[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Purification of Water and its *p*H Value

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A series of experiments relative to purification of water and the determination of its *p*H value by the glass electrode[1] is described in this article.

The Still.—The still (Fig. 1) was designed to incorporate the principles both of Bourdillon[2] and of Weiland.[3] In the still of Bourdillon purified air is passed upward through a long condenser tube, countercurrent to the condensing water. In Weiland's still purified air is passed through the hot boiler before the actual distillation is started. Thus the combination of Weiland's method with that of Bourdillon allows volatile impurities to be partly or largely driven from the boiler before or during distillation while the remainder is removed as far as possible in the condenser tube.

The condenser, including joints, was made entirely of block tin. The tapered delivery tip and the small side tube near it were cast, machined to the required dimensions, and sealed to the main condenser tube. Two water jackets of brass were joined to the condenser tube by means of solder. The top water jacket was constructed so that cold water could enter at the top and provide more efficient condensation while the one at the bottom served to control the temperature of the dsitillate. The boiler, a round-bottomed Pyrex flask of 12-liter capacity, with long ring neck ground flat on top, was joined to the machined surface of the condenser by clamps. Heat was supplied by a gas hot-plate.

The neck of the flask, inclined and filled with glass beads, served as a very efficient spray arrester. The angle of inclination left most of the cross-section fairly dry and open for the free passage of steam and air. By this method the elimination of all spray, an absolute necessity in work of this type, was accomplished satisfactorily.

The glass tube through the top of the boiler was used for three purposes: (1) for filling the boiler *in situ;* (2) for eliminating volatile impurities with purified air; (3) for the prevention of bumping. As all three purposes are important, combined they make this tube indispensable.

Purification of Air.—The air was passed through the following train: (1) a capillary flow-meter; (2) four gas washing bottles (5 cm. × 18 cm.) half full of glass beads, the first three of which contained, respectively, sulfuric acid about 6–10 normal, sulfuric acid about 1 normal, sodium hydroxide about 6–10 normal, the final bottle being used to catch spray; (3) a series of five towers (3.5 × 29 cm.) each containing soda-lime, 8–14 mesh, 15% moisture; (4) a final tower (3.5 cm. × 29 cm.) containing a filter of tightly packed glass wool and cotton.

From this purification train the air passed directly to the still through glass tubing, connected by short lengths of extra heavy-walled rubber tubing. The rubber tubing and stoppers were steamed for half an hour and impregnated with castor oil *in vacuo* at 60 to 90°.

Receiving Vessels.—Walker and Smither[4] in a study of the characteristics of various glasses, concluded that Pyrex and Libbey varieties are about equally insoluble in water, and that in this respect they both excel "Non-sol," Jena, and all the other resistance glasses studied. Pyrex has been very popular as a container for very pure water.[5]

Other materials (*e. g.*, quartz, platinum, silver, and tin) have been used occasionally as containers, but there has been no definite comparison with glass.

In these experiments three different kinds of receiving vessels were used: (1) Pyrex Erlenmeyer flasks of 500-cc. capacity with Pyrex siphons; (2) "No-solvit" bottles of 2-liter capacity with Pyrex siphons; (3) silver flasks of 1-liter capacity with silver siphons.

In general, if the container is suitable, the *p*H value of the purified water will not change on standing, or will change very slowly. Also, if the *p*H values of water collected in containers of different material agree, this confirms the conclusion that none of them contaminate the water appreciably. By both of the above criteria, the three materials used were found reasonably satisfactory. Further refinement of the experiments would justify investigation of other materials. Tin especially, should be used since the condenser itself is made of tin.

Preliminary cleaning of all vessels was accomplished by scrubbing with soap solution, rinsing thoroughly, and steaming for an hour. Siphon tubes were similarly treated. This method of cleansing was found to be more satisfactory than the other well known methods.

Collecting a Sample.—The sample was collected and kept in a purified atmosphere at all times. To accomplish this, the receiver was closed with an impregnated rubber stopper through which the delivery tip of the condenser extended (Fig. 1), so as to avoid contact of water with the rubber. Purified air passed through the siphon tube into the receiver at a rate of 20–25 liters per hour and thence up through the condenser tube by way of the by-pass and stopcock V instead of the delivery tip of small bore, 2.5 mm. On account of the small bore of the tip and the continually renewed water held therein, atmospheric contamination of the lower condenser was prevented during times that the receiver was disconnected. A very slow distillation was sufficient to keep fresh relatively pure water at the bottom of the tip.

Before the receiver was connected to the condenser, it was flushed with purified air for a period of time. For this purpose, the hose was connected at both i and o; the unoccupied hole in the stopper, ultimately occupied by the delivery tip, was closed with a glass plug; and the

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[1] Ellis and Kiehl, THIS JOURNAL, **57**, 2139 (1935).

[2] Bourdillon, *J. Chem. Soc.*, **103**, 791 (1913); Bourdillon's still was later modified by: Clevenger, *J. Ind. Eng. Chem.*, **11**, 964 (1919); Bennett and Dickson, *Science*, **50**, 397 (1919); Bengough, Stuart and Lee, *J. Chem. Soc.*, 2156 (1927).

[3] Weiland. THIS JOURNAL. **40**, 131 (1918).

[4] Walker and Smither, *Technol. Papers Bur. Standards*, No. 107 (1918).

[5] Acree and Fawcett, *Ind. Eng. Chem., Anal. Ed.*, **2**, 78 (1930); Kolthoff and Kameda, THIS JOURNAL, **53**, 825 (1931).

three-way stopcock, V, was turned so as to discharge directly into the atmosphere instead of through the condenser. After thus flushing the receiver, stopcock V was turned so as to pass the purified air stream through the condenser again. After ten minutes longer the glass plug was removed, and the receiver quickly attached.

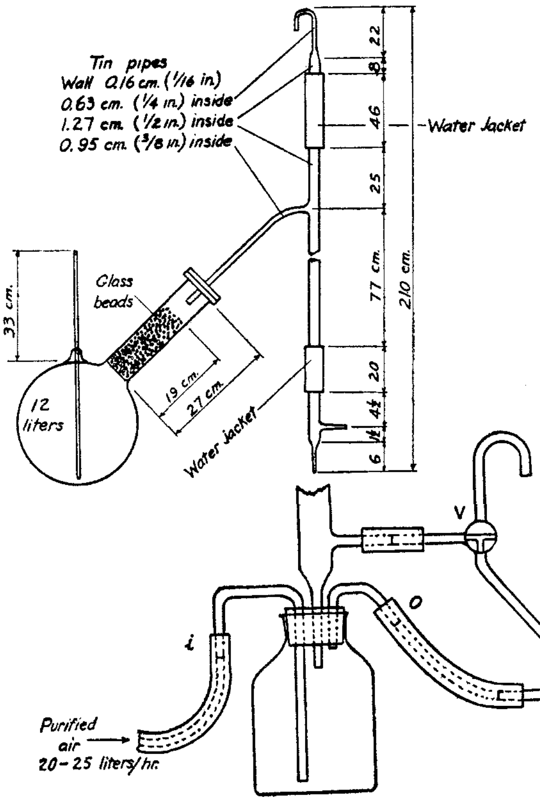

Fig. 1.

During and after disconnecting the receiver the air, uninterrupted, was forced through the hole previously occupied by the delivery tip. A three-way T-bore stopcock was then inserted and closed after the expulsion of the impure air. The hose connection at o was then broken and the glass tube tightly stoppered with a small impregnated rubber stopper or a paraffined cork. Hose connection i on the siphon tube was finally broken. The sample of purified water was then ready for use. A pressure of purified air through the three-way stopcock was used to obtain a portion of the sample through the siphon tube. The impure air was expelled from the stopcock through its side-tube, before the pure air passed into the receiver. The siphon tube in all experiments was attached directly to the top of the glass electrode.

Preliminary Experiments.—The once distilled water furnished to the chemical laboratories of Columbia University was always used for filling the boiler. This water which will be conveniently referred to as the stock distilled water, had a specific conductivity of roughly 10^{-6} reciprocal ohms, and a *p*H value of 6.1 to 6.5. Upon standing in the open, the *p*H soon dropped to approximately 5.8. A carefully conducted Nessler test on this water indicated that ammonia was present to approximately 0.004 part per million. Ammonia-free water prepared by distillation from phosphoric acid was used for comparison and for making all test solutions and standards of reference. "Aeration" of the stock distilled water by purified air caused its *p*H value to change in general from 6.3 to beyond 8.0. Continued aeration then caused this value to drop very slowly. The water contained both carbon dioxide and ammonia. Carbon dioxide is easily eliminated by aeration. Ammonia is removed very slowly. Table I illustrates the type of data which were obtained.

TABLE I

AERATION OF COLUMBIA DISTILLED WATER

Hours aerated	0	6	8	9.5	12	19.5	21
*p*H	6.3	8.05	8.13	8.18	8.22	8.17	8.13

Thirty to forty per cent. of the stock distilled water had to be distilled before a Nessler test of the distillate became negative or uncertain. The first fractions from the Bourdillon-Weiland apparatus always contained ammonia (0.1-0.2 part per million) and had a high *p*H (8.5 or more). Therefore from these experiments it appears that the Bourdillon still is capable of eliminating carbon dioxide but not ammonia.

Aeration of various fractions (32 in all) obtained from the Bourdillon-Weiland still, confirmed in a very conclusive way the general picture already described. The first fractions, those of *p*H higher than about 7.5, gave without exception a drop in *p*H when aerated. The later fractions of lower *p*H value showed very little change during prolonged aeration. Those samples with a *p*H value of 7.2 or less had a tendency slowly to become more alkaline, but seldom greater than 0.1 *p*H unit in twenty-four hours.

The *p*H values of water samples such as the above which are freed of volatile impurities may change during aeration because of contamination from containing vessels or the air stream, or because of an imperfectly closed container. The fact that very little change was actually observed over periods as long as forty-eight hours indicated that these combined effects were very small.

Purification of Water

The best method of procedure for preparing water of high purity is indicated by the data of Table II, shown graphically in Fig. 2.

When the stock distilled water was used in the boiler either alone (curve A) or with sodium hydroxide (curve B), the *p*H value of the first distillate was high (presence of ammonia). As distillation proceeded the *p*H value dropping finally tended to become constant at a value slightly higher than 7. Constancy was approached only after 50% of the charge in the boiler had been distilled. Even then there was probably a tendency to change as distillation proceeded. The *p*H value of the last fraction tended, in general, to be slightly higher than that of water distilled from phosphoric acid, which, as will be seen from curve

TABLE II (*cf.* FIG. 2)

COMPLETE DISTILLATIONS WITH VARIOUS REAGENTS IN BOILER

	A. Stock Distilled Water					
% distilled	6–10	20–25	44–49	58–64	69–85	
*p*H	8.62	8.02	7.26	7.19	7.12	
	B. Sodium Hydroxide, about 0.025 molar					
% distilled	1–5	6–13	13–18	20–39	41–49	51–57
*p*H	8.96	8.76	8.44	7.64	7.19	7.07
% distilled	58–64	64–70	70–76	77–84	85–92	
*p*H	7.19	7.21	7.11	7.26	7.29	
	C. Nessler Reagent, 25 cc. per liter of water					
% distilled	5–10	19–24	44–58	62–81		
*p*H	8.31	7.31	6.80	6.52		
	D. Stock Distilled Water Following Nessler Reagent					
% distilled	0–5	9–14	17–22	27–47	55–60	69–74
*p*H	8.24	7.54	7.05	6.30	6.58	6.59
% distilled	76–81	82–87				
*p*H	6.81	6.69				
	E. Phosphoric Acid, about 0.025 molar					
% distilled	4–10	10–14	16–21	22–33	34–39	40–44
*p*H	7.09	7.09	6.99	7.06	7.02	7.12
% distilled	45–50	51–64	65–73	73–78	78–86	
*p*H	6.98	7.00	7.02	7.15	6.94	

E, was constant throughout the distillation. It seems perfectly logical on this basis to conclude that the samples distilled from alkali or from water alone were never entirely freed of ammonia.

Confirmation of this conclusion is afforded by a study of the curves shown in Fig. 3 for the different fractions distilled from alkali. E. m. f., or apparent *p*H, is plotted against rate of flow through the glass electrode.[1] The first fraction distilled contained sufficient ammonia (easily verified by a Nessler test) to make the solution definitely alkaline and to render its measurement in a glass electrode very easy—curve A of Fig. 3. The second fraction gave a curve (not shown) very similar to A with the horizontal part not quite so perfect at lower rates of flow. The third fraction, curve B of Fig. 3, began to show a slight somewhat doubtful inflection, and a definite indication that the glass was contaminating the water at lower rates of flow. The fourth fraction gave a typical inflected curve C, with a considerable alkaline effect from the glass at lower rates of flow. Curve C remained more or less representative of all subsequent fractions—the last of which was taken when 92% of the water in the boiler had been distilled. A comparison of the curves of Fig. 3 with the types described in the previous paper[1] demonstrates their similarity to those obtained with contaminated water (*e. g.*, millionth molar KCl or Na_2HPO_4). None of them have the same shape as that for highly purified water distilled from phosphoric acid. Hence, this evidence contributes further to the conclusion that ammonia was not entirely eliminated at any time during the distillation of neutral or alkaline water.

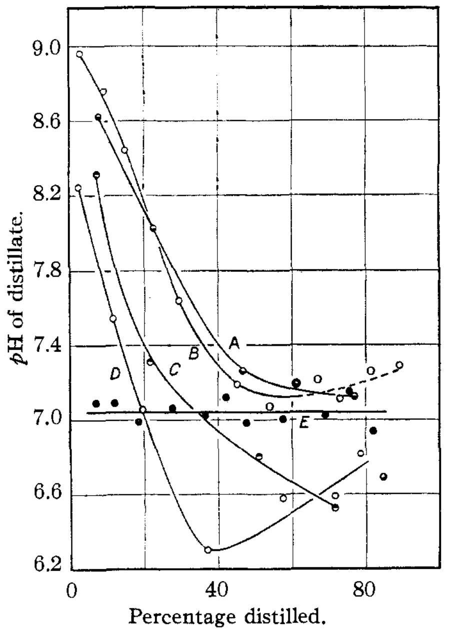

Fig. 2.—Distillations with various reagents in boiler (*cf.* Table III).

Any non-volatile reagent, which added to the boiler could hold or destroy both carbon dioxide and ammonia, would obviously be a valuable aid in purifying water. For this purpose Kendall,[6] and Fales and Nelson[7] have used Nessler reagent. Some data for Nessler reagent are plotted in curve C of Fig. 2. That it failed to hold ammonia was demonstrated not only by the high initial *p*H values, but also by direct Nessler tests for ammonia which were made on the distillate. Furthermore, as distillation proceeded, the *p*H of the supposedly purified water continued to drop. The most reasonable explanation for this anomalous gain of acidity seems to be that a small amount of iodine set free from the Nessler reagent was carried over with the current of air and steam.

After the distillation from the Nessler reagent, the boiler was disconnected from the condenser and cleaned by thorough rinsing with distilled water (a dozen or more separate rinsings). Stock distilled water was then added and a distillation completed as shown by curve D of Fig. 2. Ammonia came over with the first fractions as usual,

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(6) Kendall, THIS JOURNAL, **38**, 2460 (1916).

(7) Fales and Nelson, *ibid.*, **37**, 2782 (1915).

but the pH of the distillate continued to drop to a minimum value of 6.3, after which it rose again to about 6.8. From this behavior it would seem reasonable, as a speculation, that sufficient iodine had accumulated in the condenser from the previous distillation to contaminate the water for a considerable time afterward. In any event the experiments (C and D of Fig. 2) leave no doubt concerning the utter futility of attempting to use Nessler solution in the boiler. In consequence of the experiments with Nessler reagent it was necessary to cleanse the system thoroughly. To accomplish this the still was operated for a whole day with the cooling water off part of the time.

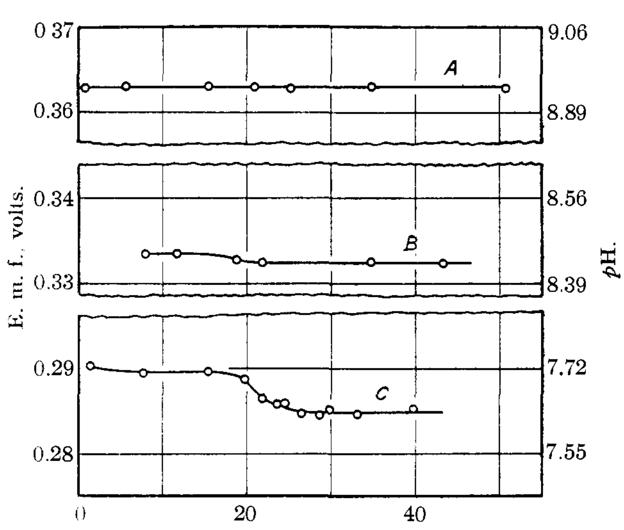

Fig. 3.—Samples of water distilled from NaOH (Table III) and measured with cylindrical glass electrode C5: A, first fraction collected, boiler emptied 1–5%; B, third fraction, boiler emptied 13–18%; C, fourth fraction, boiler emptied 20–39%.

The horizontal line E of Fig. 2, representing a distillation from phosphoric acid, shows that the acid retained all ammonia in the boiler, and that the modified Bourdillon still was capable of eliminating the carbon dioxide. The first fraction distilled had the same pH as the later fractions, and upon the rough basis of streaming potentials measured in the glass electrode,[1] they had about the same low conductivity. During the entire course of the distillation, samples of high purity could be collected. The superiority of such a distillation over the others is strikingly emphasized by the curves.

To eliminate volatile matter, the phosphoric acid was carefully heated for twenty minutes with the evolution of white fumes. Phosphorus pentoxide used without preliminary treatment was satisfactory.

Potassium permanganate both in acid and alkaline solution has been very commonly used in boilers for the purification of water. When permanganate was added to the boiler in the presence of alkali, curve B of Fig. 2 remained essentially unchanged; in other words ammonia was not thus eliminated by oxidation. When permanganate was used in the presence of acid, it likewise served no useful purpose; the acid held the ammonia in any case. The situation as regards the use of permanganate may be different if the boiler water contains appreciable quantities of organic or other oxidizable impurity. No such water has, however, been used in this research.

The pH of Purified Water

A series of measurements, summarized by Table III, was undertaken for the purpose of estimating as accurately as possible by the technique previously described the pH of purified water. During a series of four complete distillations at the rate of 800 cc. per hour from phosphoric acid (20 g. of P_2O_5 in the boiler) samples were collected in Pyrex, "No-solvit" and silver containers. The lower water jacket on the condenser was used to control the temperature of the condensate and keep it as nearly as possible that of the room. Hence the pH values could be measured immediately. Although more samples were collected in silver than in glass, the data for silver, nevertheless, cover exactly the same series of distillations as are covered by the two kinds of glass. Therefore, differences between the various containers cannot be due to differences between successive distillations. The four distillations themselves showed no significant difference of any kind.

A single glass electrode of cylindrical shape[1] made of ordinary soft (soda-lime) glass was used for all the measurements of Table III. Potassium acid phthalate (0.05 molar, pH 3.97) was employed as the reference buffer, and the difference of potential (ΔE) between it and the water is listed in the second column of the table. The buffer and the glass electrode were both checked by means of the hydrogen and quinhydrone electrodes. All measurements were made with the purified water flowing through the glass electrode[1] and each value listed in the table is the

TABLE III

THE pH OF PURIFIED WATER

Room temp., °C.	ΔE[a]	pH	Room temp., °C.	ΔE[a]	pH
			Pyrex containers		
28.5	0.1854	7.07	28.5	0.1900	7.15
27.5	.1880	7.12	26.0	.1858	7.10
28.5	.1870	7.09	25.0	.1880	7.15
31.0	.1889	7.10			
			"No-solvit" containers		
28.5	.1826	7.04	31.0	0.1864	7.06
27.0	.1861	7.09	29.5	.1822	7.00
26.0	.1880	7.14			
			Silver containers		
28.0	.1818	7.01	28.5	0.1774	6.94
28.5	.1774	6.94	24.5	.1825	7.06
28.0	.1824	7.02	25.5	.1835	7.07
27.0	.1817	7.02	26.5	.1730	6.88
27.0	.1797	6.99	25.5	.1816	7.03
27.5	.1864	7.09	27.5	.1770	6.94
29.0	.1810	6.99	27.5	.1861	7.09
31.5	.1846	7.02	24.5	.1771	6.97
30.5	.1815	6.98	25.5	.1840	7.08
29.0	.1828	7.02			

[a] ΔE represents the potential difference as determined by the glass electrode, between water and the standard phthalate buffer pH 3.97.

MEAN VALUES

Containers	Average temp., °C.	Average, pH	Average deviation from mean pH
Pyrex	27.9	7.11	0.024
"No-solvit"	28.4	7.07	.039
Pyrex and "No-solvit" comb.	28.0	7.09	.034
Silver	27.4	7.01	.045

mean of two or three (sometimes more) readings taken at different rates of flow. Obviously only rates of flow on the straight horizontal part of the e. m. f.–flow curve were used.

The significant difference between measurements made in silver and those made in glass (Table III) indicates that the glass contributes a very small alkalinity to the water. Whether or not the silver likewise contributes alkalinity is left in doubt. However, the results of experiments previously described in which samples of water were kept for comparatively long periods in the various containers would indicate that if any such effect is present it must be very slight.

The most probable pH value of water to be deduced from the data of Table III is undoubtedly the mean of the silver series, namely, 7.01 at approximately 27.5°. The precision of this figure is about 0.01 pH unit, measured in terms of the so-called "average deviation of the mean," commonly abbreviated A. D. The fluctuations of temperature as they ordinarily occur in a room could account for a greater pH change than this, but it is probable that successive series of nineteen measurements would give averages that were consistent within the meaning of this precision.

The value for the pH of water here obtained is in substantial agreement with accepted figures and with the best previous direct measurements.[4,5,8,9] The present measurements, however, are unique in that they represent a direct determination made upon a highly purified water to which no foreign material of any kind had been added, neither "isohydric" indicator nor gaseous hydrogen with platinum black.

Summary

1. Methods for the purification of water have been investigated and important information concerning this general problem has been obtained.

2. The pH value of the purest water, collected in silver vessels, has been measured directly by means of the glass electrode and found to be 7.01 at 27.5°.

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(8) Beans and Oakes, THIS JOURNAL, **42**, 2116 (1920).

(9) Kling and Lassieur, *Ann. chim.*, **15**, 201 (1931).