PERCENTAGE OF NITROGEN IN URINE.

No.	Found by aeration method.	Found by new method.	(A mixed specimen of normal urine.)
I	0.960	0.952	...
II	0.976	0.948	...

VI. Summary.

A new reagent for ammonia has been found which:

(1) Is more stable than Nessler's reagent in the presence of salts.

(2) Is fully as sensitive as Nessler's reagent.

(3) Will precipitate ammonia quantitatively.

(4) Will give accurate results nephelometrically.

(5) May be useful in water analysis.

(6) May be directly applied to normal- and micro-Kjeldahl determinations, thus doing away with the tedium and errors of distillation.

I desire to express my gratitude to Mr. P. A. Kober, for the opportunity of working out this problem.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON.]

THE USE OF THE INTERFEROMETER FOR THE ANALYSIS OF SOLUTIONS.

BY LEASON H. ADAMS.

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Chemists have long used the refractometer as an aid in analytical work, but have not made use of the interferometer to the extent that its precision and general convenience would warrant. The use of the ordinary forms of refractometer is limited by the circumstance that the change of refractive index with temperature is usually such as to require regulation of temperature to 0.01° in order to secure an accuracy of one unit in the sixth place in the measurement of refractive index. By means of the interferometer, on the other hand, it is a simple matter, requiring no special regulation of temperature, to secure an accuracy of one unit in the seventh place; this is possible because in the latter case we are comparing the refringence of one liquid (or gas) with that of another of very nearly the same composition and hence possessing almost the same temperature coefficient of refringence. In other words, with the refractometer one can determine the composition of a solution to 2 parts in 10,000 of solvent, but with the interferometer—provided that certain simple precautions be observed—to 2 parts in a million. The interferometer is adapted to the determination in any transparent mixture of a single varying component; this component may be solute or solvent, electrolyte or nonelectrolyte, indeed any substance which will not attack the

instrument. It is the purpose of the present paper to describe briefly a commercial interferometer which is convenient for chemical purposes, to discuss its mode of operation and to point out means of rendering it more generally useful. In the first place it is desirable, in the interest of a better understanding of the use of the interferometer, to recall some fundamental facts concerning the interference of light waves.

Principle of the Interferometer.—All interferometers, when reduced to their simplest terms, may be represented by Fig. 1. Light from a source, S, passes through two small openings, R_1 and R_2, and the two beams overlap as they fall on the screen at the right. At a point, O, equidistant from R_1 and R_2 the light waves arrive in the same phase, and a light spot or band results; but at all other points on the screen the paths of the two beams are of different lengths. Thus at X_1 or X_2, this path difference is exactly one-half wave-length, the two beams "interfere" and a dark band results; at Y_1 or Y_2 the retardation is a whole wave-length, the two sets of waves arrive at the screen again in the same phase, and a bright band is observed. In this way there is formed on the screen a series of alternate bright and dark bands, or so-called interference fringes.

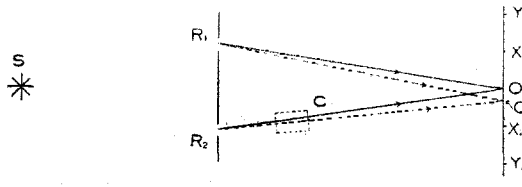

Fig. 1.—Elementary Interferometer. Two beams of light from a source, S, pass through the rectangular openings R_1 R_2 and falling on the screen at right produce a system of interference fringes which by the introduction of material at C are shifted by a certain amount depending on the thickness and refractive index of the material.

With monochromatic light as the source (*e. g.*, the light from a sodium flame) the bands are alternately black and the color of the light source (*e. g.*, yellow); with white light, on the other hand, only the central band is pure white, the next bright band beyond the adjacent dark spaces being edged with blue toward the center of the system and with red on the outside, while the bands still further away from the center appear successively more and more diffusely colored, finally fading into a uniform white.

Now if any material is placed in the path of one beam, as at C, the light waves of this beam will be retarded by an amount depending on both the thickness and refractive index of the material. The optical path is therefore lengthened, the expression for the path difference p being

$$p = l(n - n_o) \qquad (I)$$

where l is the thickness and n the refractive index of the material and n_o that of the surrounding medium. Since the optical path R_2O has now been lengthened, the two trains of light waves arrive in the same

phase no longer at O but at another point O'; the central bright band originally at O is therefore displaced to the point (O') which is optically equidistant from R_1 and R_2. Furthermore, it can readily be shown that for light of wave-length λ the number of fringes between O and O'—that is, the displacement of O measured in fringes (each made up of one bright and one dark band)—follows the simple relation,

$$N = p/\lambda,$$

whence by (I)

$$N = l(n - n_0)/\lambda \qquad \text{(II)}$$

Therefore, by counting the number of fringes, we may determine the product $l(n - n_0)$ and hence either the thickness or the difference in refractive index if the other is known.

Again, it is evident that by inserting a plate in the path of each beam, we can in this way determine the difference in refractive index of the two plates, if the thickness of each is known. Likewise, if we have a pair of similar vessels of appropriate construction, place one in the path of each beam, and observe the displacement of O (in terms of fringes) consequent upon the filling of each vessel with a transparent substance (or mixture), we can by this means determine the difference in refractive index of the two substances. Such an arrangement constitutes a differential refractometer, which is capable of giving with a very high degree of accuracy the difference of refractive index of any two mixtures (or pure substances, liquid or gaseous); and this difference can be utilized as a convenient and accurate measure of the concentration of a single varying component in a solution (or gaseous mixture). A convenient instrument designed for this purpose is the Zeiss Water Interferometer,[1] the essential features of which we proceed to outline.

Description of the Zeiss Interferometer and of Its Mode of Operation.—The simplified interferometer shown in Fig. 1 would be inconvenient in practice; a more useful arrangement is that of Fig. 2, which illustrates the set-up first used by Rayleigh, and later embodied with slight modifications in the apparatus made by Zeiss. White light from a slit is made parallel by a collimating lens, L (Fig. 2*a*). passes through the two rectangular openings R_1 R_2 as two beams which unite at O, forming a system of interference fringes which are viewed with a suitable eye-piece (not shown in this figure). Two similar chambers, C_1 C_2, of appropriate construction are placed, one in each light path; the displacement of the fringes caused by a difference in refractive index of their contents is com-

[1] Made by Carl Zeiss, Jena. Full details of the construction of this instrument may be found in papers by Löwe (*Z. Instrumentenkunde*, **1910**, 321), by Haber and Löwe (*Z. angew. Chem.*, **23**, 1393 (1910)) and in the descriptive literature published by the Zeiss firm.

pensated—*i. e.*, the central bright fringe is brought back to the zero position—by tilting the inclined glass plate P_1, P_2 being fixed.

This tilting changes the effective thickness of the compensating plate P_1; when the central bright fringe is restored to the zero position, the change in effective thickness of the compensator just neutralizes the difference in the optical path through C_1 and C_2. This arrangement is

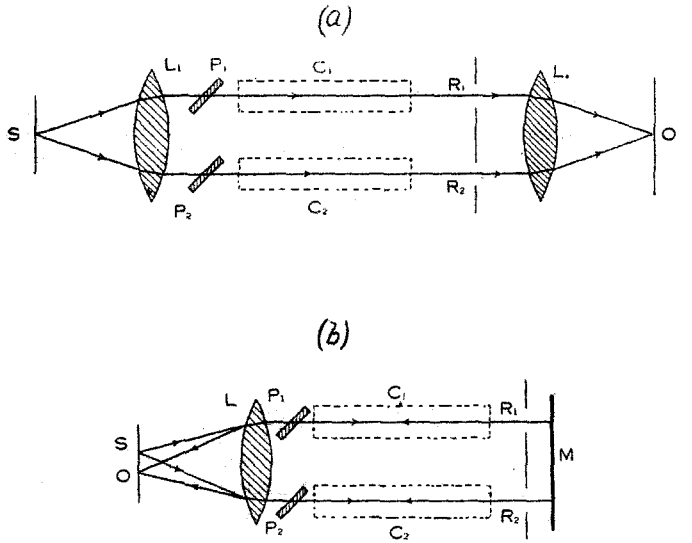

Fig. 2.—Diagram of arrangements of interferometer; the two interfering beams are separated and reunited in (*a*) by two lenses, in (*b*) by a single lens.

essentially that used in the Zeiss Laboratory Interferometer (for gases); for the sake of compactness and portability it is modified slightly in the Water Interferometer and Portable Gas Interferometer. In this modification, illustrated in Fig. 2*b*, the same lens serves the double purpose of separating and reuniting the two interfering beams.

The actual arrangement of the Water Interferometer is shown in some detail in Fig. 3, which is a diagram in plan and elevation of the instrument in use here.

White light is furnished by the small 4 volt tungsten lamp F. By means of the lens A, a mirror and the totally reflecting prism K, the image of the filament F is focused on the narrow slit S (see Fig. 3, lower half); this slit acts as a (very narrow) secondary source, the light from which is rendered parallel (just as in Fig. 2*b*) by the lens L. The light then passes throught the two compartments C_1 C_2 of the water chamber and the rectangular apertures R_1 R_2, thence to a mirror, M, where the two beams of light are reflected back upon themselves, pass through the water chamber again and finally, by means of the lens L, are reunited at O,

forming a series of interference fringes. These fringes are viewed by the cylindrical ocular E, which gives a magnification of 50 diameters, but in the horizontal direction only; the reasons for the use of a cylindrical ocular will be referred to later.

Besides the two interfering beams of light already considered, another pair proceed from the slit S in a precisely similar way, except that they pass *below* and not through the chamber C, likewise forming at O a second system of interference fringes. This latter fringe system is (practically) fixed in position; its sole purpose is to furnish a set of fiduciary lines

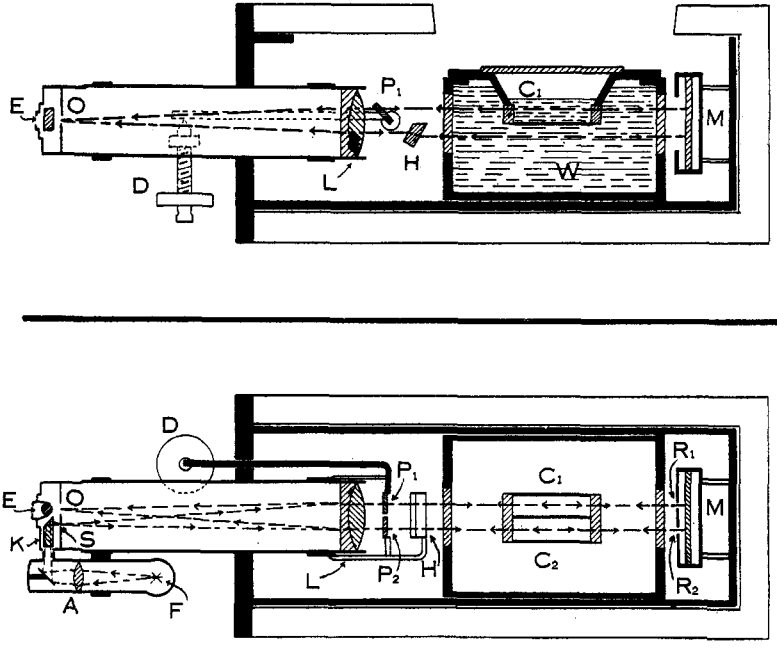

Fig. 3.—Drawing in plan (below) and elevation (above) of the Zeiss Water-Interferometer.

which take the place of the cross-hairs ordinarily used as reference marks in optical instruments. Accordingly, if the eye is placed at E, one sees two sets of alternate bright and dark bands, the two sets being separated by a narrow horizontal dark line.[1] In each set of fringes only one of the bright bands is pure white, and the bands adjacent to it are bordered with blue towards the center and with red on the outside; it is this central

[1] The width of this line is made very small by means of the auxiliary plate H. Furthermore, the cylindrical eye-piece by magnifying only in horizontal direction does not increase the apparent thickness of the horizontal line. This feature of the cylindrical ocular is quite apart from its further advantage of giving, for a 50 diameter magnification, 50 times more light than an ordinary magnifier of the same power.

achromatic band (or the black bands immediately adjacent to it) which constitute the reference point of each system.

The upper set of bands can be displaced relatively to the lower set by tilting the movable inclined plate P_1 (P_2 is fixed); this is effected by turning the micrometer screw with attached drum D, by means of which, therefore, the two achromatic bands can be brought to coincidence, and the corresponding reading on the drum observed. Now, by placing one liquid (*e. g.*, pure water) in compartment C_2 and a second (*e. g.*, a dilute salt solution) in C_1, the upper set of bands is displaced to the left; but they can be restored to their original position by turning the drum D in the proper direction. When an exact match is again obtained—*i. e.*, when the achromatic fringe is brought to a position directly above that of the corresponding fringe of the fixed lower system—the drum reading is again observed; a series of such settings can be made which will differ by no more than 1 division on the drum (which corresponds to about one-twentieth of a band or to 2 parts solute per million of water). The reading is a measure of the difference in refractive index of solution and water, and hence a measure of the concentration of the solution in C_1. The interpretation of the readings in terms of actual concentration will now be treated.

Analysis of Solutions.—Since with the interferometer we determine a single variable, namely a difference in refractive index—or rather, an arbitrary reading related to it—it is evident that its utility for the analysis of solutions is limited to (1) the determination of the concentrations of a single substance in (*a*) a given liquid or (*b*) a mixture of liquids, or of liquids and solids, of constant composition; (2) the determination of the concentration of a solution containing several solids in fixed proportion (*e. g.*, sea water); and (3) the analysis of a mixture of two soluble solids (by making up a solution of known total solid content).

Let us now consider the application of the instrument to the analysis of a simple solution—of a single salt dissolved in water; the procedure of course is substantially identical in all cases. The interferometer may be used for the analyses of solutions in two ways: (1) as a direct reading instrument, (2) as a zero instrument. In either method the zero reading of the instrument is first obtained by bringing the fringes to coincidence when water (or the same solution) is placed in each compartment of the chamber; these "zero" readings, which, however, vary only very slightly from one day to another, are in all cases subtracted from the final readings.

In the first method, which is the one generally used heretofore, a series of solutions of the salt, of known concentration, are made up, and compared on the interferometer with samples of the water used in making up the comparison solutions. The readings[1] r are plotted against the

[1] Or preferably the values of the closely related quantity r' (cf. *postea*).

values of the concentration (c); the most convenient way of doing this is to plot r against c/r and to connect the series of points by a smooth curve. The concentration of any solution of this salt can then be determined by observing the reading when it is compared with water (preferably the water from which this solution was made up) and interpolating by means of the curve.

The sensitiveness and range depend on the length of the water chamber, which is supplied in 4 sizes, 5, 10, 20 and 40 mm. in length; in all cases settings can be made to one division on the drum and there are altogether the equivalent of 3,000 divisions. With the 40 mm. chamber one division corresponds to 1.5–3.0 parts substance per million of water for most aqueous solutions; the greatest differences of concentration which can be directly compared are therefore from 0.45–0.9%. An increase of range can be obtained either by using a shorter chamber (with corresponding loss in sensitiveness) or by using throughout as the comparison substance a standard solution of the salt in place of water.

The relative sensitiveness of the usual form of Water Interferometer for various substances in aqueous solution may be seen by referring to Table I. The column headed $\Delta c/\Delta r$ gives the amount of each salt (in parts per million parts of water) corresponding to one scale division when the 40 mm. chamber is used.

TABLE I.

Sensitiveness in parts per million per scale division ($\Delta c/\Delta r$) of the Zeiss Interferometer (with 40 mm. chamber) for various substances in aqueous solution.

Substance.	$\Delta c/\Delta r$.	Substance.	$\Delta c/\Delta r$.	Substance.	$\Delta c/\Delta r$.
$NaCl$	1.9	$K_2C_2O_4$	2.5	$ZnSO_4$	1.9
$NaBr$	2.5	NH_4Cl	1.7	H_3BO_3	4.4
NaI	2.4	NH_4Br	2.3	CH_3OH	17.8
$NaNO_3$	3.0	NH_4NO_3	2.5	C_2H_5OH	5.7
Na_2SO_4	2.2	$(NH_4)_2SO_4$	2.0	Glycerine	3.4
KCl	2.5	$MgCl_2$	1.3	Mannite	2.4
KBr	2.8	$MgSO_4$	1.7	Cane sugar	2.3
KI	2.6	$CaCl_2$	1.4	Levulose	2.8
KNO_3	3.6	$SrCl_2$	1.9	Dextrine	3.0
K_2SO_4	2.7	$BaCl_2$	2.3		

In the second method the solution of unknown concentration is compared directly with two known solutions, one preferably of slightly higher, the other of slightly lower concentration, which should differ from one another by not more than 200 scale-divisions; from these two readings its concentration is then easily interpolated. This method requires the use of but a small portion of the scale of the interferometer, and presupposes an approximate knowledge of the concentration of the solution. Of the two methods the latter, while in general somewhat more laborious, is applicable to solutions of any concentration and is not subject to the

source of error noted below. The former method (1), on the other hand, while inherently more convenient and more rapid, is subject to a disadvantage connected with a phenomenon already noted by Marc[1] (in the case of colloidal solutions only)—the alteration and apparent shift of the white central band. This phenomenon, which is of general occurrence with compensation interferometers used with white light,[2] is an insidious source of error, which must be guarded against; its cause and the means of predicting in advance the exact amount of this shift will now be taken up.

Alteration in Character of the Comparison Band; its Apparent Shift.—In the central or zero position the interference pattern, as seen in the field of the eye-piece, consists of three bright bands, a central white band separated on either side by a narrow black band from the parti-colored adjacent band, each of which is blue on the side towards the center of the field. Now if, by movement of the compensator, the left-hand bright band is brought to the center, it is seen to be not pure white but edged with blue on the right and red on the left, while the neighboring band to the left will be strongly colored on both edges; thus in this case there is no uncertainty as to which is the proper band on which to make the setting. Moreover, if the water in compartment C_1 be replaced by a very dilute solution, the original central achromatic band can (by turning the drum) be brought back into the field of view and distinguished without ambiguity. But in general the situation is somewhat different.

We may best understand what happens by supposing that in some way the concentration of a solution in C_1 is increased slowly and continuously from zero onwards, and that at the same time the original achromatic band is kept central by appropriate movement of the compensator. We would then, in most cases, observe that the original achromatic band gradually becomes colored at the edges, while the adjacent bands to right and left become, respectively, more and less strongly colored; with further increase of concentration the central band becomes identical in appearance with the band on the left, and, at length, the latter is achromatic while the central band is now parti-colored just as the right-hand band was originally. The comparison band has thus *apparently* shifted one band to the left; with further increase of concentration the same sequence of events occurs, and the apparently correct comparison band is shifted one additional band to the left for a certain concentration difference, this difference for KCl being (on our instrument) about 0.07% (280 divisions).[3] Now, since in making readings on a series of solutions of a sub-

[1] R. Marc, *Chem. Ztg.*, **36**, 539 (1912).

[2] The use of monochromatic light would obviate this difficulty, but on the other hand necessitates special means to enable one to identify the original central band.

[3] The magnitude of this interval varies from one salt to another, being for instance much smaller for KNO_3 than for KCl; cf. *postea*.

stance we ought obviously to make the final setting always upon the same band, we shall err if the setting is made each time upon the most nearly achromatic band; and there will be one discontinuity for each such "concentration interval."

The explanation of this wandering of the original achromatic band is found in the relative optical dispersion of solution and water, on the one hand, and of glass (of the compensator plates $P_1 P_2$) and air, on the other hand. To obtain a quantitative expression for the magnitude of this effect it is first to be noted that in the type of instrument under consideration the lengthening of the optical path due to replacement of water by solution is compensated by the shortening of the *same* path by decreasing the effective thickness of an interposed glass plate. For the refractive indices of solution, water and glass we write n_1, n_2, and n, respectively, and put

$$\nu = n_1 - n_2$$

with appropriate subscripts attached to ν to denote the wave length to which it refers. The dispersive power (β') of the solution with respect to water[1] is defined by the relation

$$\beta' = (\nu_F - \nu_C)/\nu_D$$

and similarly,

$$\beta'' = \frac{n_F - n_C}{n_D - 1}$$

Now it can readily be shown[2] that with an interferometer of the type under discussion the position of the most nearly achromatic band will, as the concentration of the solution increases, shift one fringe to the left for a certain number r_1 of divisions on the drum, where

$$r_1 = 0.320\, r_f/(\beta' - q\beta'') \qquad \text{(III)}$$

r_f being the number of divisions corresponding to one fringe in white light[3] and q a constant depending on the refractive index of the compensator plate, and its initial inclination.[4]

Accordingly, the exact amount of the wandering of the achromatic band for any solution may be predicted in advance, and this source of

[1] It is to be noted that this quantity β' is not the same as the difference in relative dispersion of solution and water, *i. e.*,

$$\frac{n_{1F} - n_{1C}}{n_{1D} - } - \frac{n_{2F} - n_{2C}}{n_{2D} - 1} \text{ is not equal, to } \frac{\nu_F - \nu_C}{\nu_D}$$

β'' on the other hand is the ordinary relative dispersion of the glass.

[2] See L. H. Adams, *J. Wash. Acad.*, **5**, 276 (1915).

[3] Or more specifically the light of the tungsten lamp which is ordinarily used as the light-source.

[4] For the ordinary case of an initial inclination of about 45° and refractive index n,

$$q = \frac{2n(n-1)}{(2n^2-1)^{1.5} - (2n^2-1)}.$$

error thus guarded against, if the appropriate values of β' and β'' are known. The value of β'' for various kinds of glass may be found in tables of constants;[1] thus for the (crown) glass, of which the compensator plates in our instrument are made, $\beta'' = 0.015$, $n = 1.514$, and therefore $q = 0.48$.

β' has been measured for various salts in aqueous solution;[2] for KCl it is about 0.032. Consequently for a series of solutions of KCl (taking $r_f = 22$)[3] $r_1 = 0.320 \times 22/0.025 = 280$ divisions; therefore, at a concentration corresponding to 140 scale divisions the originally white central band will have become identical in appearance with the left-hand band and at 280 divisions the original left-hand band will have become the achromatic one. This difficulty could be entirely obviated by using compensator plates of such glass that $q\beta' = \beta''$ for the solutions (or mixtures) under investigation. But, unfortunately, this can be done only to a limited extent, for high dispersion in glasses is accompanied by high refractive index, so that even in the extreme case of heaviest flint glass, $\beta'' = 0.051$, $n = 1.963$, $q = 0.35$, and therefore $q\beta''$ is only 0.018, while the corresponding quantity β' may be as high as 0.045 for solutions such as the nitrates and even higher for other salts such as the bromides and iodides. But, at any rate, it would be an improvement to substitute compensator plates of heavier optical glass for the usual crown glass ones. Thus compensator plates of the glass mentioned above (Jena optical glass No. S 57) would match all sulfate solutions (β' about 0.016) very well and for use with all other solutions would be at least as suitable as crown glass plates. But in general this difficulty of the wandering of the achromatic band can only be circumvented by recourse to one of two methods of procedure: (1) the employment of the "zero method" described above, which is in general the more satisfactory mode of operation, for in that case dispersion differences are of little consequence and in most cases will not lead to error, especially if the maximum reading in the scale is never greater than 100 or 200 divisions; or (2) a careful preliminary determination of the "concentration intervals," using as a guide Equation III above and the following Table II which summarizes the available mean values of β' for salts and other substances in aqueous solution. But it may be worth while to make this series of preliminary observations and so be enabled to use the direct method in the not infrequent case when a large number of similar solutions have to be analyzed; it is for this reason that this question of the shifting of the achromatic band has been discussed here at some length.

[1] Thus Landolt-Börnstein-Roth (p. 980) gives "reciprocal relative dispersion" $1/\beta'$.

[2] W. Hallwachs, *Ann. Physik*, **47**, 381 (1891); A. H. Borgesius, *Ann. Physik*, **54**, 221 (1895); D. Dijken, *Z. physik. Chem.*, **24**, 81 (1897).

[3] On our instrument r_f for white light varies from 22 at the lower end of the scale to about 28 at the upper end.

TABLE II.

Mean Values of β' ($= (\nu_F - \nu_C)/\nu_D$) for Various Substances in Aqueous Solution.

Substance.	β'.	Substance.	β'.	Substance.	β'.
LiCl	0.037	NaBr	0.047	Na_2SO_4	0.016
NaCl	0.036	KBr	0.045	K_2SO_4	0.015
KCl	0.032	$LiNO_3$	0.048	$MgSO_4$	0.014
$MgCl_2$	0.032	$NaNO_3$	0.043	$ZnSO_4$	0.015
$ZnCl_2$	0.031	KNO_3	0.042	$(NH_4)_2SO_4$	0.016
$BaCl_2$	0.028	$Mg(NO_3)_2$	0.038	H_2SO_4	0.022
HCl	0.045	$Zn(NO_3)_2$	0.035	CH_3COOH	0.021
NH_4Cl	0.035	NH_4NO_3	0.043	Cane sugar	0.012
LiBr	0.049	Li_2SO_4	0.017		

Inspection of this table shows that there is a wide range in the values of β' for different substances in aqueous solution; however, the substances may be divided into several groups, in each of which β' is nearly constant. Thus for all of the sulfates β' is not far from 0.016; for the chlorides β' is not far from 0.035, for the bromides 0.047 and for the nitrates about 0.040. The nonelectrolyte, cane sugar (and probably also mannite) is exceptionally low.

Interpretation of the Interferometer Readings in Terms of Refractive Index.—Although the interferometer reading is a measure of a difference in refractive index, a knowledge of refractive indices *per se* is not essential for the analysis of solutions or mixtures, since the readings on an arbitrary scale are converted directly into concentrations by means of a previously determined calibration curve or table. Nevertheless, it is of interest to note the exact connection between the reading r of the instrument and the refractive index differences ν of the mixtures in question. Owing to the manner in which the micrometer screw moves the inclined compensator plate, the readings r on the drum are not quite directly proportional to ν, but by means of a small and easily applied correction they may be made so. It can readily be shown[1] that the change in optical path p caused by the rotation through an angle θ, (reckoned from the initial position at 45° to the light rays), of a plane-parallel plate of thickness h and refractive index n is found by the relation

$$p = \sqrt{2}h(\sqrt{H} - 1 - \sqrt{H + \sin 2\theta} + \cos\theta + \sin\theta)$$

where $H = 2n^2 - 1$. Furthermore, if R is the distance (in mm.) through which the micrometer screw moves and a the constant perpendicular distance from the center of rotation to the line of motion of the screw, then

$$\sin\theta = R/\sqrt{R^2 + a^2}$$

and

$$\cos\theta = a/\sqrt{R^2 + a^2}.$$

Substituting these values in the above expression we have, with sufficient approximation,

[1] See L. H. Adams, *J. Wash. Acad. Sci.*, **5**, 267–9 (1915).

$$\frac{p}{\sqrt{2h}} = \frac{R}{a}\left(1 - \frac{1}{\sqrt{H}}\right) - \frac{R^2}{2a^2}\left(1 - \frac{1}{H^{1.5}}\right). \qquad \text{(IV}a\text{)}$$

Let R' be a quantity such that

$$\frac{p}{\sqrt{2h}} = \frac{R'}{a}\left(1 - \frac{1}{\sqrt{H}}\right)$$

then

$$R' = R - \frac{R^2}{2a}\left(\frac{1 - 1/H^{1.5}}{1 - \sqrt{1/H}}\right). \qquad \text{(IV}b\text{)}$$

Now in our instrument $r = 200\,R$, $a = 110$ mm., $n = 1.51$. Making these substitutions we obtain finally the relation (for our instrument)

$$r' = r - 0.000041\,r^2. \qquad \text{(IV)}$$

R′ (and hence also r') is a number proportional to the decrease in optical path of the compensator plate, and therefore is strictly proportional to the quantity v.

Although not essential, it is advantageous to use r' rather than r in all work with the interferometer; because, as the concentration c varies, the variation of the quotient c/r' is more regular than that of c/r. In the case of practically all substances in aqueous solution, c/v, and hence c/r', *increases* slowly with increasing concentration; c/r on the other hand usually *decreases* rather rapidly, while in using the zero method one may obtain values of c/r (the concentration gradient) which increase and decrease in a very irregular way, depending on the magnitude of c and of r. The data of Table III on mannite solutions (for which I

TABLE III.

Conc. parts per million.	c. (Av.)	Δc.	r.	$\Delta c/r$.	r'.	c/r'.
504 / 0	252	504	217	2.32	215	2.34
1024 / 0	512	1024	447	2.29	438	2.34
4063 / 2541	3302	1522	669	2.27	650.5	2.34
4563 / 4063	4313	500	214	2.34	212	2.36
14154 / 13904	14029	250	105	2.38	104.5	2.39

am indebted to Mr. R. E. Hall) illustrate this point. Inspection of this table, which is self-explanatory, shows the much greater regularity of the concentration gradient obtained by converting the readings r into the "corrected" readings r' according to Equation IV. This procedure not only makes for greater convenience in plotting calibration curves and interpolating from them, but, in addition, it renders the detection of errors from various sources much more easy and certain.

As an example of the numerical relation between r' and ν we may take the following case:

A KCl solution containing 357 parts per million of water gives in the 40 mm. chamber of our instrument a reading $r = 150$, which by Equation IV corresponds to $r' = 149$. The retardation N in wave-lengths, is then[1] $N = r'/r_f = 149/22.0 = 6.78$, and by Equation II, $\nu = N\lambda/l$. Here l is twice the length of the chamber or 80 mm. Hence, taking $\lambda = 0.00058$ mm. we have the difference in refractive index between solution and water, $\nu = 0.0000497$ at 22°. This result may be compared with the results of Dijken[2] and Borgesius[3] for KCl solutions. By interpolation from their results ν_D at 22° for the same KCl concentration is 0.0000505 (Dijken), 0.000478 (Borgesius).

Concluding Remarks.—A few hints with regard to methods which have proved useful in actual working with the instrument may be worth mentioning. Changing of solutions is effected by means of a pipet (preferably provided with a rubber syringe bulb), over the tip of which is slid a small piece of rubber tubing in order to obviate damage to the water chamber. It is advisable to rinse two or three times; filter paper can be used to absorb the few drops remaining in the chamber each time, except in the final rinsing. One must wait until the temperature of the solutions is uniform, since otherwise the bands are distorted. Several independent settings of the drum should be made on each sample of solution, and it is advisable for the highest accuracy to take readings on more than one sample of each solution.

It has already been mentioned that one advantage of the interferometer is its insensitiveness to temperature changes as compared with ordinary refractometers. The temperature coefficient is not absolutely *nil*, however; for example, in the case of KCl solutions it is about —0.2% per degree (at 20–25°) and for KNO_3 solutions about —0.5% per degree; that is, if in reading one KCl solution against another we find $r = 200$ at 25°, the corresponding reading at 20° would be 202. It is evident that for small temperature fluctuations and with small readings such as are obtained when using the "zero" method, the temperature effect may be neglected; but if greater accuracy is desired the temperature coefficients may easily be determined and the necessary small corrections applied.

A number of possible applications of the interferometer to chemical work has already been suggested at various times. The instrument was originally designed for the analysis of sea-water and has been successfully used for that purpose, while Marc has employed it for the analysis of colloidal solutions. Another purpose for which the interferometer would be especially suitable is the standardization of solutions for volumetric analysis; other uses will readily suggest themselves. One such use only

[1] N, and hence ν, may be calculated without reference to r' by using formula IV*a* and knowing h and n for the compensator plate.

[2] D. Dijken, *Z. physik. Chem.*, **24**, 96 (1897).

[3] A. H. Borgesius, *Ann. Physik*, **54**, 233 (1895).

will be mentioned; namely, that mixtures of sodium and potassium salts may be rapidly analyzed with an accuracy equaling or even exceeding that of the most careful gravimetric analyses. For instance, suppose we wish to determine the amounts of soda and potash in a mixture of their sulfates, which need not weigh more than 50 mg. altogether. We dissolve this mixture in exactly 200 times its weight of water and compare it on the interferometer with a standard solution containing pure, dry K_2SO_4 dissolved in 200 times its weight of water; the reading will range from 430 to 0 as the composition of the mixture ranges from pure $NaSO_4$ to pure K_2SO_4. In this way any mixture can, with the aid of a calibration curve previously determined once for all, be analyzed in a few minutes with an accuracy of 0.1 mg. of either constituent (on a 50 mg. sample).

Summary.

The foregoing pages present a brief description of the principle and mode of operation of the interferometer, a form of instrument which enables one to determine the single varying constituent in a mixture or solution, with ease, rapidity, and very great accuracy. The only important source of error arises from differences in optical dispersion; it can readily be obviated by use of the methods discussed in the text.

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THE VISCOSITIES OF BINARY MIXTURES OF THE ASSOCIATED LIQUIDS, WATER, FORMIC ACID AND ACETIC ACID.[1]

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Jones and Murray[2] showed in 1903 that when two associated liquids are mixed, each diminishes the association of the other. They determined the molecular weight of water in formic acid on the one hand, and in acetic acid on the other. Also the molecular weight of formic acid in water, and in acetic acid, and finally the molecular weight of acetic acid in water and in formic acid.

They found that the molecular weight of water in formic acid varied from 19.7 at dilution 0.93 N to 21.9 at 6.18 N, showing that the formic acid diminished slightly the association of the water.

The molecular weight of water in acetic acid varied from 21.7 at 0.64 N to 38.8 at 12.65 N. This showed that the acetic acid diminished greatly the association of the water.

[1] This work was done in connection with an investigation which is being carried out with the aid of a Grant from the Carnegie Institution of Washington, to H. C. Jones.

[2] *Am. Chem. J.*, 30, 193 (1903).