada is not represented.

The committee refrained from soliciting comparative analyses from technical laboratories, for this ground has been fairly covered by the reports of other committees. Nevertheless it is glad to include in the tabulation below the few analyses received from these laboratories and to express its pleasure at the interest displayed by all, and appreciation of the intelligent description and discussion, by two or three, of their methods and results.

The analyses are tabulated in three classes, according as they are the work of instructors, advanced students or technical chemists. Six analyses by beginners in one institution have been omitted. Seventeen instructors from as many institutions are represented by analyses, and fourteen students from eight institutions, only two of these last being represented also by instructors. In this respect analyses 9 and 18 *a*, *b*, *c*, belong together, as also 5 and 23.

Before discussing the analyses, a few explanations are in order, so that those who find changes in their figures may understand why they were made. (1) It was requested that the analyses be calculated on the dried material, but that the hygroscopic moisture be reported separately. Most, however, included the moisture in the summations, and it was decided to follow this plan throughout, so far as possible. The change necessitated the recalculation of a few analyses. In one case, owing to failure to report the moisture, the air-dry analysis has been recalculated on the assumption of the average moisture content shown by the other coöperative analyses. (2) When, as occurred among the technical analyses, lime and magnesia were reported as carbonates, the bases have been calculated for the table, but the CO_2 ignored as not based on direct experiment. (3) When more than one analysis by the same person was reported, only the averages are given in the table, except as determinations may have been made by different methods. (4) In three or four instances among the technical analyses "ignition loss" was referred to dry material. For the sake of uniformity it has been increased in such cases by the amount of moisture reported. (5) Most of the analyses were incomplete, and many recalculations were called for as indicated above, hence totals have been omitted for all but the standard analyses and one other.

After careful consideration it has been deemed best to make public no names, either of analysts or of their respective institutions. It is hoped that the committee will not be considered lacking in courtesy on account of this decision. It takes this occasion to thank most heartily one and all who have contributed material for this presentation.

DISCUSSION OF ANALYSES.

Space does not permit of detailed discussion of the varying causes that have contributed to erroneous results in individual cases, even where these are apparent from inspection of the analyses or of the reported methods. Some of the analysts have expressed a desire, however, for criticism or comment on their work. This the chairman holds himself ready to give to the best of his ability by letter, and he cordially invites correspond-

TABLE OF ANALYSES (averages only given where duplicates were reported).

Analyst.	SiO_2.	TiO_2.	Al_2O_3.	P_2O_5.	Fe_2O_3.	MnO.	CaO (SrO).	MgO.	K_2O.	Na_2O.	H_2O 100°—.	H_2O 100°+.	S.	SO_3.	CO_2.	C.	Total.	Ign.	Remarks.
illebrand	18.11	0.23	5.78	0.18	1.75	0.04	37.68	1.96	1.17	0.36	0.16	1.48	0.26	0.015	30.59	0.66	100.26[1]	32.24	0.09 SrO incl. in the CaO by Bur. Stands.
aters	18.18	0.21	5.62	0.18	1.68	0.04	37.62	1.91	1.12	0.30	0.15	1.53	0.28	0.010	30.77	0.63	100.05[1]	32.30	
Instructors.																			
1	17.98	0.22	5.91	0.21	1.76	n.d.	38.11	2.03	1.21	0.66	0.11	0.65	0.33		30.77	0.70			
2	17.42	0.23	6.72	0.19	1.86	0.15 0.06	37.55	2.06	1.19	0.51	0.08		0.26		28.65	1.58			Higher MnO grav., lower MnO by color. C = "humus."
3	17.46	0.11	5.87	0.19	2.70	none		2.42	1.25	0.72	0.27	1.69	0.29						
4	17.90	0.17	7.35	0.18	1.54		37.83	2.03			0.08							32.38	
5	17.95	0.35	5.73	0.12	1.76	0.07	37.89	2.05	1.15	0.29	0.14	1.53[2]	0.29		30.46			32.52	MnO "probably low." CaO includes Mn_2O_3.
6[3]	17.86	0.20	7.14	0.17	1.14	0.06	37.64	2.09	1.09	0.32	0.08								MnO by colorimetry.
7	17.16	0.56	5.10	0.17	1.56	0.27	39.53	2.12	1.22	0.40	0.11			0.33				31.94	"Complete analysis."
7a	17.35	5.79		0.17	1.57		39.83	2.20											"Technical analysis."
8	17.72 18.16	5.05		0.65	2.51	1.70	38.08	2.11	1.48	1.85			none						Silica by two methods. Alkalies "probably high."
9	18.05	5.83		0.20	1.94	trace	37.95	2.11	1.33	0.58	0.11	1.32	trace	none	30.41	n.d.			
10	18.92	6.12		0.17	1.64		37.24	2.06	n.d.	n.d.			0.28		30.93	n.d.			
11[3]	17.77	9.51		0.36	2.41	trace	37.83	2.01	1.03	2.00	0.17				30.52	1.92	(105.53)		C = "Carbonaceous matter."
12	18.07	6.76			1.72		37.88	1.89	0.94	0.67	0.05		0.29		30.65				Commercial methods used, avoiding large errors.
13	17.72	6.38			1.82		37.42	2.19											

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[1] Totals corrected for the fact that pyritic iron counts in the analysis as Fe_2O_3 instead of Fe. The totals are still high by about 0.16 per cent., for the reason that most, if not all, of the residual iron should be counted as FeO instead of Fe_2O_3.

[2] Average of five determinations between the limits 1.27 and 1.78.

[3] Separate analyses made of parts soluble and insoluble in hydrochloric acid (see p. 236). These have been combined for the table.

TABLE OF ANALYSES (averages only given where duplicates were reported)—*Continued.*

Analyst.	SiO_2.	TiO_2.	Al_2O_3.	P_2O_5.	Fe_2O_3.	MnO.	CaO (SrO).	MgO.	K_2O.	Na_2O.	H_2O 100°—.	H_2O 100°+.	S.	SO_3.	CO_2.	C.	Total.	Ign.	Remarks.
14	17.99	7.32			1.81		38.23	2.06	1.38	0.25	(0.12)	1.02	0.42		30.32				No moisture reported. Analysis recalc. to undried material.
15	17.79	7.15			0.82		37.68	2.12	1.16	0.47	0.16	1.21	0.29		30.68				Al_2O_3 includes "MnO_2."
16	17.21		12.29			trace	38.00	1.31	traces		0.12				30.54				Sample treated as a clay in 17, but in 17*a* extracted by HCl, residue fused, solutions combined. Same analyst. C = "organic matter."
17	18.03		8.55				36.74	3.05	1.35	0.60	0.06				29.64	1.44			
17*a*	17.94		8.02				36.02	2.14											
								Students.											
18*a*	17.88	5.61		0.27	1.94		37.64	1.79	1.61	0.93	0.20				30.52				Undergraduates at same institution.
18*b*	17.73	5.81		0.34	2.09		37.77	2.29	1.93	0.81	0.26				30.62				
18*c*									1.46	0.82					30.34				
19	17.67	4.80		0.22	2.83[1]	none	35.26	5.20	1.77	0.04	none	0.30		none	31.65				Graduate student.
20	16.40	10.16					41.98	1.58			0.19					4.72			Grad. stud. (?). C = "organic matter."
21	17.05	0.22	4.42	0.29	2.02	trace	37.80	2.04	1.62	1.51	0.10	0.03	0.34		31.27	1.55		32.82	Grad. stud. C = "carbonaceous matter."
22*a*	18.40	0.22	7.57	0.64	1.91		38.03	1.66	0.46	0.11	0.14			0.50	29.17	0.41			Advanced students at same institution.
22*b*	18.85	0.20	5.98	0.48	1.90		38.32	0.92							29.78				
23	17.79										0.26				30.00				Advanced students at same institution. Small amounts of SrO, ZrO_2 and NiO reported by one or another.
24*a*	18.03	trace	6.19	0.25	2.05[1]	1.15	37.71	1.78	1.25	0.87	0.09	0.98	0.36		30.48				
24*b*	18.08	trace	6.75	0.20	1.72[1]	trace	37.17	2.06	1.14	0.91	0.07	0.93	0.33		30.50				
24*c*	17.29	0.82	6.35	0.21	2.26[1]	0.37	37.54	2.18	1.21	0.79	0.11	0.69	0.34		30.43				
25*a*	18.58		6.92		1.06		36.87	2.86	0.79	0.15			0.39	trace					Students at same institution.
25*b*	18.46		7.05		1.27		36.58	3.00	0.83	0.11			0.36	none					

[1] These four analysts all determined both FeO and Fe_2O_3 with most widely differing results. Their data have been reduced to total iron as Fe_2O_3.

TABLE OF ANALYSES (averages only given where duplicates were reported)—*Continued.*

<table>
<tr><th>Analyst.</th><th>SiO_2.</th><th>TiO_2.</th><th>Al_2O_3.</th><th>P_2O_5.</th><th>Fe_2O_3.</th><th>MnO.</th><th>CaO (SrO).</th><th>MgO.</th><th>K_2O.</th><th>Na_2O.</th><th>H_2O 100°—.</th><th>H_2O 100°+.</th><th>S.</th><th>SO_3.</th><th>CO_2.</th><th>C.</th><th>Total.</th><th>Ign.</th><th>Remarks.</th></tr>
<tr><td colspan="20">Technical Analysts and others.</td></tr>
<tr><td>26</td><td>17.69</td><td colspan="3">7.11</td><td>1.64</td><td></td><td>38.34</td><td>2.20</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>27</td><td>17.82</td><td colspan="3">6.80</td><td>1.76</td><td></td><td>38.01</td><td>2.32</td><td></td><td></td><td>0.11</td><td></td><td></td><td>0.69</td><td></td><td></td><td></td><td>32.88[3]</td><td>S calc. from SO_3 = 0.28.</td></tr>
<tr><td>28</td><td>17.30</td><td colspan="3">6.41</td><td>1.91</td><td></td><td>37.77</td><td>2.09</td><td>1.02</td><td>0.39</td><td></td><td></td><td>0.71</td><td></td><td>30.20</td><td>2.03</td><td></td><td>32.22</td><td></td></tr>
<tr><td>29</td><td>17.97</td><td colspan="3">5.84</td><td>2.04</td><td></td><td>37.94</td><td>2.68</td><td></td><td></td><td></td><td></td><td></td><td>0.66</td><td></td><td></td><td></td><td>32.48</td><td>S calc. from SO_3 = 0.26.</td></tr>
<tr><td>30</td><td>17.78</td><td colspan="3">6.32</td><td>1.94</td><td></td><td>37.85</td><td>1.92</td><td></td><td></td><td></td><td></td><td>0.26</td><td></td><td></td><td></td><td></td><td>32.65</td><td></td></tr>
<tr><td>31</td><td>17.36</td><td colspan="2">5.88</td><td>none</td><td>1.97</td><td></td><td>37.55</td><td>2.62</td><td colspan="2">1.62</td><td colspan="2">1.25</td><td>0.34</td><td></td><td>30.82</td><td>0.46[1]</td><td></td><td>32.52[3]</td><td>“Cl not more than 0.04.”</td></tr>
<tr><td>32</td><td>17.88</td><td colspan="2">6.81</td><td>0.18</td><td>2.10</td><td>0.06</td><td>37.40</td><td>2.25</td><td colspan="2">2.18</td><td>0.11</td><td></td><td>0.38</td><td></td><td></td><td></td><td></td><td>32.20[3]</td><td>MnO reported as 0.069 Mn_2O_3.</td></tr>
<tr><td>33</td><td>18.60</td><td>0.17</td><td>6.64</td><td>0.20</td><td>1.71</td><td></td><td>37.51</td><td>1.97</td><td></td><td></td><td>0.12</td><td></td><td>0.35</td><td></td><td></td><td>n.d.</td><td></td><td>32.23[3]</td><td>Silica regarded as high by analyst.</td></tr>
<tr><td>34</td><td>17.44</td><td colspan="4">8.18</td><td></td><td>37.50</td><td>2.11</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>32.28</td><td>CaO also 37.38 volumetrically.</td></tr>
<tr><td>35</td><td>16.58</td><td colspan="4">8.85[2]</td><td></td><td>38.24</td><td>2.49</td><td></td><td></td><td>none</td><td></td><td></td><td>0.07</td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

[1] Recalculation of the analyst's data affords 0.35 instead of 0.46 for this value.

[2] Including 0.23 P_2O_5.

[3] The ignition loss reported did not include moisture. For better comparison with other ignition losses the moisture separately reported has been included in the tabulated value.

ence with those who may wish further information than this report affords. To certain general features shown by the analyses it will be proper to direct attention at this time. In view of the expressed objects of the investigation most attention will naturally be given to those emanating from educational institutions, and among these those furnished by instructors will attract chief attention. While several of them compare favorably with the standard analyses, and as to a number of their determinations might indeed be substituted for them, there is no one that does not reveal a weak point or points, and there are a very few concerning which no good word can be said.

Silica.—The silica determinations are almost without exception low, but the greater number of these show no greater deficiency than can be accounted for by the fact that in but one or two cases was correction made for the silica passing into the filtrate after even two evaporations and filtrations. Almost without exception this double filtration was practised, and the generally favorable result of so doing is evident when comparison is made with the earlier series of analyses of cements and cement mixtures carried out under the auspices of the committee of the New York Section of the Society of Chemical Industry. In the isolated instances where the correction referred to was made, it was without the precaution insisted on in some of the chairman's published discussions of this particular feature.[1] All the precautions required for an exact silica determination do not seem to be as yet widely known, but in time will undoubtedly be more generally understood and followed where exact work is called for.

Another source of low results, to which the chairman has before called attention and which one of the instructors independently noticed, is the sticking of the silica to the sides of the evaporating dishes and its incomplete removal therefrom. This is most likely to pass unnoticed when porcelain vessels are used, and the instructor referred to found in one case a retention of 0.88 per cent. of silica by the porcelain dish, which could not be removed by rubbing with a "policeman" but was removed by treatment with ammonia.

Alumina, Etc.—The failure to correct for soluble silica is only in small part responsible for the generally high results reported

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[1] This Journal, 25, 1193, 1205, and 1206.

for alumina, as also for the collective percentages of the constituents precipitated by ammonia. Alumina being determined in practically all cases by the common method of difference, errors affecting the iron, phosphorus and titanium, where these were determined, accumulate upon this constituent. The low alumina value in analysis 8 is to be attributed to the quite abnormally high values reported for iron and phosphorus, and in 19 to that for iron.

Phosphorus.—With but two exceptions the determinations of phosphorus by instructors and technical analysts show good agreement, but the variation is great among students.

Titanium.—Although the agreement is fairly satisfactory in about half the results reported for titanium there is evidently great room for improvement. The bad results were not all obtained by gravimetric methods.

Iron.—Though many of the values for iron are good, a few are utterly bad, and the agreement is not so close among the rest as should be with a constituent susceptible of such accurate determination. Notwithstanding that considerable carbonaceous matter was evidently present, some analysts endeavored (notwithstanding the instructions to the contrary) to determine the iron present in the ferrous state, with all manner of results not listed in the table, no two agreeing even remotely. Much of the iron exists as carbonate, a little perhaps as silicate, a part as pyrite, and possibly, though not probably in this case, a further part in the ferric state. Hence it was asked that only the total iron be reported, and for the sake of convenience as Fe_2O_3.

Manganese.—Few as the determinations of this constituent are, they show the most astonishing lack of agreement and an utter failure in most cases to make an even approximately correct determination of small amounts by gravimetric methods. That such excessive amounts should be reported when but a minute quantity is present speaks badly for the observation of the analysts, for it is difficult to understand why the appearance of the precipitate obtained should not have aroused suspicion at least. The two or three determinations by colorimetry agree among themselves and differ little from the standard.

Calcium.—There is much greater uniformity among the lime values than in most of the others, and many could hardly be improved upon. The causes of the very abnormal results by analysts 7, 19 and 20 are not apparent. It does not appear from the reports that gravimetric methods have yielded better results than the volumetric method. One technical analyst reports an average 0.3 per cent. higher after a single than after double precipitation, with a corresponding difference in the opposite direction in the magnesia.

Magnesium.—In view of the results of the earlier series of analyses elsewhere referred to, the returns by instructors and technical analysts show a surprising and satisfactory agreement, though in almost every case a higher value than is shown by the standard analyses. This last is in part due to failure to correct for the lime always present in the pyrophosphate, and otherwise clearly shows the general tendency towards too high results by reason of failure to carefully remove other incompletely precipitated constituents of the sample analyzed or of the glassware and reagents used.

Alkalies.—The determinations of potash show considerable variations among themselves and deviations from the standards, but with the soda the results are almost uniformly worthless, and sometimes as astounding as those for manganese. Why this should be is not clear, but it is an observation not made for the first time. Incomplete separation of lime may be the chief cause, since the Lawrence Smith method was generally used. In one or two cases the reported corrections for alkalies in the calcium carbonate used show the reagent to have been far from excellent, and it may be that in other cases a still poorer article was employed without correction. If so, however, there is revealed a lack of proper control of reagents.

Moisture.—With few if any exceptions, moisture was determined indirectly. Quite a number of the values reported agree very closely with the indirect determinations made at the Geological Survey and the Bureau of Standards (0.11–0.12). The standard values as given in the table, however, were direct weighings of the water given off in a dry atmosphere. Although the exact determination is one of little importance in low moisture samples, the results show how far short of perfect the indirect method is. As the chairman has often pointed out, the error becomes very important with high moisture samples.

Combined Water.—For combined water the results, though not numerous, are in general as bad as those for manganese and sodium, and show a great lack of knowledge regarding this determination and the temperatures to be employed for its expulsion from silicate minerals. There is also seemingly evident much ignorance that water is a constituent of some siliceous components of limestones.

Sulphur and Sulphur Trioxide.—Few if any analysts apparently determined the condition of the sulphur in the limestone. Whereas it exists almost wholly as pyrite, some reported only SO_3. A trace of sulphur was evolved as hydrogen sulphide on boiling with dilute hydrochloric acid, not the greater part, as reported by one analyst. There has evidently been much failure to exclude sulphur from reagents or flame gases, for the variations from the standard, while not strikingly great as a rule, represent nevertheless a very appreciable weight of barium sulphate.

Carbon Dioxide.—Considering the difficulty ordinarily encountered in securing reliable results, those rendered for CO_2 are surprisingly good in the greater number of cases.

Carbon from Carbonaceous Matter.—The organic matter of the limestone is almost wholly of a coaly nature, and not "humus" as thought by a few analysts. The determinations are too few in number to merit special comment, but the methods used in a few cases were extremely faulty.

Ignition Loss.—There is here, as with CO_2, a very good general agreement with the standards. It is a determination which appeals more to the technical analysts than to others, and one which by the exercise of proper and easily applied precautions will always represent a certain algebraic sum of losses and gains in all limestones not ideally pure. For further comment on this point see p. 237.

In the limits of a single table it is impossible to bring to view all the data furnished by the reports. For instance, two analysts (instructors) decomposed the limestone by hydrochloric acid and analyzed separately the soluble and insoluble portions. Comparison of the results arrived at in the two cases, in so far as the same constituents are covered, is instructive, if not in all respects gratifying.

	Insoluble in HCl.		Soluble in HCl.	
	Analyst 6.	Analyst 11.	Analyst 6.	Analyst 11.
SiO_2	17.86	17.77	....	....
Al_2O_3	5.64[1]	7.85[1]	1.84	1.66
P_2O_5		0.14		0.22
Fe_2O_3	0.43	1.29	0.71	1.12
CaO	none	0.11	37.64	37.72
MgO	0.54	0.37	1.54	1.64
K_2O	(1.09)[2]	0.77	(none)[2]	0.26
Na_2O	(0.32)	1.31	(none)	0.79
	(25.88)	(29.61)	(41.73)	(43.41)

The above affords a striking illustration of the dangers resulting in part from wrong choice and application of analytical methods, and in part from failure to ascertain beforehand the composition of the material to be analyzed. In close agreement on several points, there is the widest divergence on others, the causes for which are partly apparent from the reported outlines of analysis, which in the case of analyst 11 is open to serious criticism.

SUMMARY.

To summarize briefly, the most striking defects revealed are inability (1) to determine alumina correctly or even to get a fairly correct collective weight for the substances that are precipitated by ammonia; (2) to determine small amounts of manganese gravimetrically with any approach to accuracy; (3) to make an acceptable alkali determination, especially as to soda; (4) to determine the so-called combined water with any approach to accuracy. Similar comment might be made regarding the carbon of carbonaceous matter, but the determinations are altogether too few to justify sweeping condemnation. In individual cases certain errors are manifestly due less to lack of skill in manipulation than to ignorance of the normal composition of a limestone as to the minor ingredients and their manner of combination, or to failure to ascertain the qualitative composition of the material beforehand and thus avoid pitfalls. This last defect is naturally rather more evident in the students' work than in that of instructors, and yet it is to be supposed that the former were super-

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[1] These values were reported as "Al_2O_3," but probably cover most if not all of the TiO_2.

[2] Localization of alkalies in the insoluble assumed by analyst from other evidence than actual test and doubtless justified.

vised by their instructors, who are therefore responsible for lapses of the kind named. Two or three instances may be given. One student found but 0.03 per cent. of water escaping between 105° and 250°, and, apparently ignorant of the fact that silicates often retain much at even higher temperatures, was led to ascribe far too high a value to carbonaceous matter, which he derived from "ignition loss" by deducting CO_2 and H_2O. Another student determined FeO by solution in sulphuric acid and titration with permanganate, unmindful of the effect of carbonaceous matter and possible soluble sulphide of iron. Still again, one determined CO_2 by loss in weight of his apparatus after using nitric acid to decompose the carbonates, ignorant perhaps of the presence of iron sulphide and ferrous carbonate and of the effect of these as well as of carbonaceous matter upon that acid.

Although the students' analyses are not all by those who were about to close their undergraduate studies, it is very evident that few if any of those who made them are fitted as yet to offer their services to the public as analysts.

In spite of the relatively small number of analyses from instructors and students, it is probable that the returns are in general indicative of the situation as to analytical chemistry throughout the country. Good work is apparent in several instances, but a great lack of it in far too many, and the charge referred to in the opening sentences of this report seems to be measurably sustained. It is evident that much greater attention should be paid to the training in analytical chemistry of those who are to fit future generations of chemists to do competent work in analysis. In order that they may accomplish this it is plain that they should be given greater opportunity to perfect themselves practically. Knowledge of the theory of analytical operations and separations is not sufficient. Among the points needing greater attention are control of reagents, impressing the importance of this upon students, and greater opportunity for them to verify the correctness of their work. Only by such means will it be possible to raise the standard of analytical chemistry above the low plane it now occupies in so many fields.

In this connection, passages in two letters of very recent date that passed between a professor of analytical chemistry in one of our eastern colleges and the chairman of the subcommittee on zinc-ore analysis, Mr. Geo. C. Stone, may be most fittingly quoted.

The first writer, freely admitting a most disgraceful state of the analytical art as evinced by the published analyses of selected samples of zinc-ore,[1] demurred to the suggestion that this might be mainly due to our poor methods of teaching. "As you well know, our students come to us from every walk of life. Some have had the advantage of a very superior secondary education, but the great majority come to us with their faculties untrained, with no sound habits of study and with no ambition for anything higher than an analytical position in some steel works laboratory. This great majority are not possessed of a critical mind or a spirit of investigation. They will perform an analytical operation a dozen times and learn nothing more than to follow directions, and in many instances they are unable to properly interpret directions, owing to their lack of a good general education. Without doubt the teaching is at fault, but it seems to me that the improvement must begin at home and continue through the primary, intermediate, grammar and high school grades before we can expect better results from our college graduates."

To this Mr. Stone replied in part: "....I fully agree with you that the improvement should begin with the lower grades. Where I do think that the colleges and universities are greatly at fault is in being so easy in their requirements that students who are not properly prepared are allowed to enter and graduate. I also think that any system of teaching analytical chemistry that allows the student to 'perform an analytical operation a dozen times and learn nothing more than to follow directions,' is wrong and will produce the sort of results that we received for samples 'A,' 'B' and 'C.'......It seems to me that the functions of our institutions for higher education should be, *1st*, to eliminate those who from lack of brains or preparation are not capable of profiting by the education, and, *2nd*, to give those who are worthy of it a thorough training."[2]

These views supplement in the clearest manner some of those

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[1] This Journal, 26, 1648–1649.

[2] Certain references in this last quotation receive singular justification by the remarks accompanying the analysis furnished by one instructor. From these it might be inferred that it is not the principles of analysis which are understood and taught in the institution, but simply rule of thumb methods applicable to the particular products of a certain section of country.—Note added by the chairman.

expressed by the chairman of this committee in his address at Philadelphia a year ago.[1]

The committee does not feel called upon to make specific recommendations based upon the showing of the above table of analyses. It prefers for the present to let the table and the above-quoted remarks speak for themselves to each and every instructor. It believes that their consideration ought to lead to much good, and that the seed of improvement already germinating will in time produce good fruit if continuously and carefully cultivated.

W. F. HILLEBRAND, *Chairman.*
CHAS. B. DUDLEY,
CLIFFORD RICHARDSON,
H. N. STOKES.

REVIEW.

SOME ABSTRACTS FROM CURRENT LITERATURE UPON INDUSTRIAL CHEMISTRY.

BY FRANK H. THORP.

Received December 23, 1905.

This article being a continuation of the Review prepared by the writer last year, the same general scheme has been followed. As in the previous article, attention has been given mainly to papers published in the foreign journals during the year just closed, and which have not been included in the *Review of American Chemical Research.* A few abstracts from American journals and patents have been given. It has been desired to make the abstracts brief and to consider only those which seemed of most general interest.

Technical Education.—Technical training and educational methods continue to receive attention in society meetings and technical journals. Prof. Sir Alexander Kennedy, in an address before the Union Society of University College, London, referred to the Academic Side of Technical Training. He argued that the teaching of various branches should be carried much further than the point which may just suffice for the needs of the professional work of the engineer. A scientific branch cannot be mastered, even to an elementary degree, without some knowledge of the more advanced phases of the subject. He holds it essential that advanced work shall be done, but this should be so selected that it will make clear and certain the knowledge of the early work. It is necessary to broaden the mental grasp of a

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[1] This Journal, 27, 300.