

Summary

1. The preparation of lithium chloroplatinate suitable for a reagent in the precipitation of potassium has been described.

2. Potassium chloroplatinate of the theoretical composition is precipitated if lithium chloroplatinate is used in place of chloroplatinic acid, with 80% ethyl alcohol as solvent.

3. Precipitates of potassium chloroplatinate formed by the lithium salt are stable at 200–260°, whereas those obtained by the usual process are unstable at temperatures above 160°.

4. A critical discussion has been given of the errors involved in the old process and an explanation offered for the better results obtained by the new procedure.

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THE DIELECTRIC CONSTANT OF WATER AS DETERMINED BY A RESONANCE METHOD

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The object of this paper is not so much the determination of the dielectric constant of water, as an investigation of the adequacy for this purpose of the resonance method when employed in the manner previously described.² Certain criticisms have been put forward with regard to this method, the principal one being that when a measurable amount of conductivity can be assigned to the dielectric under investigation, the dielectric constant value obtained is irrelevant. It will be shown in this paper that criticism of the value found for the dielectric constant of water was justified, but that the error involved was due to a cause other than the conductivity of the water and that the method can be used for the measurement of the dielectric constant of water provided its conductivity is below a certain specified value.

It was suspected that any influence of conductivity was to be found in the absorption of the electric oscillations, with consequent distortion of the point of resonance. The set-up previously described was therefore altered to include a radiotron tube of greater power and measurements were made with dielectrics whose conductivity could be varied to a known extent by the addition of a small amount of electrolyte. Apart from this a method was devised for calibrating the tuning condenser. The effect of using the harmonic instead of the fundamental for the point of resonance

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² Cuthbertson and Maass, *THIS JOURNAL*, 52, 483 (1930).

was also examined. For the determination of the absolute value of the dielectric constant of water a series of intermediate liquids was employed such that for each variation in the number of plates in the dielectric cell three liquids could be used so as to give a double check on the values obtained in each stage.

Changes in Set-Up.—The apparatus and dielectric cell used have been described in detail.³ As source of oscillations the only important change made was to make it possible to replace the UX171A radiotron tube at will by a UX210 radiotron power tube giving at least ten times the wattage rating and using 368 volts on the plate. In order to keep a constant filament current three 6-volt accumulators in parallel were employed. It was necessary to change both honeycomb and choke coils so as to carry the increased plate current, which could be varied from 15 to 75 milliamperes. Both the variable and fixed oscillators were shielded and care was taken to have a constant temperature environment during the course of related observations, which were all carried out at 25°.

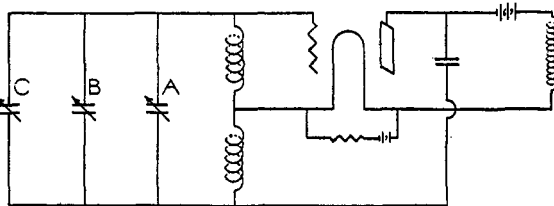


Fig. 1.—Set-up for calibrating tuning condenser A.

Calibration of Condenser.—The following procedure is worth describing as a useful method for calibrating the tuning condenser, not as far as its total capacity is concerned (which is of no interest), but in terms of its relative settings along the scale. In Fig. 1, which is similar to the variable oscillator previously described, A is the tuning condenser with a mirror mounted at the center of the dial so that scale readings could be read by reflected light on a circular scale four feet in diameter. The vernier control was manipulated by a pulley with a cord belt leading to a wheel placed at such a distance that its manipulation could be carried out without bringing in body capacity effects.

C connected in parallel is a variable condenser with the capacity arranged to correspond to a change of about 50 scale divisions on the tuning condenser between two fixed points of C. B also in parallel is a variable condenser with about the same capacity as the tuning condenser. The two fixed points of condenser C correspond to a capacity unaltered by any change in the set-up. By altering B, various parts of the scale readings of the tuning condenser could be calibrated in terms of this arbitrary but reproducible variation in the capacity of condenser C. As an analogy to this procedure one need only think of the calibration of a capillary tube by measuring the length of a mercury column as it is moved along the tube.

The tuning condenser was found to vary by several per cent. for different parts of the scale, but this variation was found to be perfectly reproducible and could therefore be corrected for in the subsequent measurements which were made. Table I gives a set of readings that were made to show the nature of the variations found.

TABLE I
CALIBRATION OF TUNING CONDENSER

Initial position										
on scale	7.0	21.0	36.4	54.5	71.6	93.6	114.2	134.8	159.0	175.9
Scale interval	50.7	51.1	51.4	51.8	52.0	52.1	52.2	52.3	52.2	52.1

With reference to the measurements previously reported which had been made with this same tuning condenser² it may be stated that, where a pair of liquids were compared over exactly the same range, the calibration is of course superfluous. Since, however, with two liquids that differ widely in dielectric constant the same range of scale may not be covered, an error may have crept in. Another advantage of the calibration was made evident by the fact that with the corrected scale readings all irregularity in the tuning condenser disappeared and since the dielectric cell condenser was also found to vary in a linear manner, the points obtained fall far better on a straight line.

Dead Space Correction.—As was to be expected, the interchange of the UX171A radiotron tube with the power tube showed no difference in the relative slopes of the curves obtained when two non-conducting media were compared in the dielectric cell. Also, the ratio of the slopes obtained for nitrobenzene and conductivity water when measured first with a 171A tube and then with the power tube agreed within the error of the measurements.

Another source of error which was suspected in the previous measurements was that in using the fundamental for the resonance point a large scale interval exists between the "no-sound" point when approached from the right or the left. If this scale interval has no variation for different settings of the dielectric cell no error may result. When the harmonic is used, which is more readily discerned with the aid of a power tube, this scale interval is reduced to an insignificant amount. In the following table data are given showing the scale readings for the fundamental when approached from the right and when approached from the left, and in the third column the scale readings given when the harmonic was used.

TABLE II
SCALE READINGS GIVING SLOPES

Dielectric cell	Right fundamental	Left fundamental	Harmonic
20	58.9	65.5	27.5
30	89.9	95.3	57.7
40	120.3	125.6	88.2
50	151.4	155.4	118.8
60	182.5	185.8	149.2
70	212.0	214.7	178.5
Slope =	153.1	149.1	151.0

Average, 151.1

It is evident that the "no-sound" scale interval ("dead space") varies with the setting of the dielectric cell. This is indicated by the values for the slopes of the lines given at the foot of each column. It will be

observed that the mean of the slopes given by the left and right fundamental "no-sound" points is the same as that of the harmonic in which there is not what may conveniently be termed "dead space." The conclusion is that where the fundamental is used and a large "dead space" exists, the average of the right and left scale readings must be taken to plot the slope. Better still the harmonic should be used when with the aid of the power tube this can be discerned. With liquids having a small dielectric constant the fundamental gives right and left "no-sound" points which are close together and which do not vary appreciably in "dead space" intervals. This had been observed, and the mistake made in the previous results was in assuming that the same would hold for liquids of high dielectric constant.

Conductivity of Medium.—If the conductivity of the medium when at all appreciable distorts the resonance point, then the resonance method is open to unanswerable criticism. To investigate this point a series of experiments was carried out both with a medium having a small dielectric constant (ether) and one having a high one (water) in each of which variation of the conductivity of the medium could be obtained by the addition of electrolytes. In the case of water actual conductivities were measured and corresponding "slopes" determined. In the case of ether carefully purified hydrogen chloride gas was added in known amounts and the slopes of the resulting solution measured. Furthermore, in the case of water the effect of altering the power of the oscillating set and its influence on the slopes of various solutions was examined.

In Table III are given the normalities of hydrogen chloride-ether solutions and the corresponding apparent dielectric constants calculated on the basis of 4.255 for pure ether. The results are plotted in Fig. 2.

TABLE III

RELATION BETWEEN CONDUCTIVITY AND DIELECTRIC CONSTANT FOR ETHER					
Normality	Slope	<i>E</i>	Normality	Slope	<i>E</i>
0	56.7	4.255	0.090	59.5	4.47
0.0061	56.7	4.255	.121	60.8	4.57
.013	56.6	4.244	.223	65.6	4.93
.024	56.7	4.255	.314	71.1	5.34
.038	57.3	4.30	.388	101.9	7.65
.052	58.0	4.35			

Conductivities of the ether solution have not been measured, but are roughly proportional to the hydrogen chloride concentration. It will be seen that the true dielectric constant of ether is approached in an asymptotic way with decreased conductivity. It may be safely assumed that provided the conductivity is below a certain value further decrease in conductivity does not measurably alter the value obtained by the resonance method.

The above was still more thoroughly investigated in the case of water. Table IV gives the values of the apparent dielectric constants of the water solutions as calculated from the slopes and based on a value of 79.20 for pure water. Column A of the table gives the results obtained with the

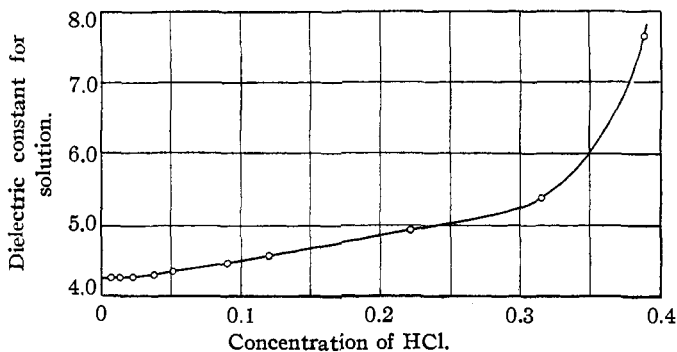


Fig. 2.

UX171A tube; column B the values obtained with the power tube using a current of 20 m. a.; column C the values obtained with the power tube using 60 m. a.

TABLE IV
EFFECT OF CONDUCTIVITY ON DIELECTRIC CONSTANT OF WATER AT 25°

Conductivity mhos 10 ⁶	Dielectric constant		
	A 171A tube	B UX210 tube 20 milliamp.	C UX210 tube 60 milliamp.
1.31	79.1		
3.3	79.0		
4.0	79.2	79.2	79.2
5.0	80.7		
5.6		80.5	80.5
6.6	82.9	81.8	81.4
7.5	84.5		
8.1		83.5	82.4
9.9	95.5		
12.0	101.8		
13.0		88.2	86.6
24.0		99.8	96.7
34.0		144.0	136.8
44.0			182.0

The results can best be correlated by means of Fig. 3, in which curves are lettered to correspond with the letter of the column in Table IV. It will be noted that in all cases the dielectric constant of conductivity water is approached asymptotically and that below a conductivity of 4×10^{-6} no difference in values is obtained; with increase in conductivity the values obtained alter with conductivity increasing rapidly in

magnitude beyond a certain point. The effect of increased power in the oscillator flattens out the curve, decreasing the influence of the conductivity of the medium. It would appear from the nature of the above curves that as long as the conductivity is below a certain value, depending on the power used, a true value of the dielectric constant is obtained. Furthermore, this is not a question of extrapolation such as would be necessary were the curve a straight line. The fact that the curve is apparently asymptotic to the value obtained for the medium when a non-conductor, greatly enhances the validity of making use of the resonance method.

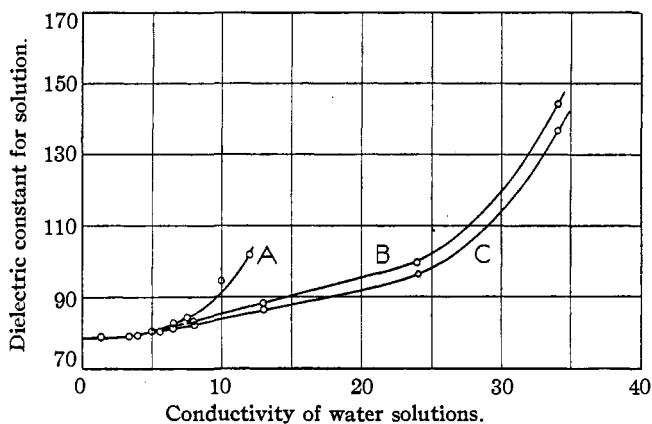


Fig. 3.

The emphasis brought about by recapitulation is perhaps warranted. It is true that the dielectric constant of water calculated from the slopes gives too high a value when the water conducts but the same limiting value is reached (independent of the power) when the conductivity is below 4×10^{-6} . It might be argued that since the purest water obtainable is still a conductor, this affects the value for the dielectric constant. In answer to this the experiments with ether show that with decreased conductivity the value obtained corresponds with that for pure ether, which is presumably a non-conductor. This value for ether, also, is in agreement with that found by other investigators.

Redetermination of the Dielectric Constant of Water.—The conclusion drawn from the above experiments is that the resonance method as described previously is not open to unanswerable objections. On the other hand, errors in the tuning condenser and dead space corrections would make it appear that the previous results referred to² need revision. Taking the necessary precaution in this connection the dielectric constant of water was redetermined by making use of benzene, ether, ethylene dichloride and nitrobenzene. The dielectric cell has been described in detail before.² This time for each set of stator and rotor plates three

media were used when possible as a counter check, and two series of investigations were made in each of which the dielectric cell was completely rebuilt.

TABLE V

DIELECTRIC CONSTANTS AT 25° OBTAINED IN VARIOUS SERIES FOR DIFFERENT CONDENSERS. EACH SET OF VALUES FOR A REBUILT CONDENSER

	17-Plate condensers	
Air	1.00	1.00
Benzene	2.273	2.270
Ether	4.250	4.258
	Benzene average	2.271
	7-Plate condensers	
Benzene	2.271	2.271
Ether	4.255	4.250
Ethylene dichloride	10.38	10.34
	Average of all ether values	4.255
	3-Plate condensers	
Ether	4.255	4.255
Ethylene dichloride	10.43	10.40
Nitrobenzene	35.30	35.20
	Average of all ethylene dichloride values	10.38
	3-Plate condensers (with twice distance between plates)	
Ethylene dichloride	10.38	10.38
Nitrobenzene	35.1	35.2
	Average of all nitrobenzene values	35.20
	3-Plate condensers (smallest capacity)	
Nitrobenzene	35.20	35.2
Water	79.40	78.9
	Average for water	79.2

In the table the first substance in each set is taken as standard, the value having been derived from the previous set. Values could be repeated with the accuracy indicated for each condenser set-up. With condensers having a large capacity greater uniformity could be obtained. The three-plate condenser of smallest capacity introduced the greatest error and two extremes are given for the water-nitrobenzene pair. In Table VI the values found for the various substances are tabulated. Each had been carefully purified.

TABLE VI

DIELECTRIC CONSTANTS, T 25°

Liquid.....	Benzene	Ether	Ethylene dichloride	Nitrobenzene	Water
Dielectric constant...	2.271	4.255	10.38	35.20	79.2

Discussion of Results

If the value for water is calculated in different ways by using various pairs of liquids, the greatest divergence is about one per cent. Without

again recapitulating the reasons that have been put forward in the first part of the paper, the authors are of the opinion that the resonance method as described can be used to give consistent results for the dielectric constant of a liquid such as water. The setting of the dielectric cell used involved a probable error of one-tenth to one-third of one per cent.; consequently in a series of stages (four in the case of water) the cumulative error may amount to 1%. Either a large number of observations will have to be taken or the dielectric cell improved. The authors are planning to investigate a cell of new design and redetermine the dielectric constant of water and also its temperature coefficient. In view of the results obtained the recalculated value for the dielectric constant of pure hydrogen peroxide at 0° is 93.5. By extrapolation of the dielectric constants of solutions of hydrogen peroxide in ether this value has been confirmed to within 0.5%.

Summary

The resonance method for the measurement of dielectric constants as described by Cuthbertson and Maass has been reinvestigated. A method for calibrating condensers, which vary in a linear manner according to their setting, is described. The effect of the power of the oscillating circuit has been examined and the precautions necessary in dealing with media of high dielectric constants specified. With a high power tube the harmonic is advocated as being better for the determination of the resonance point than the fundamental. The effect of the conductivity of the medium on the resonance point was shown to be negligible provided the conductivity was below 4×10^{-6} (in the case of water). Taking into account the necessary precautions the dielectric constant of water was found to be 79.2 at 25° by a step by step method based on 1.00 for air.

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