TURBIDIMETRIC METHOD OF DETERMINATION OF CHLORIDE IN BRACKISH WATER

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ABSTRACT

A turbidimetric method of determination of chloride in brackish waters of Rajasthan has been described. The suspending medium for the silver chloride is 1 : 1 glycerine containing 10% d-glucose. Upto 105 ppm sodium chloride can be directly determined by this new method.

A standard curve has been drawn with concentration (ppm) against percentage transmission. The curve enables one to read concentration of chloride in terms of ppm, by the use of a formula derived in this paper.

INTRODUCTION

IN DESERT areas, the salinity of brackish water, soil and atmosphere, plays a great role in potability, irrigation and air borne saline deposits. There are various methods of determinations of chloride. Skougstad and Fishman[1] reviewed, excluding fluoride, 23 methods of halide determination in their review on water analysis, of which 21 methods appeared during the years 1957 to 1960. This will tend to indicate the importance of halide determination.

The turbidity produced by a suspension of AgCl can be measured both turbidimetrically or nephelometrically. In the Lamb's [2] nephelometric method 50 per cent ethanol has been used to increase the opacity of AgCl sol and chloride concentration was determined between 4 and 300 $\times 10^{-6}$ M with an average deviation of 3 to 4 per cent. Kitano and Tsubota [3] described a nephelometric method using lead nitrate as a stabiliser. By this method chloride could be determined when cl′ content is less than 10^{-4} M.

The turbidimetric methods are few. Synghal [4] has described a turbidimetric method in a brief note in which upto about 30 ppm of NaCl was determined. Kaluszyner[5] has estimated AgCl turbidimetrically with Leitz photometer using filter No. 415. Both turbidimetric as well as nephelometri methods are used for determination of traces of chloride. The reference to nephelometric determination may not be considered out of place, since in both cases of measurement, the AgCl suspension is rquired—when the percentage transmission is measured, it is turbidimetry and when the scattering of light is measured, it is nephelometry.

The determination of salinity of brackish water is being carried out in many arid zone areas. From Turkey, analysis of 278 underground water samples were reported[6].

A recent survey of a cross section of certain regions of Rajasthan desert covering over 5,000 sq. miles showed that the salinity of underground brackish water varies considerably usually between 500 and 10,000 ppm when the total chloride is expressed as NaCl. It was felt that a rapid method of determination of chloride will be useful for samples of such high concentration and consequently experiments described below were undertaken.

In our experiment it was found that chloride could be determined by the method described by Synghal upto 25 ppm beyond which the linearity broke off. No attempt was made to find out lower limit, for two reasons. First our interest was for high chloride content. Secondly, there are good methods for determination of traces of chloride. Considering the high concentration of chloride in brackish water, the determination of chloride by reducing its concentration means for a sample of 10^4 ppm, a dilution of 4×10^2 before the turbidimetric method could be made use of in aqueous medium and the dilution required would be still greater if recourse is taken to methods for trace determination (cf: Kitano and Tsubota[3]). The large dilution required, is likely to introduce considerable error.

Since beyond 25 ppm of NaCl, AgCl suspension begins to precipitate it was thought a denser medium might help in keeping the sol in suspension. Consequently various dilution of glycerine was tried.

Although glycerine was the heaviest, it was not found suitable from the point of handling for analytical purpose because of its high viscosity. Of the diluted mediums, 1 : 1 glycerine was found to be suitable and it became possible to read 70 ppm NaCl directly.

The density of 1 : 1 glycerine was further increased by the addition of 10 per cent d-glucose (BDH, Analar) and this solution could be used to determine chloride slightly beyond 105 ppm NaCl turbidimetrically. The influence of other electrolytes such as sulphates and nitrates were studied. The effect of concentration of silver nitrate and nitric acid, temperature, time factor, stirring effect, etc. were also studied.

The experimental results are described below :

EXPERIMENTAL

Apparatus

Bausch and Lomb Spectronic 20 Colorimeter was used for all experiments.

Materials

1. Glycerine pure
2. d-glucose (BDH analar)
3. Silver nitrate solution (2·5% $AgNO_3$ in N/10 HNO_3)
4. Sodium chloride A.R.
5. Nitric Acid A.R.

Procedure

I. *For determination of chloride in aqueous medium.*

Take 1·0 cc of silver nitrate solution in a Spectronic test tube. Add 3·0 cc of appropriate concentration of sodium chloride solution with stirring at room temperature. Read the percentage transmission (%T) within 1 minute of addition at 475 $m\mu$.

II. *For determination of chloride in glucose-glycerine medium.*

Prepare a solution of 10% d-glucose in 1 : 1 glycerine (v/v) by warming if necessary. Keep it overnight.

Prepare 2·5% solution of silver nitrate in approximately N/10 HNO_3.

Set the Bausch and Lomb Spectronic 20, at 475 *mu* and set 100% transmission for distilled water.

Take 9·0 cc of G—G solution *i.e.*, 10% d-glucose in 1 : 1 glycerine in a test tube. Add 1·0 cc of the brackish water to it and mix well by stirring. Take 1·0 cc of the silver nitrate solution into a spectronic 20, tube (capacity 10cc). Draw 3·0 cc of the mixed solution, stir well and find out the percentage transmission (%T) of the silver chloride suspension well within one minute of addition and preferably between 45 to 50 seconds. It is not difficult to adhere to time factor.

Read the ppm in terms of sodium chloride, against %T from the standard graph (Fig 3).

Calculate the chloride concentration of the brackish water in terms of sodium chloride, ppm from the eqn. $Y = 10 \frac{A.x}{V}$ .. .. (1)

where Y = Actual conc. of chloride as NaCl. ppm in brackish water.

x = ppm of chloride as NaCl read from the standard curve against percentage transmission.

A = No. of times of dilution that has been made of the original brackish water, prior to addition to G—G solution.

V = Volume of brackish water or chloride solution added to the G-G solution.

The volume of chloride solution added to G–G solution is always according to the formula,

$a + b = 10{\cdot}0$ cc .. .. (2)

where a = volume of chloride solution.

b = volume of G–G solution.

If a chloride solution is diluted before mixing to G–G solution, the same formula (2) applies with reference to the diluted chloride solution only.

The use of V = 1·0 cc is recommended for convenience but volumes, more or less than 1·0 cc can also be used depending on cencentration of chloride.

The value of y is the concentration of chloride in brackish water sample expressed as sodium chloride in ppm.

RESULTS

TABLE I.

SHOWS PERCENTAGE TRANSMISSION (%T) WITH INCREASING CONCENTRATION OF NaCl (PPM) IN AQ. MEDIUM (VIDE PROCEDURE I)

NaCl (ppm)	%T
0	100
5	91
10	82
15	73
20	64
25	56
30	49
35	43
40	38

A plot of %T against concentration (Fig. 1) shows that the curve (A) breaks off beyond 25 ppm NaCl. Consequently this method cannot be used beyond this limit. The glycerine solutions were next tried as suspending medium.

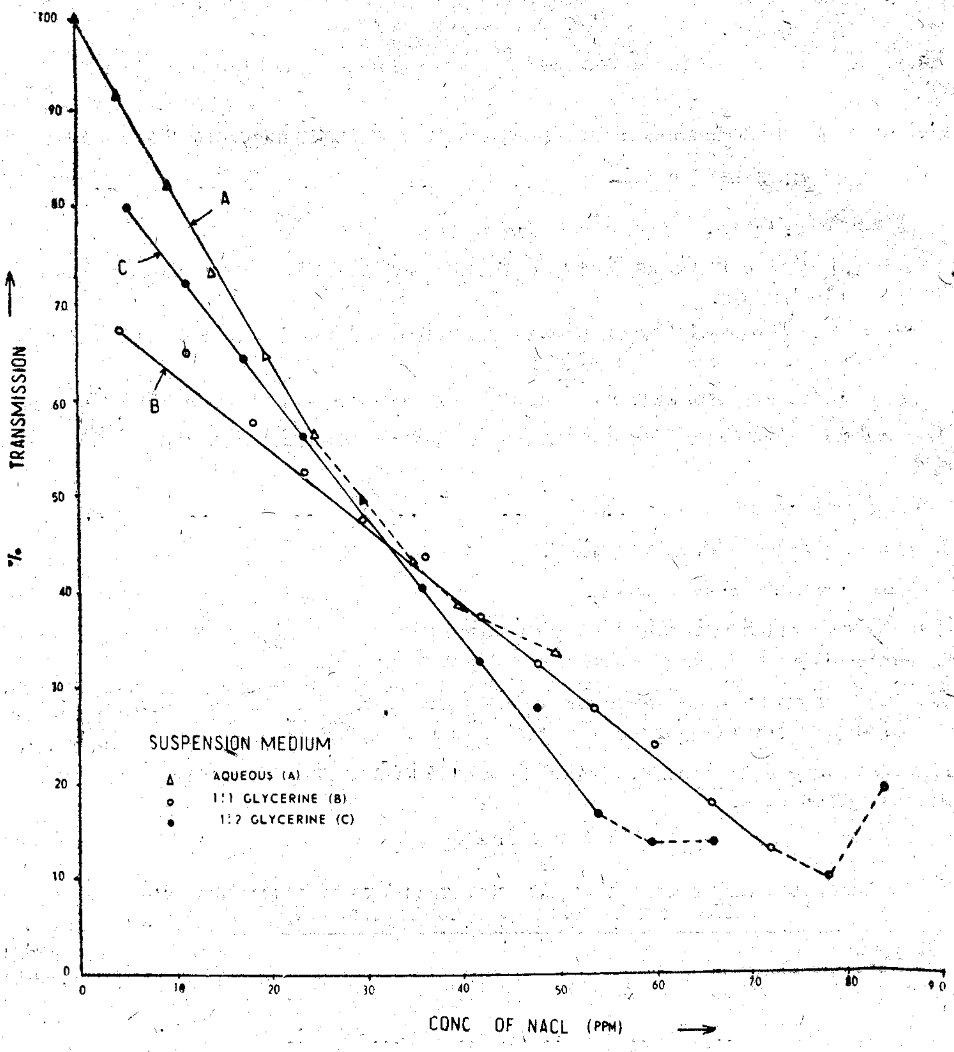

FIG 1.

Glycerine solution as suspending medium

The method consisted in taking a volume of 1 : x glycerine where x =1 or 2 and adding to it a known volume of NaCl solution directly from the stock solution so that the total volume was always 10 cc. After mixing well, 3 cc of this mixed solution was transferred to the test tube of spectronic 20 containing 1 cc of 2·5% $AgNO_3$ in N/10 HNO_3 and stirred well with a glass rod. The %T was read within 1 minute of $AgNO_3$ addition taking distilled water to be at 100 %T.

TABLE II

SHOWS %T WITH INCREASING CONCENTRATION OF NaCl (PPM) IN 1 : 1 AND 1 : 2 GLYCERINE SOLUTION

Concentration of stock solution was 606·4 ppm NaCl

Vol. of 1 : x glycerine where x=1 or 2 (cc)	Vol. of NaCl stock solution added to corresponding vol. in col. I (cc)	%T of AgCl so. in		ppm NaCl present during %T determination in 1 : 1 or 1 : 2 glycerine
		1 : 1 gly.	1 : 2 gly.	
10·0	0·0	77	90	0
9·8	0·2	65	72	12
9·6	0·4	52	56	24
9·4	0·6	43	40	36
9·2	0·8	32	27	48
9·0	1·0	23	13	60
8·8	1·2	12	12	72
8·6	1·4	18	9	84
8·4	1·6	18	..	96

A plot of %T against concentration (Fig. 1 B and C) shows that linearity is obeyed upto 72 ppm for 1 : 1 vide curve B and 54 ppm for 1 : 2 glycerine solution vide curve C beyond which there is deviation due to coagulation in traces of AgCl suspension in respective medium. 1 : 1 glycerine was therefore taken for further study.

1 : 1 *glycerine containing d-glucose as suspending meduim.*

Th next requirement was to increase the density of 1 : 1 glycerine and thereby, to obtain a greater suspension of AgCl. Glycerine itself was not found suitable because of its high viscosity, as already stated. Consequently density of 1 : 1 glycerine was increased by dissolving d-glucose (BDH Analar). The densities of various solutions are shown in Table III.

TABLE III.

(SHOWING DENSITIES OF GLYCERINE SOLUTIONS AT 15·5°C)

Pure glycerine	1·26
1 : 1 glycerine	1·12
1 : 2 glycerine	1·08
10% d-glucose in 1 : 1 glycerine	1·18

Table IV

Shows %T with increasing conc. of NaCl ppm in 5%, 10% and 15% d-glucose solution in 1 : 1 glycerine. Conc. of stock solution was 754·4 NaCl. ppm

Vol. of d-glucose solution in 1 : 1 glycerine (cc)	Vol of NaCl stock solution added to corresponding vol. in col. I (cc)	% T of AgCl sol. in d-glucose solution in 1 : 1 glycerine			ppm NaCl present during %T determination
		5% d-glucose	10% d-glucose	15% d-glucose	
9·8	0·2	51	43	..	15·1
9·7	0·3	..	..	45	22.6
9·6	0·4	44	37	..	30·2
9·4	0·6	..	31	34	45·3
9·2	0·8	27	25	..	60·4
9·1	0·9	..	..	24	67·9
9·0	1·0	20	18	..	75·4
8·8	1·2	24	13	12	90·5
8·6	1·4	..	12	15	105·6
8·4	1·6	..	12	16	120·6

A plot of %T against conc. (Fig. 2) shows that linearity is obeyed slightly beyond 105 ppm for 10% d-glucose solution in 1 : 1 glycerine. 15% d-glucose line breaks off at slightly beyond 90 ppm and 5% d-glucose line shows deviation from linearity still earlier *viz.* at about 75 ppm. Therefore optimum conc. of d-glucose was taken to be at 10%.

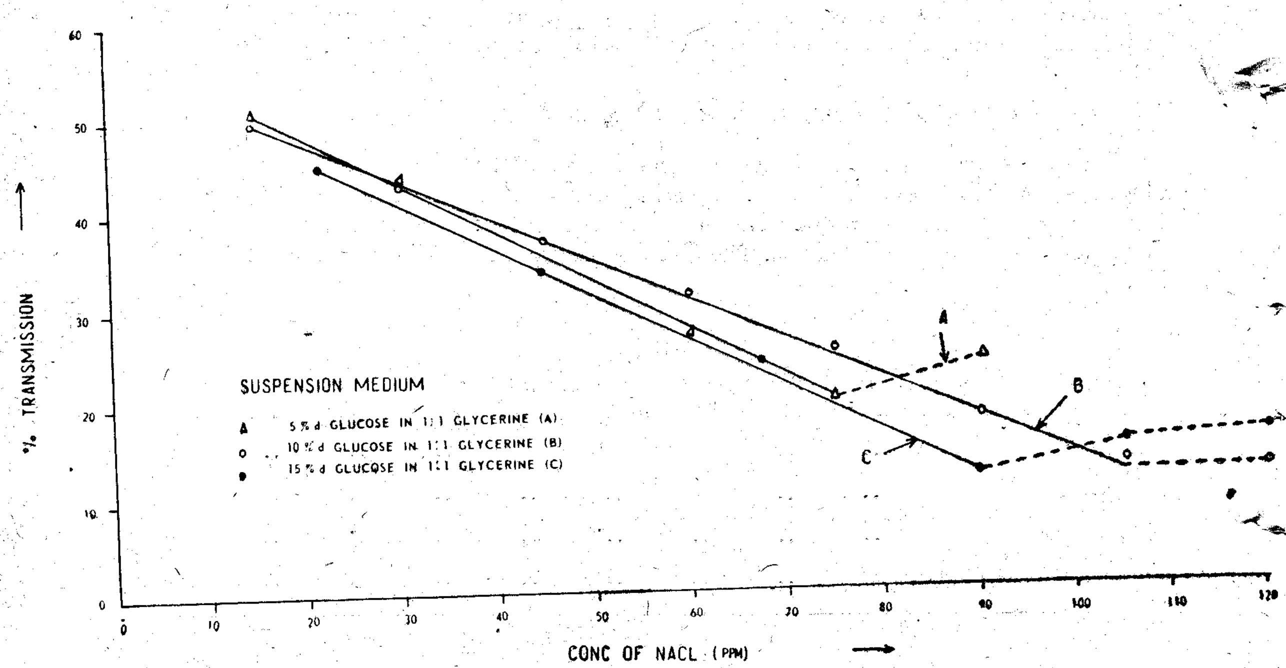

Fig 2

Standard Curve

A standard curve (fig. 3) was obtained with 1000 ppm NaCl using 10% d-glucose solution in 1 : 1 glycerine as the suspending medium. The 10% d-glucose solution of 1 : 1 glycerine has been referred to as G—G solution

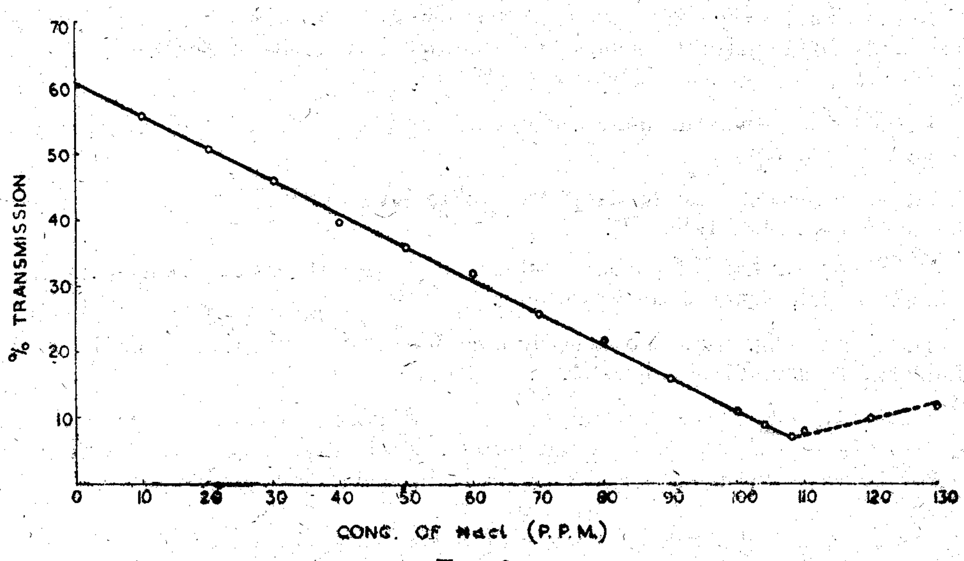

FIG. 3.

TABLE V

Vol. of G.G. solution (cc)	Vol. of NaCl solution added to corresponding vol. in col. I (cc)	%T of AgCl sol. in G—G solution	ppm NaCl present during %T determination	%T X 10/7	Optical density (log Io/I)
1	2	3	4	5	6
10·0	0·0	70	0	100	0·00
9·9	0·1	56	10	80	0·10
9·8	0·2	51	20	72·8	0·14
9·7	0·3	46	30	65·6	0·18
9·6	0·4	40	40	57·1	0·24
9·5	0·5	36	50	51·4	0·29
9·4	0·6	32	60	45·7	0·34
9·3	0·7	26	70	37·1	0·43
9·2	0·8	22	80	31·4	0·51
9·0	0·9	16	90	22·8	0·62
9·0	1·0	11	100	15·7	0·80
9·0	1·04	9	104	12·8	0·90
8·9	1·1	8	110	11·4	0·95
8·8	1·2	10	120	14·3	0·85
8·7	1·3	12	130		

"ppm NaCl present during %T determination" was calculated as shown in the following example.

Stock solution = 1000 ppm NaCl.

9cc G–G soln. + 1 cc stock soln. = 10 cc........................(*i*)

conc. of NaCl = 0·1 mgm/per cc or 100 ppm with reference to the solution (*i*) or in other words, 100 ppm NaCl was present during %T determination. Similarly, 9·5 cc G-G sol. + 0·5 cc stock soln. would give 50 ppm NaCl.

In these calculations the dilution effect caused by the addition of reagent silver nitrate, has not been considered.

The applicability of the standard curve was tested with 2000, 500 and 100 ppm sodium chloride solutions (vide Table VI).

It will be seen that %T points would lie very close to the standard curve *i.e.*, the line obtained through points of 1000 ppm only.

The curve at fig. 3 was subsequently used for the determination of chloride in other chloride solutions and brackish water.

Table VII shows results with various chloride solutions, their mixtures and influence of other electrolytes, namely sulphate and nitrate. Table VIII shows results with brackish waters obtained from the wells of desert areas of Barmer district, Rajasthan.

TABLE VI

%T WITH DIFFERENT CONCENTRATION OF SODIUM CHLORIDE

Conc. of stock soln. of sodium chloride expressed as NaCl ppm	Vol. of chloride stock soln. added to G-G soln. (cc)	%T	ppm (NaCl) read from Standard Graph	Experimental value of chloride ppm calculated from eq. $Y = \frac{10Ax}{V}$
2000	0·3	31	60	2000
	0·4	20	82	2050
	0·5	11	100	2000
	0·6	12	98	1633·3
500	0·1	59	5·0	500·0
	0·3	54	14·5	483·3
	0·6	46	30·0	500·0
	0·8	40	42·2	527·5
	1·0	36	50·0	500·0
	1·1	34	54·5	495·4
	1·2	30	62·0	516·6
	1·4	26	70·0	500·0
	1·8	16	90·0	500·0
	2·0	10	102·0	510·0
100	0·5	59	5·0	100·0
	1·0	56	10·0	100·0
	1·5	49	14·0	93·3
	2·0	51	20·0	100·0
	2·5	48	26·0	104·0
	3·0	47	28·0	93·3
	3·5	45	32·5	92·8
	4·0	42	38·0	95·5
	4·5	37	48·5	107·7
	5·0	38	46·0	92·0

TABLE VII

Nature of chloride	*Conc. of stock soln. of chloride expressed as NaCl (ppm)	Vol. of chloride stock soln. added to G-G soln. (cc)	%T	ppm (NaCl) read from Standard graph	Experimental value of chloride, ppm calculated from eq. $Y = \frac{10Ax}{V}$
$CaCl_2$	440	0·5	50	22	440
		1·0	39	44	440
$MgCl_2$	280	0·5	54	14	280
		1·0	47	28	280
$CaCl_2$ + $MgCl_2$	(a) 353·3	1·0	43	35·5	355
	(b) 326·6	1·0	45	32·0	320
$CaCl_2$ + $MgCl_2$ + NaCl	(c) 568·6	1·0	33	56	560
	(d) 600·3	1·0	31	60	600
NaCl + Na_2SO_4	(e) 1500	0·5	24	74	1480
	(f) 1000	1·0	13	96	960
NaCl + $NaNO_3$	(g) 750	1·0	24	74	740
	(h) 750	1·0	24	74	740

*ACTUAL COMPOSITION

All conc. are expressed as ppm.

	(a)	(b)
$CaCl_2$	204·9	273·2
$MgCl_2$	114·2	76·1
	(c)	(d)
$CaCl_2$	136·6	218·5
$MgCl_2$	76·1	30·4
NaCl	333·3	333·3
	(e)	(f)
NaCl	1500	1000
Na_2SO_4	500	1000
	(g)	(h)
NaCl	750	750
$NaNO_3$	250	500

TABLE VIII

SHOWING %T WITH UNDERGROUND BRACKISH WATER OBTAINED FROM THE DESERT AREAS OF BARMER DISTRICT, RAJASTHAN

Brackish well water No	Chloride expressed as NaCl (ppm) Volhard method	Dilution of bracksih water	Volume of brackish water (after dilution if any) added to G-G solution (cc)	%T	ppm (NaCl) read from graph	Experimental value for Chloride (ppm) calculated from eq. $Y = \frac{10Ax}{V}$
1	241·9	Nil	1·0	49	24·5	245
2	377·1	Nil	1·0	42	38·0	380
3	782·7	Nil	1·0	22	78·0	780
4	792·2	Nil	1·0	22	78·0	780
5	1128·2	Nil	0·5	38	56·0	1120
6	1480·0	2 times	1·0	24	74·5	1430
7	1609·0	Nil	0·5	21	80·0	1600
8	1921·5	2 times	1·0	12	98·0	1960
9	2479·1	5 times	1·0	37	48·5	2425
10	3643·0	4 times	1·0	15	92·0	3680
11	4230·4	5 times	1·0	19	84·0	4200
12	5871·6	10 times	1·0	32	58·2	5820
13	6678·4	10 times	1·0	28	66·0	6600
14	8340·2	10 times	1·0	19	84·0	8400

Effect of temperature %T.

TABLE IX

SHOWS EFFECT OF TEMPERATURE CHANGES ON %T WITH 1000 ppm NaCL SOLUTION

Vol. G-G Solution (cc)	Vol. of NaCl solution added (cc)	Temperature of AgCl sol C°	%T	Calculated NaCl ppm from eq. $Y = \frac{10Ax}{V}$
9·6	1·0 ..	40	9	1040
		35	10	1020
		28 (Room temp)	11	1000
		20	13	960
		15	14	940

It would be seen that the value is affected by change of temperature. In the condition of the laboratory, it has been noted that temperature varied to about 4°C during working hours. Effects of temp. changes have not been taken into consideration in any of the data reported in this paper.

Effect of concentration of silver nitrate and nitric acid.

TABLE X

SHOWS EFFECT OF VARIATION OF CONC. OF $AgNO_3$ AND HNO_3 ON THE %T DETERMINATION

Vol. G-G; solution ; (cc)	Vol. of NaCl solution (cc)	Conc. of ; $AgNO_3$ (%)	%T Concentration of HNO_3		
			N/5	N/10	N/25
9·0	(a) 1·0	2·5	(a) 11	(a) 11	(a) 10
9·0	(b) 0·5		(b) 37	(b) 36	(b) 36
		1·0	(a) 10	(a) 11	(a) 11
			(b) 36	(b) 37	(b) 36
		0·5	(a) 11	(a) 10	(a) 11
			(b) 35	(b) 35	(b) 37

It would be seen that concentration of silver nitrate and nitric acid can be varied over wide range *viz.*, 0·5% to 2·5% for silver nitrate and N/5 to N/25 for nitric acid. %T are shown in two ranges.

Effect of dilution of G-G solution on %T.

TABLE XI

THE FOLLOWING TABLE SHOWS THAT DILUTION OF G-G-SOLUTION UPTO 50 PER CENT HAS NO EFFECT ON %T

Vol. of G-G solution (cc)	Vol. of distilled water added to corresponding vol. of G-G solution in col. 1 (cc)	%T	Dilution of G-G solution (%)
10	0	85	0
9	1	85	10
8	2	86	20
7	3	86	30
6	4	85	40
5	5	86	50

Time factor.

The following table shows the rate of fall of %T with time. There is an average rate of decrease in %T, *viz.* 1·0% per 5 seconds, and the decrease is independent of the medium of suspension. Different transmission ranges were chosen *viz.*, 40, 50, 72 and the rate of fall is found also to be independent of the range of %T. (Vide Table No. XII).

Effect of re-stirring AgCl solution.

The %T shown with asterisk in the Table XII were recorded after re-stirring for 10 seconds, before reading %T at 75th, 90th and 120th seconds. The results show that mechanical disturbance has no influence on %T or its rate of fall, irrespective of the medium. The re-stirring effects were studied in separate experiments.

Method of preparation-glucose-glycerine solution

It has been found that method of preparation of G-G solution has no influence on %T *e.g.*, the G-G solution may be prepared in any one of the following ways.

(*i*) d-glucose dissolved in water and diluted with glycerine

(*ii*) d-glucose dissolved in glycerine and diluted with water

(*iii*) d-glucose dissolved in 1 : 1 glycerine.

TABLE XII

Time after which %T was observed (seconds)	%T with AgCl sol. in G-G soln.												%T with AgCl sol. in water					
	No of separate determination												No. of separate determination					
	I		II		III		I		II		III		I		II		III	
40 ..	38		40		40		49		50		50		73		73		72	
45 ..	37		39		39		48		48		49		72		72		71	
50 ..	36		38		38		47		47		48		71		72		70	
55 ..	36		37		37		46		46		47		70		71		69	
60 ..	35		36		37		45		45		46		69		70		68	
65 ..	35		36		36		44		44		46		69		69		68	
70 ..	34		35		35		43		44		45		68		68		67	
75 ..	33	*33	34	*34	34	*35	42	*43	42	*43	44	*44	67	*68	67	*67	67	*67
80 ..	33		33		34		42		43		43		67		66		66	
85 ..	32		33		34		42		42		43		67		65		66	
90 ..	32	*32	32	*32	33	*32	41	*40	41	*41	42	*41	66	*66	64	*65	65	*65
95 ..	32		31		33		40		40		41		65		64		64	
100 ..	31		31		32		40		40		41		65		63		64	
105 ..	31		30		32		39		39		40		64		63		63	
110 ..	30		30		31		38		39		39		63		62		63	
115 ..	30		30		31		38		38		39		62		62		62	
120 ..	29	*28	29	*28	30	*29	37	*36	37	*36	38	*36	62	*61	61	*60	61	*60

Mode of p'oducing AgCl so'ution.

The AgCl soln. may be produced either by adding G-G solution into silver nitrate solution or *vice versa.* The method of preparing the AgCl sol. has slight effect on %T. It has been found that the addition of G-G solution into silver nitrate gives slightly higher transmission than the reverse process, as the following table shows—

TABLE XIII

....AgCl soln. produced by adding	Time after which %T was measured	%T No. of separate determination				Average	Difference
		I	II	III	IV		
G-G solution to silver nitrate solution	40—45 Secs.	40	42	41	42	41·3	4·8
Silver nitrate solution to G-G solution	40—45 Secs.	37	36	37	36	36·5	

The addition of G-G solution into silver nitrate was therefore adopted.

Volume of G-G solution added to silver nitrate solution

The addition of 3·0 cc of G-G solution containing chloride solution/brackish water (mixed solution) has been recommended in the procedure II. If a larger volume of the mixed G-G solution is added to silver nitrate, %T does not change as shown in the following table. However it is preferable to use the same volume in a series of determination.

TABLE XIV.
STOCK SOLUTION=1,000 ppm NaCl

0·5 cc of stock solution was mixed with 9·5 cc of G-G solution (mixed solution)

Vol of mixed G-G. solution (cc)	Silver nitrate solution (cc)	%T
3·0	1·0	36
4·0	1·0	36
5·0	1·0	36

Influence of d-glucose

Although the increasing density of glucose-glycerine solution plays a part in retaining higher amount of AgCl in suspension, density is not considered to be the only factor, since a considerable dilution of G-G solution may be effected through the addition of stock chloride solution or brackish water without showing change in %T and it appears that d-glucose also contributes towards keeping the AgCl soln in suspension, thus enabling a high ppm of chloride to be directly determined.

The %T of AgCl soln. in 10% d-glucose dissolved in water only was therefore determined. It is found that linearity was obeyed up to 75 ppm beyond which visible coagulation of AgCl sol. began to take place. The d-glucose therefore exerts considerable influence probably as a protective colloid, but the use of glycerine is necessary for higher ppm.

Wave length

There is no optimum wave length either for G-G solution or AgCl sol. in G-G solution. The %T goes on increasing with the wave length for AgCl sol., as shown in the following table, but for G-G solution it is constant between 400 and 550 mμ.

TABLE XV

Wave length (mμ)	%T G-G solution	%T AgCl sol. in G-G solution (conc. 100 ppm)
350	80	10
375	82	15
400	85	19
425	85	26
450	85	31
475	85	36
500	85	38
525	85	40
550	85	44
575	87	47
600	88	50

Synghal reported absence of any optimum wavelength for AgCl suspension in aqueous medium.

DISCUSSION

The d-glucose (BDH, Analar) was found to contain 72·0 ppm of chloride as NaC. The firm states that it may contain max. 0·005% Cl which is equivalent to 82·0 ppm NaCl.

Due to presence of chloride in glucose, the glucose glycerine solution could not be used as a blank giving 100% transmission, because due to addition of silver nitrate th- blank would give opalescence. The glucose-glycerine solution alone gave 85%T with rese pect to water as 100% and from Table XI, it would be seen that there is practically no change in transmission due to addition of even 50% water to G-G solution. The G-G solution with the addition of 1·0 cc of 2·5% $AgNO_3$ solution gave 70%T. (Vide Table V).

The relation between log I°/I_a and concentration was obtained by multiplying %Tx data of Table V (Col. III) by a factor 10/7. Each %T was thus correspondingly shifted The G-G solution containing silver nitrate was thus shifted to 100%T (Col. VI). A plot of the corresponding optical density shows that the line passes through the original (semi-log scale) indicating that Beer's law is obeyed. (Fig. 4).

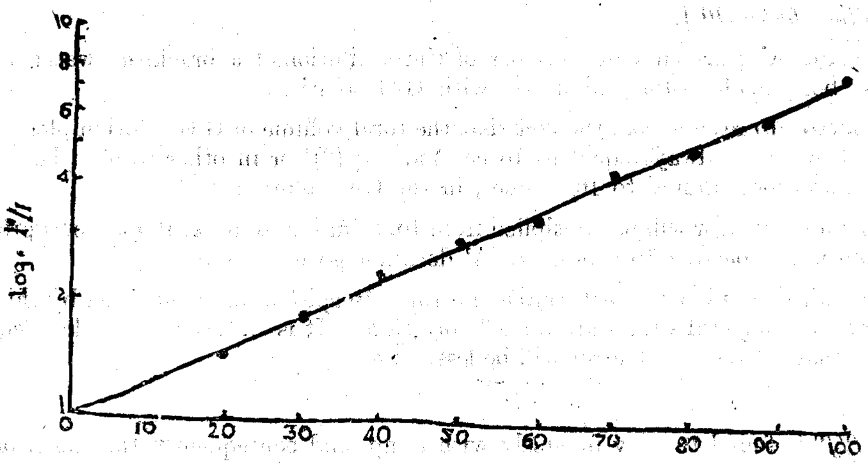

FIG. 4

It should be noted (Fig. 3) that while plotting for %T against concentration of sodium chloride, no account has been taken for the presence of chloride already present in G-G solution due to d-glucose. This does not introduce any error since the %T is plotted against known concentration of NaCl viz., 1000 ppm, as standard.

Concentration of silver nitrate and nitric acid

The concentration of silver nitrate and nitric acid can be varied over a wide range as is evident from the data in Table X.

Sources of error

The sources of error are the following—

(*i*) Time within which %T is read

(*ii*) Accuracy in %T reading

(*iii*) Multiplication factor 10 A in eqn. $y = \frac{10Ax}{v}$

(*iv*) Temperature changes

(*v*) Unknown electrolytes, organic matter and their possible effect on %T.

Time

Table XII shows that %T depends upon the time that elapses between mixing and recording transmission. The reading should be taken within 40 to 45 seconds from the moment of addition of silver nitrate solution. Other timings can be chosen provided both standard curves as well as experimental data are recorded within the same time interval.

Accuracy in %T reading

The scale reading on %T can be read with discretion upto 0·5 of a scale division. Other decimal values cannot be taken into account with desirable degree of accuracy. This is a source of error. However it is not considered to be great, since our experience shows that there can be $\pm 1{\cdot}0\%$ variation in the transmission with the sample, when used by the same operator.

The dilultion factor 10A.

The term 'A' represents the number of times dilution of a brackish water sample that has been made before mixing it with G-G solution.

The factor 10 results from the fact that the total volume of G-G solution plus volume of brackish water is always equal to 10 cc [Vide eq (2)] or in other words, the sample brackish water gets diluted to $10/v$ times, in the G-G solution.

Therefore any error will be multiplied from $10/v$ times upto max. $100/v$ times provided he dilution is not beyond 10 times, *i.e.* 'A' does not go beyond 10.

This multiplication is a great source of error. In spite of multiplication by this large factor, the experimental values are remarkably close. It is advisable to take v equal to or greater than 1·0 cc. The error will be less.

Temperature

The %T is found to vary inversely with temp. and consequently the conc. of NaC is found to decrease with temp. Taking the conc. of NaCl to be 1,000 ppm around 30°C (actual temp. is 28°C as per table IX) the rate of changes in the estimated value of NaCl is found to be $\pm$ 4 ppm per °C accordingly as the temp. is higher or lower than 30°C.

In this report temp. change has not been taken into account. In the conditions of the laboratory, the temperature varied to about 4°C during the day.

Unknown electrolytes, organic matter etc.

The presence of unknown electrolytes (other than those studied in this paper), organic matter may have a possible effect on the %T. However it is an unknown factor.

Statistical analysis of results.

1. *Standard deviation*—Table VI shows that 10 determinations of sodium chloride were made on each of the samples having conc. of 500 ppm and 100 ppm NaCl.

The s.d. of these two samples were found to be as below—

(*a*) 12·1 ppm for sample having 500 ppm conc.

(*b*) 5·3 ppm for sample having 100 ppm conc.

2. *Paired comparison*—The results obtained by the Volhord method were compared with those obtained by the turbidimetric method. The chloride of each sample of brackish water shown in Table VIII was determined by both methods and the results were statistically compared, as below—

df the degrees of freedom=13

$\bar{d}$, the average difference=11·1

Estimated standard deviation, Se, for a difference between two determinations, one determination by each procedure=39·4

$$t=1\cdot054$$

The t-test shows that the difference between the two methods of determination is nonsignificant as the value of t is much lower than what is required for P value of 0·05.

It is preferable for the analyst to draw his own standard curve with 1,000 ppm NaCl with his reagents and laboratory conditions.

The concentration of chloride in brackish water although described as high, it is usually present as a minor constituent *viz.*, 0·05 to 1·0% in the brackish water.

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