1000–1100° gave a white magnesium pyrophosphate. Both methods gave an average error of -0.05% (0.2000g. sample of phosphate).

6. The advantage in Method A is that in the absence of molybdate ions it is easier to produce a crystalline precipitate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 559]

THE ACTION OF ULTRAVIOLET LIGHT ON SOME COLLOIDAL DISPERSIONS OF GOLD[1,2]

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Introduction

The study of the effect of radiation upon colloidal dispersions of gold has been the object of numerous investigations. The earliest of these dealt with the reducing action of light upon gold salts, with the accompanying formation of a colloidal dispersion.[3] The accelerating effect of light during the reduction of gold salts by various reducing agents has also been known for some time.[4]

A comprehensive study of the significance of light in the formation and stability of colloidal gold has been made by Nordenson.[5] His paper contains a valuable survey and criticism of previous work on this problem. He investigated the effect of light upn the reduction of chlorauric acid by hydrogen peroxide. Reduction proceeds in the darkness or diffuse daylight with the formation of a coarse, bluish suspension. The exposure to the radiation of a quartz mercury-vapor lamp, during the reduction, leads to the formation of stable sols. The degree of dispersion and the color depend upon the length of the exposure. The sols prepared in this manner were examined spectrophotometrically as well as with the ultramicroscope and the dependence of the properties upon time of exposure was demonstrated. In addition he observed a coagulating effect of the

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[1] The abstract of a thesis presented to the Graduate Faculty of Columbia University by Ralph H. Muller, October, 1925, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Presented at the September, 1926, Meeting of the American Chemical Society.

[3] (a) Hellot, "Hist. de l'Acad. de Scien.," **1737,** p. 101; (b) Scheele, see Plotnikow, "Lehrbuch der Photochemie," **1920,** p. 361; (c) Krüss, *Liebig's Ann. Chem.*, **43,** 237, 238, 276 (1887); (d) Rumford, Eders "Photochemie," p. 179; (e) Juch, Eders "Photochemie," p. 179; (f) Fulhame, *Ann. chim.*, **26,** 58 (1798).

[4] (a) Pelletier, *Schweigg Jour.*, **31,** 317 (1800); (b) Herschel, "Hunt's Researches on Light," **1844;** (c) Döbereiner, *Schweigg Jour.*, **62,** 86 (1831); (d) Sonstadt, *Eders Jahrbuch f. Phot. Ind.*, **1899,** 466.

[5] Nordenson, *Inaug. Diss.*, Univ. of Upsala, **1914;** *Z. physik. Chem.*, **90,** 603 (1915).

ultraviolet light which is similar to that induced by weak electrolytes. He was convinced that the coagulation is not due to a photo-electric effect, because the result was the same with positively as with negatively charged particles. Some exception, however, must be taken to his method of reversing the charge on the gold particles. The method was that proposed by Burton[6] and also used by Svedberg[7] and consists in the addition of aluminum sulfate until the direction of migration under an electrical field is reversed. Nordenson admits the possibility of interaction of the gold with the products of hydrolysis of the aluminum sulfate, but apparently considers the change in sign of the particle charge to be the only important result. He could detect no chemical change in the dispersion medium which would account for the coagulation by light. He offered two explanations for the phenomenon. (1) The light may cause a difference in potential between adjacent particles (Becquerel effect) leading to attraction and eventually to precipitation. (2) The light may disturb the adsorption equilibrium between particle and associated ions, leading to instability and later to coagulation.

In attempting to reproduce some of the many photochemical phenomena ascribed to gold sols, we were impressed by the strict dependence of these effects upon the previous history of the dispersion. Thus it was possible to prepare sols which were utterly indifferent to prolonged irradiation from the most powerful artificial source of ultraviolet light available. Other sols were prepared which, by the customary mode of designation, were "clear red and free from coarse particles" and yet were markedly sensitive to ultraviolet light.

The object of this investigation is to study the conditions under which sols can be prepared which will exhibit the photochemical properties ascribed to them and to ascertain why certain dispersions are not sensitive to light and others are decidedly sensitive. In addition, the photochemical changes themselves are investigated as far as the available sources of ultraviolet light permit.

Materials Used

All solutions were made up in water having a specific conductivity of 1 to 2×10^{-6} mhos. The potassium chloride employed was recrystallized three times from conductivity water and fused in a platinum dish. The gold wire and arcing apparatus were the same as described by Beans and Eastlack[8] with the addition of an electric stirrer. C. P. nitric and hydrochloric acids were used in the preparation of the chloroauric acid.

Redistilled ether was used to prepare the solutions of phosphorus.

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[6] Burton, *Phil. Mag.*, **12**, 472 (1906).

[7] Svedberg, "Die Existenz der Moleküle," Leipzig, **1912**, p. 102.

[8] Beans and Eastlack, THIS JOURNAL, **37**, 2667 (1915).

Forty per cent. formalin was analyzed by the method of Blank and Finkenbeiner[9] and diluted to the desired concentration with conductivity water. Thirty per cent. hydrogen peroxide (superoxol, acetanilide free) was analyzed by means of a solution of potassium permanganate, standardized against Bureau of Standards sodium oxalate. A 50% solution of hydrazine hydrate was analyzed[10] with the same permanganate solution and both reagents were diluted to the desired concentration as needed. Fused C. P. potassium carbonate was made up to tenth normal concentration. Silver nitrate solution was checked gravimetrically and by the volumetric method of Mohr. The potassium carbonate solution was standardized against a solution of hydrochloric acid which had been accurately checked against the silver nitrate solution. Pure gallotannic acid was made up to 0.1% solutions as required. Eastman hydroquinone and pyrogallol and Eimer and Amend resublimed catechol and resorcinol were employed without further purification.

Preparation of the Gold Sols

Bredig Gold Sols.—One liter of 0.0001 M potassium chloride was arced for twenty-six minutes at 3.8 amps. The solution was surrounded by an ice-bath and the arcing interrupted occasionally to prevent an undue rise in temperature. The resulting sol was centrifuged for one hour with a force equal to 1200 times gravity and then siphoned into a well steamed nonsol bottle. A few sols that had been prepared for other purposes, in hydrochloric acid, potassium iodide and potassium bromide, were also studied.

Reduction Methods.—The technique employed in making these sols was uniform with one or two exceptions. It consisted in diluting chloroauric acid, prepared from pure gold wire, to a concentration equivalent to 0.05 g. of gold per liter. A liter of this solution was carefully neutralized with 0.1 N potassium carbonate using litmus as an indicator. The reduction was carried out at 85° in a well steamed Pyrex beaker heated by an electric hot-plate. The solution was stirred rapidly by an electric stirrer and the reducing agent added at a uniform rate from a microburet. Sols were prepared with the following reducing agents: phosphorus, formaldehyde, tannin, acetylene, hydrogen peroxide, hydrazine, pyrogallol, quinol, resorcinol and catechol.

The number of reducing agents that have been used for preparing gold sols is legion. No attempt was made to exhaust all the possibilities, but rather to make a sufficient variety of sols so that the conclusions drawn from their photochemical behavior would not be restricted to a special type of dispersion.

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[9] Blank and Finkenbeiner, *Ber.*, **31**, 2979 (1898).

[10] Zsigmondy, *Z. anal. Chem.*, **40**, 697 (1901).

Behavior of the Dispersions toward Radiation

The gold sols, prepared as described above, were exposed to the direct radiation of a quartz mercury vapor lamp. For moderate irradiation, a 110-volt Copper-Hewitt quartz lamp was employed; while more intense light and the far ultraviolet were secured with the aid of a 220-volt Hanovia quartz lamp. Exposures were made in fused quartz flasks of about 250cc. capacity. These were thoroughly cleansed before use with aqua regia and well steamed. They were stoppered with clean new corks, care being taken that the solutions did not come in contact with the corks at any time during the experiment. The flasks were placed ten to twenty centimeters from the lamp and kept cool by a blast of air from an electric fan. This was the arrangement used for a qualitative survey of the properties of the various sols. More elaborate precautions were taken in the quantitative study of the light effects to be described later.

The preliminary experiments, made with the 220-volt lamp, showed that sols made with hydrogen peroxide, tannin, quinol, catechol, resorcinol and pyrogallol turned blue during the first two days' irradiation and then became clear red at the end of eight days' total exposure to the light. The hydrazine, phosphorus, formaldehyde, acetylene and Bredig gold sols were not affected by fourteen days' exposure to the quartz mercury arc.

These results, while only qualitative, bring out some very interesting facts, the most important being the behavior of those sols which did undergo a change in the light. They turned blue and resembled a sol to which an excess of electrolyte has been added. To use Nordenson's words, "The light has a slow coagulating effect which is very similar to that of a weak electrolyte." Unfortunately he did not observe that continued irradiation will peptize the unstable sol and produce a sol identical in appearance and behavior with the original. Since the color change evoked by electrolytes and by short exposures to light is the same, the inference, that light will completely precipitate sols, is not unnatural. However, the examination of more than a hundred gold sols prepared in a dozen different ways during the course of this investigation has shown that any colloidal dispersion of gold having associated with it the necessary stabilizing ions or possessing in general the attributes of a stable sol, though temporarily unstable for any reason, can be peptized to a stable red sol by prolonged exposure to the ultraviolet radiation from the mercury arc.[11]

In other words, any sol made blue by exposure to ultraviolet light can be restored to the original red color by prolonged exposure. Any

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[11] By stability is meant the absence of coarse particles, as indicated by strong reflection of light by the sol, or by their ready removal by the natural or augmented gravitational field. To give our criterion of stability quantitative form we may adopt the one first used by D. J. Beaver (Beaver, *Diss.*, Columbia University, 1921) which is to centrifuge the sol for one hour with a force equivalent to 1200 times gravity.

sol which is blue and unstable at the time of formation, due, let us say, to too rapid reduction, but similar in all other respects to a stable sol, can be changed to a red sol by prolonged exposure.

The effect is not due to heating of the dispersion, because in all cases the sols were kept at room temperature or lower. The peptization is not a spontaneous reaction, for it was found that dispersions that had been made blue by exposure to the light did not regain their red color for months when stored in glass bottles in the sunlight, but required about two hundred hours' exposure to the ultraviolet light to effect peptization.

After peptization is effected the light seems to have no further effect. Reasons for this will be given later.

From the qualitative data given above, one cannot draw any definite conclusions as to the reasons for photochemical sensitivity or photochemical indifference. Why, for instance, should a sol prepared with hydrogen peroxide be sensitive to light, and one prepared with formaldehyde be insensitive? It will be seen later that with the exception of the Bredig sols the conditions under which the sol is formed determine its behavior toward ultraviolet light.

The function of radiation in the formation of gold sols was not investigated in detail here because Nordenson has shown the change in color caused by different periods of exposure. An attempt was made, however, to repeat some of his experiments. The rate of formation of hydrogen peroxide sols as a function of time of exposure to ultraviolet light was followed and agreed in general with his results although the results could not be checked with the precision implied by his data. His reaction mixtures, however, were made by adding a "few drops" of hydrogen peroxide to chloro-auric acid solutions. It soon became evident that the problem had not been sufficiently investigated from the chemical standpoint and, until the effect of amount of hydrogen peroxide and other factors were known, little importance could be attached to these values. Some of these factors were investigated for the hydrogen peroxide sols and are described later.

Behavior of Photosensitive Sols

Among those sols which had exhibited sensitivity to light in the preliminary experiments, the sols prepared by the tannin method were investigated more closely. In attempting to reproduce one of these sols, which had proved very suitable for the purpose, a sol was produced, identical in appearance, but absolutely indifferent toward radiation. It was found that slight variations in the hydrogen-ion concentration of the chloro-auric acid accounted for the differences in these tannin sols.

Electrometric titrations of the chloro-auric acid with 0.1 *N* potassium carbonate were therefore made at room temperature (22–25°). A curve was then plotted of cc. of potassium carbonate against *P*H of the solution for the given gold content, and from this curve solutions of definite *P*H were made, heated to 65° and reduced with tannin. Stirring and rate of addition of the reducing agent were uniform. The temperature was maintained to within ± 1° throughout the reduction and the time required for the appearance of the first trace of color was noted. The time values were not as reproducible as might be desired but, since so many factors are involved in the rate of reduction, this is to be expected unless unusually great precautions are taken. The values are, however, accurate enough to indicate the significance of time of reduction and its apparent relationship to the hydrogen-ion concentration and the color and stability of the dispersion.

Table I gives the results of these experiments.

TABLE I

RESULTS OF EXPERIMENTS

No.	G. of Au/liter	*P*H	Temp., °C.	Time of red., seconds ± 10%	Color
1	0.025	3.16	65	312	Grayish suspension
2	.025	3.43	65	217	Bluish suspension
3	.025	3.76	65	17	Purple suspension
4	.025	4.16	65	16.5	Violet sol
5	.025	4.53	65	9.3	Red sol
6	.025	4.72	65	5	Red sol
7	.025	7.66	65	14	Red sol
8	.025	8.95	65	17	Red sol, trace of blue
9	.025	9.36	65	30	Bluish-red sol
10	.025	9.63	65	58	Violet sol

It will be seen from Table I that both the color and time of reduction depend upon the hydrogen-ion concentration of the solution. The more stable red sols are formed near the neutral point and are those which are most rapidly reduced. There is a greater toleration of alkali than of acid, as it requires very high concentrations of alkali to yield a suspension. All of the unstable dispersions with the exception of the coarse suspensions (Nos. 1–3) were peptized to stable red sols by prolonged exposure to the mercury vapor lamp. The red sols (Nos. 5–8) exhibited varying sensitivity toward the light, the minimum being found, by interpolation, to be in the vicinity of *P*H 7.0. This supports Ostwald's statement that the most stable sols by the tannin method are those in which the chloro-auric acid is made neutral to litmus. The rather wide range (*P*H 4.53–8.95) for the clear red sols was found to be restricted to tannin, and not typical of sols prepared by other methods, and is possibly due to a protective effect of the tannin.

The influence of alkali upon the stability of gold sols prepared by the reduction method is mentioned in the literature, the statement being made that gold sols are more stable in alkaline solutions than in neutral or acid solutions.[12] Pihlblad,[13] who studied the effect of size of particle on the light absorption of disperse systems, measured the shift of the absorption band in gold sols, due to the addition of alkali to the reaction mixture. He showed a drift toward the violet, that is, the tendency to form red sols upon the addition of alkali, but did not extend his measurements far enough to show that the color passes through a clear red and then becomes blue again.

It was decided to investigate this matter more accurately, choosing the hydrogen peroxide sols as they seemed to offer less complexity than the tannin sols. The color of each dispersion was determined spectrophotometrically. For this purpose a Brace spectrometer with a variable rotating sector which could be varied while running was employed. The spectrometer table was calibrated with the following spectral lines: Li, 6708 Å.; Na, 5896, 5890 Å.; Hg(arc) 5791, 5770, 5461, 4358, 4046 Å. A large calibration chart was made from these values from which values of the wave length could be read.

The sols were made under carefully controlled conditions and were all reduced at 85°. The percentage transmission was determined for the following wave lengths: 4331, 4847, 5102, 5263, 5461, 5925 and 6549 Å. Each transmission value given is the average of several determinations. In the extreme red and violet ends of the spectrum it was necessary to take the average of three or four matchings, since the visibility maximum lies in the green and comparison in the red and violet is very difficult and fatiguing to the eye.

Table II gives the absorption data for sols reduced at different hydrogen-ion concentrations with hydrogen peroxide. Fig. 1 shows percentage transmission plotted against wave length. The last column of Table II gives the wave length corresponding to the head of the absorption band and is obtained graphically from the absorption curves.

Table II
Absorption Data

Sol no.	P_H	Per cent. transmission for wave length of 4331	4847	5102	5263	5461	5925	6549	Head of abs. band, Å.
6	4.35	70.5	53.8	55.4	53.0	51.0	55.2	59.6	5510
7	6.10	49.6	39.5	35.8	33.5	34.7	52.4	77.8	5315
9	7.45	40.6	33.6	29.3	30.2	38.5	66.0	90.0	5140
25	9.40	37.4	31.2	25.9	25.6	32.1	63.4	88.1	5180
39	10.00	41.0	38.0	37.5	34.9	35.3	61.1	84.3	5345
Color standard		27.3	8.3	5.9	10.0	24.3	78.7	87.5	5040

The Color Standard, the absorption spectrum of which is also included in Table II, is a convenient quantitative color reference and may be used

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[12] Freundlich, "Kapillarchemie," Leipzig, **1922**, p. 695.

[13] Pihlblad, *Inaug. Diss.*, Univ. of Upsala, **1918**.

qualitatively in judging the color of a dispersion. The standard is used by clinicians[14] and consists of 5 cc. of 20% by weight of cobaltous nitrate, $Co(NO_3)_2.6H_2O$, plus 0.30 cc. of 0.25% of potassium dichromate solution plus 10 cc. of water.

Fig. 1 shows the progressive drift of the absorption band toward the violet end of the spectrum and then back toward the red end. Fig. 3B shows the wave length corresponding to the maximum absorption plotted against the *P*H of the solution before reduction, and affords some information about the amount of colloid formed as well as its color.

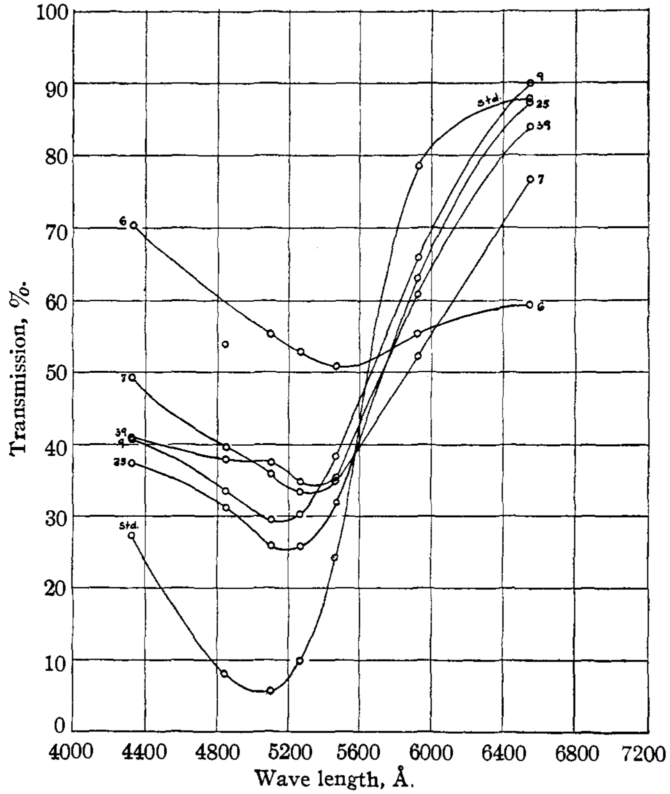

Fig. 1.

It can be seen that the transmissions at the head of the absorption bands of the bluish sols No. 6 and No. 39 are quite high, indicating little absorption of the light, while for the red sols No. 9 and No. 25 the transmissions of light at the heads of the bands are small, indicating great absorption. That this is really due to a difference in concentration of

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[14] Wood, Vogel and Famulener, "Lab. Technique," St. Luke's Hospital, New York, 1917.

TABLE III

Concd. sol		Diluted sol (1:10)	
Wave length, Å.	Trans., %	Wave length, Å.	Trans., %
4640	19.8	4587	76.1
4950	15.7	4785	69.8
5020	12.5	4933	63.1
5100	10.0	5081	42.6
5230	7.94	5180	39.4
5270	7.94	5278	40.1
5600	10.0	5475	45.7
5750	12.5	5722	61.9
5860	15.7	5869	73.0
6060	19.8	6066	84.7
6320	24.9		

the dispersed phase was shown by mapping the absorption of a very concentrated Bredig sol and then mapping the absorption of the same

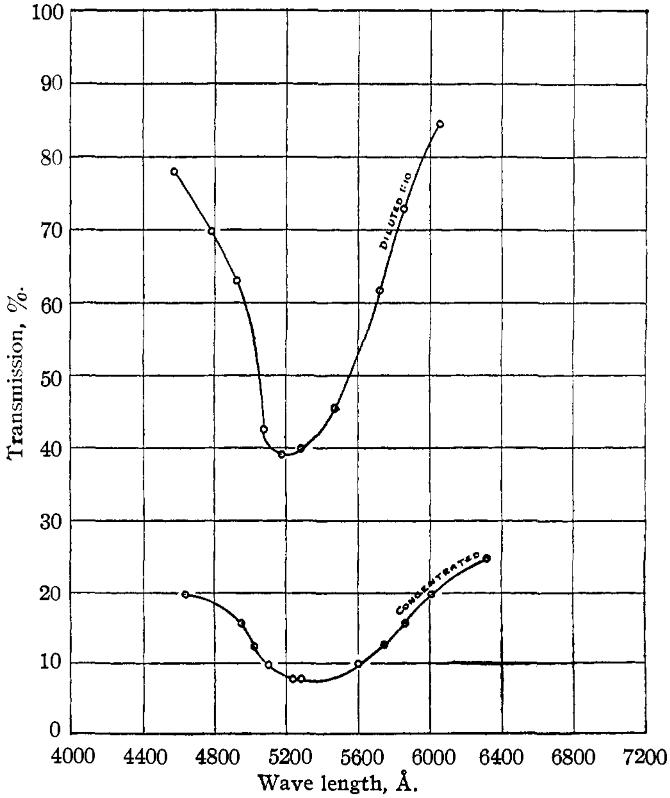


Fig. 2.

sol diluted 1:10. The maxima occur at the same wave length, but the transmissions at this wave length are 8.0 and 39.2%, respectively. The difference in shape of the curves is of little importance here, since that is influenced by reflection as well as by absorption; it is the percentage transmission at the maximum of absorption that we are concerned with. Table III and Fig. 2 illustrate this point.

Returning to the hydrogen peroxide sols, it will be seen that these experiments showed that both the color and the concentration of disperse phase are influenced by the hydrogen-ion concentration of the gold solution being reduced. This relationship is not as simple and general, however, as the above data might lead one to believe. While holding in general for the tannin sols, and quantitatively for the hydrogen peroxide sols, a similar study of dispersions made with phosphorus and hydrazine hydrate showed a continuous, but quite different, variation of color with hydrogen-ion concentration. Table IV gives the absorption determinations for sols prepared by the phosphorus method, and Table V the values for sols prepared by reduction with hydrazine hydrate. All reductions were carried out at 85°. The curves for these series are not plotted, as they are similar to the ones for hydrogen peroxide, but the dissimilarity is brought out by the plot of *P*H against the wave length corresponding to the maximum of absorption, and is shown in Fig. 3A, along with the one for hydrogen peroxide.

TABLE IV

PHOSPHORUS SOLS

Sol no.	*P*H	Per cent. transmission for wave length of 4331	4847	5102	5263	5461	5925	6549	Head of abs. band, Å.
30	3.42	35.9	32.2	24.4	25.1	31.3	62.9	85.9	5110
33	4.35	44.2	33.1	24.5	23.8	26.7	59.5	84.5	5210
8	6.10	45.4	34.3	28.5	26.2	29.5	45.6	67.3	5245
3	7.45	37.2	34.5	29.5	27.1	30.0	48.1	68.4	5260
37	7.97	36.2	33.0	25.9	21.9	27.3	40.9	63.8	5270
Color standard		27.3	8.3	5.9	10.0	24.3	78.7	87.5	5040

TABLE V

HYDRAZINE HYDRATE SOLS

Sol no.	*P*H	Per cent. transmission for wave length of 4331	4847	5102	5263	5461	5925	6549	Head of abs. band, Å.
20	3.42	41.1	43.9	41.6	35.4	37.7	38.9	44.0	5300
23	4.35	32.0	38.0	37.1	33.8	33.5	40.5	53.2	5380
26	6.10	34.0	37.1	28.8	24.1	22.3	35.1	63.7	5450
29	7.97	36.3	38.3	29.0	23.0	21.7	28.8	56.3	5440
32	9.40	34.0	38.0	27.1	23.4	22.0	40.3	66.5	5410
Color standard		27.3	8.3	5.9	10.0	24.3	78.7	87.5	5040

An examination of these curves (Fig. 3) shows immediately that the phosphorus and hydrazine hydrate sols are quite different from the hydrogen peroxide sols. In the case of phosphorus sols, the optimum conditions seem to be approached in acid solutions, below *P*H 4.0, and above this value are relatively uninfluenced by the hydrogen-ion concentration. The same seems to be true of the hydrazine sols, though the optimum is approached at both ends of the *P*H range. It is obvious in both cases that other factors are concerned. Chief among these is the temperature. Hydrazine sols are usually blue. At the particular temperature chosen, 85°, and over the *P*H range studied, they were red, with a tinge of violet. In the case of phosphorus, better sols are usually obtained by reduction in the cold, with subsequent heating to expel the ether. These curves show, then, that the given conditions are specific for the hydrogen peroxide sols. To establish all the criteria for stable sols of all types requires

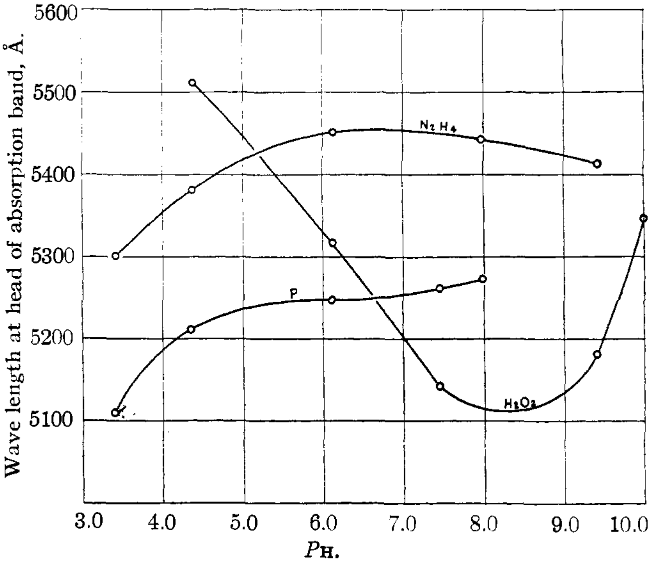


Fig. 3A.

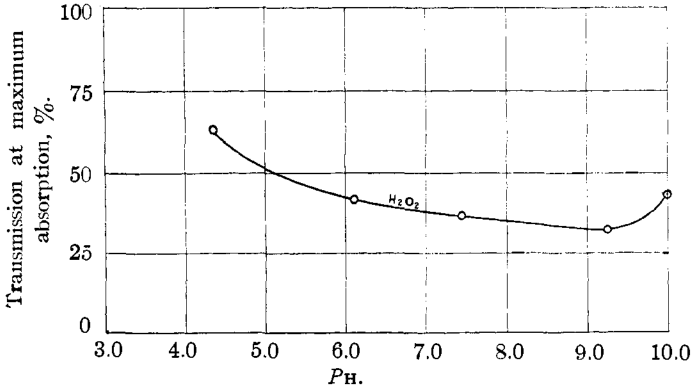


Fig. 3B.

a detailed study of all the factors concerned with each specific case, and is beyond the scope of the present investigation.

Photochemically all these dispersions behaved as described above. All dispersions with a bluish or violet tinge could be peptized permanently to red sols. The sensitivity toward radiation was progressively less as neutrality was approached, and was a minimum at slight alkalinity (*P*H 7.5–9.0) for the peroxide sols. In this range (*P*H 7.5–9.0) the sensitivity, though very slight, varied, so that a number of the sols identical in appearance exhibited different behavior toward the light. All of the peroxide sols in this range would be designated as stable sols by the usual criteria of stability, so that it is evident that nothing can be predicted about the photochemical properties of a red sol from its appearance. It is only by a knowledge of the mode of preparation, such as the curve in Fig. 3 affords, that the possibility of photochemical reaction can be estimated.

The hydrogen peroxide sols were chosen for a detailed study of the photochemical properties since the general conditions for stability had been worked out and the dependence upon these conditions demonstrated. To employ red, stable sols for this purpose restricted the choice to the narrow range of hydrogen-ion concentration just mentioned, which is the range in which the light sensitivity is very small. However, it was imperative to use red sols in order to observe the various stages of the light change. The peptization of a blue sol represents only half of the phenomenon.

It soon became apparent that the most pronounced change in a sol upon illumination is the change in color. This change was followed by Nordenson in his experiments, but unfortunately it tells us little about the mechanism of the process. It is necessary to supplement such measurements with other tests in order to get an idea of the transformations taking place in the sol. With these sols the refractive index, conductivity and absorption were measured and in addition conductivity titrations were made. With the intensities of ultraviolet light at present available, these effects are very small and the utmost precision was necessary to measure them.

The reason for the small effects found was made evident by spectrograms taken in the ultraviolet with the quartz spectrograph. A fresh red sol showed complete absorption of wave lengths below 2150 Å. The same sol made blue by radiation absorbed everything below 2070 Å. and upon further exposure and peptization of this sol it absorbed all radiation below 2010 Å. If, therefore, the radiation between 2150 and 2010 Å. is responsible for the change from red to blue, it is evident that the peptized sol can undergo no further change, because it no longer absorbs the necessary wave lengths. From spectrograms taken for every sol investigated, it was found that the photosensitive sols absorbed the radiation below

2150 Å. This spectral region represents but a small fraction of the total radiant energy of the quartz mercury vapor lamp, and decreases very rapidly with the aging of the lamp. It is only with a new lamp that the far ultraviolet is available in appreciable intensity. It is for this reason that the observed effects required more than a week's exposure.

Refractive indices were determined with a Zeiss immersion refractometer, the cell containing the sol being immersed in a thermostat regulated at 25 ± 0.001°. The changes were at no time greater than five times the experimental error. A representative run was made with a somewhat more sensitive tannin sol to show the magnitude of the effect. The refractive index changed from 1.332658 in a red-violet colored sol to 1.332674 in a blue sol and then to 1.332631 in a clear red sol, which shows that there is a slight but definite increase of the refractive index as the sol becomes blue which decreases again as the sol is peptized by the radiation. Each reading of the refractive index represents the average of ten settings, and is subject to an error of eight parts in the sixth place. The hydrogen peroxide sols require about 180 hours for the same changes but the magnitude is even less. Wintgen[15] showed that in a colloidal dispersion the refractive index is a linear function of the concentration of the electrolyte and that no variation of the refractive index with degree of dispersion could be determined. Wiegner,[16] also pointed out that the linear relationship holds and could only be disturbed if varying degrees of dispersed phase affected the adsorption of ions present. In the above experiments the amount of dispersed phase is constant, so that the observed variations in refractive index would, according to these investigators, be ascribed to the substances adsorbed or otherwise associated with the colloid particle. The conductivity of the same sol under identical conditions changes in a similar manner to the extent of about 0.3%.

For an explanation of the effect of the radiation upon the sols it is necessary first of all to set forth our conception of the structure of a normal gold sol and then consider by what means radiation could modify this structure and produce the phenomena observed. Beans and Eastlack[8] have shown that anions capable of forming stable compounds with gold, in concentrations between 0.005 and 0.00005 *M*, are necessary for the stability of Bredig gold sols. Such ions are present in the chemically prepared sols and the two cases are probably quite similar; indeed, prolonged dialysis of any gold sol will eventually lead to precipitation.

Wilson[17] has extended the complex theory by applying the Donnan membrane equilibrium theory to it. According to him, the gold particle, combined in some manner, such as residual valence, with the stabilizing

[15] Wintgen, *Kolloidchem. Beihefte*, **7**, 266 (1915).

[16] Wiegner, *Kolloid-Z.*, **20**, 7 (1917).

[17] Wilson, THIS JOURNAL, **38**, 1982 (1916).

anion, is surrounded with a liquid layer containing cations balancing the negative charges on the particle. The distribution of ions is different in this layer than in the bulk of the solution. Consequently the Donnan membrane equilibrium theory can be applied. Though the ion concentration product is equal in the surface layer and the bulk of the solution, the concentration of anion and cation is different in the surface layer, with the surface layer having a greater total concentration than the surrounding solution. This unequal distribution of ions will give rise to a difference of potential between the enveloping film and the surrounding solution. If the concentration of ions is increased in the bulk of the solution, this difference of potential decreases and with it the stability of the dispersion.

Since no other ions enter the solution in these experiments, it can be assumed that the radiation itself disturbs the equilibrium, causing ions to move into the bulk of the solution, thus lowering the difference of potential and consequently the stability. The solution should now be blue and have a slightly greater conductivity and refractive index, due to the presence of more ions in the bulk of the solution. But, as we have seen, the change to a blue color is accompanied by a decrease of the absorption in the ultraviolet so that the destructive effect of the radiation cannot continue without limit. A return to true equilibrium conditions then takes place with a decrease in the refractive index and conductivity and a return to the red color. The latter postulate of course implies that there are two frequencies that are effective; one which turns the sol blue and the other which turns it red. At present there is no satisfactory method of isolating narrow spectral regions of sufficient intensity to prove this point although, as in many other photochemical reactions, this is a possible explanation.

To test this hypothesis as unequivocally as possible, the largest quartz flask available was filled with a freshly prepared peroxide sol and the following properties of the sol were determined: absorption curve, conductance, refractive index. The chloride-ion concentration was also measured by means of a conductance titration with silver nitrate. All measurements were made on portions of the same sol in order to have them strictly comparable. With the particular sol employed the blue color was attained after eighteen hours' exposure and the final peptization to red again after 183 hours. Table VI gives the values of the conductivity and refractive index. Table VII gives the data for the absorption spectra, and Table VIII the data for the conductance titrations, the plots of which are shown in Fig. 4.

The values given here are to show the relationship of the values to each other for one and the same sol. Individual determinations of each property were made in number upon various sols with similar results.

Table VI

Value of Conductivity and Refractive Index

Peroxide sol, 0.025 g. of Au/liter. PH = 7.45. Reduced at 85°.

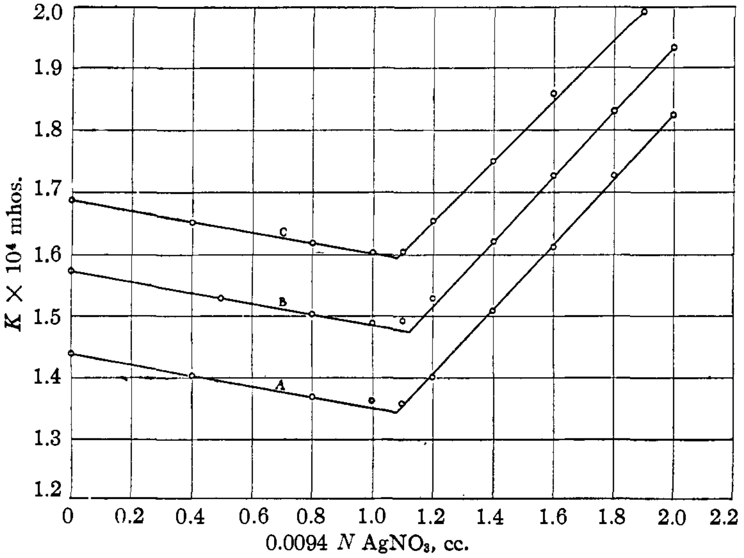
No.	Exposure, hours	Conductivity $\times 10^4$ mhos.	Refractive index, n_D	Color
2	0	1.458	1.332623	Red
2	18	1.462	1.332650	Blue
2	183	1.458	1.332623	Red

Table VII

Absorption Spectra Data

		Per cent. transmission for wave length of							
No.	Exposure, hours	4331	4847	5102	5263	5461	5925	6549	Head of abs. band, Å.
2	0	38.3	33.0	25.5	25.9	32.0	65.3	89.3	5175
2	18	49.0	43.0	35.5	31.5	33.9	52.0	69.4	5290
2	183	32.6	28.3	20.9	20.1	24.4	49.4	82.0	5210

Table VII brings out several important points. First, it will be seen that the absorption is at a maximum at 5175 Å., whereas in Table III the absorption for a sol of this PH (7.45) is given as 5140. The difference of 35 Å., which is not a visible difference, represents the limit of reproducibility of the sols.



For curve B subtract 0.1 from value of K; for curve C, subtract 0.2.

Fig. 4.

It will also be seen that the absorption for the peptized sol (at 5210 Å.) did not quite return to the original value of 5175 Å. at the end of 183 hours, although the conductivity and refractive index had returned to the original values by that time. This emphasizes again the fact that the absorption spectrum of the dispersion is one of the most sensitive indicators of the changes taking place.

TABLE VIII

CONDUCTIVITY TITRATIONS

Sol No. 2. Titrated with 0.0094 N $AgNO_3$. Cell const. = 0.3820.

(A) Original sol		(B) After 18 hours' exposure		(C) After 183 hours' exposure	
$AgNO_3$, cc.	$K \times 10^4$ mhos.	$AgNO_3$, cc.	$K \times 10^4$ mhos.	$AgNO_3$, cc.	$K \times 10^4$ mhos.
0.00	1.439	0.00	1.474	0.00	1.487
.40	1.404	.50	1.430	.40	1.451
.80	1.370	.80	1.404	.80	1.419
1.00	1.363	1.00	1.390	1.00	1.404
1.10	1.358	1.10	1.393	1.10	1.405
1.20	1.402	1.20	1.430	1.20	1.455
1.40	1.510	1.40	1.522	1.40	1.552
1.60	1.613	1.60	1.628	1.60	1.662
1.80	1.729	1.80	1.733	1.90	1.794
2.00	1.828	2.00	1.836		

Neutral point = 1.080 cc. Neutral point = 1.120 ± 0.002 cc. Neutral point = 1.080 cc.

These conductivity titrations indicate an increased concentration of chloride ion in the bulk of the solution in the blue sol, and a return to the original concentration in the peptized red sol. It will be observed that the initial conductivities in Table VIII do not check with those in Table VI, but are slightly higher. The samples for measurement were taken from the same solution. This discrepancy was observed on several occasions and is due to the absorption of carbon dioxide from the air. The error here is not serious for a test of the foregoing hypothesis, since it is the chloride ion with which we are concerned and its determination by the conductance titration with silver nitrate would not be influenced by the presence of dissolved carbon dioxide, due to the relatively higher solubility of silver carbonate.

The hypothesis outlined above required that the ionic concentration in the bulk of the solution should increase as the sol turns blue. The shift in color was shown and the increase in conductance as well as the greater value for the conductance titration were also demonstrated. Prolonged exposure reduced these values again and the absorption spectra showed the return to the original color.

Though the original and final red state seem to be identical, it is evident from the photochemical indifference of the latter that they are not the same. Spectrograms in the far ultraviolet bear this out, as the peptized sol no longer absorbs the effective radiation. It is possible that when peptization is effected, the ions are more firmly associated with the complex, which would account for the greater stability toward light as well as the lack of absorption bands in the effective region of the spectrum.

In addition to the above chemical sols, quantitative measurements were made on Bredig sols prepared according to the method of Beans and Eastlack.[8] Since these sols were uniformly stable to light, an attempt was made to see if their rate of precipitation by dilute solutions of electrolytes is affected by radiation.

Spear, Jones, Neave and Shlager[18] showed that the precipitation of colloidal platinum containing electrolytes is greatly accelerated by the action of ultraviolet light.

Gold sols prepared by the above method were exposed to the radiation from a quartz mercury lamp for various lengths of time and with different amounts of electrolyte (0.001 M $Th(NO_3)_4$), and the conductivity change measured very accurately. At the same time similar determinations were made on sols kept in the dark. In twenty-seven series of measurements the conductivity, which is a measure of the amount of sol precipitated, decreased at the same rate in the "illuminated" and in the "dark" sols. A plot of time divided by specific conductivity against time yielded straight lines the slopes of which depended on the amount of the electrolyte added but were independent of the kind of illumination or lack of it.

Using a photometric comparison method it was also shown that the rate of precipitation of the above Bredig gold sols was the same in the light and in the dark.

Nowhere is there a greater need for a powerful source of ultraviolet light, especially monochromatic light, than in the study of such effects as we are dealing with here. In view of the peptizing ability of the radiation as herein described, it should be possible, once such a source is available, to peptize sols during their formation or immediately after, and obtain dispersions with quite different properties.

Summary

1. The photochemical properties of gold sols depend upon the nature and method of preparation of the sols.

2. Of the sols studied, those which are sensitive to ultraviolet light are made blue and unstable by exposure, but by prolonged irradiation are peptized to stable red sols.

3. With other factors kept constant, the color, rate of formation and photochemical properties of chemically prepared gold sols were found to vary continuously with the hydrogen-ion concentration of the reduction mixture.

4. By assuming Wilson's theory of the structure of the colloidal gold particle and, further, that light can disturb the equilibria involved, it has been shown that the ion concentrations change in accordance with the requirements of the hypothesis.

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[18] Spear, Jones, Neave and Shlager, THIS JOURNAL, **43**, 1385 (1921).

5. The necessity for a more powerful light source for this type of investigation is emphasized.
6. The rate of precipitation of Bredig sols is not influenced by radiation.

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[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

THE PYROPHOSPHATE METHOD FOR THE DETERMINATION OF MAGNESIUM AND PHOSPHORIC ANHYDRIDE[1]

BY ALICE WHITSON EPPERSON

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Probably no determination in analytical chemistry has been the subject of a greater number of conflicting statements than that involving the precipitation of magnesium ammonium phosphate. It is the purpose of this paper to give the results of extensive tests of such statements, and to urge the establishment of a standard procedure which defines, so far as they are known, the most favorable conditions for obtaining a normal precipitate of $MgNH_4PO_4$, and the subsequent ignition of that precipitate to pyrophosphate, $Mg_2P_2O_7$.

In investigating the conditions most favorable for the precipitation of magnesium ammonium phosphate, methods recommended for the determination of magnesium and of phosphoric anhydride were studied. Various procedures suggested in publications on the subject since 1873 were tested, and the effects of those impurities most likely to occur in the regular course of analysis were determined. In most cases short (four hours) single precipitations were made to determine the maximum effect of any variation, and overnight (sixteen hours) single precipitations were made to determine whether standing would cause the precipitate to regain normal composition. Reprecipitation under the conditions to be recommended was tried in many cases.

Since the final treatment of the magnesium ammonium phosphate should be the same whether the precipitate is obtained in the determination of magnesium or of phosphoric anhydride, some commonly recommended methods for obtaining pure pyrophosphate were first investigated and the following observations were made. (1) Solution of the magnesium ammonium phosphate in nitric acid, followed by evaporation to dryness and igniton, has no apparent effect on the final pyrophosphate. (2) Moistening the ignited pyrophosphate with one or two drops of nitric acid, followed by re-ignition, has no effect, either good or harmful. (3) Solution of the ignited pyrophosphate in nitric acid and evaporation of the solution was found to be literally impossible, confirming the experience of Lundell and

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[1] Published by permission of the Director, National Bureau of Standards, U. S. Department of Commerce, Washington, D. C.