stead of hydrobromic being used as a solvent for the metallic salt and to form the acid halogen salt of pyridine.

The analysis gave:

	Calculated for $C_5H_5N.SnCl_2.3HCl$.	Found.
Tin	28.07	28.5
Chlorine	50.20	50.75
Pyridine and hydrogen	21.73	20.75

Properties. — $C_5H_5N.SnCl_2.3HCl$ crystallizes in small white needle-shaped crystals. It is decomposed by water into a basic hydroxide or oxide of tin, and by nitric acid into the oxide of tin. When heated, the oxide of tin is the decomposition product. It is soluble in dilute hydrochloric acid, insoluble in ether, benzene, and chloroform, and very slightly soluble in 95 per cent. alcohol.

THE COMPOUND $C_5H_5N.MnCl_2.HCl$.

Preparation.—The process is the same as for the preparation of the tin salt. A great deal of care has to be taken in the purification by 95 per cent. alcohol as the compound is quite soluble. The manganese was determined by precipitation with sodium carbonate and was weighed as Mn_3O_4.

The analysis gave:

	Calculated for $C_5H_5N.MnCl_2.HCl$.	Found.
Manganese	22.70	21.57
Chlorine	44.00	44.10
Pyridine and hydrogen	33.30	34.33

Properties.—$C_5H_5N.MnCl_2.HCl$ crystallizes in salmon-colored plates. It is soluble in 95 per cent. alcohol and hydrochloric acid, slightly soluble in ether and insoluble in chloroform. When heated, decomposition takes place with the formation of the oxide of manganese.

UNIVERSITY OF MAINE CHEMICAL LABORATORY,
June, 1901.

COMMON ERRORS IN THE DETERMINATION OF SILICA.

BY W. F. HILLEBRAND.

Received January 6, 1902.

TO some it may seem as if a threadbare subject had been reopened in the above title, and that concerning a determination of such common occurrence in both technical and scientific

[1] Read at the Philadelphia meeting of the American Chemical Society.

operations little remained to be said or done. But that this is not so the following presentation will, I think, make sufficiently clear. Although not much of what I shall offer is really new, even that which is not will well bear repetition, having escaped the attention which it deserves. It seems to be advisable and necessary that public attention should be from time to time called to important facts which have not impressed themselves sufficiently to become a matter of common knowledge and application.

Regarding certain features of the silica determination I have long entertained doubts, but it is only very recently that convenient opportunity has presented itself for an investigation of these points as well as others, the direct incentive being afforded by an experience of the past summer as an outgrowth of the labors of a Committee of the New York Section of the Society of Chemical Industry having for its object the promotion of uniformity in technical analysis.

Uniform samples of raw cement-mixture and of finished cement were sent to a large number of analysts for determination of the commoner constituents by the usual technical methods. The same samples were analyzed in greater detail by myself and with the same regard to exactness that is usual in analyzing rocks and minerals in the laboratory of the United States Geological Survey. Fourteen of the chemists besides myself returned reports which showed in most cases a marked lack of agreement. The results for silica[1] only are here presented in tabular form with one exception, which is omitted for the reason that it does not profess to represent silica only, but rather the residue from evaporation of the limestone with acid, hence containing much undecomposed mineral matter.

TABLE I. SILICA FOUND BY DIFFERENT ANALYSTS IN THE SAME SAMPLES OF RAW MIXTURE AND FINISHED CEMENT.

	Limestone mixture.	Finished cement.
Standard	15.18	21.31
I	15.75	20.90
Ia	15.37	——
2	14.68	20.92

[1] The full data together with copies of the outlines of methods employed were submitted to me for review and suggestion without knowledge on my part of the names of the analysts. My report was transmitted through the Director of the Geological Survey to the committee of the New York Section of the Society of Chemical Industry, and its report was rendered at the Section meeting on December 20, 1901, and published in the *J. Soc. Chem. Ind.*, Jan. 15, 1902.

	Limestone mixture.	Finished cement.
3	13.92	20.06
4	——	20.00
5	14.18	20.26
6	14.70	20.96
7	12.78	20.84
8	13.97	19.82
9	14.44	20.76
10	13.60	19.18
11	14.64	21.46
12	14.18	20.76
13	14.92	21.56
14	13.56	19.53
Highest	15.75	21.56
Lowest	12.78	19.18
Difference	2.87	2.38

Without detailing the various means employed for rendering silica insoluble it may be said that all the workers strove to bring this about by the usual more or less approved methods of drying at temperatures ranging from that of the steam-bath for a long time to 120° and even higher for a shorter time. Despite their efforts there is not only a wide discordance in results, but, with two exceptions in each series, they are all too low. The actual failure to recover all silica is, however, in the majority of cases greater than the figures indicate, by reason of neglect of blast-ignition, or of correction by hydrofluoric acid, or both.

It is evident then that none of the methods in common use for rendering silica insoluble can be at all depended on to effect this result. None of the analysts except No. 1 and myself seems to have employed two evaporations with an intervening filtration. All others made but a single filtration, and in this simple difference lies the main solution of the trouble, a fact pointed out by Alex. Cameron with quantitative demonstrations nearly eight years ago,[1] but which has apparently almost escaped the notice of chemists. Indeed I must admit a certain degree of remissness myself, for I have but an indistinct recollection that it was the reading of Cameron's paper when it first appeared which led me to adopt the practice of double evaporations with intervening filtrations which I have followed for a good many years. What influenced this change had escaped my mind until mention of

[1] *Chem. News*, **69**, 171 (1894).

Cameron's paper in a recent number of this Journal, followed by its reperusal, recalled the matter to recollection.

Other earlier writers, as Lindo, Craig, and Gilbert, have recognized the impossibility of recovering all silica by one evaporation, without, however, recommending a repetition after filtration. Instead, dehydration by hot sulphuric acid is often used in iron and steel works, but its use precludes satisfactory determination of other constituents in the same sample.

Cameron used in most of his experiments 2 grams of silica, about 98½ per cent. pure, fused this with 9 grams of fusion mixture, dissolved the fused mass in hydrochloric acid, and evaporated in porcelain on the water-bath. The drying was continued on the bath in several experiments for some time after all acid fumes had ceased; in others the dehydration was effected by the blue flame of an Argand burner. He found that with the lower temperature four, and even five, evaporations and filtrations were needed to reduce the silica recovered to a negligible quantity, but that with the higher heat three, or even sometimes two, sufficed. Furthermore, he showed by one experiment that a very common practice of evaporating several times to dryness with fresh portions of acid without intervening filtrations did not reduce the silica in the filtrate, and that the presence of aluminum, iron and calcium was without influence on the results.

My own experiments to test all these points were entirely confirmatory of Cameron's, though less unfavorable as to the number of evaporations needed. This I attribute to the facts that I employed from one-half to one-fourth as much silica as he did, thus conforming more nearly to the ordinary conditions of a silicate analysis, and platinum instead of porcelain evaporating dishes. On the water- or steam-bath drying is not so speedily reached in porcelain as in platinum, and very possibly his later siliceous residues came in large part from the vessel itself.

The material employed in my tests was very nearly pure quartz crystal containing 99.88 per cent. silica. Amounts of this lying usually within the limits 0.5 and 1 gram were fused with 5 grams sodium carbonate, the fused masses dissolved in hot water, then acidified by hydrochloric acid, and the solutions evaporated in platinum vessels for different lengths of time on a steam-bath. Then the residues were digested for a short time with hydrochloric acid and hot water. Prolonged digestion was unnecessary, as

only sodium chloride with mere traces of other salts had to be extracted.

TABLE II. SILICA FOUND IN FILTRATES.

	Weight of quartz	SiO_2 in first filtrate.	Per cent.	SiO_2 in second filtrate.	
1..	0.8943	0.0078	= 0.87	0.0012	Duration of first drying not known.
2..	0.8208	0.0321	= 3.91	0.0006	Duration of first drying brief, not exceeding one to two hours, and in one case the residue still somewhat moist in parts.
3..	0.6401	0.0218	= 3.41	0.0005	
4..	0.5738	0.0197	= 3.43	0.0009	
5..	0.7028			0.6000	
6..	0.5931	0.0167	= 2.82	0.0001	Duration of first and second dryings twenty-one hours each. In 9 the mass was ground to powder as soon as free from visible moisture, without marked improvement in the result.
7..	0.7309	0.0211	= 2.89	0.0001	
8..	0.8495	0.0204	= 2.40	0	
9..	0.7841	0.0142	= 1.81	?	
10..	0.7092	0.0089	= 1.25	0.0004	Several evaporations with fresh acid before first filtration. Total duration of dryings and evaporations twenty hours.
11..	0.7324	0.0047	= 0.64	0.0005	Repeated (4) evaporations with water only before first filtration, twenty hours' drying before third filtration.
12..	2.0000	0.0193	= 0.96	0.0008	

Experiment 10 was made in order to test the somewhat prevalent practice of evaporating several times with fresh acid before filtering. The result is an improvement over all but the first of the earlier ones, but still leaves much to be desired.

Experiments 11 and 12, in which repeated evaporations with water only were made, show a still better but by no means satisfactory result. The improvement in these last cases is not surprising, but it is to be expected that in ordinary analysis the foreign matter remaining with the silica would be increased by this treatment with water only instead of acid.

In order to learn, if possible, something about the effect of the large amount of sodium chloride in preventing the dehydration of silica, a soluble gelatinizing zeolite (thomsonite with 41.17 per cent. silica) was experimented with. The foreign chlorides in solution were here, of course, very much reduced in amount. The results are shown opposite 1, 2, 3 of table III.

TABLE III. SHOWING DIFFERENT SOLUBILITIES OF THE SILICA SEPARATED IN GELATINOUS AND GRANULAR FORM FROM ZEOLITES.

	SiO_2 in weight of zeolite taken.	SiO_2 in first filtrate.	Per cent.	
1	0.4185	0.0065	1.55	Duration of drying 2 hours.
2	0.4142	0.0048	1.16	Duration of drying 21 hours.
3	0.8265	0.0072	0.87	Duration of drying 21 hours.
4	0.5736	0.0020	0.35	Duration of drying brief.
5	0.5760	0.0023	0.40	Duration of drying prolonged.

Since the separation of silica from soluble silicates occurs in two forms, gelatinous and granular, according to the species acted on, it seemed worth while to try a non-gelatinizing zeolite (heulandite) containing 57.18 per cent. silica. The results appear opposite Nos. 4 and 5 of Table III. Manifestly the instantaneous separation of silica in granular form, without first entering into solution, is far more perfect than when it gelatinizes.

We have thus seen how the serious errors in silica determinations shown by Table I can be avoided by two evaporations with intervening filtrations. In extreme cases a third evaporation may at times be advisable. Furthermore, that prolonged drying is a useless waste of time, except perhaps after the second evaporation, when, if results like 6, 7, and 8 of Table II can be depended on, it may be of value in very exact work.

CAUSES OF THE SOLUBILITY OF SILICA UNDER THE CONDITIONS GIVEN.

In explaining the partial solubility of silica after drying at temperatures much above that of the water-bath it has been customary to assume the formation of soluble silicates by action between some of the silica and salts present. This is an undoubted cause and one which should become more active with increasing temperature, though Gilbert's work does not seem to indicate this except when magnesium is present in quantity. But if true at 120° it must probably still be true to some extent at 100°.

Another explanation for the incomplete dehydration at 100° is assumed to be the protecting influence of other salts, and to remedy this, repeated additions of acid, or perhaps better still of water, are sometimes resorted to (See Exp. 10–12 of Table II).

Again it may be that the silica separated is itself soluble enough in acid to cause an appreciable error. The experiments reported below show clearly what the action of hydrochloric acid is on silica which had been obtained by fusing quartz with sodium carbonate and drying the evaporated hydrochloric solution for twen-

ty-one hours on the steam-bath. This silica (about 0.65 gram) was first extracted with a little acid, then thoroughly washed with hot water, rinsed back into the dish, and digested with hydrochloric acid of about 1.10 sp. gr. under varying conditions.

a. Digested twenty-five minutes on steam-bath with about 25 cc. acid. Silica in filtrate 0.0029 gram.

b. Same silica further treated as in *a* for one and one-half hours. Silica in filtrate 0.0026 gram.

c. Same silica gently boiled in platinum for thirty minutes with above acid. Silica in filtrate 0.0022 gram.

There was thus extracted with ease nearly 1.2 per cent. of the total silica without counting the probably larger amount held by the original filtrate, and it is to be presumed that the effect of the boiling would have been greater had it preceded instead of followed the quiet digestion.

It is thus plain how a portion of the silica always found in the filtrates gets there and that it is hopeless to try to prevent this by a single prolonged drying. Once the bulk of the silica is removed by filtration, however, then, after a second evaporation, because of its tendency to collect in clots of sensible size and consequent small surface exposure, the amount of silica going into solution is very small and by no means in proportion to that of the acid used.

DETERMINATION OF SILICA THAT HAS ESCAPED SEPARATION BY THE USUAL PROCESSES OF DEHYDRATION.

I pass now to another phase of the determination of silica, which so far as I am aware, has never been investigated.

While it has long been known that some silica passed into the filtrate in silicate work, it was supposed to be recovered in the ordinary course of analysis with the ammonia or basic acetate precipitate, whence after ignition and weighing it could be obtained in insoluble form by fusing the mixture with potassium pyrosulphate. I purpose showing that these suppositions are both in part erroneous, that the residual silica is, as Lindo says,[1] not

[1] Lindo (*Chem. News*, **60**, 14 (1889)) gives no quantitative data and in all his experiments (with glass) the ammonia precipitates were, of course, very small. It is fair to conclude from his addition of ferric chloride to the filtrates from them in order to recover by its precipitation by ammonia the "last trace" (*loc. cit.*, p. 40) of silica, that he would not have suspected the presence of any silica in these filtrates when analyzing mixtures containing considerable aluminum or iron oxide. Lindo's observations are of value, but his analytical results are not, for the reason that he operated largely in glass vessels and his alkaline solutions remained long in contact with glass, hence must have taken silica from them, notwithstanding which his analyses show without exception a large loss.

wholly precipitated by ammonia, and that the ordinary treatment of the pyrosulphate fusion mass recovers but a minor part of that which was thrown down with the oxides of iron and aluminum.

The experiments of the following table were made with a hydrochloric solution containing 0.0101 gram of silica in 10 cc. and with a solution of aluminum chloride free from silica. The amounts used were chosen to represent approximately the conditions most frequently prevailing in silicate analysis after but a single evaporation to separate silica. Precipitation was effected by ammonia at boiling temperature in a solution of about 300–400 cc. volume containing 25 cc. hydrochloric acid of 1.10 sp. gr. As soon as settled the alumina was filtered, washed, ignited, and fused with potassium pyrosulphate free from silica. The fused mass was generally dissolved in hot water acidulated with sulphuric acid, and once in warm water only, and the residual silica was collected, weighed, and corrected by hydrofluoric acid. In two cases (8 and 9) the filtrates were evaporated with excess of sulphuric acid, heated till fumes came off in quantity, and the separated silica collected after cooling and dilution of the solution. The filtrates from the alumina were evaporated, ignited to remove ammonium chloride, and the silica recovered by evaporation with a few drops of hydrochloric acid and further treatment as usual.

TABLE IV. SILICA IN ALUMINA AND IN FILTRATE FROM ALUMINA AFTER ONE PRECIPITATION BY AMMONIA.

	Al_2O_3 used.	SiO_2 used.	SiO_2 in filtrate.	SiO_2 recovered from Al_2O_3.	SiO_2 recovered from $K_2S_2O_7$ solution.
1	0.19	none	none	none	....
2	0.19	0.0101	....	0.003	....
3	0.19	0.0101	....	0.0037	....
4	0.19	0.0101	0.0020	....	....
5	0.19	0.0101	0.0021	....	....
6	0.19	0.0101	0.0007	0.0034	....
7	0.19	0.0101	0.0019	0.0021	....
8	0.20[1]	0.0101	0.0007	0.0033	0.0060
9	0.19	0.0101	0.0021	0.0023	0.0058

Treatment of about 0.01 gram of ignited precipitated silica with fused pyrosulphate resulted in the solution of 2 mg. of it and of 2.2 mg. in another test. Not being evenly distributed through a mass of other oxides undergoing solution the solvent

[1] Fe_2O_3.

effect of the pyrosulphate in these cases may reasonably be supposed to be less than in the tests of the table.

We here see how in practically all ordinary silicate analyses a portion of the silica, sometimes very small, escapes being weighed at all, since it mostly passes on into the filtrate from the magnesia. When a double precipitation by ammonia or sodium acetate is made, instead of one as in the above tests, the loss will be greater than the table shows.

We further see how, when correction is made for the silica with the alumina, it is only in small part recovered and the alumina is consequently made to appear too high when determined indirectly. Here we have an added argument in favor of endeavoring to collect all silica at the outset, for it is shown that the expectation of recovering the whole of a missing portion later is based on erroneous assumptions. Therefore Gilbert's conclusion, because he found very little silica with the alumina after fusion with pyrosulphate, that there is "no tendency for silica to recombine with the lime and alumina" (in non-magnesia silicates) "even at a temperature of 280° C."[1] is perhaps not well founded. Since his further conclusion that silica is almost completely dehydrated at 120°[2] is based on this same reason, his analytical results lose much of their value.

As showing the errors in the silica results that may be incurred in the analysis of certain siliceous ores where potassium pyrosulphate is employed as the means for breaking them up, I will here give the figures for two titaniferous magnetites. The lower values give the silica obtained in the usual way from the mixture of silica and silicates left after fusion with pyrosulphate, and the higher those afforded by direct fusion of the ores with sodium carbonate.

	I.	II.
Silica	{ 11.73	20.82
	{ 12.42	21.42

Complete analysis of the ores showed such a deficiency when pyrosulphate was used that the cause was sought and found to be as stated above. It was this observation which led to a portion of the work summarized in Table IV.

[1] *Technology Quarterly*, **3**, 63 (1890).

[2] *Loc. cit.*, p. 64.

THE PROPER TEMPERATURE FOR IGNITION OF SILICA.

Most authorities, Fresenius included, have directed that blast temperatures be used in order to obtain the correct weight of ignited silica. It is only recently that doubt has arisen as to this because of the experiments of Lunge and Millberg,[1] who, employing silica derived from silicon tetrafluoride, observed no further loss in weight over the blast after sufficient exposure to the full flame of a good Bunsen lamp. This was in direct conflict with all my experience in silicate work, and as a result of friendly correspondence Professor Lunge caused the matter to be reinvestigated in his laboratory a year ago and sent me the following table of results, which I take the liberty of making public.

TABLE V.—LOSS IN WEIGHT OF PURE SILICA FROM SiF_4, AT DIFFERENT TEMPERATURES AS DETERMINED BY DR. LOHÖFER, IN PROFESSOR LUNGE'S LABORATORY.

Temperature.	Time. Minutes.	*a.*	*b.*	*c.*
105°	..	0.1840	0.1778	0.2020
Dark redness	30	0.1643	0.1584	0.1803
Dark redness	30	0.1640	0.1584	0.1800
Full flame of burner	30	0.1622	0.1566	0.1779
Full flame of burner	30	0.1620	0.1564	0.1778
Blast	30	0.1619	0.1564	0.1776

It is but natural that Professor Lunge should write: "From these results I must conclude that Millberg and myself were right."

The following two tests by myself on silica similarly obtained confirm the above, and show, after blasting, further slight losses comparable with those appearing in Professor Lunge's table and of the same order as those produced by more than half an hour's blasting with silica precipitated by acid (see Table VIII).

TABLE VI.—SHOWING LOSS IN WEIGHT OF PURE SILICA FROM SiF_4, ACCORDING TO TESTS MADE BY MYSELF.

	a.
	0.5053
Full burner flame 30 minutes	0.5017
Blast flame 30 minutes	0.5014
	b.
	0.5030
Full burner flame 45 minutes	0.4997
Full flame 45 minutes	0.4995
Blast flame 40 minutes	0.4991[2]

[1] *Ztschr. angew. Chem.*, p. 425 (1897).

[2] This loss is partly chargeable to the crucible itself.

These slight losses are not due to mechanical carrying off of silica, for the latter had utterly lost its extraordinarily down-like character during the early heating and become converted by the blasting into a coherent cake of enormously reduced bulk.

Let me now, however, present another series of results furnished by silica otherwise precipitated. The silica used was obtained by three evaporations from the quartz that served for the earlier experiments of this paper, and the initial weights are those found after an exposure of about one hour to the full Bunsen flame. The weights given represent the silica as corrected by hydrofluoric and sulphuric acids for the few tenths of a milligram of non-volatile salts always present. The crucibles were found not to lose weight themselves over the blast. The quartz powder employed was 99.88 per cent. pure, as found by careful evaporation with hydrofluoric and sulphuric acids.

TABLE VII.—SHOWING DIFFERENCES IN WEIGHTS OF SILICA PRECIPITATED FROM SODIUM SILICATE WHEN IGNITED OVER BUNSEN BURNER AND BLAST-LAMP.

No.	Weight of quartz.	Silica found.		Loss in weight.	Percentages found.	
		Burner 1 hr.	Blast ½ hr.		Burner.	Blast.
1	0.5738	0.5761	0.5735	0.0026	100.40	99.95
2	0.5931	0.5945	0.5930	0.0015	100.24	99.98
3	0.6401	0.6450	0.6394	0.0056	100.76	99.90
4	0.6638	0.6668	0.6628	0.0040	100.45	99.85
5	0.7028	0.7058[1]	.....	.....	100.25	....
6	0.7309	0.7342	0.7306	0.0036	100.45	99.96
7	0.8208	0.8271	0.8206	0.0065	100.77	99.98
8	0.8495	0.8521	0.8484	0.0037	100.31	99.88
9	0.8943	0.8996	0.8936	0.0060	100.59	99.92
10	.....	0.9989	0.9898	0.0091	.....	....

Results similar to the above are repeated in every silicate analysis that is made in our laboratory, and others have told me their experience is the same. It is as clear as daylight that the blast is a necessity if the work is to be at all accurate. In every one of the above instances the percentage found without blast is far in excess of 99.88, the true value for silica in the quartz, and is as invariably brought very near this value and with far smaller variations from a mean when the blast is applied (see further, p. 373). The above values for "burner" percentages very well represent the usual lack of exact agreement in series of duplicate silica determinations, when the blast has not been used (see Gil-

[1] Two hours.

bert's paper), while those of the next column show of what accuracy the determination is susceptible when all the conditions of success are understood and applied.

From the foregoing it appears that the silica separated by water from silicon tetrafluoride and that by hydrochloric acid from sodium silicate are in different conditions and behave differently when strongly heated ; that Professor Lunge's conclusion that silica need not be blasted, while correct for one form of silica, cannot be applied, as he supposed, in analytical work.

I have always, until lately, regarded one-half hour's blasting as sufficient in all cases for as much as a gram of silica, but that this length of time is often insufficient to secure constant weight is indicated by some of the results in Tables V and VI and still more by those in the following :

TABLE VIII.—SHOWING NEED OF VERY LONG BLASTING AT TIMES.

Heat.	Time in minutes.	Weights of silica. 1.	2.	3.	4.	5.	6.
Burner	60	0.6691	0.7041	0.9989	.....	0.4175	0.4220
Blast	30	0.6657	0.6982	0.9905	0.7208	0.4154	0.4192
Blast	30	0.6656	0.6979	0.9902	0.7201	.....	0.4187
Blast	30	0.6651	.....	0.9899	0.7193	0.4152	0.4185
Blast	30	.....	.....	0.9897	0.7194	.....	.....
Blast	30	.....	.....	.....	0.7194	.....	.....

The progressive losses shown here are not chargeable to the crucibles, nor were they due to mechanical loss of silica or to volatilization of included salts, and they explain very well the fact that nearly all the figures of the first column in Table V slightly exceed the true value for silica in the quantity used, for they were obtained by blasting for only one-half hour. They may also serve to explain in small part the excessive summations often encountered in rock analyses. These later losses can exert little effect when the silica percentages are small, but when large as in rock analysis, they may at times be of moment and necessitate blasting for more than half an hour.

In the foregoing I have entered into such detail as the exact scientific worker needs for his enlightenment and have carried my separations and ignitions farther than the technical chemist ordinarily cares to or can proceed. But in its main features, what I have said concerns him not less than the research chemist and I trust that in some respects it may help to ease his path.

SUMMARY.

Statements of earlier writers are fully confirmed, that silica cannot be rendered wholly insoluble by a single or any number of evaporations with hydrochloric acid when followed by a single filtration, no matter what temperature may be employed, but that two or more evaporations alternating with filtrations are necessary to secure satisfactory results.

It is shown that the generally accepted view that any silica passing into the filtrate is wholly thrown down by ammonia or sodium acetate in presence of much aluminum or iron is incorrect. Also that silica is appreciably soluble in melted potassium pyrosulphate and that consequently when siliceous oxides of iron and aluminum obtained in analysis are then fused their silica contents are only in small part left undissolved when the fused mass is taken up with water or acid. Both these sources of error are avoided by separating all silica at the start as above.

The need of blast ignition in order to get the correct weight of silica obtained in analysis is proved. The opposite conclusion of Lunge and Millberg, being based on what seems to be a different behavior of the silica derived from silicon tetrafluoride, is therefore not justified.

LABORATORY U. S. GEOLOGICAL SURVEY.
December, 1901.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REDETERMINATION OF THE ATOMIC WEIGHT OF CALCIUM—PRELIMINARY PAPER.

BY THEODORE WILLIAM RICHARDS.

Received February 16, 1902.

DURING the years 1897 to 1899 an investigation upon the atomic weight of calcium was conducted in the Chemical Laboratory of Harvard College. This investigation was more carefully conducted, and in some respects more elaborate than any previous research of a similar kind conducted in this laboratory. The details are so many that time has not yet been found for a verbal presentation of them, but a brief report of the results was made to the American Association for the Advancement of Science in August, 1899, of which a notice is published in the journal.[1]

[1] This Journal, **22**, 72 (1900).