compound ethyl alcohol, and the non-ionizing compound ethyl ether, shift the band of acetone by —102, —22 and +27 units, respectively. Another example of this is given by the ionizing compound acetic acid, which displaces the acetone band 47 units towards the ultra violet, whereas the replacement of the hydrogen atom to give ethyl acetate entirely neutralized this effect, no shift being observed when acetone is dissolved in the ester.

## Summary.

1. All of the aliphatic ketones except acetone and methylethyl ketone follow Beer's law, *i. e.*, the molecular extinction is independent of the concentration, and solvent.

With acetone and methylethyl ketone there are deviations when ionizing solvents are used, due to partial disruption of the associated molecules.

2. Kundt's Rule, which states that with increasing refractivity of solvent the band moves towards the red, holds good if regarded as a rough generalization.

3. When a pure substance is dissolved in an ionizing type of solvent the absorption center moves toward the ultra violet; if a pure substance is dissolved in a neutral non-ionizing type of solvent the absorption center is unaffected or moves towards the red end of the spectrum. It is probable that this is a general rule which holds good for all classes of absorbing substances.

The whole of the experimental part of this work was carried out in the Spectroscopic Department of Liverpool University, England. The author desires to express his sincere thanks to Prof. E. C. C. Baly for permitting him to make such full use of the facilities available there for this work.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

# THE DETERMINATION OF POTASSIUM AS PERCHLORATE. II.

BY GREGORY P. BAXTER AND MATSUSUKE KOBAYASHI.

Received February 2, 1920.

Not long ago[1] we reported the results of experiments upon the quantitative handling of potassium perchlorate with special reference to its solubility in various washing media. After presenting additional evidence of the fact, already known, that the salt is soluble to a marked degree in even very concentrated alcohol containing perchloric acid, we supported the proposal of Davis[2] of using as a washing liquid alcohol containing

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[1] THIS JOURNAL, 39, 249 (1917).

[2] *J. Agr. Sci.*, 5, 52 (1912).

perchloric acid and previously saturated with potassium perchlorate. A further suggestion of working at 0° was made, since the uncertainty is almost halved owing to the lesser solubility at this temperature. The experiments showed beyond question that the procedure is adequate to prevent loss of potassium through solution in the washing liquid. When sodium perchlorate was present, however, the potassium perchlorate recovered was always in excess of the quantity originally taken, almost in proportion to the sodium perchlorate present. Part of this excess was unquestionably due to mechanical inclusion of the sodium salt in the particles of potassium perchlorate during evaporation of the aqueous solution of the original salts to dryness, since re-solution of the precipitate and evaporation, after extraction and removal of the sodium perchlorate, reduced this excess to a small fraction of the value it otherwise would have had. At the time we imputed the residual excess to inclusion, and it still seems probable that inclusion is responsible for a large part of the excess.

It was later pointed out, however, by Gooch and Blake[1] that a saturated alcoholic solution of potassium perchlorate may be caused to deposit a large part of the salt by dissolving in it sodium perchlorate. Apparently this takes place much more readily when the solution is in contact with solid potassium perchlorate. We had considered this point and, finding that the addition of sodium perchlorate to the saturated alcoholic solution produced no visible precipitate, concluded that no difficulty was to be feared from this source. Since the appearance of the paper by Gooch and Blake we have tested the matter further, with results which are in accordance with theirs.

In our earlier experiments, however, the difficulty could not have exceeded a few tenths of a milligram, for the total quantity of dissolved potassium perchlorate in the washing liquid is less than 2 mg. per 100 cc. Since the volume of washing liquid used in the initial extraction of the sodium perchlorate was always 20 cc., it is hard to believe that the error from this source could exceed 0.4 mg. in any case. This is exactly the error found in experiments with moderate quantities of sodium salts, if the original precipitate was dissolved and re-formed to avoid inclusion, although the maximum error, in the presence of nearly enough sodium perchlorate to saturate the extraction liquid, was 4 times as large. It is likely that a part of this larger error was due to inclusion even during the second evaporation.

It is, therefore, necessary to modify the treatment of the precipitate insofar as the initial extraction of the sodium salt is concerned, although the subsequent rinsing of the potassium perchlorate is best carried out with a saturated alcoholic solution of the salt as previously advocated.

[1] *Am. J. Sci.*, 44, 381 (1917).

Since the uncertainties involved are of small magnitude, the materials with which the following experiments were performed were very carefully purified. *Potassium perchlorate* was twice recrystallized from water. Fairly pure *perchloric acid* was distilled under reduced pressure in an all-glass apparatus, and was preserved in a quartz flask. *Sodium perchlorate* was prepared from sodium chloride. The latter substance was several times precipitated from aqueous solution with hydrogen chloride, the first and last solutions being freed from insoluble matter by filtration through a platinum-sponge crucible. In order to change the chloride to perchlorate, a solution of the salt was evaporated to dryness with an excess of perchloric acid, and the residue was several times dissolved and the solution evaporated to dryness with small amounts of perchloric acid. After the salt had been dissolved and the solution filtered through platinum sponge, the solution was again evaporated to dryness and the residue dissolved in alcohol containing 0.1% of perchloric acid. Filtration followed and the processes of evaporation, solution in alcohol and filtration were repeated. The final alcoholic solution was evaporated to dryness, and the residue was dissolved in water to make a 10% solution from which suitable quantities could be measured out for the separate experiments. *Alcohol* was dehydrated over lime and redistilled.

The first experiments were directed to determine how completely potassium perchlorate is salted out by sodium perchlorate. Sodium perchlorate solution was evaporated to dryness in a platinum dish and the salt was dissolved at 0° in alcohol containing 0.1% of perchloric acid and saturated with potassium perchlorate. Such an alcoholic solution will, in the following pages be designated *washing liquid*, and is indicated in the tables of results with the letter W. After standing 20 minutes the solution was filtered through a weighed platinum-sponge crucible, and the dish and crucible were thoroughly rinsed with washing liquid. Then the crucible was dried upon an electric stove at about 200°. The gain in weight of the crucible, which represents the potassium perchlorate salted out, gradually increases from an almost negligible quantity (0.1 to 0.3 mg.) with moderate concentrations of sodium perchlorate, (0.25 g. in 20 cc. washing liquid), to very nearly all of the dissolved potassium perchlorate when the washing liquid is nearly saturated with sodium perchlorate (one g. in 20 cc.). The data obtained in these experiments are given in Table I, Expts. 1 to 7.

Apparently the salting out of potassium perchlorate from the washing liquid is not to be feared if the quantity of sodium perchlorate is no more than a few tenths of a gram, while it cannot exceed 0.4 mg. for each 20 cc. of washing liquid used in the initial extraction, since this is the total quantity of dissolved salt. After the first extract has been decanted, so little sodium perchlorate remains that the second addition of washing liquid will not result in further salting out.

In order to show that the sodium perchlorate itself was not responsible for any appreciable part of the gain of the crucible, similar experiments were performed using alcohol containing perchloric acid but no potassium perchlorate. Such a solution is indicated in the tables by the letter A. The gain in weight of the crucible did not exceed 0.1 mg. in any case. (Expts. 8 to 13.)

In order to determine whether sodium perchlorate can be completely washed out of a precipitate of the potassium salt, in Expts. 14 to 18 the dry sodium perchlorate was dissolved at 0° in absolute alcohol containing 0.1% of perchloric acid, and was poured upon a weighed quantity of finely powdered potassium perchlorate in a platinum dish. After being stirred the solution was allowed to stand a few minutes and then was filtered through a platinum-sponge crucible. The residue was washed by decantation many times with small portions of chilled washing liquid, and was dried and weighed. It is unlikely that the gain in weight, which occurred in every case, is due to potassium perchlorate salted out of the washing liquid, for the greater portion of the sodium perchlorate had been eliminated before even the first portion of washing liquid was added. Furthermore, the gain in weight seems to be roughly proportional not only to the quantity of sodium perchlorate, but also to that of the potassium salt. It seems more probable, therefore, that this gain is due to adsorption of the sodium perchlorate by the precipitate. In practice such a difficulty need not be feared, however, since solution of the original precipitate and re-evaporation may be depended upon to eliminate such impurity.

This effect is apparently somewhat irregular. At any rate, in Expt. 19, which was identical with Expt. 15 except that the initial extraction was made with washing liquid instead of alcohol, the excess in weight of recovered material was no greater than in the latter experiment.

The foregoing experiments confirm Gooch and Blake's observation that if washing liquid is used in the initial extraction of the potassium perchlorate, when a considerable amount of sodium perchlorate is present appreciable amounts of potassium perchlorate may be salted out of the washing liquid. On the other hand, the error introduced in this way under no circumstances is likely to exceed one mg., since even at room temperature alcohol containing perchloric acid will dissolve no more than this weight of potassium perchlorate in a 20 cc. portion, while at 0° the possible error is limited to half this quantity. It should be noted that the higher figures given by Gooch and Blake refer to 50 cc. of alcohol at room temperature and containing no perchloric acid.

TABLE I.

| Expt. | First extract. Cc. | Washings. Cc. | NaClO$_4$ taken. G. | KClO$_4$ taken. G. | KClO$_4$ found. G. | Error. G. |
|---|---|---|---|---|---|---|
| 1 | W 20 | W 50 | 0.25 | ...... | 0.0001 | ...... |
| 2 | W 20 | W 50 | 0.25 | ...... | 0.0003 | ...... |
| 3 | W 20 | W 50 | 0.5 | ...... | 0.0002 | ...... |
| 4 | W 20 | W 50 | 0.5 | ...... | 0.0004 | ...... |
| 5 | W 40 | W 50 | 1.0 | ...... | 0.0006 | ...... |
| 6 | W 40 | W 50 | 2.0 | ...... | 0.0006 | ...... |
| 7 | W 40 | W 50 | 2.0 | ...... | 0.0007 | ...... |
| 8 | A 20 | W 50 | 0.5 | ...... | 0.0001 | ...... |
| 9 | A 20 | W 50 | 0.5 | ...... | 0.0001 | ...... |
| 10 | A 20 | W 50 | 1.0 | ...... | 0.0001 | ...... |
| 11 | A 20 | W 50 | 1.0 | ...... | 0.0001 | ...... |
| 12 | A 40 | W 50 | 2.0 | ...... | 0.0001 | ...... |
| 13 | A 40 | W 50 | 2.0 | ...... | 0.0001 | ...... |
| 14 | A 20 | W 95 | 0.25 | 1.0011 | 1.0015 | +0.0004 |
| 15 | A 20 | W 100 | 1.0 | 0.3021 | 0.3024 | +0.0003 |
| 16 | A 20 | W 100 | 1.0 | 0.1033 | 0.1034 | +0.0001 |
| 17 | A 20 | W 110 | 1.0 | 1.0019 | 1.0030 | +0.0011 |
| 18 | A 20 | W 105 | 1.9 | 1.0009 | 1.0016 | +0.0007 |
| 19 | W 20 | W 80 | 1.0 | 0.3010 | 0.3013 | +0.0003 |

Next several experiments were performed to determine, under the conditions of our experiments, the magnitude of the loss of potassium perchlorate through solubility, if the alcohol is not previously saturated with this salt. A weighed quantity of potassium perchlorate was dissolved in water together with approximate quantities of sodium perchlorate, and the solution was evaporated to dryness with an excess of perchloric acid. The residue was extracted at 0° with alcohol containing 0.1% of perchloric acid, and was washed by decantation twice with small portions of a similar solution. In order to avoid inclusion of sodium salt, the precipitate was dissolved in water and the solution was again evaporated to dryness with a small quantity of perchloric acid. Extraction and washing with an alcoholic solution of perchloric acid followed, and the precipitate was collected and dried. In these experiments, Table II, Nos. 20 to 25, a negative error occurred in every case. Two similar experiments at room temperature, Nos. 26 and 27, showed somewhat larger losses. It is obvious that the apparent error from solubility will be less with larger amounts of sodium perchlorate, partly owing to the lessened solubility of the precipitate, partly owing to compensation by inclusion of the sodium salt by the precipitate, even when solution and re-formation of the precipitate during the washing occurs. With more dil. alcohol, also, the error will become larger.

TABLE II.

| Expt. | First extract. Cc. | Washings. Cc. | $NaClO_4$ taken. G. | $KClO_4$ taken. G. | $KClO_4$ found. G. | Error. G. |
|---|---|---|---|---|---|---|
| 20 | A 20 | A 105 | 0.1 | 0.3007 | 0.2995 | —0.0012 |
| 21 | A 20 | A 100 | 0.5 | 0.3007 | 0.3005 | —0.0002 |
| 22 | A 20 | A 105 | 0.5 | 0.3011 | 0.3007 | —0.0004 |
| 23 | A 20 | A 110 | 1.0 | 0.3004 | 0.3001 | —0.0003 |
| 24 | A 20 | A 110 | 1.0 | 0.3007 | 0.2992 | —0.0015 |
| 25 | A 20 | A 90 | 1.0 | 0.3007 | 0.3007 | —0.0000 |
| 26 | A 20 | A 100 | 0.1 | 0.3005 | 0.2991 | —0.0015 |
| 27 | A 20 | A 95 | 1.0 | 0.3018 | 0.3014 | —0.0004 |

There can be no question, therefore, of the necessity for precautions to avoid loss of potassium perchlorate through solubility beyond that of using an alcoholic solution of perchloric acid as washing liquid. Finally we made a series of experiments under varied conditions in an effort to discover the procedure best adapted to yield accurate results. In all these experiments an exactly weighed quantity of potassium perchlorate, together with an approximately weighed portion of sodium perchlorate, was dissolved in water and the solution was evaporated to dryness with a small quantity of perchloric acid. In Expt. 28, Table III, the residue was extracted at 0° with an alcoholic solution of perchloric acid, and then was washed by decantation and transferred to the platinum-sponge crucible with chilled washing liquid. The excess in weight of recovered potassium perchlorate is undoubtedly due chiefly to mechanical inclusion, since the precipitate was not redissolved in the course of the washing.

In Expts. 29, 30 and 31, the dry residue was first extracted at 0° with washing liquid, and after 3 rinsings with washing liquid it was dissolved in water and the solution was evaporated to dryness with a little perchloric acid. A second extraction and rinsing with washing liquid followed. These experiments were comparable with those in the last table of our previous paper. As is to be expected, a consistent error persists, although somewhat less in magnitude than that indicated in the earlier results. We attribute the difference, in part at any rate, to the better quality of the sodium perchlorate used in these experiments.

In Expts. 32 to 36 the initial extraction of the dry salt was done with alcohol containing 0.1% of perchloric acid. Otherwise the experiments were identical with the preceding 3. The excess in weight of recovered perchlorate may be ascribed to either adsorption or inclusion of the sodium salt by the precipitate, rather than to salting out of material from the mother liquor.

Three additional rinsings of the first precipitate before solution and re-evaporation produced no perceptible effect on the results in Expts. 37 and 38.

In Expts. 39 and 40 the precipitate was dissolved and the solution evaporated after the third rinsing, and again after the fifth, washing liquid being used always, except in the initial extraction. This procedure, though troublesome, diminished the positive error to a point which for most purposes is very satisfactory.

In Expts. 41 and 42 the initial extraction with alcoholic perchloric acid was followed by 2 rinsings with the same liquid, but the precipitate was only once re-dissolved. The results compare favorably with those of the preceding 2 experiments, owing possibly in part to compensation between solution of the precipitate in the first 2 rinsings and inclusion.

TABLE III.

| Expt. | First ext. act. Cc. | Washings. Cc. | $NaClO_4$ taken. G. | $KClO_4$ taken. G. | $KClO_4$ found. G. | Error. G. |
|---|---|---|---|---|---|---|
| 28........ | A 20 | W 95 | 0.1 | 0.3030 | 0.3038 | +0.0008 |
| 29........ | W 20 | W 110 | 0.3 | 0.3012 | 0.3017 | +0.0005 |
| 30........ | W 20 | W 110 | 0.5 | 0.3003 | 0.3009 | +0.0006 |
| 31........ | W 20 | W 107 | 1.0 | 0.3035 | 0.3044 | +0.0009 |
| 32........ | A 20 | W 118 | 0.1 | 0.3003 | 0.3005 | +0.0002 |
| 33........ | A 20 | W 100 | 0.1 | 0.3021 | 0.3023 | +0.0002 |
| 34........ | A 20 | W 105 | 0.3 | 0.3021 | 0.3025 | +0.0004 |
| 35........ | A 20 | W 95 | 0.5 | 0.3003 | 0.3007 | +0.0004 |
| 36........ | A 20 | W 95 | 1.0 | 0.3013 | 0.3019 | +0.0006 |
| 37........ | A 20 | W 100 | 0.5 | 0.3006 | 0.3009 | +0.0003 |
| 38........ | A 20 | W 108 | 1.0 | 0.3009 | 0.3016 | +0.0007 |
| 39........ | A 20 | W 102 | 0.5 | 0.3010 | 0.3012 | +0.0002 |
| 40........ | A 20 | W 100 | 1.0 | 0.3007 | 0.3010 | +0.0003 |
| 41........ | A 20 + 10 + 10 | W 85 | 0.1 | 0.3013 | 0.3012 | —0.0001 |
| 42........ | A 20 + 10 + 10 | W 77 | 1.0 | 0.3019 | 0.3023 | +0.0004 |

In view of the foregoing evidence we, therefore, reiterate our earlier recommendations, with the modification that the initial extraction of the sodium perchlorate be carried out with alcohol containing perchloric acid but no potassium perchlorate, instead of with a saturated solution of the latter substance. In case the quantity of sodium is small, the use of a saturated solution of potassium perchlorate for the initial extraction is safe; in case the quantity of sodium is large, the potassium salt is best washed once or twice with alcohol containing perchloric acid before the use of saturated solution of the precipitate is commenced.

Aside from the above the chief recommendations are as follows:

1. The use of absolute alcohol.
2. The use of a low temperature in washing (0°).
3. The use of a platinum-sponge crucible.
4. At least one solution of the precipitate in water and re-evaporation in the course of the washing.

5. The use of alcohol containing perchloric acid and saturated with potassium perchlorate at the temperature of use for washing the precipitate after the sodium salt has been extracted with alcohol containing perchloric acid.

The saturated solution of potassium perchlorate is best prepared by dissolving the necessary amount of salt in hot conc. aqueous solution of perchloric acid and adding the solution to anhydrous alcohol.

By this procedure the error can undoubtedly be kept within a very few tenths of a milligram, and seems to us preferable to, although more troublesome than that of Gooch and Blake, who have advocated the procedure of keeping the volume of washing liquid, consisting of an alcoholic solution of perchloric acid, very small. The errors in their experiments varied from negative values of from 0.5 to 0.9 mg. in the absence of sodium salts, to positive values up to 2.6 mg. in the presence of sodium salts.

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[CONTRIBUTION FORM THE LABORATORIES OF SOIL FERTILITY, BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE.]

# COLORIMETRIC DETERMINATION OF TITRATION CURVES WITHOUT BUFFER MIXTURES.

BY LOUIS J. GILLESPIE.

Received February 4, 1920.

The writer is led to present this material by the experience of the late Dr. E. H. Walters (First Lieutenant, Sanitary Corps) and Dr. L. E. Wise, formerly in this laboratory, who found the titrimetric determination of molecular weight to be very useful in the identification of small quantities of unknown acids in cases where phenolphthalein could not be used and where no neutralization equivalents were given in the literature. The usefulness of the titration curves has been explained by Hildebrand,[1] who gave a comparatively simple electrometric procedure. The writer has aided both Dr. Wise and Mr. R. N. Harger in determining titration curves colorimetrically, using the assortment of indicators recommended by W. M. Clark and Lubs[2], and the 0.05 *M* buffer mixtures studied by them.[3] For titration curves a large number of buffer mixtures were required, and we in fact resorted only to the colorimetric method because the neutralization equivalent was required for an organic acid containing arsenic, which badly poisoned the hydrogen electrode. Since that time the writer has developed a system for the colorimetric determination of

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[1] THIS JOURNAL, **35**, 847 (1913).

[2] H. A. Lubs and W. Mansfield Clark, *J. Wash. Acad. Sci.*, **6**, 481 (1916); W. M. Clark and H. A. Lubs, *J. Bact.*, **2**, 1, 109, 191 (1917).

[3] W. M. Clark and H. A. Lubs, *J. Biol. Chem.*, **25**, 479 (1916); also described in *J. Bact., loc. cit.*