THE PERCHLORIC METHOD OF DETERMINING POTASSIUM, AS APPLIED TO WATER ANALYSIS.

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Potassium is determined gravimetrically as potassium chloroplatinate (K_2PtCl_6), as potassium cobaltinitrite ($K_3Co(NO_2)_6$), and as potassium perchlorate ($KClO_4$).

The potassium chloroplatinate method is most commonly used. It is accurate, but there are difficulties because of the solubility of the salt in alcohol, the non-uniformity of the precipitate, the loss by ignition, and the cost of material. The cost of chloroplatinic acid equivalent to 1 g. of potassium in the precipitate, K_2PtCl_6, amounts to $4.90. While this material can be recovered, the cost of recovery is considerable.

The determination as potassium cobaltinitrite[1] in its present form is not satisfactory. The results are unreliable.

The potassium perchlorate method, more commonly called the Wense[2]-Caspari[3] method, has been applied to the analysis of fertilizers and similar material containing alkalies, alkaline earths, iron, aluminium, magnesium, and phosphates. The chief difficulty in this method has been the obtaining of the perchloric acid. The danger of preparing the pure acid, as was attempted, is very great. For this reason the method has not been available to many chemists. Recently a 20% solution at $3.00 a Kilo, a 30% solution at $4.80 a Kilo, and even stronger solutions of perchloric acid have been placed on the market.

The quantity of perchloric acid necessary to combine with 1 g. of potassium costs 3.8 cents. The cost of an equivalent amount of chloroplatinic acid is $4.90. The cost of perchloric acid in the perchlorate method is not only lower than the cost of platinum in the chloroplatinate method, but is much lower than the cost of recovering the platinum. The precipitate $KClO_4$, is of constant composition, its solubility in 96% alcohol containing 0.2% $HClO_4$ is almost zero, and the loss by ignition is eliminated. The fertilizer chemists[4] of Germany have tested the method and have obtained such accurate results that they have placed it on an equal basis with the chloroplatinate method by adopting it as an official method.[5]

In this method the sulfates are precipitated in a slightly acid solution. This solution of chlorides is then treated with an excess of perchloric acid, (1.5 times that required to combine with all bases present), and evaporated with constant stirring until white fumes appear. A small amount of water is then added and again evaporated with stirring. This is continued

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[1] H. B. McDonnel, Bur. Chem., *Bull.* 162, 19 (1912).

[2] W. Wense, *Z. angew. Chem.*, 4, 691 (1891); 5, 233 (1892).

[3] R. Caspari, *Ibid.*, 6, 68 (1893).

[4] *Landw. Ver. Sta.*, 59, 313 (1903); 67, 145 (1907).

[5] *Fifth Internat. Congr. of Appl. Chem.*, 1, 216 (1903); 4, 940 (1903).

until all volatile acids are absent. The perchloric acid lost by volatilization is replaced from time to time. The precipitate ($KClO_4$) obtained is washed with 95% alcohol immediately before drying.

The author has modified this method as follows: Precipitate the sulfates in a strong hydrochloric acid solution, avoiding a large excess of barium chloride. Evaporate the resulting solution with only a slight excess of perchloric acid without stirring. Dissolve the residue and again evaporate with perchloric acid. Wash the precipitate only with alcohol containing 0.2% perchloric acid before drying.

The revised method as applied to the determination of potassium in water is as follows: Evaporate an aliquot portion of the water to about 150 cc. Acidify with 10 cc. of concentrated hydrochloric acid and heat to boiling. To the boiling solution add drop by drop (avoiding a large excess), a 10% solution of barium chloride until all the sulfates are precipitated. Boil for fifteen minutes and then filter. If no precipitate forms, filtration may be omitted.

Evaporate the filtrate to dryness. Heat until all the ammonium salts are driven off. Dissolve in 20 cc. of hot water and add a quantity of a 20% solution of perchloric acid, slightly in excess of that required to combine with nearly all bases present. One cc. of perchloric acid is equivalent to 90 mg. of potassium (K). Evaporate to dryness. Add 10 cc. of hot water and a small amount of perchloric acid. Again evaporate to dryness. If white fumes do not appear, take up with 10 cc. of water, add more perchloric acid and evaporate to dryness. Repeat until white fumes do appear. Take up with 25 cc. of 96–97% alcohol, containing 0.2% perchloric acid (1 cc. of 20% $HClO_4$ per 100 cc. of 97–98% alcohol). Break up the residue with a stirring rod. Decant the supernatant liquid through a Gooch crucible containing a matt that has been washed with 0.2% perchloric acid in alcohol. If there is an unusually large precipitate, dissolve it in hot water and repeat the evaporation with perchloric acid. (Large quantities of barium chloride are difficult to change to the perchlorate.) Wash once by decantation with 0.2% perchloric acid in alcohol, and transfer the precipitate to the crucible. Wash several times with 0.2% perchloric acid in alcohol. Dry the crucible in an oven at 120–130° for an hour. Remove, cool and weigh. The increase in the weight of the crucible is $KClO_4$. (In using the Gooch crucibles, do not disturb the matt after analysis. Dissolve the potassium perchlorate with hot water, leaving the matt intact. Using the crucible repeatedly in this manner eliminates the errors due to the action of perchloric acid on fresh asbestos.)

If both sodium and potassium are to be determined, obtain the combined chlorides by the usual methods, and estimate the potassium as potassium perchlorate, as described, omitting the precipitation of the sulfates with barium chloride.

It is of advantage to evaporate to dryness with only a slight excess of perchloric acid, and to repeat the process a second and possibly third time, in order to insure the removal of nearly all volatile acids, and in order to make stirring while evaporating unnecessary.

The recommendation of 97% alcohol for washing is due to the solubility of potassium perchlorate in alcoholic solutions of perchloric acid containing 95% or less alcohol. The difference between the efficiency of 97% and 100% alcohol is immaterial.

It is undesirable to wash the crucible with ether or alcohol just before drying. A slight amount of potassium perchlorate would be dissolved. Dry as much as possible with air suction and then dry in an oven. The small amount of perchloric acid left in the asbestos will be volatilized without causing any error, especially if the same asbestos matt is used repeatedly.

A series of analyses was first made using only potassium chloride. (See Table I.) This potassium chloride, the purest of a well-known firm, was dried at 180° for several hours before using. A standard solution was then prepared and definite amounts measured out with a standardized pipet.

TABLE I.—ANALYSES OF SOLUTIONS CONTAINING ONLY POTASSIUM CHLORIDE.

No.	Potassium added, g.	$KClO_4$ obtained, g.	Potassium obtained, g.	Error, g.
1	0.0050	0.0174	0.0049	—0.0001
2	0.0100	0.0353	0.0100	....
3	0.0150	0.0530	0.0150	....
4	0.0200	0.0701	0.0198	—0.0002
5	0.0300	0.1049	0.0296	—0.0004
6	0.0350	0.1241	0.0350	....
7	0.0500	0.1769	0.0499	—0.0001

Since the amount of potassium found agreed with the amount taken, a second series was analyzed, using comparatively large amounts of sodium chloride in addition to the potassium. (See Table II.)

The variations are small and lie within the limits of experimental error. The largest is —0.9 mg. The average for the fifteen analyses is 0.2 mg. less than the theoretical amount. The balance used is not capable of weighing less than 0.1 of a mg. The error in percentage, is large with small quantities (amounting to as much as 2.0%). Increasing the quantity of potassium decreases the error in percentage.

An artificial mineralized water was then made by adding the following constituents to distilled water: $CaCO_3$, $MgCO_3$, $MgCl_2$, Na_2CO_3, NaCl and Na_2NO_3. The insoluble constituents were dissolved with a small amount of hydrochloric acid. Portions of this solution containing 0.1

TABLE II.—ANALYSES OF SOLUTIONS CONTAINING LARGE QUANTITIES OF SODIUM CHLORIDE.

No.	Potassium added, g.	Sodium chloride in solution, g.	$KClO_4$ obtained, g.	Potassium obtained, g.	Error.	
					G.	%.
1	0.0050	0.0500	0.0181	0.0051	+0.0001	+2.0
2	0.0100	0.1000	0.0350	0.0099	—0.0001	—1.0
3	0.0200	0.2000	0.0712	0.0201	+0.0001	+0.50
4	0.0300	0.3000	0.1073	0.0302	+0.0002	+0.66
5	0.0400	0.4000	0.1423	0.0401	+0.0001	+0.25
6	0.0500	0.5000	0.1783	0.0503	+0.0003	+0.60
7	0.0600	0.6000	0.2129	0.0600	0.0000	0.00
8	0.0700	0.7000	0.2471	0.0697	—0.0003	—0.40
9	0.0800	0.8000	0.2830	0.0799	—0.0001	—0.11
10	0.1000	1.0000	0.3534	0.0997	—0.0003	—0.30
11	0.2000	1.0000	0.7090	0.2001	+0.0001	+0.05
12	0.3000	1.0000	1.0626	0.2999	—0.0001	—0.03
13	0.4000	1.0000	1.4171	0.3999	—0.0001	—0.03
14	0.5000	1.0000	1.7686	0.4991	—0.0009	—0.18
15	1.0000	1.0000	3.5438	1.0000	0.0000	0.00

g. of each substance ($CaCO_3$ and $MgCO_3$ now being present as $CaCl_2$ and $MgCl_2$, respectively), were measured out. Known amounts of potassium were then added to each portion and determined without removing any of the ions. The results are shown in Table III. In this series most of the errors, although not large, are minus in character.

TABLE III.—ANALYSES OF WATERS OF HIGH MINERAL CONTENT

No.	Potassium added, g.	Mineral content g.	$KClO_4$ obtained, g.	Potassium obtained, g.	Error.	
					G.	%.
1	0.0500	0.6000	0.1757	0.0496	—0.0004	—0.80
2	0.1500	0.6000	0.5301	0.1497	—0.0003	—0.20
3	0.2500	0.6000	0.8887	0.2508	+0.0008	+0.32
4	0.3000	0.6000	1.0612	0.2995	—0.0005	—0.17
5	0.3500	0.6000	1.2378	0.3493	—0.0007	—0.20

To each of several portions of the same artificial water 0.1 g. of Na_3PO_4 was added, and the potassium determined as above, with results as shown in Table IV.

TABLE IV.—ANALYSES OF HIGHLY MINERALIZED WATER CONTAINING PHOSPHATE.

No.	Potassium added, g.	Mineral content, g.	$KClO_4$ obtained, g.	Potassium obtained, g.	Error.	
					G.	%.
1	0.0500	0.7000	0.1784	0.0503	+0.0003	+0.60
2	0.1000	0.7000	0.3540	0.0999	—0.0001	—0.10
3	0.1500	0.7000	0.5323	0.1502	+0.0002	+0.13
4	0.2500	0.7000	0.8867	0.2501	+0.0001	+0.04
5	0.3500	0.7000	1.2385	0.3494	—0.0006	—0.17

Though sodium phosphate is insoluble in alcohol, it does not produce an error in the determination of potassium (see Table IV). When sodium phosphate is evaporated with $HClO_4$ the following reaction takes place:

$$Na_3PO_4 + 3HClO_4 = 3NaClO_4 + H_3PO_4$$

Sodium perchlorate and phosphoric acid are soluble in alcohol and do not cause an error in the determination of potassium.

The sulfate and ammonium ions were found to produce an error, but the error caused by the sulfate was not equivalent to all the sulfate ion that was present. It is necessary to remove all of the ammonium salts and most of the sulfates.

Summary.

The method of determining potassium as the perchlorate is accurate.

Sulfate and ammonium ions produce an error and must be removed. The sulfate is precipitated with barium chloride in a strongly acid solution avoiding a large excess. The ammonium salts are expelled by heating.

The phosphate ion does not produce an error and need not be removed.

The solution containing chlorides should be evaporated to dryness with a slight excess of perchloric acid, without stirring.

The precipitate should be washed only with alcohol containing 0.2% perchloric acid.

The time of making an analysis is short, the manipulations are simple, and the cost is almost negligible.

The method can be recommended for use in water analyses and in other analytical work where the content of potassium is desired.

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A NEW METHOD FOR THE PRECISE STANDARDIZATION OF HYDROCHLORIC ACID SOLUTIONS.

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When the greatest precision is desired in standardizing a volumetric solution, those methods should be avoided, which: (1) involve transferring or washing a precipitate; (2) depend upon the peculiarities of any particular indicator; (3) require the use of standard substances containing water of crystallization, or those that may contain impurities difficult to detect, *i. e.*, almost all organic compounds, or that can not be positively dried without danger of decomposition; (4) demand any peculiarities of technique or any exercise of personal judgment that may make it difficult for different observers to obtain nearly identical results.

With these criteria in mind, I have devised and for several years used in practice a method, the accuracy of which is only limited by the unavoidable errors of weighing. It depends upon the loss of weight caused by the replacement of NO_3 in silver nitrate by Cl. Since hydrochloric acid solutions kept in glass vessels, always contain traces of chlorides and of other non-volatile impurities derived from the glass, the process must be so conducted as to avoid error from this source. The method is carried out as follows, when the solution to be standardized is 0.2 *N:*