racemate. Assuming the rotation of the racemate to be very nearly one-half the sum of the rotations of *l*-amyl *d*-tartrate and *l*-amyl *l*-tartrate,[1] the rotations of the racemate and the mesotartrate should be *very nearly* the same if the principle of superposition were correct. In reality Walden found:[2]

l-amyl racemate............... $[M]_D = 9.77°$
l-amyl mesotartrate.......... $13.83°$

The difference is great.

Less decisive is the case of the *l*-amyl esters of the racemic and meso-modifications of dimethylsuccinic acid.[3] Here the molecular rotations found by Walden are, respectively, 10.47° and 9.79°. The difference, however, which happens to be small, might be due either to the influence of configuration or to extramolecular influences in the racemate mixture. The point can only be decided by examining the esters of the *d*- and *l*-acids separately.

I am instituting a series of experiments, designed to further test the principle provisionally formulated in this paper, and hope to communicate the results before very long.

It is a pleasure, in concluding, to acknowledge my indebtedness to Professor Morris Loeb, of this University, for a number of important suggestions concerning both the subject-matter of the present paper and its presentation.

DETERMINATION OF THE SODIUM PHOSPHATES.

BY C. CHESTER AHLUM.

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BECAUSE of the close similarity of the reactions of disodium hydrogen phosphate and trisodium phosphate, the quantitative determination of these salts when in mixture requires special and modified methods.

It is known that both of these phosphates may be titrated with standard acid and if isolated may be determined with accuracy by this means. Both disodium hydrogen phosphate and tri-

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[1] This assumption, again, is justified by the very observations that were intended to prove the principle of superposition. It is further justified by the observations of Hammerschmidt (see Landolt: loc. cit. p. 213).

[2] Loc. cit.

[3] Landolt: loc. cit. p. 258.

sodium phosphate are alkaline to methyl orange while sodium dihydrogen phosphate is neutral; therefore, the point of neutralization or end reaction occurs when either or both of the alkaline phosphates are converted into the acid phosphate.

$$HCl + Na_2HPO_4 = NaH_2PO_4 + NaCl$$
$$2HCl + Na_3PO_4 = NaH_2PO_4 + 2NaCl.$$

From the above reactions it is observed that trisodium phosphate requires two molecules of acid while the disodium hydrogen phosphate requires but one. Therefore, 1 cc. of N/10 hydrochloric acid will be equivalent to 0.0082 gram of Na_3PO_4 or 0.0142 gram of Na_2HPO_4.

If carbon dioxide is passed into a solution of trisodium phosphate the latter will be converted into disodium hydrogen phosphate with the formation of a definite quantity of sodium carbonate,

$$CO_2 + 2Na_3PO_4 + H_2O = 2Na_2HPO_4 + Na_2CO_3.$$

As the sodium carbonate formed is directly proportional to the trisodium phosphate, a determination of the latter salt, when in mixture with disodium hydrogen phosphate, can be very easily accomplished, *i. e.*, by passing carbon dioxide into a solution of the mixed salts and determining the sodium carbonate formed.

Two grams of the mixed salt are dissolved in water and carbon dioxide passed through the solution until the reaction is complete (about ten or fifteen minutes). The solution is then evaporated to dryness and the sodium carbonate estimated by the Schrötter apparatus. The amount of carbon dioxide eliminated multiplied by 7.4545 gives the amount of trisodium phosphate present in the mixture.

One gram of the mixed salts is dissolved in water and titrated with N/10 hydrochloric acid. The number of cubic centimeters required by the trisodium phosphate is obtained by dividing the amount (in grams) of trisodium phosphate found in the above determination by 0.0164 (2×0.0082). The number of cubic centimeters required by the disodium hydrogen phosphate is the difference between the number obtained in the titration and the number required by the trisodium phosphate. The number of cubic centimeters required by the disodium hydrogen phosphate multiplied by 0.0142 gives the amount of disodium hydrogen phosphate in the mixture.

If the original mixture contains sodium carbonate, a determination of this ingredient will be necessary in order to estimate the amount of sodium carbonate formed from the trisodium phosphate and also to make a correction in the titration.

Alternative Method.—If a solution containing disodium hydrogen phosphate and trisodium phosphate is acidified and then neutralized with sodium carbonate, adding an excess of the latter, we have as a result a solution containing disodium hydrogen phosphate and sodium carbonate.

If a titration were to be made of the mixed salts before treatment and a titration made after, making allowance for the amount of sodium carbonate found in excess, we find the amount of acid required by the phosphates after treatment is less than that required before, the difference being directly proportional to the amount of trisodium phosphate present.

This is made clear by referring to the reactions above, noting that disodium hydrogen phosphate requires but one molecule of acid while the trisodium phosphate requires two.

This method in detail is as follows: 0.5 gram is dissolved in 50 cc. of water and titrated with N/10 hydrochloric acid. 1.0 gram is dissolved in 50 cc. of water containing a drop of methyl orange. Hydrochloric acid is added in slight excess and the solution boiled for ten minutes. Sodium carbonate is added in excess and the solution concentrated by boiling as far as possible. It is then transferred to a weighed platinum dish, evaporated to dryness on a steam-bath, dried in an oven and weighed.

The mass in the dish is broken up and pulverized with a porcelain pestle, guarding against loss. One-half of the amount of solid matter found is weighed off and the carbon dioxide determined by the Schrötter apparatus. The remaining half of the solids is dissolved in 50 cc. of water and titrated with N/10 hydrochloric acid.

The following example will be explanatory: 0.5 gram was titrated with N/10 hydrochloric acid, requiring 23.1 cc. One gram was treated in the manner described above, titrating a solution of one-half of the solids and estimating the carbon dioxide in the other half. The amount of carbon dioxide found was 0.0149 gram. The amount of sodium carbonate equivalent to the carbon dioxide eliminated $= 0.0149 \times 2.4115 = 0.0359$ gram.

The number of cubic centimeters of N/10 hydrochloric acid equivalent to the sodium carbonate present = 0.0359 ÷ 0.0053 = 6.7. The number of cubic centimeters of N/10 hydrochloric acid required after treatment was found to be 20.1.

	cc.
Total N/10 acid required	20.1
N/10 acid required by Na_2CO_3	6.7
N/10 acid required by Na_2HPO_4	13.4

	cc.
N/10 HCl required by the $Na_3PO_4 + Na_2HPO_4$	23.1
N/10 HCl required by the Na_2HPO_4 (the original Na_2HPO_4 with that formed from the trisodium phosphate)	13.4
Difference	9.7

The difference in the amount of acid required is due to the loss in alkalinity of the trisodium phosphate, caused by the conversion of this salt into disodium hydrogen phosphate, thereby requiring just one-half of the acid as when in the tribasic state.

In the above example the amount of N/10 hydrochloric acid necessary to completely act upon the trisodium phosphate would be $9.7 \times 2 = 19.4$ cc. As each cubic centimeter is equivalent to 0.0082 gram of trisodium phosphate, the amount of this salt in the mixture will be $19.4 \times 0.0082 \times 200 = 31.9$ per cent.

The number of cubic centimeters required by the disodium hydrogen phosphate is obtained by subtracting the number of cubic centimeters required by the trisodium phosphate from the number of cubic centimeters obtained in the original titration.

In the above example this would be 23.1 cc.—19.4 cc. = 3.7 cc. As each cubic centimeter of N/10 hydrochloric acid is equivalent to 0.0142 gram of disodium hydrogen phosphate, the amount of this salt present in the mixture would be $3.7 \times 0.0142 \times 200 = 10.5$ per cent.

The accuracy of the determinations depends upon the determination of the sodium carbonate. As all sources of error may be traced to this determination, this should be performed with care and results checked.

A number of mixtures made up of disodium hydrogen phosphate and trisodium phosphate of known purity, were analyzed according to this method, with results tabulated below. Both salts employed were chemically pure crystals containing twelve molecules of water.

Per cent. known to be present.		Per cent. found.	
Na_3PO_4.	Na_2HPO_4.	Na_3PO_4.	Na_2HPO_4.
8.63	31.72	8.11	32.81
12.94	27.76	11.23	28.46
17.26	23.79	17.98	23.10
23.74	17.84	24.21	16.89
30.11	11.89	31.93	11.09
32.37	9.92	32.71	10.16
34.52	7.93	33.32	9.11
36.68	5.94	36.84	6.17

If alkaline carbonates are present in the original salts they must be determined by the Schrötter apparatus and the necessary correction applied to the titration.

LABORATORIES OF GEO. W. LORD COMPANY, PHILADELPHIA.

A DESCRIPTION OF IMPROVED APPARATUS AND OF A MODIFICATION OF DREHSCHMIDT'S METHOD FOR THE DETERMINATION OF TOTAL SULPHUR IN COAL GAS.[1]

BY EVERHART PERCY HARDING.

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OF ALL methods[2] discussed and used during the last half century for the determination of total sulphur in coal gas the one proposed and used by Drehschmidt appears[3] to be the most convenient and to give the most reliable results.

The method of Drehschmidt consists in the oxidation of the sulphur to sulphur dioxide in a supply of air freed from hydrogen sulphide, of the conversion of the sulphur dioxide into potassium sulphite by its absorption in a 5 per cent. solution of potassium carbonate, of the oxidation of the sulphite to potassium sulphate with bromine and of the subsequent precipitation of the sulphur with a solution of barium chloride, and the calculation of the amount of sulphur from the weight of the ignited barium sulphate.

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[1] The writer is indebted to Mr. O. L. Bernhagen for the drawing of the apparatus used in this paper.

[2] Chem. News, 1861, p. 38; 1863, p. 73; 1868, p. 89; Z. anal. Chem. 15, 175; 21, 335 ; 22, 171. Hempel : "Gas Analyse," Dritte Auflage,s. 304.

[3] Chem. Ztg. 11, 1382 (1887.)