was slowly added during a period of about fifty minutes, being careful not to let the temperature rise above +5°. Stirring was continued for an additional two hours, during which the temperature was allowed to rise to 15°. The mixture was then washed with three 100-ml. portions of water and the benzene distilled off on a steam-bath. The residue was then distilled at lowest possible pressures. The product distilled at 165–185° at 2 mm.; yield, 70.6 g., 79%. Found: N (Kjeldahl), 6.26; calcd. N for $C_{12}H_{17}O_3N$, 6.28.

t-Octylnitrophenol.—This was prepared from *t*-octylphenol in a similar manner. The product distilled at 157–168° at 1 mm.; 97% yield. Found: N, 5.58; calcd. N for $C_{14}H_{21}O_3N$, 5.61.

The nitration of *s*-hexyl-*m*-cresol was carried out similarly and every evidence indicated that the reaction proceeded normally. However, at the distillation temperature, the product began to decompose, and the decomposition progressed spontaneously and could not be stopped by cooling the distillation flask.

Neither compound showed any decided fungicidal activity when tested against a mold culture by the Agar Cup Plate Method.[3]

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(3) These tests were made by S. R. Pence and W. A. Feirer, to whom the authors acknowledge their thanks.

MEDICAL-RESEARCH DIVISION
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The Qualitative Determination of Cadmium in the Presence of Copper

BY ALBERT C. HOLLER

This paper describes a qualitative determination of cadmium in the presence of copper. The principle is that described by Sachs,[1] who states that a number of insoluble hydroxides are colored by a 1% alcoholic solution of phenolphthalein. He ascribes this to the activated adsorption of phenolphthalein on the hydroxide.

The procedure was worked out to fit into the method used to analyze group II as described by Engelder,[2] but may be applicable to other schemes.

The copper and cadmium were present in approximately equal amounts (about 30 mg. of each). It has been determined that cadmium can be detected in the presence of copper when the copper–cadmium ratio is as large as 10 to 1.

Procedure.—The filtrate from the lead separation is neutralized with ammonium hydroxide and the bismuth hydroxide is filtered off in the usual way.[2] If copper is present the filtrate will be colored deep blue. The solution is neutralized with nitric acid and 5 cc. of concd. nitric acid added. The solution is evaporated to dryness and the residue ignited below a dull red heat until the volatilization of ammonium salts is complete. The baked residue is then dissolved in 1.5 cc. of dilute nitric acid and the volume adjusted with water to 25 cc. Twelve cc. of 0.5 *N* sodium hydroxide is added to the solution. The hydroxides of cadmium and copper are filtered off and washed once with water. The hydroxides are then spotted with a 1% alcoholic solution of phenolphthalein and moistened with a few drops of water.

A crimson color indicates the presence of cadmium.

Copper hydroxide does not adsorb phenolphthalein when the hydroxide is prepared using a 10% excess of the salt (cupric nitrate) and thus does not form a colored compound.

I wish to express my appreciation to Mr. H. R. Heiple who helped me prepare this paper.

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RECEIVED JANUARY 14, 1941

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(1) Sachs, THIS JOURNAL, **62**, 3514 (1940).

(2) Engelder, "Elementary Qualitative Analysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1933, pp. 119 and 124.

The Exchange of Sulfate Ion with Water

BY JAMES L. HYDE

The oxygen exchange of sulfate ion has been studied in acid, neutral and alkaline solutions. Heavy oxygen water, prepared by fractional distillation,[1] was obtained through the courtesy of Professor Merle Randall, and was distilled from alkaline permanganate before use. Analysis of the water[2] was performed with a mass spectrometer. After placing each sample, whose composition is shown in the table below, in a sealed tube in a thermostated bath for the indicated time, two cubic centimeters of water was distilled off *in vacuo*, and this water analyzed in the same way. The precision of analysis was ± 1%.

The alkaline exchange experiment was performed in a sealed platinum bulb similar to the silver one used by Winter, Carlton and Briscoe[3] in order to avoid any possible interference by glass. The results are tabulated below.

In a recent publication Hall and Alexander,[4] who used solutions containing lower concentrations of hydrogen ion and hydroxyl ion, respectively, reported results which were similar except for the fact that their exchange in acid solution was incomplete.

Our results are also in agreement with those of all other observers[3,5,6] for the neutral solution.

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(1) Randall and Webb, *Ind. Eng. Chem.*, **31**, 227 (1939).

(2) Cohn and Urey, THIS JOURNAL, **60**, 679 (1938).

(3) Winter, Carlton and Briscoe, *J. Chem. Soc.*, 131 (1940).

(4) Hall and Alexander, THIS JOURNAL, **62**, 3455 (1940).

(5) Datta, Day and Ingold, *J. Chem. Soc.*, 1968 (1937).

(6) Titani and Goto, *Bull. Chem. Soc. Japan*, **13**, 667 (1938); **14**, 77 (1939).

TABLE I

	H_2SO_4 (96%)	Na_2SO_4	NaOH	Na_2SO_4
Solutes, g.	9.125	2.10	2.84	1.68
Water, g.	9.93	5.00	4.00	
% O^{18} in water	0.79	0.79	0.84	
% O^{18} in water of orig. soln. (calcd.)	0.77	0.79	0.675	
Temp., °C.	100	100	100	
Time (hrs.)	59	87	84	
Vessel	Pyrex	Pyrex	Platinum	
% O^{18} in water recovered	0.55	0.79	0.67	
Obsd. decr. in % O^{18}	0.22	0.00	0.005	
% decr. calcd. for compl. exch.	0.22	0.11	0.06	
Amt. of exch.	Complete	None	None	

We also agree with Winter, Carlton and Briscoe for alkaline solution, but disagree with Datta, Day and Ingold.

Partial exchange has been observed for potassium acid sulfate by Titani and Goto and by Mills.[7] Winter, Carlton and Briscoe observed no exchange of sulfate in acid solution, but we must disagree with this observation.

Our results, coupled with those of Mills for potassium acid sulfate, lead us to postulate, as the mechanism for the exchange of sulfate, the same type of reversible anhydride formation which has satisfactorily accounted for the exchange of carbonate under all conditions of acidity.[8] The difference in the rates appears to be chiefly due to the fact that sulfuric acid is a stronger acid than carbonic, and that a much smaller quantity of the anhydride is present in solution.

[7] Mills, THIS JOURNAL, **62**, 2833 (1940).

[8] Mills and Urey, *ibid.*, **62**, 1019 (1940).

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Density of Perchloric Acid Solutions

BY AARON E. MARKHAM

Data in the literature on the density of perchloric acid cover only a limited range of concentration. In this work, the density at 25° has been determined over the range up to 65% concentration. Measurements were in a 25-cc. pycnometer, the volume found by weighing filled with water, weights reduced to vacuum. The solutions were made from a stock solution of C. P. acid, meeting A. C. S. specifications. Its concentration was found by density and the data of Smith and Goehler[1] to be 71.209%. Titration confirmed this concentration.

The estimated maximum error, based on the differences of duplicate determinations, is about five in the last figure.

Measurements at 30° at intervals of 10% give a basis for estimating the temperature coefficient of density, over the range 25° to 30°. Empirically, $\Delta d/\Delta t = -(28 + 1.4x)10^{-5}$ in which x is the per cent. of acid.

The empirical equation which most nearly fits these data is:

$$d^{25}{}_4 = 0.99707 + 0.00562796x + 0.0000230045x^2 + 0.00000049593x^3$$

The maximum deviations of this equation over portions of the concentration range are:

Range	Maximum error in $d^{25}{}_4$	Maximum error in x
0 – 20%	0.00027	0.045
20 – 40	0.00006	0.006
40 – 65	0.00298	0.222

Wt. per cent. acid	$d^{25}{}_4$	$d^{30}{}_4$
0	(0.99707)	(0.99568)
1	1.00265	
2	1.00828	
4	1.01975	
6	1.03154	
8	1.04355	
10	1.05591	1.05388
12	1.06862	
14	1.08163	
16	1.09498	
18	1.10866	
20	1.12280	1.11999
22	1.13734	
24	1.15224	
26	1.16761	
28	1.18359	
30	1.20002	1.19651
32	1.21697	
34	1.23446	
36	1.25259	
38	1.27130	
40	1.29073	1.28658
45	1.34252	
50	1.39937	1.39435
55	1.46134	
60	1.52766	1.52177
65	1.59628	

The value which Smith and Goehler gave for the density at 65% concentration was 1.59665. This value was found by interpolation between two points at some distance apart, using a straight line. Since the analysis of the acid used depends on their data, closer agreement than this with

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[1] Smith and Goehler, *Ind. Eng. Chem., Anal. Ed.*, **3**, 61 (1931).