

**NOTES ON THE SO-CALLED ACTION OF WATER ON LEAD.**

By JOHN C. THRESH, M.D., D.Sc., F.I.C., ETC.

*(Read at the Meeting, April 6, 1921.)*

THE historical part of this subject was so fully dealt with by Mr. Heap in a paper read before the Society of Chemical Industry (*J. Soc. Chem. Ind.*, 1913, **32**, 771, 811, 847), that anyone interested in this history can easily refer thereto. It will be found that the statements made by different observers are very conflicting, and that there are many anomalies which require explanation.

At my laboratory there are notes, extending over a period of twenty years, on waters which acted upon lead, and when recently a series of waters had to be

## THRESH : NOTES ON THE SO-CALLED ACTION OF WATER ON LEAD 271

examined these records were looked up. Amongst others were notes of the action of samples of distilled water prepared in the laboratory, and some were recorded as "eroding" lead, some as exerting a "solvent" action, some which both "eroded" and "dissolved" lead, and some which apparently did neither. Different fractions from the same distillation had different effects, and it was quite obvious that ammonia-free distilled water must vary considerably in its character. That such was the case was easily demonstrated by examining a number of such waters by the determination of the electric conductivity. The most carefully distilled water had at 20° C. a conductivity of 2, but most gave 3 to 4, and one had a conductivity as high as 14. Certain waters yielded a distillate containing the merest trace of carbon dioxide, others yielded distillates containing considerable quantities, and the degree of oxygenation also differed considerably. It seemed probable, therefore, that these variations accounted for the differences recorded in the action of distilled waters on lead.

The examination of the natural waters above referred to raised other points. One sample was of a river water which, when filtered, contained no lead, whereas, unfiltered and acidulated, it yielded an appreciable colour with hydrogen sulphide. (Lead in large quantities was found in the flocculent sediment in the river, and the drinking of this water by cattle had caused lead poisoning.) Another water, rain water collected in a large concrete-lined tank, and having a long leaden suction pipe to the pump, gave the following perplexing results: Lead per 100 c.c. in water, no acid added, 0.10 mgrm.; after acidifying, 0.25 mgrm.; decanted after standing twenty-four hours, 0.12 mgrm.; after centrifugalisation, 0.10 mgrm.; after filtration through paper, 0.025 mgrm.; and after filtration through Gooch and Pasteur filter, *nil*.

EFFECT OF FILTRATION ON LEAD IN WATER.—To ascertain the effect of filtration, two solutions were made of neutral lead acetate, one with distilled water nearly free from carbon dioxide, and the other with a rain water containing some carbon dioxide and a trace of carbonate. The former solution was quite clear, and the latter faintly turbid. After standing twenty-four hours, successive 50 c.c. were removed by means of a pipette and filtered. (The original solutions contained 0.2 mgrm. of lead in 50 c.c., and the first 50 c.c. of each were examined without filtration.)

	Solution in Distilled Water. Lead found.	Solution in Rain Water. Lead found.
	Mgrm.	Mgrm.
1st 50 c.c. not filtered ... ..	0.20	0.125
2nd " filtered through paper ...	0.06	0.04
3rd " " " " ...	0.08	0.065
4th " " " " ...	0.14	0.10
5th " filtered through asbestos ...	0.025	0.01
6th " " " " ...	0.085	0.03
7th " " " " ...	0.13	0.04
8th " filtered through porcelain ...	0.00	0.00
9th " " " " ...	0.025	0.00
10th " " " " ...	0.08	0.02

The cylinders in which the waters had stood appeared hazy, as though some deposit was on the glass. This proved to be the case, as, after rinsing, and then adding 50 c.c. of slightly acidified water, both yielded solutions containing lead. The distilled water cylinder yielded 0.375 mgrm., and the rain water 0.30 mgrm. In another experiment with a solution of lead acetate in distilled water (2 mgrms. Pb per 100 c.c.), a minute fragment of sodium was added to give an alkaline reaction. Fifty c.c. of this passed through a filter-paper yielded 0.2 mgrm. of lead, and 50 c.c. passed through a Pasteur filter was free from lead. In another experiment lead foil was placed in a litre of specially distilled water containing the merest trace of carbon dioxide, but saturated with air. The water was contained in a bottle completely filled and stoppered so as to exclude air. After two days the lead was removed, and the liquid poured off was found to contain about 12 mgrms. of lead in 100 c.c. It was diluted so that each 50 c.c. contained 2 mgrms. This liquid was alkaline to naphtholphthalein, and became turbid upon addition of a trace of sodium carbonate. Filtered through the finest filter-paper obtainable, the lead in the filtrate did not exceed 0.005 mgrm., and that passed through a Gooch asbestos filter and a Pasteur filter was quite free from lead. The remainder was passed in successive 50 c.c. through a coarser filter-paper. The first 50 c.c. contained 0.07 mgrm., the second 0.10 mgrm., and the amount passed gradually increased to 0.35 mgrm. in the thirteenth portion, after which the filter practically ceased to pass the water, the pores being choked.

It should here be added that in all cases when the lead solution was rendered faintly acid with acetic or hydrochloric acid, the liquid passed through the filters with its full complement of lead. It is fairly obvious that these neutral or alkaline solutions contain the lead compound in a colloid condition, and that the filtration effects are due to "adsorption."

When pure distilled water containing oxygen in solution acts upon lead, a soluble lead oxide or hydroxide is slowly formed. At first probably there is molecular solution, but molecular aggregates are formed, and the dispersion is then of colloid dimensions; later, larger aggregates may be formed, the dispersion becoming coarser until the liquid appears turbid. When dealing with these minute quantities, forces come into play which are of little importance when considerable masses are being dealt with, as in an ordinary analysis, but which cannot be ignored when dealing with very dilute solutions.

FACTORS AFFECTING THE COLORIMETRIC ESTIMATION OF LEAD.—In estimating quantities of lead from 0.01 to 0.4 parts per 100,000 in various kinds of water, it was observed that the colours produced with hydrogen sulphide varied not merely in depth, but in tint from a reddish-brown to a deep orange, and that frequently the addition of the reagent was rapidly followed by the production of an opalescence which entirely prevented any accurate determination of the lead contents. After a long series of comparative experiments, the conclusion arrived at was that by far the best results were obtained in the absence of a mineral acid (removed by addition of a trace of sodium acetate), and using *N* acetic acid containing as a stabiliser 0.1 per cent. of gold leaf gelatin. The quantity of free acid also affects the depth of colour of the colloidal lead sulphide. The following table shows the effects noted in one series

of experiments in which the quantity of acid used varied. The solution experimented with contained 0.2 mgrm. of lead as oxide or hydroxide in 100 c.c.

Solution: Neutral	With 1% $\frac{N}{10}$ HCl	2% $\frac{N}{10}$ HCl	4% $\frac{N}{10}$ HCl	With 1% $\frac{N}{10}$ acetic acid	2% $\frac{N}{10}$ acetic acid	4% $\frac{N}{10}$ acetic acid	1% $\frac{N}{10}$ acetic acid
Colour with H <sub>2</sub> S: 100	160	185	175	120	175	185	185

The effect due to the variation in quantity of acetic acid above a certain amount is much less than the variation with a mineral acid. The effect of gelatin is even more marked. A natural water containing lead, neutral and not acidified, gave with hydrogen sulphide a coloration of 40; acidified with acetic acid, a coloration of 60; and acidified with acetic acid containing gelatin, a coloration of 100.

The colour produced in the presence of the stabiliser is not only excellent for comparative purposes, but the liquid remains perfectly bright for considerable periods, which is a great advantage when a number of samples are being examined. In the presence of free mineral acid nitrites interfere, but in the quantities ever found in water the effect on the acetic solution is practically *nil*.

**INFLUENCE OF HEAT AND AGITATION ON THE SOLUTION OF LEAD.**—In making quantitative estimations of the lead taken up by water, it was found that the action was accelerated by heat, but the effect is not such as to necessitate the use of apparatus for maintaining a uniform temperature, the variations at the laboratory temperature being comparatively small, especially compared with other conditions, the chief of which is agitation. The following experiments bring out this point, and also show that the marked effect of agitation is due to the colloid condition of the lead in certain solutions; the colloid lead refuses to diffuse. A tall cylinder (150 c.c.) was filled with distilled water, and a coil of lead-foil placed at the bottom. The upper edge of the lead was opposite the 40 c.c. graduation. After standing at rest for an hour or two, a faint turbidity was noted extending up to this point. After twenty-four hours this had disappeared, but by viewing in different lights there was an obvious difference between the water above the 42 c.c. graduation and below. The upper 50 c.c. were drawn off, and contained no lead; after another twenty-four hours 25 c.c. were drawn off, and contained no lead. After sixty hours another portion of 25 c.c. was pipetted off, and was free from lead. After seventy-two hours 10 c.c. were taken off, and found to contain the merest trace of lead. Then 5 c.c. of remaining liquid were drawn off, and found to contain lead in the proportion of 10.0 mgrms. per 100 c.c., and finally the liquid remaining in the cylinder was acidified with acetic acid, and found to contain 16.5 mgrms. Pb per 100 c.c.

Time.	Agitation.	Lead acted upon by the Water.	Water.
15 minutes	In rotatory machine	2.5 mgrms. per 100 c.c.	Distilled
15 "	Shaken occasionally	2.0 " "	The same water
15 "	At complete rest	1.0 " "	" " "
4 hours	In machine	2.54 " "	A carbonated water
4 "	At rest	1.88 " "	The same carbonated water

In order to obtain uniformity of agitation, a small water-wheel was constructed with a hollow cylindrical axis in which bottles containing water could be placed. With the laboratory water-supply a rate of revolution of between 60 and 70 per minute was easily maintained. This little apparatus has been found most useful. With it the results given on page 273 were obtained.

**INFLUENCE OF SURFACE AREA.**—The area of lead surface exposed has a marked effect during the first few minutes, but after some hours it is very slight. The unit employed throughout was 25 sq. cms. per 100 c.c., and in all comparative experiments it is necessary to use bottles of the same shape and of approximately the same size. The effect of variation of area of lead exposed is shown in the following tabular results of one series of experiments, made with distilled water containing 0.852 mgrm. of oxygen per 100 c.c.

Unit of Lead Surface per 100 c.c.	Time.	Lead Removed.
Sq. Cm.		Mgrams.
0.5	10 minutes	0.46
1.0	10 "	0.94
1.5	10 "	2.1
2.0	10 "	2.4
0.6	15 " (rotated)	2.0
1.0	15 "	2.5
0.5	6 hours	7.25
1.0	6 "	7.9

The way in which the lead surface is cleaned has a pronounced effect upon the rate at which action commences and continues for about the first hour, but afterwards the effect is only slightly marked. Lead which has been dipped in dilute acid and then polished with a dry cloth has the greatest initial velocity, and the same lead dipped into  $\frac{N}{100}$  sodium carbonate solution after treatment with  $\frac{N}{10}$  hydrochloric acid had the least initial velocity, but the results were very variable. After numerous experiments, it was concluded that the most uniform results were obtained by using lead which had first been well rubbed with finely-powdered pumice and then polished with clean dry linen.

**ACTION OF DISTILLED WATER.**—The factors likely to affect the results having been studied, experiments were conducted with distilled water, and after many failures an apparatus was devised for distilling water and collecting the distillate without the access of air, and thus obtaining a water free from dissolved gases, especially oxygen and carbon dioxide. When such a water is obtained and the unit of lead introduced through an atmosphere free from oxygen and carbon dioxide, and the containing vessel is sealed, the water remains clear and the metal bright; and when the water is poured off quickly and tested, no trace of lead can be found in solution.

If to such a sample of water air deprived of carbon dioxide be admitted, the liquid remains clear for two or three days, after which a deposit forms on the bottom of the bottle, and when shaken the deposit exhibits a crystalline character. Under

the microscope it is seen to be very minute and acicular, single and in tufts. It settles quickly and the liquid is bright. If now ordinary air be permitted to gain entrance, the liquid soon becomes turbid from the absorption of carbon dioxide. The solution is alkaline to phenolphthalein and naphtholphthalein, and precipitates with the slightest trace of a solution of a carbonate.

Obviously this is a solution of lead oxide or hydroxide, and the saturated solution contains about 20 mgrms. of lead in 100 c.c. Apparently the amount varies from 19.5 to 20.6 mgrms., and this may be regarded as the solubility of this compound at 8° to 12° C. With free access of carbon-dioxide-free air, the formation of the oxide or hydroxide continues, but when air is excluded, the action stops when the available oxygen is used up. This applies also to distilled water to which any acid has been added. If the acid forms a soluble lead salt, this remains in solution, whilst if the acid forms a practically insoluble lead salt, this insoluble salt is deposited as soon as the water has become saturated therewith. Carbonic acid appears to form the most insoluble salts, followed by silicic acid, then, at a distance, by phosphoric, sulphuric acid, etc. So far as the solvent action of water on lead is concerned, carbonic and silicic acids are the only ones to be considered. When the action between oxygen-laden but otherwise pure distilled water and lead takes place in stoppered bottles, quite full and protected from the access of air, it is always found: (1) That the oxygen taken up by the lead corresponds to the lead which has entered into solution as estimated by hydrogen sulphide. (2) That the loss of weight suffered by the metal is very approximately a measure of the amount of lead which has been oxidised. (3) That the amount of lead dissolved can be estimated with fair approximation by titrating the solution with  $\frac{N}{10}$  acid, using methyl orange as the indicator.

(1) This requires that the oxygen contained in the water at the commencement and end of the experiment should be accurately determined, and Winkler's method has been used (save in certain cases where experiments were being made with nitrated waters, when my process was utilised). The following are the results of a series of experiments, commencing with water exhausted as far as possible by an air-pump, and concluding with water through which pure oxygen gas had been passed:

	Lead, Mgrms. per 100 c.c.																
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	Aver.
Estimated from loss of O (1 mgrm. = 12.94 Pb)	0.0	1.42	2.2	2.7	4.1	7.4	7.3	7.25	9.75	11.1	12.3	14.9	20.7	21.6	35.0	42.8	11.08
By means of H <sub>2</sub> S	0.03	1.55	2.1	2.5	4.25	7.3	7.35	8.0	9.4	11.0	12.0	15.6	19.0	22.0	35.3	42.0	11.17

The above results show that the amount of lead chemically acted upon is determined by the amount of oxygen taken out of solution, and that the extent of this action can be accurately gauged by the amount of oxygen lost.

(2) This is more troublesome, and is of no practical use. Save with pure distilled water or acidified water the results are useless, as insoluble salts deposit upon the lead and vitiate the results. The following experiments were made with distilled water containing the merest trace of carbon dioxide:

	1.	2.	3.	4.	5.	6.	7.
Weight lost by lead foil (mgrms.)	...	...	6.2	7.5	9.0	13.2	15.0
Lead found in solution and suspension (mgrms.)	...	...	7.1	8.8	8.45	13.45	13.75
	...	...	14.3	15.0	14.5	15.0	15.0

(3) This is not of much utility, since the presence of lead salts in solution interferes with the delicacy of the end reaction, but it is worthy of notice that in distilled

waters containing only oxygen and carbon dioxide the amount of lead taken up can be approximately estimated in this way. The attempts to estimate the relative proportion of oxide and carbonate by using phenolphthalein as well as methyl orange all ended in failure.

With distilled water the velocity of the reaction between the oxygen and the lead appears to depend upon the amount of oxygen present, and the same remark applies in the presence of any free acid forming soluble lead compounds, but in the presence of acid the velocity is greater in the earlier stages. For example :

Time	Lead acted upon—	
	Neutral Distilled Water.	Distilled Water + 4 per Cent. $\frac{N}{17}$ HCl.
	Mgrms.	Mgrms.
$\frac{1}{2}$ hour	1.65	3.1
3 hours	4.7	8.0
5 "	7.1	9.7
24 "	11.0	12.4
48 "	12.2	13.0

**RATE OF UTILISATION OF OXYGEN.**—The following gives in a little more detail information concerning a series of experiments showing the rate at which oxygen is taken up, and that action ceases when all the oxygen has been used. The bottles used all held approximately 160 c.c., and were completely filled so as to exclude air. After standing the requisite time, 5 c.c. of water were taken from the bottle, the solutions of manganese chloride added (3 c.c.), and some of the original water added again to fill the bottle. In the 5 c.c., diluted to 50 c.c., 100 c.c., or more according to circumstances, the lead was determined, and the residual oxygen was determined in the remainder of the water. The correction for oxygen in the water and chemicals added was usually so small as to be negligible. In many cases duplicate bottles of water were put on, so that the lead could be estimated in one and the residual oxygen in the other. The discrepancies which occurred when this method was used led to the discovery of the marked effect of unequal agitation.

Record of experiments made November 19 and 20, 1920. Temperature, 13° C. Oxygen in 100 c.c. of the distilled water, 1.030 mgrms.; free CO<sub>2</sub>, 0.33 mgrm. :

Time.	Oxygen Left.	Oxygen Lost.	Lead Equivalent.	Lead found by H <sub>2</sub> S.
	Mgrm.	Mgrms.	Mgrms.	Mgrms.
$\frac{1}{2}$ hour	0.95	0.08	1.03	0.6
$\frac{1}{2}$ "	0.90	0.13	1.68	1.66
1 "	0.80	0.23	2.98	2.8
2 hours	0.66	0.37	4.79	4.55
3 "	0.54	0.49	6.34	6.1
6 "	0.44	0.59	7.6	7.1
21 "	0.18	0.85	11.0	11.1
72 "	0.03	1.00	12.95	13.6

**EFFECT OF CARBON DIOXIDE.**—Carbon dioxide produces very insoluble lead salts; yet it is capable of dissolving a small quantity of lead when it is present in unusual amounts. It is a most important factor in the action of water on lead, since the so-called "erosive" action is entirely due to it. It does not prevent the action of the oxygen dissolved in the water, but it enters into combination with the oxide formed. If the amount of carbon dioxide does not greatly exceed 1 part per 100,000 of water, when lead is inserted action is distinctly visible within a few minutes. The formation of an insoluble lead carbonate layer can be seen at the surface of the metal, and this glides down and forms a turbid layer at the bottom of the bottle. As the action proceeds, the turbid layer increases in thickness until it just covers the upper surface of the lead. After this, if unshaken, the suspended matter slowly deposits and the water again becomes clear.

When the carbon dioxide exceeds 1.5 parts per 100,000 this turbidity is not produced, the water remains perfectly clear and bright, some lead is taken into solution if sufficient carbon dioxide be present, but a very insoluble carbonate is deposited on the metal, which assumes a dark grey colour. The amount of lead acted upon can be easily ascertained from the oxygen loss. It is very difficult in many cases to determine it directly by hydrogen sulphide, since a considerable amount of strong acid must be added to dissolve the deposit, and if much oxygen is left in the water the action of this acid has to be allowed for. When action has proceeded until nearly all the dissolved oxygen has been used up, the determination is easy, but when much oxygen remains a correction must be made for the amount of lead affected by the acid added. This is best done by taking duplicate samples, which are prepared and kept under identical conditions, and at the expiration of the required time one bottle is used for estimating the residual oxygen, and into the second is introduced 1 per cent. of 99 per cent. acetic acid and the bottle shaken until all the deposit is dissolved off the lead. This usually takes two to five minutes. Now 5 c.c. of the acid water are removed for the determination of the lead by means of hydrogen sulphide, and the remainder is used for the estimation of the residual oxygen. The difference between the two oxygen determinations is the measure of the lead acted upon by the acid, and affords the necessary correction. The following table is explanatory :

Time.	Oxygen in 100 c.c. of Water used.	Oxygen Lost.	Lead Equivalent.	Lead found by H <sub>2</sub> S.
	Mgrms.	Mgrm.	Mgrms.	Mgrms.
3½ days	1.103	0.52	6.75	—
3½ "	1.103	0.63	8.1	8.0 - 1.35 = 6.65
4 "	1.106	0.21	2.75	4.0 - 1.7 = 2.3
6 "	1.106	0.495	6.3	8.4 - 1.6 = 6.8
7 "	0.515	0.135	1.75	3.15 - 1.6 = 1.55

In the following table the results obtained with oxygenated water containing various quantities of free carbon dioxide are recorded. In the cases where the free



carbon dioxide was less than 1 part per 100,000 the liquid was turbid; where it contained 1.15 parts it was dull; in all the others the water remained clear.

Oxygen in Original Water per 100 c.c.	Free Carbon Dioxide. Parts per 100,000.	Total Lead acted upon calculated from O lost and by H <sub>2</sub> S.	Lead in Clear poured-off Liquid.	Lead in Filtrate.	
				Pasteur.	Paper.
Mgrms.		Mgrms.	Mgrms.	Mgrm.	Mgrm.
0.70	0.75	7.0	0.20	0.00	—
1.053	1.15	11.65	0.275	—	0.03
1.053	2.65	12.7	0.25	0.03	—
1.031	3.0	13.3	0.30	0.00	—
1.045	4.0	10.7	0.40	0.00	—
1.045	7.9	10.9	1.9	0.00	—
1.045	14.3	9.45	2.85	0.00	0.60

**INFLUENCE OF CARBONATES.**—When bicarbonates are present action is retarded, and calcium carbonate in carbon dioxide solution has a much greater retarding action than the sodium salt. Of the hundreds of experiments made, a few only can be quoted here. These show that when small quantities of carbonates only are present, the lead when immersed in the water causes more or less turbidity, but when the amount of calcium carbonate present exceeds about 1 part per 100,000 the water remains clear. A larger quantity of sodium bicarbonate is usually necessary to produce this effect.

Time.	Amount of Salt Present, Calculated on Bicarbonate.	Free CO <sub>2</sub> .	Oxygen Lost.	Lead Equivalent.	Lead by H <sub>2</sub> S.	Notes.
1 day	(CaC <sub>2</sub> O <sub>5</sub> ) 0.4	0.0	0.51	6.6	—	Turbid. No lead in solution.
"	" 0.9	0.0	0.18	2.3	—	Less turbid. Ditto
"	" 1.35	0.0	0.20	2.6	—	Clear and bright. Ditto
2 days	" 0.5	0.15	0.73	9.45	10.5	Turbid. Trace Pb in solution
"	" 1.0	0.3	—	—	4.8	Clear and bright. No Pb in sol.
"	" 1.45	0.45	0.59	7.65	8.0	" " "
"	" 1.7	0.5	0.22	2.85	2.85	" " "
4 days	" 19.0	0.55	0.22	2.85	2.8	" " "
2 days	(NaHCO <sub>3</sub> ) 0.5	0.0	0.77	10.2	10.15	Turbid. No Pb in solution
"	" 1.0	0.0	0.44	5.7	—	Clear and bright. Ditto
"	" 2.0	0.0	0.36	4.65	—	" " "
"	" 5.0	0.0	—	—	—	" " "

When water containing carbonate is kept in constant motion whilst in contact with lead, the water becomes turbid, or at least dull, and if poured off and acidified lead is found to be present. The following experimental results show how markedly the results may be affected by agitation. The water used was a pure chalk water of over 20° hardness.

Time.	Agitation.	Oxygen Present.	Free CO <sub>2</sub> .	O used.	Lead Equivalent.	Notes.
3 hours	Rotated	1.030	0.0	0.10	1.3	Water dull, but does not deposit
24 hours	At rest	1.030	0.0	0.363	4.7	Water bright. No lead in poured-off liquid

The rotated water gave the following results :

50 c.c. poured off and treated with hydrogen sulphide without acidification : lead absent.

50 c.c. poured off and treated with hydrogen sulphide after acidification : 0.32 mgrm. Pb per 100 c.c.

50 c.c. poured off and filtered through paper after acidification : 0.10 mgrm. Pb per 100 c.c.

GENERAL CONCLUSIONS.—The effect of numerous salts has been studied, but the results must be reserved for another occasion. The experiments above recorded prove that water has no action whatever on lead ; that it is the foreign matters dissolved in water which affect the metal, the oxygen combining with it to form a soluble oxide or hydroxide, which remains in solution (to the point of saturation) in the absence of other substances capable of combining with it. This solution is of a colloidal nature and of such coarse degree of dispersion or so liable to adsorption that it will not pass through a Pasteur filter, and may not even pass a fine paper filter. In the presence of acids forming soluble lead salts, such salts are formed and will pass through any filter. If the acid forms insoluble salts, these are thrown down, and may be deposited on the metal in such a way as to prevent any further action. Any soluble salts present in the water may likewise act upon the lead hydroxide. Water is merely an inert medium, by means of which these foreign substances are enabled to act upon each other, the water itself taking no part other than that of a solvent.

