

# POLARISTROBOMETRIC-CHEMICAL ANALYSIS.

By H. LANDOLT.

(Concluded.)

Translated by J. F. Geisler.

(*Ztschr. anal. Chem.*, **28**, 203-234.)

## II.

### *Solutions of one active substance in two inactive solvents.*

As is well known, the specific rotatory power of optically active substances is unequally affected by different solvents. If the individual action of two solvents is expressed by  $[a] = A + Bq$  and  $[a]_1 = A + B_1 q_1$ , in which the constants  $A$ , representing the specific rotatory power of the pure active substance, must agree, then if  $q$  and  $q_1$  express the parts by weight in 100 parts by weight of the solution, the equation may be expressed by

$$[a]_m = A + Bq + B_1 q_1 \quad (10).$$

It would be taken for granted that each of the solvents in the mixture would have the same effect as if used alone. This is generally not to be expected, since, as is also indicated by changes in the density of mixed solvents, a physical change takes place in the molecules, thus causing a different effect upon the active substance. If this effect is but slight, the value of  $[a]_m$  will be between  $[a]$  and  $[a]_1$  and can then be determined more or less closely by the above formula. It may happen, however, that the mixture causes an altogether different effect, and may possibly increase the rotatory power above that of either of the solvents, in which case a maximum must result from a given mixture of the solvents.

As an example of the first instance, the behavior of narcotin, as observed by Hesse\* in using about equal concentrations ( $c = 0.74$  to  $2$ ), is cited:

|   |                  |
|---|------------------|
| Solution in alcohol of 97 vol. %  | $[a]_D = -185.0$ |
| “ “ chloroform  | $[a]_D = -207.4$ |
| Solution in mixture of 1 vol.<br>of alcohol and 2 vols.<br>chloroform ..... | $[a]_D = -191.5$ |

---

\* *Ann. Chem. (Liebig)*, **176**, p. 192.

An increase in the rotatory power by the use of mixed solvents is shown in the following instances:

According to Hesse,\* cinchonidine gives for a concentration of  $c = 2$ .

When dissolved in alcohol of 97% vol.  $[a]_D = -106.9$

“ “ “ chloroform  $[a]_D = -83.9$

When dissolved in alcohol-chloroform

(1:2) .....  $[a]_D = -108.9$

For dry cinchonidine nitrate and hydrochloride Oudemant† obtained:

|                                  | Nitrate. | Hydrochloride. |
|----------------------------------|----------|----------------|
| Solvent.....c =                  | 1.855    | c = 1.722      |
| Water ..... $[a]_D = -$          | 99.9     | — 99.9         |
| Absolute alcohol.... $[a]_D = -$ | 103.2    | — 104.6        |
| 80% (wt.) alcohol +              |          |                |
| 20% water..... $[a]_D = -$       | 127.0    | — 128.7        |
| 89% (wt.) alcohol +              |          |                |
| 11% water ..... $[a]_D = -$      | 119.0    | — 119.6        |

Quinidine hydrochloride shows, according to Oudemant, for a concentration of 1.89 of the dried salt

Dissolved in water.....  $[a]_D = +190.8$

“ “ absolute alcohol.....  $[a]_D = 199.4$

“ “ alcohol 90.5% (by wt.).....  $[a]_D = 213.0$

In solutions of quinine hydrochloride ( $2H_2O$ ) Hesse‡ found that in mixtures of alcohol and water (vol. %) the maximum rotation occurs with a concentration

of  $c = 2$ , when the vol. % of water  $q = 60$

|             |       |       |       |       |       |       |       |       |             |
|-------------|-------|-------|-------|-------|-------|-------|-------|-------|-------------|
| q=0 (water) | 20    | 40    | 50    | 60    | 70    | 80    | 85    | 90    | 97          |
| $[a]_D = -$ | 138.8 | 166.6 | 182.8 | 187.5 | 187.8 | 182.3 | 174.8 | 168.3 | 160.8 143.9 |

For the sp. rot. power of cinchonine in mixtures of chloroform and alcohol Oudemant§ gives the following:

\* Ann. Chem. (Liebig), **176**, p. 219.

† Ann. Chem. (Liebig), **182**, p. 49, 50.

‡ Ann. Chem. (Liebig), **176**, p. 210.

§ Schiebler, Neue Ztschr. f. Rüb. Ind., III., p. 130.

|                  | 1      | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11     |
|------------------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| Chloroform,      | 100.00 | 99.66 | 98.74 | 94.48 | 86.95 | 82.26 | 65.00 | 44.29 | 27.54 | 17.02 | 0.00   |
| Alcohol,         | 0.00   | 0.34  | 1.26  | 5.52  | 13.05 | 17.74 | 35.00 | 55.71 | 72.46 | 82.98 | 100.00 |
| $[\alpha]_D = +$ | 212.0  | 216.3 | 226.4 | 236.6 | 237.0 | 234.7 | 229.5 | 226.6 | 227.6 | 227.8 | 228.0  |

Here the maximum rotation is observed when the mixture contains 10% of alcohol. This shows, moreover, that in an alcoholic solution of cinchonine, fully one-half of the alcohol could be replaced by chloroform without causing any great difference in the angular rotation, whereas in a chloroform solution of the alkaloid the mere replacement of  $\frac{1}{30}$  of the chloroform by alcohol would cause an increase of about 4°.

Hence the determination of the angular rotation by such a mixed solvent is only practicable when the proportions of the mixed solvents remain constant, so that it will act as a homogeneous solution. Hesse used, mostiy, a solution composed of 1 vol. alcohol of 97% by vol. and 2 vols. of chloroform as a solvent for alkaloids. Cane sugar seems to be about the only substance whose rotatory power is not affected by mixed solvents. According to Seyferth,\* the angular rotation for cane sugar in varying mixtures of alcohol and water is practically constant, whereas Tollens† found that alcohol slightly increased the angular rotation, also methyl alcohol and acetone to a somewhat greater extent. Thus for 10% solutions of cane sugar in mixtures composed of 3 parts by vol. of the above solvents and 1 part by vol. of water, Tollens found the rotatory power to be:

|                                |                        |
|--------------------------------|------------------------|
| In water solution.....         | $[a]_D = 66.66\bar{7}$ |
| Water and alcohol.....         | $[a]_D = 66.82\bar{7}$ |
| Acetone and water.....         | $[a]_D = 67.396$       |
| Methyl, alcohol and water..... | $[a]_D = 68.628$       |

The above conditions may arise when solutions of an active substance consist of but one solvent, but contain also one or more inactive substances. In such cases the effect of the latter must be determined by experiment.

### III.

#### *Solutions of two active substances in one inactive solvent.*

Under these conditions the solvent may affect the specific

---

\* Ann. Chem. (Liebig), **169**, p. 71.

† Ber. d. chem. Ges., 1880, p. 2297.

rotatory power of each of the active substances and these latter, moreover, affect each other. A quantitative determination of the two substances is then possible only when the variation is so small that the angular rotations may be considered as constant for the concentration limits.

The method of analysis will depend upon whether the combined weight of the two substances is known or not.

A. The compound is a solid consisting of two optically active substances.

Weigh out  $g$  grms. of the compound, dissolve and dilute to 100 c.c., determine the angular rotation  $a$  in a 1 dm. tube, and calculate from this the specific rotatory power

$$[a] = \frac{100a}{l \cdot g}$$

If the mixture contain  $X\%$  of a substance of which the spec. rot. pow. is  $[a]_x$  and  $y = 100 - x$  per cent. of the other substance with the sp. rot. pow.  $[a]_y$ , then

$$[a]_x \cdot X + [a]_y (100 - X) = 100 [a], \text{ whence}$$

$$X = 100 \frac{[a] - [a]_y}{[a]_x - [a]_y},$$

$$y = 100 - X = 100 \frac{[a] + - [a]}{[a] + - [a]}_y \quad (11)$$

As an example, several mixtures of cane sugar and raffinose are given for which Clerget\* found the degrees by Ventzke's scale and by multiplying by 0.3465 calculated the angular degrees.

|      | In 100 c. c. 20 g<br>of a<br>mixture. |                  | Observed deviation<br>for 1 dm. tube<br>l = 2 dm. |                            | Spec. rot. of<br>the<br>mixture.<br>[a] |
|------|---------------------------------------|------------------|---|----------------------------|---|
|      | Cane<br>Sugar.                        | Raffinose.       | Ventzke.  | Ang. degrees<br>$\alpha_D$ |   |
| I.   | 16 g                                  | 4 g <sup>‡</sup> | +85.45  | +29.608                    | +74.02                                  |
| II.  | 17 g                                  | 3 "              | 83.45   | 28.915                     | 72.29                                   |
| III. | 18 g                                  | 2 "              | 81.13   | 28.112                     | 70.28                                   |
| IV.  | 19 g                                  | 1 "              | 79.00   | 27.374                     | 68.43                                   |

\* Z. V. f. R. Z. I., 1887, 153.

Taking the following rotations as constants

$$\text{Cane sugar, } [\alpha]_D = + 66.5 = [\alpha]_x$$

$$\text{Raffinose, } [\alpha]_D = + 104.5 = [\alpha]_y$$

Then the % of cane by the formula would be

|            | I.    | II.   | III.  | IV.     |
|------------|-------|-------|-------|---------|
|            | 80.21 | 84.76 | 90.05 | 94.92 % |
| instead of | 80.   | 85.   | 90.   | 95. %   |

If the calculation were to be made with Ventzke's degrees then the given rot. power for cane sugar and raffinose would have to be divided by 0.3465.

If the sp. rotation of the respective substances may not be considered constant, but the variation is known through the equation  $[\alpha] = A + Bc$ , calculate from the values which are nearest those for the concentration used, and then substitute them in equation (11). In this manner Hesse\*\* effected the analysis of various mixtures of alkaloids and their salts, of which the following is cited :

A mixture of quinine sulphate ( $C_{20} H_{24} N_2 O_2 \cdot H_2 SO_4 + 7 H_2 O$ ) and cinchonine sulphate ( $C_{20} H_{24} N_2 O_2 \cdot H_2 SO_4 + 4 H_2 O$ ), for a solution of 4 grms. of the same per 100 c. c., showed a specific rotation of  $[\alpha]_D = - 71.87$ .

For the individual salts the sp. rotation was found to be affected by the concentration of the aqueous solution as follows :

$$\text{Quinine sulphate } [\alpha]_D = - 164.85 + 0.31.c.$$

$$\text{Cinchonine " } [\alpha]_D = + 212.0 - 0.8.c.$$

If it be taken for granted that the two constituents are present in equal proportions for each  $c = 2$ , then according to equation (11) the % of quinine sulphate in the mixture is

$$\frac{- 71.81 - 210.4}{-164.23 - 210.4} = 75.3\% \text{ as against } 75.\%$$

the amount really present.

The uncertainties which might arise through the value of  $c$  are avoided by working with low concentrations.

B. The combined weight of the two active substances is not known, and either the number of grammes of the same in 100 c. c. of solution, or their % in a solid substance is to be ascertained.

---

\*\* Ann. Chem. (Liebig), 182, 148.

Under these conditions the analysis can often be accomplished by determining first the angular rotation of the original solution, and again after one, or both, of the active substances has been converted by chemical agents into a new active body. The method was first applied by Clerget in the analysis of mixtures of cane sugar and invert sugar, and is known as the Inversion method.

The two cases are the following :

(a.) By the chemical reaction only one of the two substances is converted into a new active compound, while the other remains unchanged.

Representing by  $c_1$  and  $c_{11}$  the unknown concentrations of the two substances, and  $[a]_1$  and  $[a]_{11}$  their rotatory power,

$[a]_{111}$  the sp. rotation of the product of the inversion,

$k$  the quantity of the chemical equivalent which one part by weight of the changeable substance will yield,

$a$ , the observed angular rotation of the original solution,

$a_1$ , the angular rotation after the inversion,

$l$ , the length of the tubes in decimeters,

Then the following two equations express the conditions before and after inversion, when the factors  $[a]_{111}$  and  $k$  are based on the spec. rotation  $[a]_1$ ,

$$[a]_1 c_1 + [a]_{11} c_{11} = \frac{100. a}{l (c_1 + c_{11})} (c_1 + c_{11}),$$

$$[a]_{111} kc_1 + [a]_{11} c_{11} = \frac{100. a_1}{l (kc_1 + c_{11})} (kc_1 + c_{11}),$$

whence

$$c_1 = \frac{100 (a - a_1)}{l ([a]_1 - [a]_{111} k)}, \quad (12)$$

$$c_{11} = \frac{100 ([a]_1 a_1 - [a]_{111} ka)}{l [a]_{11} ([a]_1 - [a]_{111} k)}.$$

The calculation can also be made in the following manner : From the specific rotation of each of the substances find by the formula

$$a = \frac{[a] lc}{100}$$

the angular rotation of a solution of the concentration in a tube of a given length (2 dm.)

Representing by

$\varphi_1$  and  $\varphi_{11}$  the angular rotations as found for the two substances,

$\rho$  the angular rotation of the inverted substance,

then, having calculated all the angular rotations for tubes of the same length, we have

$$\begin{aligned} \text{Before the inversion, } & \varphi_1 c_1 + \varphi_{11} c_{11} = a, \\ \text{After " " " " } & \rho k c_1 + \varphi_{11} c_{11} = a_1, \end{aligned}$$

which lead to the formulas

$$\begin{aligned} c_1 &= \frac{a - a_1}{\varphi_1 - \rho k}, \\ c_{11} &= \frac{\varphi_1 a_1 - \rho k a}{\varphi_{11} (\varphi_1 - \rho k)} \text{ or } = \frac{a - \varphi_1 c_1}{\varphi_{11}}. \end{aligned} \quad (13)$$

If the specific rotations of the respective substances and hence, also the angular rotations  $\varphi_1$   $\varphi_{11}$   $\rho$  are not constant, the concentrations  $c_1$  and  $c_{11}$  must first be ascertained by means of medium values, and then the necessary figures from  $[a] = \mathbf{A} + \mathbf{B}c$  inserted in the above equations.

When the specific rotation of the inverted product is unknown, where possibly the product is a mixture of several substances, the angular rotation of a definite quantity of the original substance *after inversion, must first be ascertained by preliminary trials.* This angle, calculated for the concentration of 1 grm. in 100 c.c., represents the product  $\rho k$  and must be inserted in place of the same in the formula (13). If the angle is variable then it must be ascertained for various concentrations of the original active substance. Concerning the practical application of the method, it must be borne in mind that in the chemical treatment the added reagents change the concentration of the substances, so that after the reaction the solution must be diluted to a definite volume, to which volume the solution before the inversion should also be diluted and then polarized, so as to have the conditions as to concentration as near alike as possible.

As an example of the above the well-known Clerget's method for the determination of cane sugar in presence of invert sugar is given. The angular rotation  $a$  is first found for the original solution, 50 c. c., then inverted, after the addition of 5 c. c. conc. hydrochloric acid, by heating for 15 min. at 67-70°, whereby all cane sugar is changed to invert sugar, and after cooling the angular rotation observed for  $a_1$  making allowance\* for the dilution.

The temperature of the solutions should be kept as near 20° as possible for the polarizations. Taking for granted that for the trials a polaristobometer with Na — light and tubes of 2 dm. length were used, the following factors may be inserted in formulas (12) and (13):

$[a]_1 = +66.5$  as spec. rot.  $[a]_D$  of cane sugar, whence  $\varphi_1 = +1.33$  as the angular rotation, which 1 grm. of sugar in 100 c. c. would exert in a 2 dm. tube.

$[a]_{11} = -20.0$  as medium spec. rot.  $[a]_D$  of invert sugar in dilute solutions at 20°. Whence  $\varphi_{11} = -0.4$  for the angular rot. of 1 g in 2 dm. tube.  $k = 1.0526$ , *i. e.* the number of grammes of invert sugar which 1 grm. of cane sugar will yield according to the equation  $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$ .

$[a]_{111}$  under these conditions  $= [a]_{11}$ , and  $\rho = \varphi_{11}$ .

Finally the difference  $a - a_1$  becomes the sum  $S$  of the two observed angular rotations, when as is generally the case, the solution was dextro-rotatory before and lævo-rotatory after the inversion. With these constants there result for the calculation of the number of grammes of cane sugar  $c_1 = r$  and invert sugar  $c_{11} = i$  in 100 c. c. of the original solution the formulas:

$$r = \frac{a - a_1}{1.75} = 0.5714 S = \frac{4S}{7},$$

$$i = -0.6015 a - 1.9. a_1 = \frac{a - 1.33 r}{-0.4}.$$

The % of invert sugar obtained by the above formula is usually

---

\* (In saccharimetry this allowance is, in a measure, met by using 1.1 or 2.2 dm. tubes for the polarization of the inverted solution.) J. F. G.



a trifle too high (from  $+0.07$  to  $+55\%$  as shown by tables in the orig. article). Better results are obtained by the formula

$$i = -0.6005 a - 1.8729a_1.$$

For cane sugar close results are obtained by the formula

$$r = \frac{4S}{t}$$

If a quartz-wedge saccharimeter with a Soleil or Ventzke's scale be employed for the inversion method, the following should be observed: According to the original investigations of Clerget an invert sugar solution prepared from 16.35 g cane sugar in 100 c. c. should cause a lavo-rotation of  $44$  degrees at  $0^\circ$  on the scale of a Soleil instrument, and to diminish  $\frac{1}{2}$  degree for each 1 degree rise in temperature. From this Clerget obtained the formula

$$R = \frac{100 S}{144 - \frac{1}{2} t}.$$

which gives the % of cane sugar in the original substance when 16.35 (according to later statements 16.192g) of the latter are used for the Soleil or 26.048g for the Ventske saccharimeter. At the temperature  $20^\circ$  the normal solutions would have to polarize  $-34^\circ$  after inversion. Later researches, however, of Creydt\* and Dr. Rathgen give us an average  $-32.4$ , whence the corrected Clerget's formula becomes

$$R = \frac{100 S}{142.4 - \frac{1}{2} t}.$$

In the technical examination of cane sugars and molasses the inversion method is subject to uncertainties, since the nature of the invert sugar may not be known,† which as already mentioned may show considerable variation in its rotatory power. In such a case the direct polarization may be subject to some error, but the polar. after inversion be correct, since after the acid treatment the invert sugar shows its normal rotation.

When besides cane and invert sugar a solution contains other optically active substances of a nature not affected in their optical properties by the inversion with hydrochloric acid then Clerget's method is applicable. Casamajor. ‡).

\* Z. V. R. Z, I. 1887, p. 149.

† See Degener (Z. V. R. Z. I. 1886, 347) and Herzfeld loc. cit., 1887, 911.

‡ Chem. News, 45, 150.

If  $D$  = original polarization of the mixture

$D_1$  = Rotation after inversion

+  $R$  the rotation caused by the cane sugar

—  $J$  the rotation caused by the invert sugar in the orig. solution

+  $G$  the rotation caused by the foreign dextro-rotatory constituents

—  $H$  the rotation caused by the foreign lævo-rot. constituents.

—  $i$  the rotation caused by invert sugar produced from the cane by inversion, we have the expressions

Before inversion:  $D = +R - J + G - H,$

After “  $D_1 = -i - J + G - H.$

and the difference is therefore:

$$D - D_1 = R + i$$

*i. e.* according to the representations in equation (13) :  $a - a_1 = (\varphi_1 c_1) - (\rho k c_1)$ , where in the above case the third member of the equation is negative, on account of lævo-rotation, and therefore enters as positive in the equation.

b By the chemical reaction both substances are changed into new active combination. Representing by

$\varphi_1$  the angular rotation, which 1 g of the substance A dissolved in 100 c. c. exerts in a 1 dm. tube,

$\rho$  the angular rotation which 1 g of the substance A exerts after the inversion.

$\varphi_{11}$  and  $\rho_{11}$  the same angles for the other substance B

$c_1$  and  $c_{11}$  the respective unknown concentrations of the substances A and B, assuming that tubes of the same length were used, the angular rotations of the mixture before inversion  $a$ , and for that after inversion  $a_1$ , are represented by the conditional equations:

$$\begin{aligned} \varphi_1 c_1 + \varphi_{11} c_{11} &= a \\ \rho_1 c_1 + \rho_{11} c_{11} &= a_1, \quad \text{whence} \\ c_1 &= \frac{\rho_{11} a - \varphi_{11} a_1}{\rho_{11} \varphi_1 - \rho_1 \varphi_{11}} \\ c_{11} &= \frac{\rho_1 a - \varphi_1 a_1}{\rho_1 \varphi_{11} - \rho_{11} \varphi_1} \end{aligned} \quad (14)$$

A case of this kind has been treated by Clerget,\* namely the analysis of a mixture of cane sugar and raffinose. When treated with hydrochloric acid the cane sugar is changed to invert sugar, and the raffinose according to investigations of Hädicke and Tollens into a dextro-rotatory mixture of galactose and laevulose. For the calculations the following figures are used as a basis conditional upon  $l=2$  dm.,  $t=20^\circ$  and the light D:

$\varphi_1 = +1.33^\circ$  angular rot. for 1 g cane sugar, obtained from  $[a]_D = 66.5^\circ$ .

$\rho_1 = -0.425^\circ$  angle resulting from 1 grm. cane sugar after the inversion; calculated for the sp. rotation of invert sugar for a concentration of  $c=15$ , where  $[a]_D = -20.2$ , and 1.0526 g invert sugar = 1 g cane sugar.

$\varphi_{11} = +2.09^\circ$  angular rotation for 1 g raffinose from  $[a]_D = +104.5$ .

$\rho_{11} = +1.06^\circ$  angular rot., for 1 grm. raffinose after inversion, calculated from  $\rho_{11}$ , according to Creydt, that the polarizations of raffinose before and after inversion are in the ratio of 100 : 50.7.

By use of these factors in equation (14) there results for the number of grammes for the two active substances in 100 c. c. the formulas:

$$\text{Cane sugar } c_1 = \frac{1.06a - 2.09a_1}{2.298},$$

$$\text{Raffinose } c_{11} = \frac{0.425a + 1.33a_1}{2.298}.$$

In the investigations of Creydt the inversions were made by heating 50 c. c. of the solution with 5 c. c. of hydrochloric acid of sp. gr. 1.188 for 15 minutes, and after diluting to 100 c. c., observing the deviation in a Ventzke sacchar. at  $20^\circ$ . For converting the degrees into angular degrees the author used for the cane sugar in the original solution the factor 0.3465 and for the inverted solution a medium factor 0.345.

When the Ventzke saccharimeter is used Creydt gives the following formulas for the calculations in which A represents the polarization of the original solution and C the sum of the polar-

---

\* L. V. R. Z. I., 1887, 164.

izations before and after the inversion as shown by the saccharimeter :

$$\text{Cane sugar } Z = \frac{C - 0.493 A}{0.827},$$

$$\text{Raffinose } R = \frac{A - Z}{1.57},$$

which give % in 100 parts of the substance in case 26.048 grms. of the latter were dissolved to 100 c. c. dilution.

#### IV.

*Use of the Polaristrobometer for the Analysis of Inactive Substances.*

Certain active substances, such as tartaric, malic and asparagic acids, most of the alkaloids, santonin, camphor, etc., show the peculiarity of having their optical activity considerably altered when some inactive substance is added to the solution.

1. For determining the quantity in solution. Preliminary tests are made with solutions of various concentrations of the inactive substance containing always the same quantity of the active substance diluted to the same volume, from the data of which a formula is readily found. As an example the determination of boracic acid in aqueous solution is given. This is accomplished through the aid of tartaric acid whose rotatory power is materially affected by increasing quantities of boracic acid. 20 grms. of tartaric acid were dissolved and diluted to 100 c. c. in solutions of different concentrations of boracic acid and the angular rotation determined with a Laurent half shadow instrument in a 4 dm. tube at 20°. It was found that when  $C$  represented the number of grammes of boracic acid in one litre of solution, and  $a$  the angular rotation of the solution after the addition of the tartaric acid, the relation of the two is expressed by the simple formula

$$C = 1.4a - 14.4.$$

The results as shown from determinations are quite satisfactory, which suggests the use of the method for the rapid determination of boracic acid. It would only be necessary to introduce 20 g. tartaric acid into a 100 c. c. flask, dissolve in the boracic acid solu-

tion, fill up to the mark, and polarize in a 4 dm. tube. By the aid of tartaric acid, or the soluble tartrates, the acids of arsenic and antimony, and also, according to observations of Gernez,\* molybdic and tungstic acids, or their salts, may be determined by means of the angular rotation. Formamide, acetamide and urea, according to Gernez, exert a similar influence as the tartrates. Malic acid is said to be much more sensitive than tartaric acid to the influence of these substances. By the aid of invert sugar the quantity of acetate of lead and possibly other metals could be determined in solutions.

2. Mixtures of two inactive substances may be analyzed by first determining the effect of a number of mixtures of known composition upon the rotatory power of the active substance, using always the same quantity of the latter. The results will be the more favorable the greater the influence of the separate constituents. In this manner possibly the analysis of mixtures of sodium and potassium chloride may be effected.

3. In like manner in certain cases the analysis of a mixture of two inactive solutions may be possible, provided the variations in specific rotation of the added active substance is regular. Thus, according to Oudemans, cinchonine may be used to quantitatively determine small amounts of alcohol in chloroform. Further investigations are needed to determine the usefulness of these methods in special cases.

---

\* Compt. rend. **104**, 783.