New Method of Determination of Thallium with Cobalt Hexammine Trichloride.

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Introduction. Thallium is usually found in small quantities in association with large amounts of alkali metals and other elements and also contained in chamber muds in plants commercializing sulfuric acid, and in the flue-dust formed during the calcination of iron pyrites, lead ores and zinc blend.

In 1863, W. Crookes proposed the iodide method[1]. However, several defects were pointed out by some workers,[2] and as a substitute for the iodide method the chromate method was recommended by Moser and Brunkle[3] as being most accurate in the determination of thallium. This chromate method had been in general use for a long time, but as the preliminary separation of many metals that are commonly present with thallium is troublesome, besides having to allow a little over 12 hours for complete precipitation, several other methods were in continuous study by many workers. No one proposed method yet has been approved for wide use. On the other hand, the application of the organic reagents, such as thionalide,[4] mercapto-benzothiazol[5] and thiourea[6], to the determination of thallium has been recommended because of their good sensitivity. However, when not more than 10 mg. in a 50 gr. sample of flue-dust and chamber muds containing a large quantity of common metals is to be determined, none of the so-far suggested methods is qualified as a sufficient answer to the problem.

Among the above mentioned methods, the thionalide method is the most sensitive, though it does not show specific reaction to the thallium (Mehrdeutigkeit) and a rough estimation as to the test sample is required before the thionalate formation can be made. In a case of minute

(1) W. Crookes, *Chem. News*, **7** (1863), 133; *J. Chem. Soc.*, **17** (1864), 115; G. Werther, *Z. anal. Chem.*, **3** (1864), 1; H. Baubigny, *Compt. rend.*, **113** (1891), 544; W. Lepper, *Z. anal. Chem.*, **79** (1930), 323.

(2) F. Mach and W. Lepper, *Z. anal. Chem.*, **68** (1926) 40; F. Cuta, Collection Czechoslovak. Chemical Communications, **7** (1935), 33; W. Lepper, *Z. anal. Chem.*, **79** (1930), 323, H. Baubigny, *Chem. News*, **64** (1891), 239.

(3) L. Moser and A. Brukle, *Monatsh.*, **47** (1926), 709; J. Bondanar and A. Terenyi, *Z. anal. Chem.*, **69** (1926), 32; A. Cernotzky, *Z. anal. Chem.*, **93** (1933), 349.

(4) R. Berg and Fahrenkamp, *Z. anal. Chem.*, **109** (1937) 305; R. Berg and W. Roebling, *Angew. Chem.*, **48** (1935), 430.

(5) G. Spacu and K. Kuras, *Z. anal. Chem.*, **109** (1936), 90.

(6) C. Mahr and O. Ohle, *Z. anal. Chem.*, **115** (1939), 256.

thallium determination in such samples as in flue-dust and chamber muds occurring with an abundance of many other metals, it is very difficult and impractical according to the author's experience. The thiourea method with which perchloric acid is required has its defects, due to the formation of an elastic compound resembling india-rubber when confronted with specially large quantities of copper, zinc and lead. Moreover the Tl-thiourea complex has a perceptible solubility even in ice cold water. It is an unsatisfactory method for determination of such minute amounts of thallium as was attempted by the author.

In the face of these difficulties the author has taken interest in a suggestive report by Spacu *et al*[7] stating that thallium can be determined as $Co(NH_3)_6(TlCl_6)$ which is practically insoluble in a slightly acidic medium. In this paper, though the result of the gravimetric determination of considerable amounts of thallium (80 to 100 mg.) only in a pure salt solution is reported, the experimental conditions are not given in details and examination of the interference of many metals, which is of the most practical importance, was not performed. However it is easy to suppose that the determination of a minute quantity of thallium in such samples with accurate results is possible as the factor for thallium in $Co(NH_3)_6(TlCl_6)$ is the least (0.35346) of all factors in the gravimetric method.

This investigation is based upon the above report and was undertaken for the following purposes: (a) To determine the interference of other metals, if any. (b) To note the experimental conditions and to determine as little as 5 to 10 mg. of thallium. (c) To determine whether it is applicable to the determination of thallium in flue-dust and chamber muds.

Experimental.

(a) **Reagent used.** *Thallium standard solution.* Thallium sulfate, Merck reagent (For Analysis), was recrystallized twice and heated to about 400°C in an electric furnace. The standard solution was prepared by dissolving the salt thus obtained.

Cobalt hexammine trichloride $Co(NH_3)_6Cl_3$ (for the sake of convenience, called luteo salt hereafter). Luteo salt is easily prepared from cobalt chloride, ammonium chloride, silver nitrate and ammonia according to Biltz,[8] and recrystallized from saturated solution by the addition of hydrochloric acid. The saturated solution, the concentration of which is about 20 M at room temperature, was used. It is desirable that any contaminable matter be filtered off before using and to preserve it in amber-colored bottle as decomposition will take place with exposure to light.

(b) **Addition of ammonium chloride.** The original report stated the greater possibility of success by making a precipitation under 2.5N hydrochloric acid solution. The suitable acid concentration in this case was tested as shown in Table 1.

These results indicated that it may be safer to use a 2.5N acid solution as previously reported. However, the lower results were obtained due to incomplete pre-

(7) G. Spacu and A. Pope *Z. anal. Chem.*, **120** (1940), 322.

(8) H. Biltz, „Übungsbeispiele aus der unorg. Experimentalchemie", S. 165, Leipzig (1913).

Table 1. Acid Concentration

Acid Concentration	$Co(NH_3)_6TlCl_6$ (g.)	Tl-found (g.)	Tl-present (g.)	Difference (g.)	Remarks
0.33N HCl	0.0284	0.01004	0.01002	+0.00002	added some NH_4Cl
0.66N HCl	0.0288	0.01018	0,01002	+0.00016	instantly pptd.
1.32N HCl	0.0283	0.01000	0.01002	−0.00002	,,
1.98N HCl	0.0288	0.01018	0.01002	+0.00016	
3.30N HCl	0.0298	0.01060	0.01002	+0.00058	luteo salt pptd.
0.82N HNO_3	0.0265	0.00937	0.00970	−0.00033	
2.26N HNO_3	0.0290	0.01025	0.00970	+0.00055	
3.86N HNO_3	0.0064	0.00227	0.00970	−0.00743	precipitate dissolved
5.46N HNO_3	0.0005	0.00047	0.00970	−0.00923	,,
1.02N H_2SO_4	—	—	0.00970	−0.00970	not precipitated
2.46N H_2SO_4	0.0237	0.00837	0.00970	−0.00133	
4.26N H_2SO_4	0.0168	0.00594	0.00970	−0.00376	
7.86N H_2SO_4	—	—	0.00970	−0.00970	,,

cipitation as sometimes happen especially with sulfuric acid or nitric acid solution owing to the amount of chloride ion present being insufficient to form $TlCl_6'''$. But this difficulty is easily removed by the addition of ammonium chloride as shown in Table 2 and the range of acid concentration is safely extended to about 3N. Moreover the determination can be made in any kind of acid medium.

It was also found that the addition of about 0.5 g. ammonium chloride is responsible for the perfect change of thallium ion into $TlCl_6'''$. Furthermore it makes possible the determination of thallium as slight as 5 mg. gravimetrically indeterminable by any other method up to date. Thallium is not easily oxidized with nitric acid alone, but its complete oxidation can be effected in the presence of any chloride ion. As there is a tendency that hydrolysis of thallic nitrate or sulfate will occur, especially when hot, the formation of $TlCl_6'''$ is sometimes difficult. But ammonium chloride removes also these difficulties. Consequently the addition of ammonium chloride newly recommended is remarkably useful in this instance, especially with sulfuric acid solution most commonly used.

Table 2. Effectiveness of the Addition of NH_4Cl

Acid Concentration	HCl (ml.)	NH_4Cl (g.)	Tl-complex (g.)	Tl-found (g.)	Tl-present (g.)	Difference (g.)
2.0N H_2SO_4	15	0.5	0.0324	0.01145	0.01149	−0.00004
2.0N H_2SO_4	15	none	0.0311	0.01099	0.01149	−0.00050
2.0N H_2SO_4	none	0.5	0.0325	0.01149	0.01149	−0.00000
2.0N H_2SO_4	none	none	0.0229	0.00081	0.01149	−0.01068
1.9N HNO_3	15	0.5	0.0326	0.01152	0.01149	+0.00003
1.9N HNO_3	15	none	0.0235	0.01007	0.01149	−0.00142
1.9N HNO_3	none	0.5	0.0308	0.01089	0.01149	−0.00060
1.9N HNO_3	none	none	0.0237	0.00105	0.01149	−0.01044
2.5N H_3PO_4	none	0.5	0.0301	0.01064	0.01032	+0.00032
2.5N H_2SO_4	5	0.5	0.0304	0.01075	0.01032	+0.00043
2.5N H_2SO_4	5	none	0.0232	0.00997	0.01032	−0.00035

(c) **General procedure.** Oxidation can be easily carried out with some particles of potassium chlorate and about 0.5 g. ammonium chloride added to the boiling solution. Boiling is continued until the volume is reduced to one half, and then it is allowed to stand at room temperature. Thus the solution is ready for the precipitation. If luteo salt solution is added, a brown orange precipitate forms instantanously. When the temperature

of the solution exceeds 50°C, thallic oxide may be precipitated, the formation of which should be avoided.

Twice the amount of luteo salt solution should be added, though theoretically it is sufficient to add 1.3 times the amount of thallium expected in the solution. The precipitate is decanted with 2% HCl solution and transferred to a glass filter G4. Washing must be continued until the washing solution becomes colorless, usually requiring more than 200 ml. for 10 mg. thallium. The precipitate then is washed three times with 5 ml. each of 95% alcohol followed by three times with ether. The precipitate is then dried at 105°C from a half to an hour, and transferred in desicator to cool at room temperature. Thallium now is weighed as $Co(NH_3)_6(TlC_6)$ (F = 0.35346).

The result agrees with the true value within the errors allowed as shown in Table 3. However deviation may be caused, maximum deviation of results was found less than 1.5% of thallium. The remarkable characteristics of this method is that a minute amount of thallium can be determined with fairly good results by the addition of ammonium chloride without any hazardous operation.

Table 3. Accuracy

Tl-present (g.)	$Co(NH_3)_6(TlCl_6)$ (g.)	Tl-found (g.)	Difference (g.)	Error %
0.00574	0.0163	0.00576	+0.00002	+0.35
0.00484	0.0135	0.00480	−0.00004	−0.82
0.00968	0.0275	0.00972	+0.00004	+0.41
0.00968	0.0270	0.00954	−0.00014	−1.4
0.00968	0.0269	0.00950	−0.00018	−1.8
0.01148	0.0321	0.01149	+0.00001	+0.00
0.01937	0.0551	0.01949	+0.00010	+0.51
0.01937	0.0543	0.01919	−0.00018	−0.92
0.01937	0.0546	0.01930	−0.00007	−0.35
0.01937	0.0547	0.01940	+0.00003	+0.16
0.02903	0.0822	0.02905	+0.00002	+0.07
0.03980	0.1126	0.03973	−0.00007	−0.18

Proposed Method. For practical application, it is necessary to get sufficient knowledge on the behavior of various other ions on luteo salt. However as this proposed method isolates some ions precipitating with luteo salt, for the sake of convenience, this new method will be discussed before the interference is discussed.

(*a*) *Proposed Method.* Finely ground sample such as flue-dust and chamber muds is perfectly decomposed by treating with an acid mixture, consisting of one part of water, two parts of HCl and HNO_3, respectively, and four parts of sulfuric acid, being mixed in the named order. Complete evaporation is important for complete isolation of lead, silica, bismuth and others. Then the cooled residue is disintegrated with 1N hot H_2SO_4, to which a few drops of H_2O_2 is added to reduce any $Tl^{\cdots}$ that may have been formed. After a while it is filtered to separate the insoluble matter. Complete extracting with the sulfuric acid is necessary for success. To neutralize the greater part of the free acid, the extracted solution is treated with concentrated sodium hydroxide solution. At this stage a precipitate is formed, which diss-

solves slightly on stirring. The remainder of the free acid is accurately neutralized with sodium carbonate solution. The end point is easily perceived by the slow evolving of carbon dioxide gas.

The solution is then heated to boiling and sulfur dioxide is passed until it cools to room temperature. The precipitate, if present, is filtered off. In this condition, thallium exists as thallous ion. Through the procedure until this stage, lead, bismuth, tin, antimony, and mercury etc. have already been removed. Then the solution is acidified to 1N acid concentration with hydrochloric acid and heated to expel any traces of sulfur dioxide. The solution is now ready for oxidation and precipitation in the same way as has been given in the general procedure, including the washing and weighing.

(*b*) *Interference.* Interferences by several common ions were tested with proposed method, but no serious interference has been noted under the conditions recommended above. The results have a tendency to be slightly higher than the true value as shown in Table 4. The chief sources of error arise from incomplete neutralization and incomplete treatment with sulfur dioxide or from insufficient washing neglecting to remove any contaminable matter. For example, the luteo salt reacts with cadmium to form an orange-colored complex compound. For best results, twice the amount of washing solution already mentioned as required for washing is necessary. However no fatal dissolution of the thallium complex compound was perceptible due to profuse washing. It is evident from table 4 that minute amounts of thallium as small as 10 mg. or even less can be determined in the presence of many other ions a thousand times greater in quantity.

Discussion. The iodide or chromate method was widely used among the many methods. However, the former tends to give slightly lower results than the real value and requires about 18 hours for the complete precipitation owing to its colloid forming tendency. The latter has an advantage over the former in some respects, but it requires also at least 12 hours for standing and is fatally defective in that thallium chromate formed is by nature perceptibly soluble. Moreover the factor is larger than double that of the proposed method. Thus it is easily conceivable that the determination of such minute amounts of thallium less than 50mg. per 100 ml.[9] is impossible. But in this respect, the proposed method was found to be definitely satisfactory as shown in Table 4, even in the case of a minute amount as 5 mg. per 100 ml.

Mach *et al*[10] had found that the determination of thallium in small

(9) J. Bondanar and A. Tereniyi, *Z. anal. Chem.*, **69** (1926), 32.

(10) F. Mach and W. Lepper, *Z. anal. Chem.*, **69** (1926), 42; R.J. Meyer, *Z. anorg. allgem. Chem.*, **24** (1900). 364.

amounts impossible with the above method, can be undertaken as Tl_2O_3. But even the use of this method in flue-dust is definitely unsatisfactory due to the analogous reasons as mentioned above with the chromate method.

Five most widely used methods involving these methods were discussed by Strecker *et al*[11] who concluded that Tl(I)-Co(III)-nitrite is most satisfactory. But the minimum amount determined was 0.1 g. Tl and

Table 4. Determination in the Presence of Other Metals

Ion	Salt used (Amount in g.)	$Co(NH_3)_6(TlCl_6)$ (g.)	Tl-found (g.)	Tl-present (g.)	Diff. (g.)	Precipitate
K^+	KCl (10)	0.0326	0.01152	0.01149	+0.00003	
Na^+	NaCl (10)	0.0324	0.01145	0.01149	−0.00004	
K^+Al^{+++}	Alum (10)	0.0282	0.00997	0.01000	−0.00003	
SiO_3''	Na_2SiO_3 (5)	0.0300	0.01060	0.01032	+0.00028	filtered
		0.0290	0.01025	0.01032	−0.00007	,,
Ca^{++}	$CaCl_2$ (5)	0.0287	0.01014	0.01003	+0 00011	
Ti^{+++}	$Ti(SO_4)_2$	0.0284	0.01004	0.01003	+0 00001	,,
Cr^{+++}	$CrCl_3$ (5)	0.0284	0.01004	0.01003	+0 00001	
Mn^{++}	$MnSO_4$ (5)	0.0301	0.01064	0.01032	+0.00032	
		0.0291	0.01029	0.01032	−0.00003	
Fe^{+++}	$FeCl_3$ (10)	0.0304	0.01071	0.01032	+0.00039	
		0.0326	0.01152	0.01149	+0.00003	
Co^{++}	$CoSO_4$ (5)	0.0296	0.01046	0.01032	+0.00014	
Co^{++}	$CoCl_2$ (5)	0.0236	0.01011	0,01003	+0.00008	
Ni^{++}	$NiCl_2 6H_2O$ (5)	0.0289	0 01022	0.01003	+0.00019	
		0.0299	0.01053	0.01032	+0.00020	
Cu^{++}	$CuSO_45H_2O$ (10)	0.0283	0.01000	0.01000	0.00000	
Zn^{++}	$Zn(C_2H_3O_2)$ (5)	0.0284	0.01034	0.01032	+0.00002	
		0.0330	0.01166	0.01 49	+0.00017	
AsO_3'''	As_2O_3 (5)	0.0287	0.01014	0.01003	+0.00011	
MoO_4''	$(NH_4)_6Mo_7O_{24}4H_2O$ (5)	0.0284	0.01004	0.01003	+0.00001	,,
Ag^+	$AgNO_3$ (10)	0.0281	0.00993	0.01000	−0.00007	,,
Co^{++}	$Cd(NO_3)_2$ (10)	0.0284	0.01004	0.01003	+0 00001	
Sn^{++}	$SnCl_22H_2O$ (5)	0.0283	0.01000	0.01000	0.00000	,,
		0.0261	0.00923	0.00986	−0.00063	,,
Sb^{+++}	$SbCl_3$ (5)	0.0279	0.00986	0.01000	−0.00014	,,
Ba^{++}	$BaCl_22H_2O$ (10)	0.0259	0.00916	0.00986	−0 00070	,,
		0.0290	0.01024	0.01000	+0.00024	,,
Hg^+	$Hg_2(NO_3)_2$ (5)	0.0289	0.01022	0.01000	+0.00022	,,
Pb^{++}	$Pb(NO_3)_2$ (10)	0.0234	0.01004	0.01000	+0.00004	,,
Bi^{+++}	$BiCl_3$ (5)	0.0283	0.01000	0.01000	0.00000	,,
Mg^{++}	$Mg(NO_3)_26H_2O$ (5)	0.0283	0.01000	0.01000	0.00000	
Zn^{++}	$ZnSO_4$ (5)	0.0329	0.01163	0.01149	+0.00014	
Zn^{++}	$Zn(C_2H_2O_2)_2$ (5)	0.0320	0.01141	0.01132	+0.00009	
NO_3'	HNO_3	0.0326	0.01152	0.01149	+0.00003	
SO_3''	H_2SO_4	0.0324	0.01145	0.01149	−0.00004	
PO_4'''	H_3PO_4	0.0286	0.01011	0.01000	+0.00011	
PO_4'''	$(NH_4)_2HPO_4$	0.0301	0.01064	0.01032	+0.00032	

* Precipitate formed when treated with sulfur dioxide.

(11) W. Strecker and P. de la Pena, *Z. anal. Chem.*, **67** (1926), 257.

the factor exceedingly large (0.6469). Owing to this reason and for the necessity of preliminary separation, it is also unsatisfactory for application to flue-dust. The thionalide method, recommended in the determination of such a little amount as 5 mg., cannot be used in the presence of many metals frequently occurring in flue-dust. Matsubara and Kuwabara[12] found that the thionalide method and chromate method can only give an approximate quantitive result in such a sample because of the presence of many metals. From such standpoints it may be concluded that the proposed method is remarkably superior to the above mentioned and can be easily applied for the determination of minute amounts of thallium.

The superiority will be summarized in the following:

(a) The addition of ammonium chloride realizes the determination of 5 mg. thallium in any mineral acid medium with fairly good results.

(b) The proposed method is time-sparing, usually only requiring two or three hours from the time the sample is brought into solution. It simplified the procedure for the determination particularly in such a substance as flue-dust which is usually in association with numerous other metals. The veracity of this concluded superiority can be proved by comparing it with the thionalide method having the least factor among many of the other methods already mentioned.

(c) It does not require a troublesome separation, thus eliminating another possible source of error which results from the minute amount of thallium being absorbed on voluminous and absorptive precipitates of iron, manganese etc. as is frequently the case noted in other methods.

(d) The factor is the smallest among any other gravimetric method, thus making possible the determination of a minute amount of thallium present in the sample such as flue-dust which is impossible with any other method.

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(12) S. Matsubara and T. Kuwabara, *J. Min. Soc. Japan*, **61** (1945), 7.