

Use of complex compounds in chemical analysis.

I. Determination of Lead with 6-nitro complex salts.

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A. The permanganometric titration.

I. Introduction.

The analytical determination of metals with 6-nitro complex salt have long been known. Especially, sodium 6-nitro-cobaltic salt ($\text{Na}_3[\text{Co}(\text{NO}_2)_6]$) is used for the determination of Potassium and regarding this we have many reports in the present time.¹⁾

Professor Kato²⁾ reports that the difficultly soluble complex salt $\text{K}_2\text{NiZn}(\text{NO}_2)_6$, $\text{K}_2\text{NiPb}(\text{NO}_2)_6$, or $\text{K}_2\text{CuPb}(\text{NO}_2)_6$,—a Complex with the general formula $\text{K}_2\text{MM}'(\text{NO}_2)_6$ in which the sum of the valencies of M and M' is four—may be equally used as Cobaltic salt.

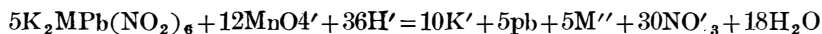
The present authr has investigated a method of determination of bi-valent metals (especially Lead), making the metal form the above mentioned type of complex in the manner $\text{K}_2\text{MPb}(\text{NO}_2)_6$.

The method depends upon the principle;—(1) the formation of the above salt $\text{K}_2\text{MPb}(\text{NO}_2)_6$, and (2) the titration of this precipitation with permanganate.

The sensitivity of this complex formation is 1:20000 for Nickel, and 1:5000 for Copper.

According to professor Kato³⁾, when the precipitate is titrated with permanganate, the endpoint is interfered by the presence of colouring Nickel- or Copper-ions; therefore, cobaltic salt is more suitable for the determination of potassium. But in the present study, no difference has been found between usual permanganometry and ammonium ferrous sulfate-permanganometry with Diphenylamine as the indicator, and hence, the former method was used under care.

The titration proceeds in the following way the oxidizing due to the central metal as in the case of cobaltic salt does not exist and 12 oxidizing units are necessary for NO_2 contained in 1mol $\text{K}_2\text{MPb}(\text{NO}_2)_6$.

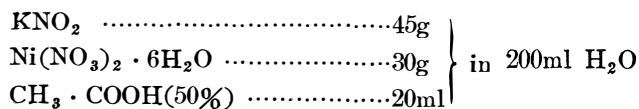


$$\therefore 0.1\text{N KMnO}_4 \text{ 1ml} = 0.00172675\text{g Pb}$$

II. Experimental Procedure.

Reagents : KNO_2 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were purified by recrystallizing several times from water. If the reagents were added to sample solution separately, the precipitation formed differs in appearance. Accordingly, the reagents were previously dissolved in the following manner and used after ageing for 1 or 2 days, the precipitate caused by impurities being filtered.

(I) Nickel-reagent



(II) Copper-reagent

KNO ₂	50g	} in 200ml H ₂ O
Cu(NO ₃) ₂ · 3H ₂ O	20g	
CH ₃ · COOH(50%)	20ml	

Sample : 16.5g of Pb(NO₃)₂, recrystallized several times from water, was dissolved in 1 L water, The exact amount of Pb existing was determined by means of 8-oxychinoline and the solution was made to the concentration 10.25mg/. cc.

Analytical procedure. To the sample solution in a small beaker, Nickel- or Copper-reagent was added, stirred sufficiently, and after standing for about 2 hours, perfectly precipitated brownish yellow Pb-Ni salt or dark grey Pb-Cu salt was filtered through glass filter G. 4, washed several times with the saturated solution of the same salt and finally with 95%-alcohol.

The salt was then transferred into a closed vessel with hot water. The air in the vessel being substituted with CO₂, 10–40ml of 18N-H₂SO₄ was added and made into the dilution 3–6N with O₂-free water.

When the complex salt sufficiently decomposed in the closed vessel, N/10-KMnO₄ solution was added, decolorized with N/10-Na₂C₂O₄ solution, and the excess of Na₂C₂O₄ was titrated with N/10-KMnO₄.

III. Experiments and Results.

The conditions governing the formation of the complex salt precipitate by the mixed reagents were studied.

(1) Amount of the reagent to be added.

Different volumes of Ni- and Cu- reagents were tried to see their amounts which make Pb precipitate completely.

As shown in Table I. and II., the results were very unsatisfactory even in cases where the reagents are quite excess.

Table I.
Nickel reagent.

Exp. No.	Sample taken (Pb mg)	Reagent added (ml)	N/10 KMnO ₄ used (ml)	Pb found (mg)
1	51.3	1	0.11	0.2
2	"	2	1.35	2.3
3	"	5	4.64	8.0
4	"	10	19.83	34.2
5	"	15	24.22	41.8
6	"	20	26.85	46.4

Table II.
Copper reagent

Exp. No.	Sample taken (Pb mg)	Reagent added (ml)	N/10 KMnO_4 used (ml)	Pb found (mg)
1	20.5	1	2.30	4.1
2	"	2	5.43	9.4
3	"	3	5.48	9.5
4	"	5	8.40	14.5
5	"	10	8.71	15.0
6	"	15	9.88	17.0

(2) Effect of the standing time.

After the reagent was added and stirred enough, it was allowed to stand various hours in the room temperature. As seen in Tables III. and IV., the longer the time of standing, the more complete is the precipitate formation, but the result is still unsatisfactory.

Table III.

Sample taken : 51.3mg Pb, Ni-reagent added : 20ml, Total volume : 35ml

Exp. No.	Time (h)	N/10 KMnO_4 used (ml)	Pb found (mg)
1	1	27.68	47.8
2	2	28.54	49.3
3	4	28.94	50.0
4	8	29.12	50.3
5	24	29.12	50.3

Table IV.

Sample taken : 20.5mg Pb. Cu-reagent added : 15ml, Total volume : 18ml.

Exp. No.	Time (h)	N/10 KMnO_4 used (ml)	Pb found (mg)
1	0.5	9.83	16.9
2	1	10.70	18.5
3	2	11.78	20.3
4	5	11.88	20.5

(3) Effect of the total volume of the solution.

The time of standing was limited to 2 hours constant and the total volume of the solution was varied by evaporation to find the point where the complete precipitation is attained. In Tables V. and VI., we see that the Lead in the solution should exceed the amount ca. 2 mg/ml. for the purpose.

Table V.

Sample taken 51.3g Pb Ni-reagent ; 20ml, Time 2hs.

Exp. No.	Total Volume (ml)	N/10 KMnO ₄ used (ml)	Pb found (mg)
1	evap. to 20	29.69	51.3
2	50	29.39	50.8
3	100	24.88	43.0
4	250	trace	—

Table VI.
Sample taken 20.5mg pb, Cu-reagent 15ml, Time 2hs.

Exp. No.	Total Volume (ml)	N/10 KMnO ₄ used (ml)	Pb found (mg)
1	evap. to 15.5	11.77	20.3
2	17	11.77	20.3
3	20	10.50	18.1
4	30	6.20	10.7
5	50	3.89	6.7

(4) Experimental results.

On the basis of the studies above mentioned, the experiment has been made in the following procedure :

The solution containing 10mg-100mg Pb is concentrated on steam bath, sufficient amount of the reagent is added dropwise, allowed to stand for about 2 hours at room temperature, and is titrated with standard N/10-KMnO₄ solution in the closed vessel. The results obtained are quite satisfactory they shown in Tables VII and VIII.

Table VII.

Exp. No.	Sample taken (Pb mg)	Reagent added (ml)	N/10 KMnO ₄ added F = 1.16853 (ml)	N/10 Na ₂ C ₂ O ₄ added F = 0.98975 (ml)	N/10 KMnO ₄ Titer F = 1.16853 (ml)	N/10 KMnO ₄ O ₄ used (ml)	Pb found (mg)	Error (mg)
1	10.3	5	10	10	3.51	5.89	10.2	-0.1
2	"	"	"	"	3.50	5.88	10.1	-0.2
3	20.5	15	25	25	6.35	11.88	20.5	0.0
4	"	"	"	"	6.35	11.86	20.5	0.0
5	41.0	30	25	25	16.48	23.73	40.9	-0.1
6	"	"	"	"	16.46	23.71	40.7	-0.3
7	51.3	30	50	35	4.95	29.66	51.2	-0.1
8	"	"	"	"	4.95	29.66	51.2	-0.1
9	102.5	40	75	35	5.00	58.84	101.6	-0.9
10	"	"	"	"	4.98	58.81	101.5	-1.0

Table VIII.

Exp. No.	Sample taken (Pb mg)	Reagent added (ml)	N/10 KMnO ₄ added F=1.02452 (ml)	N/10Na ₂ C ₂ O ₄ added F=0.99994 (ml)	N/10 KMnO ₄ Titer F=1.02452 (ml)	N/10KMnO ₄ O ₄ used (ml)	Pb found (mg)	Error (mg)
1	10.3	5	25	25	5.25	5.99	10.3	0.0
2	"	"	"	"	5.20	5.94	10.3	0.0
3	20.5	10	25	25	10.95	11.83	20.4	0.1
4	"	"	"	"	10.95	11.83	20.4	0.1
5	30.8	15	25	25	16.85	17.88	30.9	0.1
6	"	"	"	"	16.80	17.83	30.8	0.0
7	41.0	20	25	25	22.50	23.71	40.8	0.2
8	"	"	"	"	22.48	23.65	40.8	0.2
9	51.3	25	35	25	18.08	29.35	50.7	0.6
10	"	"	"	"	18.12	29.42	50.8	0.5

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B. Indirect colorimetric determination of Lead.

I. Introduction.

The indirect colorimetric determination for Sodium by means of the complex Na₂MUO₂(CH₃COO)₄ is well known.¹⁾

Recently, Tsyvina²⁾ and Shigematu-Kimura³⁾ report the similar method for calcium and sodium depending upon the complex K₂CaNi(NO₂)₆, and Na₂NiUO₂(CH₃·COO)₄ respectively.

The present method is an application of the colorimetric determination of Nickel or Copper, which forms complex Dimethylglyoxime salt in a neutral or a weak alkaline solution. Namely, the indirect determination of Lead is made by means of the same colour reaction using Nickel or Copper, respectively existing in the complex K₂NiPb(NO₂)₆ or K₂CuPb(NO₂)₆ described already in the above part of the report.

II. Experimental procedure.

Reagents ;

- 1). Nickel and Copper reagents are the same as used in above experiment A.
- 2). 1% alcohol solution of Dimethylglyoxime.
- 3). 0.5% AgNO₃ aqueous solution.
- 4). (NH₄)₂S₂O₈ crystal.
- 5). 10% pyridin aqueous solution.

Colorimeter : Dubosq type colorimeter used under the sun light.

Analytical procedure :

The sample solution containing 50~250 γ Pb was concentrate nearly to dryness, 3-5ml of the Nickel or Copper reagent was added, stood for about 2-3hs, filtered, washed with 2-5ml of 25% KNO₂ solution previously saturated with the complex salt. Dissolve the precipitate in hot water (about 80°C) and dilute to 100ml-200ml in measuring flask.

The colouring condition was regulated according to the method described by Shigematu and Kimura for Nickel, and by Clark and Jones⁴⁾ for Copper.

As the standard solutions, definite amounts of Pb-Ni, Pb-Cu complex salts prepared previously and dried sufficiently on filter paper were dissolved in water and encolored under the same condition.

III. Experiments and Results.

(1) Effect of co-existent Pb⁺⁺ ion.

In the colorimetric determination of Nickel with 1% Dimethylglyoxime alcohol solution, the effect of co-existent Pb⁺⁺ ion was found for the first time when it was present in a quantity more than 15 times.

Similarly, in the case of Cu existence of Pb⁺⁺ ion hardly affected the results.

Table I.

Exp. No.	Nickel taken (γ)	Co-existent Pb ⁺⁺ (γ)	Color. det. of Nickel (γ)
1	197	--	194
2	"	103	194
3	"	206	192
4	"	515	194
5	"	1030	192
6	"	2575	151

Table II.

Exp. No.	Copper taken (γ)	Co-existent Pb ⁺⁺ (γ)	Color. det. of Copper (γ)
1	92	--	90
2	"	103	92
3	"	206	91
4	"	515	91
5	"	1030	90
6	"	2575	93

(2) Effect of acidity.

In application of Clark and Jones method to the colorimetric determination of Copper, the effect of 5% acetic acid added in order to decompose K₂PbCu(NO₂)₆ on the intensity of the colour was observed.

The best results were obtained when the salt is decomposed with 0.5–2ml of 5% acetic acid and diluted to 200ml.

Table III.

Exp No.	Copper taken (γ)	amounts of 5% HAC added (ml)	Color. det. of Copper (γ)
1	90	0.5	93
2	"	1	88
3	"	2	86
4	"	5	50
5	"	10	43

(3) Determination of Lead.

The results of indirect colorimetric determination of Lead in the solution containing 50–250 γ Pb were obtained as shown in following table.

Table IV.

Exp. No.	Sample taken (pb γ)	Reagent added (ml)	Color. det. of Pb (γ)	Error (γ)
1	50	3	55.5	+5.5
2	"	"	51.0	+1.0
3	100	"	103.0	+3.0
4	"	"	98.5	-1.5
5	150	"	151.5	+1.5
6	"	"	152.5	+2.5
7	200	"	208.0	+8.0
8	"	"	211.5	+11.5
9	250	"	245	-5.0
10	"	"	258	+8.0

Table V.

Exp. No.	Sample taken (pb γ)	Reagent added (ml)	Color. det. of Pb (γ)	Error (γ)
1	50	3	53.5	+3.5
2	"	"	49	-1.0
3	100	"	104.5	+4.5
4	"	"	108.7	+8.7
5	200	5	196	-4.0
6	"	"	201	+1.0
7	250	"	238.3	-11.7
8	"	"	244	-6.0

Summary.

50--250 γ of Lead was precipitated with 6-nitro salt, and the determination of Lead by means of colorimetric determination of Nickel or Copper in the precipitate was performed.

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