A NEW GRAVIMETRIC METHOD FOR THE DETERMINATION OF LEAD AS LEAD SALICYLALDOXIME AND ITS SOLUBILITY MEASUREMENT BY USING ThB AS RADIOACTIVE INDICATOR.

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I. Gravimetric Determination of Lead as Salicylaldoxime Compound.

An excellent method of quantitatively determining copper as a salicylaldoxime compound has been proposed by F. Ephraim.(1) The present authors

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(1) F. Ephraim, *Ber*, **63** (1930), 1928.

have now found a new gravimetric method for the analysis of lead using salicylaldoxime.

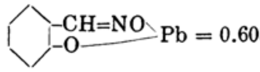
Material Used. The sample used was Kahlbaum's lead acetate for analysis, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, the composition of which was proved to be quite exact by the gravimetric determination of lead as the chromate. Of this substance, 7.3228 g. was dissolved in 1 liter; and this solution contains 0.0400 g. of lead in 10 ml.

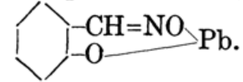
Salicylaldoxime was prepared from salicylaldehyde and hydroxylamine hydrochloride and purified by repeated recrystallization from ligroin. The colourless crystals thus obtained had the melting point 63°C. The substance had some tendency to get somewhat coloured when stored. One gram of it is dissolved at room temperature in 5 ml. of alcohol and the solution is slowly poured into 95 ml. of pure water warmed to about 80°C. A little of the oxime which may remain at first as a turbid suspension is gradually dissolved away. The solution is now filtered after a thorough stirring and the 1% solution of the oxime thus prepared is used for precipitating the lead salt.

Procedure. Twenty-five ml. of the lead acetate solution is diluted with pure water to about 50 ml. and treated with a slight excess of salicylaldoxime. Ten per cent. ammonia water is then slowly added so as to make the pH of the solution greater than 6.5. For this purpose, neutral red ($p\text{H} = 6.8-8.0$) or phenolphthalein ($p\text{H} = 8.2-10.0$) is used as a convenient indicator. After clarifying the turbid mother liquor by stirring, it is allowed to stand about an hour. The easily filtrable precipitate of slightly yellow colour is transferred to a glass filter, washed with 20% alcohol, and filtered by suction. It is thoroughly dried at about 105°C., cooled, and weighed as usual. The result is shown in Table 1.

Table 1.

No.	Salicylaldoxime added (g.)	Pb-Salicylaldoxime found (g.)	Pb		Difference (g.)
			added (g.)	found (g.)	
1	0.08	0.1648	0.1000	0.1000	0.0000
2	0.08	0.1647	0.1000	0.0997	−0.0003
3	0.08	0.1646	0.1000	0.0996	−0.0004
4	0.08	0.1647	0.1000	0.0997	−0.0003
5	0.08	0.1645	0.1000	0.0996	−0.0004

Pb :  = 0.6054.

For deciding upon the composition of lead salicyladoxime, the quantitative determination of lead and nitrogen in it was made. Lead in a weighed quantity of the substance dried at 105°C. was precipitated in acetic acid solution as lead chromate and weighed. Nitrogen was determined as ammonia by the Kjeldahl method. As shown in Table 2 the results prove that the probable composition is Pb($C_7H_5O_2N$) and suggest that the allowable constitution is 

It is to be noted here that, in copper salicylaldoxime, one atom of copper is combined with two molecules of salicylaldoxime, while, in lead salicylaldoxime, one atom of lead is combined with only one molecule of the aldoxime. Similar examples are found among other oxime compounds of metals, which we intend to report in another connection.

Table 2.

Pb-Salicylaldoxime taken (g.)	$PbCrO_4$ found (g.)	Pb			Difference %
		g.	%	as Pb($C_7H_5O_2N$) %	
0.1640	0.1558	0.09988	60.81	60.54	+0.27
Pb-Salicylaldoxime taken (g.)	**NH_3 found (g.)**	**N**			**Difference %**
		g.	%	as Pb($C_7H_5O_2N$) %	
0.1642	0.007627	0.006272	3.82	4.09	−0.27

The hydrogen ion concentration of the precipitating solution, from which lead salicylaldoxime was completely precipitated, was determined with indicators in the following way. A strong acetic acid solution of lead acetate was first prepared, in which the addition of an excess of the salicylaldoxime solution formed no precipitate. This acid mixture was divided into several portions, to each of which a separate indicator was added and ammonia water was poured drop by drop so as to produce a definite colour grade showing a definite pH value. The reaction mixtures were allowed to stand for an hour, and then filtered. Each of the filtrates was now tested for lead with sodium sulphide solution to ascertain the degree of completeness of precipitation. Indicators used for this purpose were tropeolin 00 ($p\mathrm{H} = 1.3-3.0$), methyl orange ($p\mathrm{H} = 3.1-4.4$), methyl red ($p\mathrm{H} = 4.2-6.3$), neutral red ($p\mathrm{H} = 6.8-8.0$), and phenolphthalein ($p\mathrm{H} = 8.2-10.0$). It was found that, at $p\mathrm{H} \geqq 6.5$, the filtrate formed no precipitation of lead sulphide showing that the preceding precipitation of lead salicylaldoxime was complete. By utilizing the differences of pH values produced in this way, the authors⑵ succeeded in separating and determining copper and lead in a mixture.

II. Solubility Determination of Lead Salicylaldoxime by Using Th B as the Radioactive Indicator. There are four methods used ordinarily in determining solubilities of difficultly soluble compounds; namely, (1) a definite quantity of the saturated solution is evaporated to dryness and the dry residue weighed; (2) the electrical conductivity of the saturated solution is determined and the solubility calculated; (3) the single potential between the electrode and ions of the dissolved salt is measured and the solubility calculated; (4) the solubility product is first found from the equilibrium constant and the solubility calculated.

Each of these methods is accompanied by a theoretical limitation and consequently the result gives only a conditional value. The fifth method described below is free from this defect. (5) G. v. Hevesy and F. Paneth⑶ first used in the determination of the solubility of lead chromate Ra D as indicator. Generally, when a radioactive isotope of the metal, whose salt is to be measured, is used as an indicator, the solubility found represents the total quantity of the dissolved part no matter whether that part is ionized or hydrolyzed or not. Moreover, the manipulation of this method is not complex at all and the result is believed to be far more rational than that obtained with the four ordinary methods.

The solubilities of some of difficultly soluble organo-metallic complex salts are known, but, as they were determined by the first method cited above, there is no safeguard as to their exactness. The present authors have succeeded in obtaining exact solubility of lead salicylaldoxime in water with the use of Th B ($T = 10.6$ h.), the radioactive isotope of lead.

Radio-thorium was taken as the mother substance of Th B. In the upper part of the receptacle for radio-thorium, a small plate of platinum, which is easily inserted or removed, is suspended. Between the receptacle (+) and the platinum plate (−) a pure water resistance is inserted and a potential of 200 volts is applied with both the terminals connected with the earth. As soon as thorium-emanation is evolved from radio-thorium through the step of Th X, it is caught on the platinum plate and Th A, Th B, Th C, etc. are caused to deposit on it. On taking off the platinum plate, Th A ($T = 0.14$ sec.) is rapidly disintegrated and leaves Th B, Th C, etc. behind. It is to be

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(2) M. Ishibashi and H. Kishi, *J. Chem. Soc. Japan*, **55** (1934), 1067.

(3) G. v. Hevesy and F. Paneth, *Z. anorg. allgem. Chem.*, **82** (1913), 223.

noted here that the radio-activity (β-ray) of Th B is too weak and insufficient, so that what we measure practically is the intensity of α- and β-rays evolved from Th C produced from Th B. For this reason, it is necessary that Th B and Th C are in transient equilibrium ; if the radio-activity of radio-thorium is strong and the duration of exposure of the platinum plate short, an allowance of a certain period of time will be necessary before the attainment of this transient equilibrium. In our case, however, the quantity of radio-thorium was small and the radio-activity weak, so that about one week's exposure of the platinum plate was necessary for performing one experiment. In such a case, it is to be easily presumed, and is also proved, that the transient equilibrium is practically attained at the moment of the removal of the platinum plate.

The measuring apparatuses used were the radioscope of the Rikagaku-kenkyujo, an accurate watch, and a stop-watch. According to the theoretical formula expressing the decline of radioactivity, $I_t = I_0 e^{-\lambda t}$, the value for a definite instant was calculated from the experimental values at various instants. I_0 is the radioactivity at the start, I_t that at the end of a period t, λ the disintegration coefficient, which is 0.0654 (h.$^{-1}$) for Th B.

Procedure. The platinum plate suspended above radio-thorium for about one week was treated with about 5 ml. of hot concentrated acetic acid to dissolve the deposited Th B, Th C, etc. The solution was diluted to about 50 ml. with pure water and exactly one ml. of it was taken from a burette on a watch glass. It was now evaporated up on the water bath and dried in the air bath at about 120°C. The radioactivity was measured with the residue after its complete cooling (Table 3). Radioactivity measurements made later on were calculated back to that of this first instant.

On the other hand, 20 ml. of the same radioactive indicator solution were measured off from the burette and poured into a beaker of 100 ml. capacity ; a weighed quantity of lead acetate was added to it and dissolved by stirring with a glass rod so as to distribute the acetates of Th B and Th C homogeneously in the lead acetate solution. The salicylaldoxime solution was now added in excess. After adding phenolphthalein, ammonia water was slowly added with constant agitation until pink colour was produced. After allowing to stand for about an hour, the precipitate was collected and washed in the usual way.

The wet lead salicylaldoxime thus prepared was placed in an Erlenmeyer flask of about 200 ml. capacity, about 100 ml. of pure water was added to it, and the flask was tightly closed with a rubber stopper and introduced to a thermostat at 25°C. It was kept in rotation for 24 hours for the purpose of the complete saturation. Finally it was taken out from the thermostat and filtered. About 20 ml. of the first filtrate were thrown away for avoiding the concentration change caused by the adsorption on filter paper. Out of the remaining 80 ml. of the filtrate, 50 ml. are accurately measured out into the evaporating dish, evaporated on the water bath, and dried in the air bath as before. After cooling, the radioactivity was measured (Table 4 and Table 5).

Table 3.

Natural discharge			Radioactivity for 1 ml.			
Measuring time elapsed (min.)	Reading of scale divisions	Number of scale divisions per min.	Measuring time elapsed (min.)	Reading of scale divisions	Number of scale divisions per min.	Corrected value (I_0)
0.00	60.0	0.50	0.00	60.0	26.0	26.0–0.5 = 25.5
20.00	50.0		0.77	40.0		

Table 4.

Radioactivity for 20 ml.	$Pb(C_7H_5O_2N)$ equivalent to 0.0318 g. of $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ (g.)	$Pb(C_7H_5O_2N)$ corresponding to radioactivity of one scale division per min. (g.)
Number of scale divisions per min. $25.5 \times 20 = 510$	$\frac{0.0318 \times 0.5463}{0.6054} = 0.0287$ $\begin{cases} Pb/Pb(C_2H_3O_2) \cdot 3H_2O = 0.5463 \\ Pb/Pb(C_7H_5O_2N) = 0.6054 \end{cases}$	$0.0287/510 = 0.0000564$

Table 5.

Natural discharge			Radioactivity for 50 ml.				
Measuring time elapsed (min.)	Reading of scale divisions	Number of scale divisions per min.	Measuring time elapsed (min.)	Reading of scale divisions	Number of scale divisions per min.	Corrected value	
						I_t	I_0
0.00	50.0	0.41	0.00	50.0	0.56	0.56–0.41 = 0.15	1.14
24.39	40.0		17.86	40.0			(t=31 hs.)

It is seen from Table 5 that the radioactivity of the dried material from 50 ml. of the saturated solution of lead salicylaldoxime is 1.14, and hence the radioactivity for one liter of it is $1.14 \times 20 = 22.8$. From Table 4 it is known that the weight of lead salicylaldoxime corresponding to unit radioactivity is 0.0000564 g. and hence the solubility in 1 liter of pure water at 25°C. must be $22.8 \times 0.0000564 = 0.0001287$ g. $\fallingdotseq 1.29 \times 10^{-3}$ g.

In the same way, the result of the second experiment with the saturation time of 15 hours was found to be 1.61×10^{-3} g., and that of the third experiment with the saturation time of 27 hours was found to be 1.22×10^{-3}g. The minimum time necessary for the complete saturation is thus found to be somewhere within 15 hours of rotatory agitation.

Table 6. Solubility per liter at 25°C.

Pb-Salicylaldoxime				Pb	
(g.)		(mol)		(g.)	
1.29×10^{-3}	mean 1.37×10^{-3}	3.8×10^{-6}	mean 4.0×10^{-6}	7.79×10^{-4}	mean 8.31×10^{-4}
1.61×10^{-3}		4.7×10^{-6}		9.75×10^{-4}	
1.22×10^{-3}		3.6×10^{-6}		7.39×10^{-4}	

Summary.

(1) Lead is quantitatively precipitated as salicylaldoxime compound from a neutral and a strongly ammoniacal solution of $p\mathrm{H} \overset{=}{>} 6.5$.

(2) The composition of the material precipitated and dried at about 105°C. is possibly $\mathrm{Pb(C_7H_5O_2N)}$.

(3) The solubility of lead salicylaldoxime in pure water at 25°C., measured by the use of radioactive isotope Th B as indicator, is 1.37×10^{-3} g. per liter, i.e., 4.0×10^{-6} mol/l.

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