rate can happen with a slag, considering that its type as silicate is determined beforehand in the charges of a blast furnace, by furnishing to the silica of ores, stone, and ash of coal, perfectly definite basic elements, in certain proportions primarily calculated, which necessarily determine a composition which the ultimate analysis of the slag, as run from the furnace, corroborates very closely in the great majority of cases. When it does not happen, it has also to be attributed to disturbing factors, and they can be found, for instance, in this fact that calcium, combined with sulphur, which the slags often contain in very serious quantities, has been calculated as oxide of calcium or *lime*. The same can be said of magnesium and manganese. 5% of sulphur in a slag is by no means an exceptional circumstance; 8% of manganese sulphide is frequently met with in Scotch slags. In other cases alumina, owing to certain condition of the furnace, or the proportions of fluxes, will play the part of an acid, and, in these conditions, ought not to figure in the determinations of the type as saturating silica.

(*To be continued.*)

DETERMINATION OF LITHIA IN MINERAL WATERS.

By E. Waller, Ph. D.

Practically, three methods are now available. 1. The phosphate method (Mayer's modification) (*Ann. Chem. u. Pharm.* **98,** 193). 2. The amylalcohol method (*Gooch, Am. Chem. Jour.,* **9,** 33). 3. The fluoride method (*Carnot, Bull. Soc. Chim.* [3] **1,** 280).

Rammelsberg's method (*Pogg. Ann.,* **66,** 79) somewhat similar in principle to that of Gooch, in that it depends upon the comparatively greater solubility of lithium chloride in an organic solvent, has been comparatively little used, on account of the difficulty and expense involved in obtaining the pure anhydrous alcohol and ether necessary for the process. Moreover the experiments of J. L. Smith (*Am. Jour. Sci.* [2] **16,** 56), rearranged in convenient form for reference by Gooch (*loc. cit.*) do not indicate that it is very satisfactory in its application, even with the best of care. Some indirect processes, such as the weighing of mixed chlorides of sodium, potassium and lithium, and then determining the chlorine and potassium (Bunsen, *Ann. Chem. u. Pharm.*, **122**, 348), have been also proposed, but they are troublesome in execution, and likely to be unsatisfactory in result.

For all of these processes, it is necessary to obtain from some known quantity of the water, the alkalies as chlorides free from admixture with other bases, and in most cases, a considerable proportion of the sodium and potassium salts, which usually predominate largely over those of lithium, must be removed. To accomplish this the usual method may be followed, acidification with hydrochloric acid, evaporation, treatment with barium hydrate solution, removal of the excess of baryta by ammonium carbonate, driving off the ammonium salts, and extraction with alcohol or alcohol and ether, to take out the lithium chloride which is inevitably accompanied by some sodium and potassium chlorides. Throughout this treatment, the spectroscope must constantly be used to determine when the extraction or washing is complete and these preliminary operations often prove very tedious. Some suggestions in this connection may be of value. The small platinum wires used to test the precipitates, solutions, etc., need critical examination. A wire which has been once used with lithium salts may perhaps be held in the flame until it will give no trace of color to the flame, nor show the lithium line by the spectroscope, but on moistening with hydrochloric acid and inserting in the flame, the line will show almost as brightly and distinctly as if no lithium had been removed from it. Repeated scouring, immersion in acid and insertion in the flame, or long soaking in acid may be necessary to remove this trace of lithium from the wires. It has been found convenient to keep several wires dipping into a test tube partially filled with dilute hydrochloric acid, and to use them in succession, so that each wire shall have a tolerably long immersion in the acid, before being tested again, as a preliminary to using it for a test on a precipitate, etc.

Barium precipitates ($Ba\ CO_3$ and $Ba\ SO_4$) when formed in the presence of lithium compounds, carry down and retain perceptible quantities of lithia (by spectroscope test) with great persistency. The well known tendency of the barium sulphate to drag other salts with it *seems* to be greater in the case of lithia than in that of other alkaline salts, although this may perhaps be due to the exceeding delicacy of the spectroscopic reaction. Precipitation in a rather dilute solution, and rather liberal washing is usually the most convenient course to pursue in the case of the precipitation of $Ba\ SO_4$ in presence of lithium salts. With $Ba\ CO_3$, re-solution in HCl, and re-precipitation with ammonia and ammonium carbonate is most effective. If the proportion of lithium is large, re-solution, and re-precipitation a third time may be advisable. The precipitate produced by barium hydrate, unless consisting largely of sulphate, does not give so much difficulty in the washing out of the lithia, except when it has been exposed for some time to the air of the laboratory containing CO_2.

A word further as to the decomposition of $Li\ Cl$ by heat. Direct quantitative estimations upon the subject were not made in this investigation, but the phenomena noted tend to confirm Mayer's remark that under the influence of heat in presence of water, lithium chloride has a tendency to exchange chlorine for oxygen.

A solution containing lithium chloride is evaporated to dryness with difficulty when placed on the water bath, and if it finally is made to *appear* dry after prolonged treatment in this manner, more of the material is slow to re-dissolve in water (apparently because of the formation of lithium hydrate) than if the same solution is evaporated nearly to dryness and the moisture driven out by careful ignition over a naked flame.

Assuming in every case that one has obtained a concentrated aqueous solution from a known quantity of the water, containing all of the lithium and some of the potassium and sodium as chlorides, but no other bases, the phosphate method would be as follows :

Add an excess of hydro-disodium phosphate, and then a moderate excess of pure sodium hydrate, evaporate to dryness, re-dissolve in water by the aid of a gentle heat, add an equal volume of strong ammonia, digest warm for some time, allow to stand for twelve hours, filter and wash with a mixture of equal volumes of ammonia and water, and finally ignite and weigh as $Li_3 PO_4$. A second or third portion of precipitate may be recovered, by evaporating the filtrate and washings, adding ammonia and allowing to stand as before, filtering, etc. The chief difficulty with the accuracy of the process, consists in the practical impossibility of obtaining all the lithium as phosphate, free from any other alkaline salts. Too much washing will cause appreciable amounts of lithium phosphate to go into solution. Indeed, in my experience the filtrate and washings have always showed a decided lithia line in the spectroscope, from the start. On the other hand, too little washing leaves some alkaline salt along with the lithium phosphate—shown by its tendency to cake on ignition—but whether it cakes or not, lithium phosphate separated by this method when tested by the flame, almost invariably gives so strong a sodium flame, as practically to obscure the red of the lithium to the naked eye. Consequently it becomes to a considerable extent a matter of judgment, to decide when the washing is completed, and *then* the amount of lithium phosphate obtained is a compromise between the precipitate dissolved off by washing, and alkaline salts left with it. However, by the aid of a little experience, the error can be usually brought within moderate limits, if the proportion of water which the chlorides represent is sufficiently large (ordinarily 10 to 20 litres). The use of such large quantities of water is naturally attended with more or less labor, in evaporation, removal of bases, etc., and is in itself objectionable aside from the sources of error inherent in the method of determination. This method has, however, until recently been practically the only one in general use.

The method of Gooch (*loc. cit.*) used by him in the examination of the waters of the Yellowstone Park (*Bull. U. S. Geol. Survey*, No. 47, also *Chem. News*, **59**, *113*, *et seq.*), may be described as follows: The concentrated solution of the alkaline chlorides should contain only about 0.2 grm. of salts in all. To this solution, in a casserole or dish, is added 30 to 50 c. c. of pure *anhydrous* amyl alcohol. The vessel is then heated on a sand bath over a low flame, so as to boil off the water through the amyl alcohol, leaving the undissolved salts adhering to the sides of the dish. The heat is kept up until the volume of amyl alcohol has been reduced to about 15 or 18 c. c. after cooling. A few drops of hydrochloric acid are added to restore to the form of chloride any lithium oxide or hydrate which may have been formed, and the heating is repeated for a short time. The amyl alcohol is then filtered through paper, or through a Gooch crucible, into a measuring cylinder, and its volume noted (usually 10 to 15 c. c.). In case the proportion of lithium is large the undissolved salts should be taken up with a little water, and the treatment repeated in the same way as just described, the amount of amyl alcohol which has been heated with the chlorides being measured as before. The salts are then washed with cold amyl alcohol until no trace of lithium is perceptible in them by the spectroscope; the filtrate and washings are evaporated in a weighed platinum dish, and the chlorides converted into sulphates, ignited and weighed. From this weight, for every 10 c. c. of amyl alcohol which remained in contact with the chlorides after heating, the following deduction is made:

When only sodium and lithium chlorides were present, 0.00050 grm.
" " potassium " " " " 0.00059 "
When both sodium and potassium, as well as lithium
chlorides were present, - - - 0.00109 "

The cold amyl alcohol used for washing dissolves so little that it is needless to take it into account.

The relative solubilities of Na Cl, KCl and Li Cl in amyl alcohol, as determined by Gooch, are essentially:

Na Cl.................	1 in 30,000, or 0.0041	grm. in	100 c. c.
K Cl..................	1 " 24,000, or 0.0051	"	100 "
Li Cl.................	1 " 15, or 6.60	"	100 "

Temperature seems to have but little influence upon the solubility of Na Cl and KCl.

Pure amyl alcohol freed from water by boiling, if necessary, is indispensable.

Gooch's test experiments with mixtures of pure salts may be here quoted, arranged in a form slightly different from that given in his paper. The $Li_2 SO_4$ obtained was calculated back to Li Cl in every case. The error is noticeably greater in the presence of potassium chloride.

Ex. pt. No.	Conditions.		Li Cl taken.	Errors in corrected weight of Li Cl found.
(23)	Na Cl only	Single	0.1298 grm.	0.0002— grm.
(24)	" "	Extr'n	0.1227 "	0.0002— "
(32)	" "	Double	0.1287 "	0.0007— "
(33)	" "	Extr'n	0.1347 "	0.0006+ "
(26)	KCl only	Single	0.1256 "	0.0008— "
(27)	" "	Extr'n	0.1287 "	0.0010— "
(34)	" "	Double	0.1125 "	0.0003+ "
(35)	" "	Extr'n	0.1251 "	0.00011+ "

The average of these errors is 0.0001— with a range from 0.001 — to 0.0011+ or if we calculate to the equivalent in $LiHCO_3$ from 0.0016— to 0.00176+, a difference of 0.00376 grm.

The process has the advantage that the sodium and potassium chlorides are left in a condition for the determination of those bases, in which case, however, an allowance must be made for the small amounts dissolved by the amyl alcohol which was heated with the chlorides. One disadvantage of the process is to be found in the fumes of the amyl alcohol which, even in a well ventilated laboratory is a source of great discomfort to most analysts.

The small amount of water, 100 to 200 c. c. that can be used for this process is advantageous, though for those accustomed to the use of the phosphate process, the amount seems hardly large enough to give a fair average, and to average on a larger amount requires the concentration of the Li Cl by extraction with alcohol or alcohol and ether. In some of the first trials made with the process, the amount of mixed chlorides experimented upon considerably exceeded 0.2 grm., probably nearly 1. grm. and in some cases more. This was because Prof. Gooch's paper seemed to imply that the operation might be reasonably expected to be successful, when applied to quantities ordinarily handled in analytical work. In the case of one water it did prove so, but with another water, containing more lithia as well as alkaline salts it was not. The removal of all the water in the manner described, was a matter of extreme difficulty, and curiously enough, a limit seemed to be reached, beyond which the Li Cl was extracted, but slowly and with great difficulty. The results may prove interesting.

The alkaline salts from two equal quantities of a water, each lot amounting to between one and two grammes, were treated as described :

Obtained from A..............	0.2400	grm. $Li_2\ SO_4$	from B	0.2354	$Li_2\ SO_4$
Found in insoluble part. f. A.	0.0974	"	" B	0.0943	"
Total............	0.3374	"		0.3297	"

The control process used in this case was Carnot's fluoride method, which cannot however be regarded as absolutely free from imperfections. It is as follows : the mixed alkaline chlorides after evaporation nearly to dryness, are extracted with a mixture of about equal volumes of alcohol (of 90% or over) and ether, so as to obtain the Li Cl comparatively free from the others. It was found most convenient to add the alcohol ether mixture, and allow to stand for some time with frequent stirring, and then after standing over night to filter through a small filter, and wash with alcohol, one extraction will often suffice. A second extraction may however be necessary, the work being of course controlled by the indications of the spectroscope. After evaporating off the alcohol and ether, the salts are dissolved in the least possible quantity of water, and filtered into a weighed platinum dish. The filtrate and washings should then be concentrated to small bulk (5 or 10 c.c.) and pure ammonium fluoride and ammonia added: after thorough mixing the dish is set aside over night for the Li F to precipitate. The solution is then decanted through a small filter, and the precipitate is washed by decantation three or four times (5 to 7 c.c. at a time), with a solution consisting of the reagent mixed with 5 to 10 times its bulk of ammonia ; between decantations the solution must be allowed to stand some little time with stirring. The bulk of filtrate and washing (30 to 50 c.c.) is noted, the filter paper and contents placed in the dish, sulphuric acid added, and heat applied until the paper has been incinerated, and the lithium converted to sulphate, in which form it is weighed. To this weight is added 0.0040 grm. for every 7 c.c. of filtrate and washings, and the result estimated as $Li_2\ SO_4$ is calculated to Li, Li HCO_3, etc., according to the requirements of the case.

Care is necessary in preparing the reagent, and wash liquor.

Carnot seems to have found that the ammonium fluoride ordinarily supplied for laboratory use, is the only member of the combination liable to contain impurities which would interfere (chiefly fluosilicic acid, which might precipitate alkaline fluosilicates), but experiments have shown that ammonia, which has been standing for some time in contact with glass, will give a cloud (presumably ammonium fluosilicate) with a mixture of solutions of ammonium fluoride and ammonia after boiling and filtering clear. This solution, so long as it contains a fair amount of free ammonia, appears to be without action upon glass. It has been found advisable therefore to make up (and cork up) the reagent and washing solution some time beforehand, and to filter off such portions as may be required at the time of using. Naturally, it is necessary to use for the final filtration, a filter paper which has been extracted with hydrofluoric acid. Schleicher & Schull's papers were found satisfactory in this connection. Carnot also recommends that the resulting Li_2SO_4 should be dissolved in 40 to 50 c.c. of water, and a test made for the presence of magnesium, which may have remained with the alkaline chlorides. If any is found to be present, it must be determined as phosphate and a correction made accordingly.

In connection with this process it was observed that lithium sulphate ignited in contact with the carbon of the filter paper, is especially prone to reduce to sulphide and especial caution is necessary at this stage of the operation. The sulphide, when heated in contact with the platinum, attacks it in a very marked manner.

The process seems to be very good, although not rapid.

Its tendency is to yield results a little high, apparently because the allowance for solubility is usually larger than the actual amounts of precipitate dissolved. Test analysis tended to show also that unless the amounts of potassium and sodium chlorides present with the lithia are kept within narrow limits, the results will be high.

Unfortunately a number of the tests and comparison experiments with these methods have not yet been completed, and will have to be deferred to a second communication.

I order to test these methods upon water containing lithia, samples of several of the best known and widely advertised waters were purchased and submitted to examination.

The results were somewhat surprising, and showed unquestionably that either the original analyses, on the strength of which those waters are now sold, were erroneous, on account of imperfection in the methods used, or, what is more probable, that the proportions of lithium in those waters are liable to great fluctuations.

The results given were chiefly obtained by Carnot's fluoride method, but were in several cases confirmed by the use of other methods. The most scrupulous care was exercised to be sure of obtaining *all* of the lithium in the waters under examination, the spectroscopic indications having been used at every stage of the process.

In the Farmville Lithia Water, purchased at the office of the company, no lithium could be detected by the spectroscope on moderate amounts of the water. On evaporating eight litres of the water, and treating in the manner described for the concentration of the lithia into a solution of small bulk, a lithia line was obtained in the spectroscope, but the amount was found to be too small to permit of a quantitative estimation. The experiment was repeated with ten litres of the water, with essentially the same result.

With the Buffalo Lithia Water the reaction for lithium was more distinct, when considerable quantities of the water were concentrated. From 20 litres of the water was obtained lithium sulphate corresponding to 0.0185 part $LiHCO_3$ per 100,000.

In the Londonderry water, the lithia reaction could be obtained without great difficulty. Analysis of the water purchased by myself showed a little over 4 parts per 100,000. The company puts up some of the water in half-gallon bottles not charged with CO_2, and also some in pint bottles (called in their circulars "sulpho-carbonated"), which is charged with CO_2, and has also received the addition of some salts. The amounts of salts added appears to be somewhat irregular. For instance, the following results were obtained (results given in parts per 100,000):

	Total solids.	Loss on ign.
Londonderry, half-gallon bottles (aver.)	37.35	2.25
" pint bottle, A	149.4	4.9
" " B	104.2	4.5
Average of eleven others	224.7	6.4

The variations in the eleven bottles were 221.3 to 231.4, for total solids. The proportion of lithium was essentially the same as for the still water.

I was told that several lots of water, purporting to come from these springs, had at times appeared on the market in which no lithia could be detected. As I learned that Dr. Endemann had obtained some water of that kind, I requested him to send me a bottle. He complied, and although the bottle bore all the labels and marks similar to those purchased by myself, no lithia could be detected in it. The water contained 5.2 parts total solids per 100,000. I have heard of others who had similar experiences.

I naturally desired to obtain samples of these waters direct from the springs, taken by some one whom I knew to be disinterested. Attempts thus far have been unsuccessful. In the case of the Londonderry springs, all access is denied to visitors, and applications for water are referred to the bottling establishment in Nashua.

Of all the waters examined, purporting to be natural, the Saratoga Hathorn proved to be the strongest in lithia. The result of tests on this water are not at present in such form that they can be here recorded, but it suffices to say that the water contains fully as much as the analyses call for (12 to 14 parts Li HCO_3 per 100,000, corresponding to 7 or 8 grains per U. S. gallon).

Tests were also made on the waters manufactured and sold by Carl H. Schultz as containing lithia. They were found to contain a little more lithia than claimed. E. g., the formula on his "Vichy with Lithia," calls for an amount corresponding to about 57 parts Li HCO_3 per 100,000. The analyses showed 60 to 62 parts.

The results enumerated may be thus tabulated :

Designation of Water, etc.	Total Sds. Per 100,000.	Loss on Ign.	Non-Volatile.	Used for Determination.	Li HCO_3		
					Per 100,000	Grs. U. S. Gal.	Grs. Imp. Gal.
Farmville Lithia, half gal. bottles	16.4	1.1	15.3	8:L	traces.		
" "	....	....	....	10.L	traces.		
Buffalo Lithia, half gal. bottles...	93.2	6.5	88.7	20.L	0.0185	0.011	0.013
" "	....	....	....	20.L	0.0135	0.008	0.009
Londonderry Lithia hf. gal. bot's.	37.35	2.25	35.1	10.L	4.171	2.432	2.920
" "	....	....	....	10.L	4.075	2.376	2.852
" "	....	....	....	2.L	4.130	2.408	2.891
" " pts (c'h'g'd CO_2)	....	....	...	2.L	4.129	2.407	2.890
" " "	....	....	....	4.L	4.074	2.376	2.851
" " (hf. gal. Dr. E.)	5.1	1.	4.1	1.L	none		