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Studies on Aging and Coprecipitation. XXXII. The Adsorptive Properties and the Determination of the Specific Surface of Lead Chromate

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The particle size of lead chromate precipitated under ordinary conditions as a rule is so small that the specific surface cannot be measured microscopically. In the present paper procedures are described for the determination of the specific surface of fresh and aged precipitates of lead chromate by means of the wool violet² and thorium B³ methods. In studying the exchange between radioactive lead and inactive lead on the surface of lead chromate in an alcoholic medium, it was found that lead acetate was strongly adsorbed on the surface of lead chromate. This led to the development of a simple new method for the determination of the specific surface of lead chromate.

Experimental

Materials Used.—C. P. lead nitrate and potassium chromate were recrystallized from water and dried to constant weight. The wool violet 5 BN used was obtained from the National Aniline Company and had been purified in their laboratories. All other chemicals were C. P. products.

Lead Chromate Samples. A.—Prepared by slowly adding from a dropping funnel, and with mechanical stirring, one liter of 1.02 *M* lead nitrate to 2 liters of 0.5 *M* potassium chromate. The latter solution contained 5 ml. of glacial acetic acid. After the precipitate had been filtered and washed, it was purified and aged by shaking it in 5 liters of distilled water for two weeks. During this period it was washed frequently by decantation. The final washings gave no test for lead or chromate. The product was filtered, washed with ethanol, and dried for two days by drawing air through the precipitate.

B.—Product A aged twenty-four hours in 0.1 *M* nitric acid, then filtered, washed with water and ethanol, and air-dried.

C.—A fresh undried precipitate prepared by adding with mechanical stirring 10 ml. of 0.05 *M* lead nitrate to 10 ml. of 0.05 *M* potassium chromate, the latter solution being contained in a 60-ml. wide-mouth round bottle. The suspension was centrifuged, decanted, and the specific surface measurement performed when the precipitate was six minutes (in some cases eight minutes) old.

D.—A three-hour old undried sample. Sample C was aged by shaking the fresh precipitate after centrifuging

and decantation with 20 ml. of distilled water. It was then centrifuged once again, decanted, and the specific surface measurement made.

E.—A twenty-four-hour old undried precipitate. Treated in the same manner as described for sample D except that the time of aging in water was twenty-four hours.

A new precipitate was prepared for each experiment except in the case of products A and B, when samples of a stock supply were used. With extreme care in the preparation of the precipitates, it was possible to obtain satisfactory agreement of duplicate experiments.

The mechanical shaker used in the experiments oscillated at a rate of 220 times per minute with a vertical throw of 5 to 10 cm. depending upon the position of the bottle in the shaker.

The temperature was 24–27° unless otherwise indicated.

Wool Violet Adsorption.—To the lead chromate sample contained in a 60-ml. bottle was added in order 10 ml. of a lead nitrate solution and 10 ml. of a wool violet solution, the concentrations of both solutions being known. The bottles were stoppered with a paraffined cork, mechanically shaken for a time (usually one-half hour), and centrifuged until clear (requiring ten to twenty minutes). Five-ml. portions of the centrifugates were diluted to between 0.5 and 2 mg. of W. V. per liter and analyzed colorimetrically with a Lange photoelectric colorimeter. When the precipitate had not been dried the amount of solution was determined by weighing the bottle and contents and subtracting from this the weight of the solid and the bottle. This was necessary in order to calculate the final amount of dye in the solution from the dye analysis.

Thorium B Exchange.—In the experiments involving thorium B exchange the technique was essentially the same as that employed by Kolthoff and Rosenblum⁴ in their study of lead sulfate.

A measured volume of a lead nitrate solution of known concentration and containing thorium B was added to a known amount of lead chromate. The resulting suspension was agitated on a mechanical shaker for the desired time and centrifuged at a speed of 2000 r. p. m. for two minutes. After evaporation of the clear supernatant liquid the activity was determined and compared to that of a standard prepared by dilution of the original ThB solution to an approximately equal activity.

Paraffined vessels and pipets were used when the concentration of the active lead in the solution was less than 0.0005 *M*. If the lead concentration was lower than this it was found that the walls of the vessels and pipets adsorbed an appreciable fraction of the lead. Above a concentration of 0.0005 *M* adsorption of lead was negligible. Paraffined corks were used as stoppers for the bottles in all experiments.

(1) From a thesis submitted by Frank T. Eggertsen to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree (1939).

(2) For the application of this method to the determination of the specific surface of lead sulfate, barium sulfate, silver chloride and silver bromide, see Kolthoff and co-workers, *THIS JOURNAL*, **56**, 1832 (1934); **59**, 1215, 1639 (1937); **61**, 3409 (1939).

(3) F. Paneth, *Physik. Z.*, **15**, 924 (1914); Paneth and W. Vorwerk, *Z. physik. Chem.*, **101**, 445 (1922).

(4) I. M. Kolthoff and C. Rosenblum, *THIS JOURNAL*, **55**, 2656 (1933).

Experimental Results

Maximum Adsorption of Wool Violet.—With the object of attaining a surface saturated with the dye, adsorption experiments were carried out on the aged air-dried product A and on the fresh product C. The amounts of dye adsorbed from solutions of varying lead nitrate and wool violet concentrations are shown in Tables I and II. The time of shaking of the suspensions was one-half hour.

TABLE I
ADSORPTION OF WOOL VIOLET ON PRODUCT A

Series	Sample in g.	Initial Pb ⁺⁺ × 10 ⁴ M	Initial W. V., mg. p. l.	Final W. V., mg. p. l.	W. V. adsorbed, mg.	W. V. adsorbed in mg. per g.
1	1.00	0.00	200	198	0.04	0.04
			300	208	1.8	1.8
			400	325	1.5	3.0
			400	320	1.6	1.6
			400	312	1.8	1.2
			500	402	1.9	1.9
2	1.00	1.25	300	288	3.3	3.3
			400	288	2.3	4.6
			400	228	3.5	3.5
			400	230	3.4	2.3
			500	310	3.8	3.8
			600	420	3.6	3.6
3	1.00	2.50	300	97	4.1	4.1
			400	286	2.3	4.6
			400	164	4.7	4.7
			500	268	4.7	4.7
			600	364	4.7	4.7
			600	350	5.0	5.0
4	1.00	5.00	400	149	5.0	5.0
			500	248	5.1	5.1
			400	128	5.5	5.5
			500	216	5.7	5.7
			600	300	6.0	6.0
			600	300	6.0	6.0
5	0.50	12.50	300	170	2.6	5.2
			400	276	2.5	5.0
			500	368	2.6	5.2
			300	64	4.7	4.7
			400	156	4.9	4.9
			500	268	4.7	4.7
6	1.00	25.0	400	149	5.0	5.0
			500	248	5.1	5.1
			400	128	5.5	5.5
			500	216	5.7	5.7
			600	300	6.0	6.0
			600	300	6.0	6.0
7	1.00	50.0	400	128	5.5	5.5
			500	216	5.7	5.7
			600	300	6.0	6.0
			600	300	6.0	6.0
			600	300	6.0	6.0
			600	300	6.0	6.0

It is seen that practically no wool violet was adsorbed by either product from a water solution in the absence of excess lead. With increasing concentration of lead nitrate the adsorption increased until at $5 \times 10^{-4} M$ the amount of dye adsorbed reached a value which increased only slowly with further increases in lead concentration. From the results in Tables I and II it can be inferred that the wool violet is adsorbed as the lead salt on the surface of the lead chromate.

TABLE II
ADSORPTION OF WOOL VIOLET ON PRODUCT C
Weight of sample was 0.1616 g.

Initial Pb ⁺⁺ × 10 ⁴ M	Initial W. V., mg./l.	Final W. V., mg./l.	Mg. W. V. adsorbed	W. V. adsorbed per g.
0.0	38	35	0.06	0.4
.0	377	360	.36	2.2
1.1	480	455	.52	3.2
2.4	383	184	4.15	25.7
2.4	480	272	4.35	26.9
4.8	287	56	4.83	29.9
4.8	384	108	5.77	35.7
4.8	432	148	5.94	36.8
4.8	480	202	5.82	36.0
4.8	575	284	6.10	37.7
7.2	382	94	6.06	37.6
	432	140	6.10	37.8
	480	188	6.10	37.8
9.6	575	260	6.60	40.8
	480	162	6.64	41.1
	432	100	6.94	43.0
12.0	480	154	6.81	42.1
	480	154	6.81	42.1
	575	238	7.07	43.8

In order to get the surface saturated with the dye it is necessary that the initial amount of lead in the solution be at least equivalent to the maximum amount of dye that can be adsorbed.

The above suggested mechanism is substantiated by means of a simple calculation. In series 2 of Table I, for example, the amount of wool violet adsorbed was 1.8 mg. Since the molecular weight of wool violet is 800, 2.25×10^{-6} mole of the dye was adsorbed. The amount of lead in solution in these experiments was 2.5×10^{-6} mole. In other words, the quantity of wool violet adsorbed was equivalent to the amount of lead ion present in the solution from which the adsorption took place.

The removal of lead from the solution with the dye was proved by the following experiments. To 1 g. of the air-dried product (A) was added 10 ml. of a radioactive 0.0005 M lead nitrate solution. After shaking the suspension in a paraffined bottle for one hour, which time is sufficient for the attainment of a surface-solution distribution equilibrium of the ThB, 10 ml. of a 0.08% wool violet solution was added, and the suspension was shaken one-half hour longer. It was then centrifuged and the activity of the centrifugate determined. 6.0% of the active lead was found to remain in the solution. Two other experiments were performed in the same way except that 10 ml. of water was added instead of the wool violet

solution. After adding the water, one of the suspensions was shaken for the extra half-hour period and centrifuged. The other one was shaken by hand for only one minute before centrifuging. It was found that 21.4% of the ThB was left in solution in the one-hour experiment, and 20.7% after one and one-half hours of shaking. The figure 21.4 represents the total amount of lead in solution at the time when wool violet was added to the suspension. The decrease in the amount of ThB left in solution to 20.7% after one and one-half hours of shaking shows that only a slight recrystallization and penetration of ThB into the solid occurred. However, in the presence of wool violet during the last half hour of shaking with ThB, only 6.0% of the lead remained in solution. This means that a considerable amount of the lead was removed from the solution upon dye adsorption.

The ratio 6.0/21.4 represents the fraction of the original lead which was still present in the solution after wool violet adsorption. Therefore 15.4/21.4 was the fraction of the total lead removed from the solution with the dye, which corresponds to 3.6×10^{-6} mole of lead. The amount of wool violet adsorbed in this experiment was 3.7 mg. or 4.5×10^{-6} mole. Thus, approximately equivalent amounts of lead and wool violet were removed from the solution during the adsorption process.

From the results of Tables I and II it is seen that the amount of dye adsorbed increased slowly above lead concentrations of 5×10^{-4} M. This was due to a slight precipitation of the dye by lead nitrate as is shown by the following experiments.

Ten-ml. portions of lead nitrate solutions of varying concentrations were added to 10-ml. portions of a 500 mg. per liter wool violet solution. The bottles were stoppered with paraffined corks and the contents shaken for one-half hour on a mechanical shaker, after which they were centrifuged at 2000 r. p. m. for ten minutes. The centrifugates were then analyzed for wool violet colorimetrically. The results of these experiments are given in Table III.

TABLE III

PRECIPITATION OF WOOL VIOLET WITH LEAD NITRATE									
Lead concn., $M \times 10^4$	1.2	2.5	5	7.5	10	12.5	25	50	
W. V. pptd., mg.	0.04	0.24	0.28	0.34	0.38	0.42	0.44	0.96	

In all of the solutions except the one to which

no lead was added a precipitate was visible after centrifuging.

From the results of Table III, it seems quite certain that the slowly increasing adsorption values at high lead concentrations in Tables I and II can be attributed to a direct precipitation of the dye. From a practical viewpoint it is important to conclude that under the following conditions the surface of lead chromate becomes saturated with the dye. A weighed amount of the solid is shaken with 20 ml. of a solution which is 5×10^{-4} M in lead and which contains so much wool violet that the final concentration of the dye is at least 150 mg. per liter. The weight of lead chromate should be such that no more than 6 mg. of dye is adsorbed. If more dye is found to be adsorbed a larger volume of the above lead-wool violet solution or a smaller amount of lead chromate should be used. Adsorption equilibrium with undried precipitates of lead chromate was found to be attained within half an hour of shaking. With dried precipitates a two-hour period of shaking was found necessary in order to disintegrate the agglomerates completely.

The dye adsorption was found to decrease with increasing concentrations of potassium nitrate in the solution. For example, a precipitate whose maximum adsorption was 4.8 mg. per gram adsorbed 4.4 mg. of dye from a solution which was 0.01 M in potassium nitrate, 4.0 mg. from 0.05 M, and 3.9 mg. from 0.2 M potassium nitrate. According to these results, specific surface measurements by the dye method should be carried out in the absence of appreciable quantities of electrolytes.

Specific Surface Measurement by ThB Exchange in Water Medium.—The radioactive indicator method for specific surface determination of crystalline powders originates with Paneth and Vorwerk.³

When kinetic equilibrium is established between the lead in the surface and in the solution, the distribution of the active lead is given by the equation

$$\frac{\text{ThB (surface)}}{\text{ThB (solution)}} = \frac{\text{Pb (surface)}}{\text{Pb (solution)}} \quad (1)$$

In the application of this method the exchange should be limited to the surface layer only and recrystallization of the solid should be prevented. The distribution of the radioactive lead (left-hand term in expression 1) is determined experimentally. Pb (solution) is equal to the original amount

of inactive lead in the solution if the lead is not adsorbed on the lead chromate. If adsorption occurs it is easily seen that

$$\Sigma \text{Pb (surface)} = \text{Pb (surface)} + \text{Pb (adsorbed)} \quad (2)$$

In this expression Pb (surface) represents the amount of lead in the surface of lead chromate when no adsorption occurs. In the case when lead is adsorbed expression (1) can be written as

$$\frac{\Sigma \text{ThB (surface)}}{\text{ThB (solution)}} = \frac{\text{Pb (surface)} + \text{Pb (adsorbed)}}{\text{Pb (solution after adsorption)}} \quad (3)$$

In his determination of the specific surfaces of aged lead chromate samples Paneth³ noted a continual increase in the amount of ThB exchanged with time of shaking. This he attributed to a disintegration of aggregates as well as to a slow diffusion of ThB into cracks and fissures in the crystals. It has been proved by Kolthoff and Rosenblum⁵ that in the case of aged lead sulfate a part of this effect, at least, is due to recrystallization. Upon shaking the aged air-dried sample A of lead chromate with a radioactive lead solution, an increase in the amount of ThB (exchanged) with time of shaking was observed just as Paneth found with the products used by him. By the following experiments it was shown that part of this effect was due to recrystallization.

To 0.5 g. of product A was added 25 ml. of inactive 0.0005 *M* lead nitrate. After shaking this suspension for various periods of time, 10 ml. of an active lead solution of the same concentration was added, and the shaking continued for another half hour. It was found that after one hour of preshaking with an inactive lead solution the percentage of ThB exchanged remained practically constant. For example, 26.7% of ThB was exchanged when there was no preshaking period; the value was 29.2% after preshaking one-half hour, 29.8% after one hour, 30.0% after five hours, and 30.8% after seven hours.

Table IV shows the increase of ThB exchanged with time of shaking with the radioactive lead solution. In these experiments 10 ml. of an active 0.0005 *M* lead nitrate solution was added to a

suspension of 0.5 g. of product A in 25 ml. of the same inactive lead solution which had been preshaken for one and one-half hours. Thus the effect of disintegration of the agglomerates had been eliminated by the preshaking process.

The results of the above experiments show that the amount of ThB exchanged increased steadily with time of shaking.

The experiments of Table IV were repeated at a temperature of 95° instead of at room temperature. It was found that the amounts of ThB exchanged at corresponding times were much greater at the higher temperature. For example, 72% of the ThB was exchanged after five hours of shaking at 95°.

From the above and other experimental data it may be concluded that in water medium and at room temperature a recrystallization of product A occurred, resulting in a penetration of ThB into the solid beyond the first surface layer. The rate of penetration of ThB, and hence the rate of recrystallization, is greater at higher temperatures.

By extrapolating the Pb (exchanged) values of Table IV to zero time of shaking, the specific surface of the sample A was found to be 2.6 mg. of lead per g. of lead chromate. In the calculations a correction was made for adsorption. Under the conditions of these experiments 3.8% of the lead in solution, or 0.26 mg. of Pb per g. of lead chromate, was adsorbed after three hours of shaking. For the purpose of computing the values of Pb (exchanged) equation (3) was used. The results in Table IV seem to indicate that surface exchange equilibrium was not attained until at least after half an hour of shaking. Therefore, the first values were disregarded in the extrapolation.

It was found that fresh precipitates recrystallized so rapidly in water medium that it was not possible to measure their specific surfaces by the method described above. For example, when product C (six minutes old) was shaken for twenty minutes with 20 ml. of a 0.001 *M* radioactive lead solution, the calculated apparent Pb (exchanged) value was 325 mg. of lead per g. of lead chromate. This value was found to be 8150 after one hour of shaking, 1200 after two hours, and 2010 after four hours. It is evident that in this case the establishment of a surface-solution equilibrium distribution was superseded by a rapid recrystallization process, and that it is not possible to compute the value of the specific surface from the data obtained.

TABLE IV

EXCHANGE ON LEAD CHROMATE, PRODUCT A							
Shaking, hours	0.25	0.50	1	2	3	5	
ThB exchanged, %	27.5	29.2	30.3	31.7	32.9	35.2	
Pb (exchanged), mg. p. g.	2.44	2.62	2.78	3.00	3.18	3.54	

(5) I. M. Kolthoff and C. Rosenblum, *THIS JOURNAL*, **56**, 1658 (1934).

In order to inhibit the recrystallization, use was made of the following methods. (1) The exchange was carried out in 95% ethanol medium; (2) the fresh lead chromate was allowed to adsorb a layer of wool violet and the ThB exchange took place on the dye-coated precipitate.

Specific Surface Measurement by ThB Exchange in Ethanol Medium.—In these experiments the following procedure was used.

A solution 0.001 *M* (approximately) in lead acetate was prepared in 95% ethanol. The final solution contained 1 ml. of glacial acetic acid per liter, the latter being added to prevent hydrolysis of the lead acetate and the adsorption of lead on the glass. To 0.1616 g. of products C and D and to 1 g. of product A were added 30.65-ml. portions of the above solution containing ThB. The bottles were stoppered with paraffined corks. Before adding the active solution to the undried products the latter were washed once, immediately after their preparation, with 95% ethanol by centrifuging and decantation. This treatment arrests the aging process, as will be shown in a subsequent paper.

It was found that lead acetate is strongly adsorbed from 95% ethanol by lead chromate. It was necessary to determine the extent of such adsorption before specific calculations could be made from the ThB exchange data. The lead was determined (after eliminating the alcohol by evaporation) by precipitating as the chromate, dissolving the precipitate in hydrochloric acid and titrating with ferrous sulfate using diphenylamine as an indicator.

The results of the ThB exchange and of the adsorption experiments are given in Table V, and the Pb (exchanged) values are plotted against time of shaking in Fig. 1. For the sake of brevity only part of the data is given, a more complete set being presented in the thesis of the junior author.¹ Specific surface values were computed by extrapolating each set of Pb (exchanged) values to zero time of shaking and dividing by the weight of the precipitate. In this way the following values of the specific surface expressed in mg. of lead per gram of lead chromate were found: 24.8 for product C, 8.7 for product D, and 2.1 for product A. It should be noted that these values are almost identical with the amounts of lead adsorbed as acetate after twenty-four hours of shaking. These figures were (expressed in mg. of Pb p. g.): 18.9 (product C); 8.7 (product D) and 2.1 (prod-

TABLE V
EXCHANGE OF ThB AND ADSORPTION OF LEAD ACETATE
IN 95% ETHANOL

Shaking, hours	ThB exchanged in %	Pb (exchanged) + (adsorbed), mg.		Pb (adsorbed), mg. ^b	Pb (exchanged), mg.	Pb (exchanged), p. g.
		Pb (solution), mg.	Pb (adsorbed), mg.			
Lead Chromate Sample C, 0.1616 g.						
0.25	51.2	4.30	4.54	2.48	2.06	12.7
.63	52.1	4.26	4.64	2.52	2.12	13.1
1.5	55.8	4.22	5.33	2.56	2.77	17.2
4	61.1	4.08	6.41	2.70	3.71	23.0
8	67.6	3.87	8.08	2.77	5.31	32.9
16	70.4	3.72	8.84	2.92	5.92	36.6
21	71.8	3.64	9.26	3.00	6.26	38.8
Sample D, 0.1616 g.						
0.25	23.4	5.70	1.74	1.08	0.66	4.1
.67	26.1	5.70	2.01	1.08	.93	5.8
1.5	28.1	5.68	2.22	1.10	1.12	6.9
8	29.4	5.46	2.28	1.18	1.10	6.8
12	32.2	5.40	2.56	1.24	1.32	8.2
21	34.0	5.28	2.72	1.36	1.36	8.4
Sample A, ^a 1 g.						
0.25	30.7	5.34	2.37	1.44	0.93	0.9
.67	36.0	5.30	2.98	1.48	1.50	1.5
1.5	38.6	5.23	3.29	1.55	1.74	1.7
8	44.3	4.80	3.82	1.84	1.98	2.0
12	45.7	4.72	3.98	1.92	2.06	2.1
16	47.2	4.66	4.17	1.98	2.19	2.2
21	47.2	4.59	4.11	2.05	2.06	2.1

^a Preshaken for four hours with 20 ml. of inactive lead solution to disintegrate the agglomerates. ^b Only the values after 0.5, 4, and 24 hours were actually determined. The others were obtained by interpolation.

uct A). These results show that the specific surface of lead chromate can be determined simply by shaking for twenty-four hours a suitable sample with a 0.001 *M* solution of lead acetate in 95% ethanol which contains 0.1% glacial acetic acid and determining the amount adsorbed. This

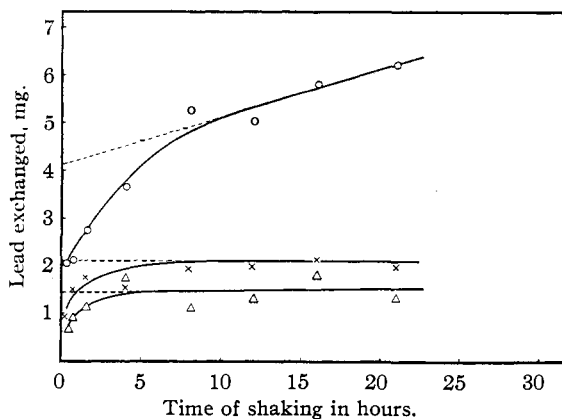


Fig. 1.—ThB exchange in 95% ethanol: ○, fresh precipitate; △, 3-hour-old product; ×, aged air-dried product.

amount corresponds to a monomolecular layer of adsorbed lead acetate.

Furthermore, the results of Table V show that the rate of recrystallization, even of the fresh precipitate, is very small in ethanol medium. It is also evident that the surface-solution exchange process is extremely slow, about four hours being required for the attainment of a distribution equilibrium. This is in decided contrast to the behavior of the same precipitates in water medium.

ThB Exchange Method with a Precipitate Having an Adsorbed Dye Layer.—It was found that the specific surfaces of lead chromate precipitates, fresh or aged, can be determined by the ThB exchange method if their surfaces are first allowed to adsorb a layer of wool violet, the dye preventing recrystallization. The procedure discussed below was followed, using 0.1616 g. of product C and 1 g. of product A.

To each of the samples was added in order 10 ml. of 0.001 *M* lead nitrate and 10 ml. of 0.8 g. per liter wool violet. The suspensions were shaken for one-half hour in case of product C and two hours in case of product A; they were then centrifuged for fifteen minutes. Under the conditions of the adsorption a surface saturation of the samples was attained. After decanting the dye solution the precipitates were washed by centrifuging and decantation with 20 ml. of a solution which was 0.0005 *M* in lead nitrate and 0.02% in wool violet. Then 20 ml. of an active solution having the same composition as the wash solution was added. The resulting suspensions were shaken for a given period of time, centrifuged until clear, and the activities of the supernatant liquids determined in the usual fashion.

The results of these experiments are recorded in Table VI. From the data given it is evident

TABLE VI
EXCHANGE OF ThB ON LEAD CHROMATE COVERED WITH ADSORBED WOOL VIOLET

Product	Shaking, hours	ThB exchanged, %	Pb (exchanged), mg.	Pb (exchanged), mg. p. g.
C	0.33	64.7	3.82	23.6
	1	68.0	4.46	27.6
	3	68.5	4.59	28.4
	5	67.5	4.40	27.2
	8	67.3	4.35	26.9
A	0.33	51.2	2.14	2.1
	1	53.5	2.35	2.4
	3	55.8	2.58	2.6
	5	56.4	2.71	2.7
	8	57.0	2.77	2.8

that surface-solution distribution equilibrium of ThB was established in about one hour and that virtually no recrystallization of the dye-coated precipitates occurred. After correction for the slight precipitation of lead (see Table III) the values of the specific surface were calculated with the aid of equation (1); the results agree satisfactorily with those computed from Table V.

Discussion

(1) From the specific surface data found for product A by the radioactive (Table IV) and wool violet (Table I) methods it can be derived that 1 mg. of dye is adsorbed per 0.54 mg. of lead on the surface. This corresponds to an adsorption of one wool violet ion per 2 molecules of lead chromate on the surface when the latter is saturated with dye. In the case of lead sulfate⁶ one wool violet ion was found to be adsorbed per 1.5 lead sulfate molecules on the surface of lead sulfate. In the latter case the surface became saturated upon shaking of the suspension of lead sulfate in water with the wool violet solution without addition of an excess of lead nitrate. In the case of lead chromate the amount of lead in the solution had at least to be equal to the amount of wool violet adsorbed in order to saturate the surface with the dye, equivalent amounts of wool violet and lead being removed from the solution. This would indicate that the dye is adsorbed as lead wool violet on the surface of lead chromate. In the case of lead sulfate it was concluded⁶ that the dye ion was adsorbed by exchange with sulfate ions on the surface. However, it is quite possible that in this case also the dye was adsorbed as the lead salt, the necessary lead ions being furnished by the lead sulfate itself. The difference in behavior between lead sulfate and lead chromate then might be attributed to the much greater solubility of the former than of the latter in water.

In the present paper it was found (Table VI) that the amount of lead exchanged was of the same order of magnitude with a wool violet coated product as with an uncoated product. These results would seem to indicate that for every surface lead ion which was covered by adsorbed dye and thus prevented from exchanging, a lead ion was adsorbed from the solution with the dye in such a way that it could participate in the radioactive exchange.

(2) The various methods described for the

(6) I. M. Kolthoff, W. Von Fischer and C. Rosenblum, *THIS JOURNAL*, **56**, 832 (1934).

determination of the specific surface have been applied to products of lead chromate of different age and degree of perfection. The agreement between the results is very satisfactory, as is evident from the summarized data in Table VII. In terms of mg. of wool violet per gram the surfaces of the various products were: Product A, 4.8; B, 4.1; C (six minutes old), 38; C (eight minutes old), 35; D, 17.2; E, 15.4. These values were

converted into the units of Table VII by means of the factor 0.54. One mg. of wool violet is equivalent to 0.54 mg. of lead in the surface according to the results obtained with product A.

Summary

1. The wool violet method is very suitable for the determination of the specific surface of lead chromate. Equivalent amounts of dye and lead are removed from the solution. On the saturated surface one wool violet ion is adsorbed per 2 molecules of lead chromate. The mechanism of the dye adsorption has been discussed.

2. Lead acetate is adsorbed in a monomolecular layer on the surface of lead chromate from dilute solutions of the salt in 95% ethanol. Use of this fact has been made in the development of a new method for the determination of the specific surface.

3. Two new procedures have been described for the determination of the specific surface of fresh and imperfect precipitates of lead chromate by the radioactive method.

MINNEAPOLIS, MINNESOTA

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TABLE VII

SPECIFIC SURFACE EXPRESSED IN MG. OF Pb P. G. OF DIFFERENT SAMPLES OF LEAD CHROMATE BY VARIOUS METHODS

Sample	W. V. method	Adsorption lead acetate from alcohol	Thorium B methods		
			In water	In ethanol	Dye coated products
A	2.6	2.1	2.6 2.9 ^a 2.2 ^a	2.1	2.7
B	2.2				
C ^b	20.5			25	
C ^c	19	18.9			27
D	9.3	8.7	7.5	8.7	
E	8.3		7.4		

^a No correction was made for the slight amount of lead adsorbed. The values reported may be slightly high for this reason. ^b Product was six minutes old. ^c Product was eight minutes old.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY]

The Systems Magnesium Chromate-Water and Ammonium Chromate-Water from 0 to 75°

BY ARTHUR E. HILL, GLENN C. SOTH AND JOHN E. RICCI

In connection with certain phase rule studies involving magnesium and ammonium chromates the aqueous solubilities of these salts were determined in the temperature range 0 to 75°.

I. The literature contains little information on magnesium chromate and its hydrates. The only figure on the solubility of the salt appears to be that of Kohlrausch,^{1a} who reported that at 18° 100 ml. of saturated solution contained 60 g. of magnesium chromate. Kopp² reported that magnesium chromate crystallized from aqueous solution at room temperature as the heptahydrate; according to Wyrouboff³ the pentahydrate could be prepared by allowing the heptahydrate to stand in air, or by recrystallization from water above 30°.

(1) This paper is being published, following the death of Professor Hill, by his collaborators.

(1a) Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, London, 1931, p. 275.

(2) Kopp, *Ann.*, **42**, 97 (1842).

(3) Wyrouboff, *Bull. Soc. Min.*, **12**, 69 (1890).

The present measurements were made on "Analyzed" grade magnesium chromate recrystallized as follows. A quantity of the salt was dissolved in water and filtered by gravity to remove the insoluble material. The solution was evaporated on a steam-bath under reduced pressure, at about 60°, until crystals began to form in the solution. The material was poured out immediately into a beaker and allowed to cool to room temperature with continuous stirring for twelve hours. The precipitated salt was filtered by suction, centrifuged for twenty minutes, and air-dried for three days. It was then kept in a desiccator over some partly dehydrated salt. This gave, after a week, magnesium chromate pentahydrate of sufficient purity (100.0 ± 0.1% by chromate analysis). The treatment described is rendered necessary by the fact that the concentration of solutions of magnesium chromate by normal boiling causes the precipitation of a solid phase of still unknown composition which may possibly be a basic product of hydrolysis. Concentrated solutions of the salt, moreover, have high viscosity, so that adequate stirring to prevent superheating and serious bumping of the solution during recrystallization is difficult.

The solubilities were determined from both super- and