fracture of the Töpler pump chamber and delivery tube. Stopcocks have been eliminated from the pumping cycle and a minimum quantity of dried and filtered air comes in contact with the mercury in the pump reservoir; the mercury is consequently not fouled through contact with lubricants or moist air. The mercury delivered by the Töpler pump is automatically returned to the cycle, while the gas pumped is automatically collected and may be transferred as desired to other units.

The control system is entirely independent of the vacuum pump and may find other applications in which alternating vacuum and pressure are desired.

WASHINGTON, D. C.

SOME PROPERTIES OF COLLOIDAL LEAD

BY HELEN QUINCY WOODARD

In the course of the preparation of colloidal lead suitable for clinical use a number of the properties of lead sols prepared by the Bredig method[1] have been studied. The more outstanding of these properties are presented below.

Apparatus and Method.—The apparatus was the same as that described by the author elsewhere.[2] The anode was $1/16$-inch commercial sheet lead from the National Lead Co. The cathode was a roll of "Pueblo" lead foil from the American Smelting and Refining Co. Baker's "C. P." reagents and Eimer and Amend's "C. P." and "Tested Purity" reagents were used and were not further purified. The approximate currents used at different times are given below, temporary fluctuations up to $\pm 10\%$ of the values given being caused by irregularities in the arc: 1.4 amps., 40 volts; 3.8 amps., 50 volts; 7.0 amps., 60 volts. The temperature range was 10–35°.

Properties.—The colloidal lead was dark gray and fluorescent when first prepared, turning blue-black after being centrifuged or being allowed to stand for a few hours. It was brown by transmitted light. The particles carried a positive charge, as shown by their migration in an electric field. When a current passed directly through a sol, the lead coagulated to tree-like growths on the electrodes.

When protected from air by paraffin seals about 5 mm. thick the sols would keep for from three to nine weeks before coagulating. If, however, they were left with a large surface in contact with the air, they rapidly

[1] Bredig, *Z. angew. Chem.*, **12**, 951 (1898).
[2] Woodard, *Ann. Sur.*, 607, Oct., 1927.

developed an area of clear supernatant liquid, as observed by Stenström and Reinhard.[3] Sols left uncovered in this way soon settled out.

The colloidal lead was readily coagulated by electrolytes. Sulfuric acid, sodium carbonate, sodium bicarbonate, potassium hydroxide and sodium chloride, when added to sols stabilized by potassium hydroxide in amounts sufficient to bring the final concentration of added electrolyte to 0.001 N or higher, caused visible coagulation in a few minutes. The electrolytes mentioned had about equal precipitating power in equinormal concentrations, but acetic acid had much less effect. The coagulation time could not be determined accurately but was roughly inversely proportional to the age of the sol.

All the sols could be coagulated by shaking with air or with carbon dioxide. The time of shaking required to coagulate a sol under given conditions decreased with increasing age of the sol.

Series of sols were made by arcing in different electrolyte solutions. The concentrations of stable colloidal lead prepared under different conditions are shown in Table I, the criterion of stability being the ability of

TABLE I

Electrolyte	P_H of initial soln.	Current, amps.	Number of sols	Average concn., % Pb	Average dev. from av., %
0.00025 M HCl	3.6	1.4	15	0.038	±20
.000125 M H₂SO₄	3.6	1.4	5	.039	±19
.00022 M CH₃COOH	5.2	1.4	6	.050	±24
H₂O only	5.5	1.4	6	.050	±14
.000124 M NaCl		1.4	5	.082	±11
.00025 M NaCl	5.6	1.4	6	.100	± 8
.00050 M NaCl		1.4	5	.091	±18
.00099 M NaCl		1.4	3	.040	±12
.000125 M NaHCO₃	8.3	1.4	5	.083	±17
.000125 M Na₂CO₃	9.2	1.4	5	.098	±13
.00011 M KOH	8.8	1.4	5	.104	±15
.00022 M KOH	10.0	1.4	63	.122	±15
.00044 M KOH	..	1.4	6	.130	±14
.00087 M KOH	..	1.4	3	.067	±12
.00022 M KOH	..	3.8	13	.152	±19
.00022 M KOH	..	7.0	29	.187	±18

the sol to withstand centrifuging for five minutes at a force of 1000 × gravity. The average deviations from the average concentrations of sols in each electrolyte series are rather large in comparison to the differences in the average concentrations of sols in different series. Nevertheless, a comparison of the different series brings out the following relationships fairly clearly.

(1) The concentration of colloidal lead stabilized by 0.00022 M potassium hydroxide at currents of 1.4–7.0 amps. is directly proportional to the current used.

[3] Stenström and Reinhard, J. Biol. Chem., 69, 607 (1926).

(2) For the entire range of electrolyte solutions examined with the exception of the neutral salt sodium chloride, the concentration of colloidal lead stabilized by equi-normal solutions of different electrolytes is a function of the P_H of the initial solution; see Fig. 1. (Note that the P_H values given in the table were obtained from solutions that had cooled from the boiling point in the apparatus in contact with the electrodes. Considerable lead is dissolved under these conditions.)

(3) For the electrolytes potassium hydroxide and sodium chloride, the concentration of stable colloidal lead dispersed by a given current rises with increasing electrolyte concentration up to a maximum which is reached in the neighborhood of 0.0003 M, and then falls; see Fig. 2. It could not be determined whether the curves finally drop to zero, owing to the extreme difficulty of maintaining an arc in high electrolyte concentrations, and the latter portions of the curves are ill defined for the same reason.
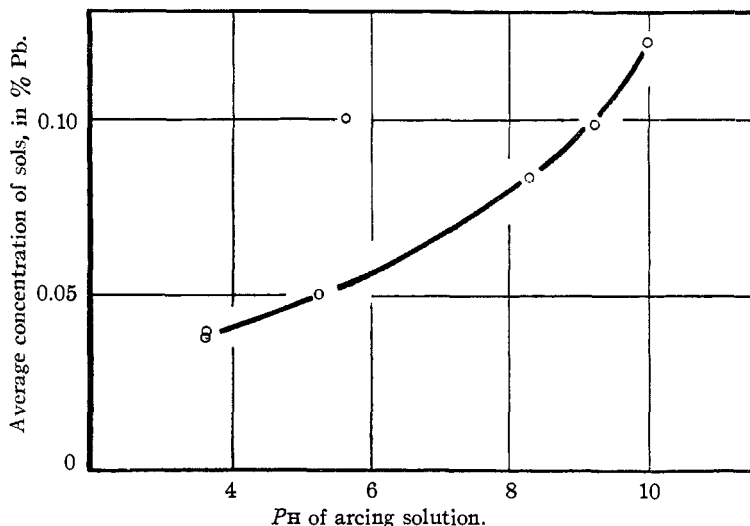

Fig. 1.—Lead sols in approximately 0.00025 N solutions of different electrolytes. Relation of concentration of sol to P_H of arcing solution.

The relation of the concentration of lead sols to the weight of lead dis-integrated from the cathode during the preparation of the sols offers an interesting contrast to the relationship found by the author and others for the similar sols of gold, silver and platinum.[4] Thus, the concentration of gold, silver and platinum sols rises to a maximum during arcing, and then, on further arcing, falls, sometimes rather rapidly, to zero. With lead sols, on the other hand, the concentration rises rapidly to a maximum during arcing, and further arcing, even when quite prolonged, does not show any tendency to cause the concentration of colloidal lead which is stable to five minutes centrifuging with a force of 1000 $\times$ gravity to fall below this maximum. This is true of sols in all the different electrolyte solutions examined. Table II gives a typical example. The relation for uncen-

[4] Briggs, *Dissertation*, Columbia, **1923**; Woodard, *Dissertation*, Columbia, **1925**; Baeyertz, *Dissertation*, Columbia, **1924**.

<div align="center">

TABLE II

CENTRIFUGED SOLS IN 0.00025 M NaCl AT 1.4 AMPS.

</div>

Lead disintegrated, g.	Concn. sol, % Pb	Lead disintegrated, g.	Concn. sol, % Pb
1.30	0.104	2.13	0.089
1.66	.099	2.69	.110
2.06	.109	3.63	.089

trifuged sols is much less consistent than for centrifuged ones, and the maximum of concentration is reached later.
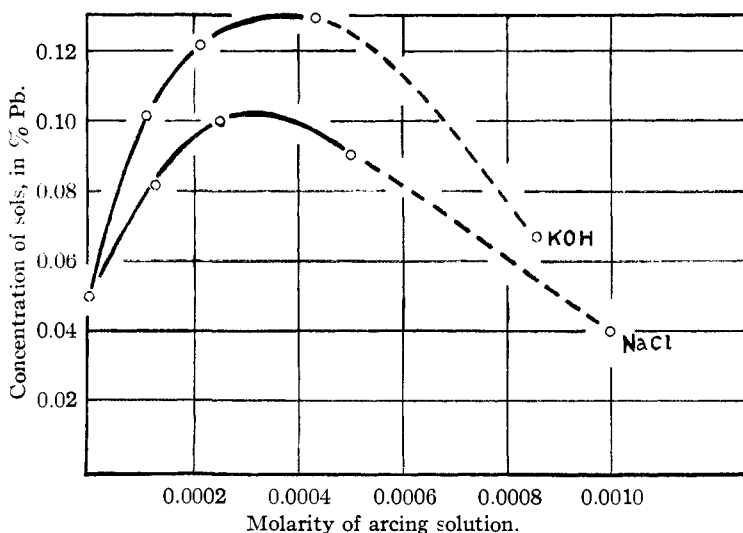

Fig. 2.—Lead sols in solutions of potassium hydroxide and sodium chloride. Relation of concentration of sol to concentration of arcing solution.

The behavior of lead sols under the influence of gravitational force also differs from the analogous behavior of gold sols under centrifugal force, and in general from the settling of dispersions of mixtures of particles of different degrees of stability.[5] This was shown by a study of uncentrifuged sols which were allowed to stand in cylinders 30 cm. high with an internal diameter of 4–4.5 cm. The surfaces of the sols were covered with paraffin. Samples were withdrawn for analysis from the center of the column of liquid from time to time. Typical curves obtained by plotting concentration against time of standing are shown in Fig. 3. These curves show, as expected, an initial rapid drop in concentration as the unstable particles settle out. This is followed by a period of nearly constant concentration, as with colloidal gold. After a time the influence of a cumulative precipitating is apparent. Visible coagulation begins and the con-

[5] Ayres, *Chem. Met. Eng.*, **16**, 190 (1917); Davidson, *Dissertation*, Columbia, **1924**.

centration falls rapidly to zero.   This was observed in sols stabilized by acids, neutral salts and alkalies alike.   A similar but less marked effect
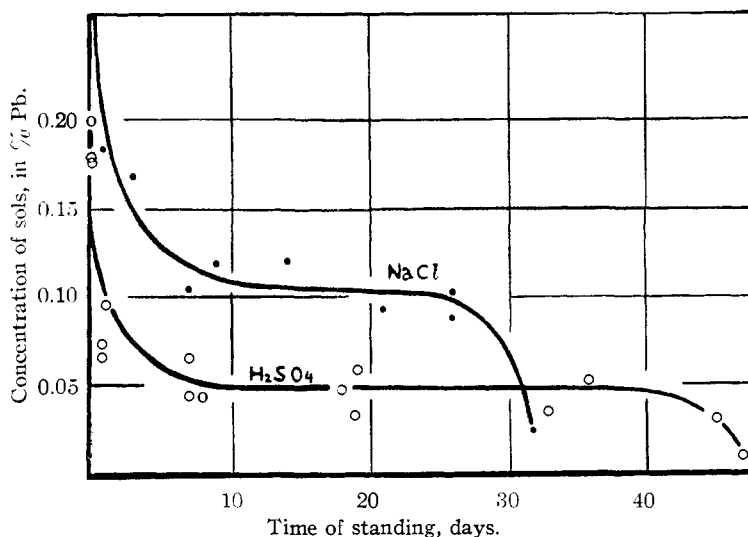

Fig. 3.—Lead sols in 0.000125 M H$_2$SO$_4$ and in 0.00025 M NaCl.   Change of concentration on standing.

was observed in sols which had been centrifuged for five minutes;   see Table III.   In view of the readiness with which the sols can be coagulated

TABLE III

CHANGE IN CONCENTRATION OF CENTRIFUGED SOLS IN 0.00022 M KOH AT 7.0 AMPS.

No. sols	Time, days	Original concn. remaining, %	No. sols	Time, days	Original concn. remaining, %
8	5	100	5	30	70
8	10	98	5	35	55
8	15	93	5	40	38
8	20	89	5	45	17
8	25	83	5	50	9

by shaking with air, it seems probable that the precipitation is caused by the oxygen and carbon dioxide which are absorbed through the paraffin seals.

Summary

The concentration of stable colloidal lead prepared by the Bredig method has been found to be proportional to the current used in the preparation of the colloid and to the PH of the initial solution in which the arcing is done.

The concentration of colloidal lead has been found to rise to a maximum with increasing concentration of stabilizing electrolyte used, and then to fall as the concentration of stabilizing electrolyte is further increased.

Some properties of Bredig colloidal lead have been compared with the corresponding properties of colloidal gold, silver and platinum.

NEW YORK CITY

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF LITHIUM NITRATE IN CERTAIN MIXED SOLVENTS[1]

BY J. L. WHITMAN AND S. R. SPENCER

As part of some investigations being carried on in this Laboratory, it was found desirable to make a series of measurements of the conductivity and viscosity of solutions of lithium nitrate in mixtures of methyl alcohol and ethyl alcohol, and of methyl alcohol and water. Such measurements have previously been made by Jones and Lindsay[2] and by Jones and Carroll,[3] but it seems desirable to report the more extended series of measurements which we have made.[4]

Materials

Lithium Nitrate.—This was prepared from pure lithium carbonate and c. p. nitric acid, was recrystallized five times from conductivity water and was then shown to be free from impurities by a spectroscopic test. The drying of the salt was found to be more difficult than would be indicated from the literature. Anhydrous material could only be obtained by prolonged heating at 150° in a vacuum. This probably accounts for the fact that the values here recorded are uniformly higher than the values previously reported.

Water.—Laboratory distilled water was electrically redistilled from alkaline permanganate and had a conductivity of 1 to 1.2×10^{-6}.

Alcohol.—A good grade of ethyl alcohol was successively treated with lime, metallic calcium, silver nitrate and finally again with lime prepared according to Danner and Hildebrand.[5] Thus prepared it had a conductivity of about 3×10^{-7}, while methyl alcohol prepared in a similar manner had a conductivity of 2×10^{-6}.

Solutions.—Dry lithium nitrate was weighed into a quartz flask, solvent of the required composition then being added to give a solution of the greatest desired concentration. More dilute solutions were made by adding solvent in the required amount to this stock solution.

Apparatus and Measurements

A Leeds and Northrup Kohlrausch slide wire bridge with extension coils, a microphone hummer, tunable head phones, Curtis coil resistance boxes, adjustable air con-

[1] The data reported in this paper constitute a portion of a Dissertation presented to the Graduate Faculty of the State University of Iowa by S. R. Spencer, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Jones and Lindsay, Am. Chem. J., 28, 329 (1902).

[3] Jones and Carroll, ibid., 32, 521 (1904).

[4] For a summary and review of the work of Jones in the field of conductivity in mixed solvents see Jones and Kreider, ibid., 45, 282 (1911).

[5] Danner and Hildebrand, THIS JOURNAL, 44, 2824 (1922).