

A STUDY OF THE PREPARATION OF TELLURIC
ACID AND ITS APPLICATION IN ANALYTICAL CHEMISTRY

by

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TABLE OF CONTENTS

INTRODUCTION	1
EXPERIMENTAL	5
Volumetric Determination of Tellurium Dioxide	5
Purification of Tellurium Dioxide	13
Determination of the Solubility of Telluric Acid and Tellurium Dioxide in Concentrated Ammonium Hydroxide	13
Preparation of Telluric Acid	14
Determination of the Purity of Telluric Acid	20
The Determination of Barium by Homogeneous Precipitation as Barium Tellurate	21
DISCUSSION	25
SUMMARY	27
ACKNOWLEDGMENT	29
LITERATURE CITED	30

INTRODUCTION

The studies reported upon in this paper were directed towards (1) The preparation of telluric acid, and (2) the homogeneous precipitation of barium and similar ions as tellurates.

A review of the literature shows that there have been several methods of preparing telluric acid. Meyer and Franke (4) oxidized the elementary tellurium with a mixture of barium chlorate and sulfuric acid. Krepelka and Kubik (2) oxidized the elementary tellurium with 30 percent hydrogen peroxide, but their method necessitated using a 10-15 fold excess of the oxidizing agent. Staundenmaier (9) reacted a mixture of nitric and chromic acids with tellurium dioxide to effect oxidation to telluric acid. The procedure as developed by Mathers et al. (3) is the most widely used. Crude tellurium dioxide is purified and then oxidized by a slight excess of permanganate in a hot solution of about five molar nitric acid. Manganese dioxide is dissolved by the addition of 3 percent hydrogen peroxide. Upon purification the yield is found to be 75-76 percent.

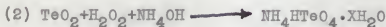
A controversy continues to prevail concerning the molecular structure of telluric acid. In the literature it is referred to as both the hydrate form, $H_2TeO_4 \cdot 2H_2O$, and the hexabasic form, H_6TeO_6 . Pauling (5) has recognized the latter as being the correct formula. According to that investigator, X-ray data have shown definitely that the six oxygen atoms in the

molecule are equivalently related to the tellurium atom. Representative salts are Ag_6TeO_6 , Hg_3TeO_6 , $Ag_3H_3TeO_6$, $K_2H_4TeO_6 \cdot 3H_2O$. Many complex crystals such as $(NH_4)_4(HPO_4)_2Te(OH)_6$ and $2KIO_3 \cdot Te(OH)_6$ contain telluric acid. Tellurates combine with MoO_3 or WO_3 to form compounds such as $K_6Te(MoO_4)_6$.

The method as developed during this investigation involved the oxidation of the tellurium dioxide in a basic solution of ammonium hydroxide through the use of 30 percent hydrogen peroxide as the oxidizing agent. The commercial grade tellurium dioxide was purified as suggested by Mathers et al. (3). The four possible theoretical equations for the oxidation reaction are as follows:



or



or



or



Reaction of the ammonium tellurate with dilute nitric acid converts the compound to telluric acid.

Before starting the preparation it was deemed necessary to ascertain the approximate solubility of the tellurium dioxide and the telluric acid in concentrated ammonium hydroxide. These solubilities were determined only qualitatively.

As a result of the preceding study it was decided to attempt the oxidation of tellurium dioxide to telluric acid as postulated. From qualitative solubility studies it was reasoned that the tellurium dioxide would dissolve sufficiently to be attacked by the hydrogen peroxide. After oxidation occurred the ammonium salt of the acid would precipitate and more of the tellurium dioxide could enter into solution, thereby permitting the reaction to go to completion. The purity of the product was determined by the method of Rosenheim and Weinheber (7).

Since it was desirable to know the purity of the tellurium dioxide used as the starting material, it was analyzed by the procedure developed by Brauner (1). This process involved the titration of an acid solution of the tellurium dioxide with standardized potassium permanganate and the back-titration with oxalic acid. After several analyses it became evident that reproducible results could not be obtained by this method. Two other methods for volumetric analysis of tellurium were presented in the literature. Schrenk and Browning (8) utilized potassium dichromate to titrate tellurium electrometrically in the presence of ferric ion, selenium, and copper. Willard and Young (12) employed ceric sulfate in the presence of chromic ion as a catalyst and obtained very good results. Since manganese ion should be capable of inducing the oxidation of Te^{IV} to Te^{VI} , it was decided to use this ion as a catalyst in the ceric sulfate titration. It was found to perform excellently for inducing

the oxidation if it were used in a certain minimum concentration. During the development of this modification, Watson (10) published a note on the use of manganous sulfate as a catalyst in the standardization of ceric sulfate against sodium oxalate.

The second phase of the problem involved the precipitation of barium from a basic solution produced by the decomposition of urea at elevated temperatures. Willard and Tang (11) and Willard and Fogg (13) have made the principal contributions to the study of homogeneous precipitation. The theory suggested by these authors is based upon the following. Urea decomposes into carbon dioxide and ammonia, when its solution is heated. Since urea is very soluble in water, and its rate of decomposition into ammonia and carbon dioxide, which is relatively slow, is dependent upon the temperature and duration of heating, a good control of the pH of the solution is possible, especially if it is buffered. The increase in pH can be stopped at any time by simply cooling, since no decomposition of urea takes place in the cold. The pH of the solution cannot rise very high and the more basic elements will not be precipitated, since the ammonia produced is driven from the hot solution if the pH is much above seven. The slow evolution of carbon dioxide, produced by the decomposition of the urea, effectively prevents bumping. In such a solution the change in pH will be uniform throughout, insofar as the temperature is the same, and no local excess of the reagent will be present at any point. No undesirable foreign ion will be introduced, except in some

cases when a buffer is employed, and the excess of the precipitant can be decomposed easily.

EXPERIMENTAL

Volumetric Determination of Tellurium Dioxide

The determination of the purity of tellurium dioxide was first attempted by the method of Brauner (1). The tellurium dioxide in 2N sulfuric acid solution was titrated with excess potassium permanganate and the excess permanganate was back-titrated with a standard solution of oxalic acid. Careful adherence to the method as described by Brauner gave results shown in Table 1.

Table 1. The analysis of commercial grade tellurium dioxide utilizing the method of Brauner.

Sample	Weight of sample taken (g)	Weight of TeO_2 found (g)	Percent TeO_2
1	0.2753	0.1739	63.17
2	0.3617	0.2080	57.54
3	0.3800	0.2775	73.02
4	0.3331	0.2979	89.45
5	0.3784	0.3271	86.41
6	0.2018	0.1820	90.17

The data recorded in the preceding table did not provide satisfactorily the desired information. It was decided to

conduct further investigations to learn the reason for the wide range of results. The following series of experiments were conducted with tellurium dioxide that was purified by the method of Mathers et al. (3).

Since the oxidation of the tellurium dioxide by the potassium permanganate is slow it is necessary to permit the solution to stand for some time before conducting the back-titration. The data for a series of determinations when the amount of permanganate added was held constant, and the time of standing before back-titrating was varied, are recorded in Table 2.

Table 2. The analysis of purified tellurium dioxide utilizing the method of Brauner.

Sample	Weight of sample taken (g)	Time of standing (min.) ¹	Weight of TeO ₂ found (g)	Percent TeO ₂
1	0.2020	10	0.1895	89.63
2	0.2101	10	0.1890	89.96
3	0.2100	10	0.1881	89.58
4	0.2149	10	0.1873	87.16
5	0.2020	15	0.1859	92.00
6	0.1950	15	0.1856	95.23
7	0.1970	15	0.1818	92.28
8	0.2068	30	0.2132	103.09
9	0.1986	30	0.2047	103.07

¹ After addition of excess potassium permanganate and before back-titration with oxalic acid.

A preliminary survey of the data obtained from samples 1-7 would indicate that fairly reproducible results could be obtained if the solution were permitted to stand for a prescribed length

of time before attempting back-titration. However, the results shown in 8-9 reveal clearly that the potassium permanganate is reduced by something in addition to the tellurium dioxide.

When the first few drops of permanganate are added to the solution containing the tellurium dioxide, a brown coloration appears and as the process is continued a brown precipitate is formed. This precipitate is either manganese dioxide or a mixture of manganese dioxide and manganic sulfate. Since manganese dioxide is known to further catalytically the decomposition of potassium permanganate it was suspected that this was the reason for the higher results when the tellurium dioxide was permitted to stand in the presence of the potassium permanganate for increasing amounts of time.

To provide additional support for this supposition another series of determinations were run whereby the time of exposure was constant but the amount of potassium permanganate added was varied. Again an increase in the percent tellurium dioxide was noted with each increase in permanganate but the differences were not as marked as when the time element was varied. This information was considered to supplement the supposition previously described. The data from these determinations are given in Table 3.

Table 3. The analysis of purified tellurium dioxide utilizing the method of Brauner.

Sample	Weight of sample taken (g)	Amount of KMnO_4 added (ml)	Percent TeO_2
1	0.2074	25.00	83.89
2	0.1973	35.00	87.57
3	0.1931	40.00	88.81
4	0.1789	45.00	90.86

The results of the preceding investigation were considered conclusive enough to warrant rejection of the method. At this point it was decided to employ a different oxidizing agent.

Since Willard and Young (12) had used ceric sulfate for the analysis of tellurium while employing chromic ion as a catalyst it was decided to use the same oxidizing agent but to select a different catalyst. Manganous sulfate was chosen since ceric sulfate is capable of oxidizing progressively the Mn^{II} to Mn^{III} , Mn^{IV} or Mn^{VII} .

Results obtained by utilizing ceric sulfate as the oxidizing agent and manganous sulfate as a catalyst are shown in Table 4.

Table 4. The analysis of purified tellurium dioxide utilizing ceric sulfate as the oxidizing agent in the presence of manganous sulfate as a catalyst.

Sample:	Weight of sample taken (g)	Weight of TeO ₂ found (g)	Percent TeO ₂
1	0.1808	0.1768	97.76
2	0.1849	0.1814	98.11
3	0.1848	0.1811	97.98
4	0.1867	0.1824	97.72
5	0.1807	0.1767	97.67
6	0.2043	0.2009	98.35
7	0.1926	0.1879	97.57
8	0.1924	0.1882	97.84
9	0.1955	0.1910	97.90
10	0.1970	0.1924	97.66

The average percent TeO₂ for the above series was 97.84 with an average deviation of 0.19 percent or 1.9 parts per thousand.

Variations in the excess of ceric sulfate added were found to cause no fluctuations in the results. Time of boiling in excess of the specified time also produced no variance in the percent tellurium dioxide found.

Another series of titrations were made on commercial grade tellurium dioxide to ascertain if the impurities present could have been responsible for the wide variety of results obtained when Brauner's (1) method was employed. These results are shown in Table 5.

Table 5. The analysis of commercial grade tellurium dioxide utilizing the ceric sulfate method.

Sample:	Weight of sample taken (g)	Weight of TeO_2 found (g)	Percent TeO_2
1	0.1950	0.1495	76.64
2	0.1893	0.1453	76.64
3	0.1982	0.1523	76.89
4	0.1876	0.1435	76.53
5	0.1869	0.1428	76.46

The average percent tellurium dioxide for this series was 76.65 with an average deviation of 0.13 percent or 1.3 parts per thousand.

As a further check on the ceric sulfate method, using manganous ion as a catalyst, it was desired to obtain some tellurium dioxide of known purity. Pure samples of tellurium dioxide were obtained by reducing 100 percent pure telluric acid with 3-4M hydrochloric acid and then eliminating excess chloride ions by adding concentrated nitric acid. When tellurium dioxide, recovered in this manner, was used in the titrations, the results obtained are listed in Table 6.

Table 6. The analysis of tellurium dioxide of known composition utilizing the ceric sulfate method.

Sample	Weight of sample taken (g)	Weight of TeO_2 found (g)	Percent TeO_2
1	0.2016	0.2015	99.95
2	0.1846	0.1844	99.89
3	0.1906	0.1904	99.90
4	0.1776	0.1775	99.95
5	0.1920	0.1918	99.89

The average percent tellurium dioxide for this series was 99.92 with an average deviation of 0.03 percent or 0.3 part per thousand.

Reagents Required. The preparation and concentration of the reagents used in the preceding ceric sulfate analysis of tellurium dioxide are described in the following paragraphs.

1. Ceric sulfate solution. An approximately 0.1N solution is prepared by dissolving about 63.25 grams of the ceric sulfate ammonium salt in 500 ml of 2N sulfuric acid. The resulting solution was then diluted to 1 liter and filtered through asbestos to remove any phosphates which precipitate. Iron wire of known assay value was used for standardization.

2. Ferrous sulfate solution. This solution was prepared by dissolving approximately 19.5 grams of the ferrous ammonium sulfate salt in 250 ml of water to which 5 ml of 2N sulfuric acid to prevent hydrolysis had been added. The solution was then diluted to 500 ml.

3. Ortho-phenanthroline ferrous complex. To prepare the indicator solution, 1.5 grams of ortho-phenanthroline monohydrate was dissolved in 100 ml of 0.025M freshly prepared ferrous sulfate solution.

4. Manganous sulfate solution. A 1M solution was prepared by dissolving 22.305 grams of manganous sulfate in 100 ml of a water solution.

Procedure. Approximately 0.2 gram of tellurium dioxide was placed in a 600 ml beaker and 100 ml of 1N sulfuric acid was added. To this mixture 0.3 ml of 1M manganous sulfate solution was added. The contents of the beaker were heated to boiling and the standardized ceric sulfate solution was added in excess. The first addition of the oxidizing agent forms a brown coloration, due to the oxidation of the manganous ion to Mn^{III} or Mn^{IV} .

After the ceric sulfate solution was added in excess the resulting mixture was boiled for 20 minutes with occasional stirring. At the end of the boiling period the solution was back-titrated with ferrous sulfate solution in the presence of orth-phenanthroline ferrous complex as indicator. As the back-titration proceeded the brown coloration gradually disappeared and the solution became blue. The ferrous ion was added until the blue color changed to red.

The total amount of ceric sulfate required for oxidation of the tellurium dioxide was then determined and the percent of tellurium dioxide present in the sample calculated.

Purification of Tellurium Dioxide

The commercial grade tellurium dioxide, approximately 76 percent pure, was further purified by dissolving a 25 gram sample in 5N sodium hydroxide and then reprecipitating the tellurium dioxide by adding 10N nitric acid until the solution was acid to phenolphthalein.

After precipitation the dioxide was permitted to stand for 48 hours to allow complete sedimentation. The supernatant liquid was then decanted and the tellurium dioxide washed five times with distilled water. The purified material was placed in a 150 ml beaker, covered with an inverted 250 ml beaker, and placed in an oven for 24 hours at a temperature of 110° C.

This method produces a compound of about 98 percent purity. Subsequent repetitions of the above procedure made no appreciable change in the purity.

Determination of the Solubility of Telluric Acid and Tellurium Dioxide in Concentrated Ammonium Hydroxide

Accurately weighed amounts of the two compounds were placed in individual 250 ml Erlenmeyer flasks and 100 ml of concentrated ammonium hydroxide was added to each flask. The flasks were stoppered, held at a temperature of approximately 25° C. and agitated occasionally during the following 72 hours. After the elapse of the prescribed period, the liquid was

separated by filtration and subsequently evaporated to obtain the amount of solid which had gone into solution. The residue which remained undissolved was dried also and weighed. In this manner the weight of solute which had been dissolved could be checked. As a result of this study the following data were obtained concerning the solubility of telluric acid and tellurium dioxide in concentrated ammonium hydroxide. One hundred ml of ammonium hydroxide was found to dissolve 0.27 gram of telluric acid and it would dissolve also 3.82 grams of tellurium dioxide.

Preparation of Telluric Acid

It was first decided to attempt almost immediate oxidation through instigation of the reaction by heating. After heating to 75-78° C., a reaction began which continued for some time after the removal of the source of heat. This was evidenced by profuse bubbling due to the liberation of oxygen.

In the first series of experiments the volume of oxidizing agent was held constant and the ratios of ammonium hydroxide and water were varied. One gram samples of purified tellurium dioxide were used. The results of this series of oxidations are shown in Table 1.

Table 1. The oxidation of tellurium dioxide by 30 percent hydrogen peroxide¹ in the presence of water and ammonium hydroxide².

Trial :	NH ₄ OH (ml)	:	H ₂ O (ml) :	Result
1	0.00		60.00	No reaction.
2	1.00		59.00	Very slight oxidation. Gum formed.
3	5.00		55.00	Slight oxidation. Gum formed.
4	10.00		50.00	Slow and partial oxidation. Gum formed.
5	25.00		35.00	Oxidation fairly complete. Some gum formed.

¹ 10.00 ml of 30 percent hydrogen peroxide used in each trial.

² Ratio of water and ammonium hydroxide varied.

From these results it was evident that, in reaction carried out in the presence of dilute ammonium hydroxide, the tellurium dioxide formed a gummy mass which appeared to inhibit the oxidation process. Apparently moisture was adsorbed on the surface of the finely divided tellurium dioxide and formed a coating which prevented the penetration of and oxidation by the hydrogen peroxide. Subsequent reactions were conducted only in the presence of concentrated ammonium hydroxide and 30 percent hydrogen peroxide.

Table 2 shows the results of a number of trials in which the volume of hydrogen peroxide was varied and the volume of

concentrated ammonium hydroxide was held constant. Again one gram samples of purified tellurium dioxide were used and heat was applied as in the previous series.

Table 2. The oxidation of tellurium dioxide by 30 percent hydrogen peroxide¹ in the presence of concentrated ammonium hydroxide².

Trial :	H ₂ O ₂ (ml)	:	Result
1	1.00		Slight oxidation. Very slow.
2	2.00		Slight oxidation. Very slow.
3	2.50		Slight oxidation. Slow.
4	3.00		Oxidation more extensive.
5	3.50		Oxidation nearly complete.
6	4.00		Complete oxidation.
7	4.00		Complete oxidation.

¹ Volume of hydrogen peroxide varied.

² 25.00 ml of concentrated ammonium hydroxide used in each trial.

The results shown in Table 2 are not quantitative and the amount of oxidation was determined by noting the amount of tellurium dioxide that remained at the completion of the process after the ammonium salt of the acid was removed by acidification with dilute nitric acid.

This method involves the use of 4.00 ml of 30 percent hydrogen peroxide per gram of tellurium dioxide, and since this is nearly an eight fold excess, it was decided to dispense with

the heating and permit the oxidation to proceed under its own momentum. The reason for the large excess of hydrogen peroxide was due to the decomposition of the peroxide by heat.

The next series of trials were conducted by permitting the tellurium dioxide to remain in the presence of the ammonium hydroxide - hydrogen peroxide mixture for a period of 24 hours with occasional shaking. No heat was applied. The amount of tellurium dioxide used in each trial was one gram. The results are shown in Table 3.

Table 3. The oxidation of tellurium dioxide by 30 percent hydrogen peroxide¹ in the²presence of concentrated ammonium hydroxide and in the absence of heat.

Trial :	H ₂ O ₂ (ml)	:	Result
1	10.00		Complete oxidation
2	7.00		Complete oxidation
3	5.00		Complete oxidation
4	2.00		Complete oxidation
5	1.00		Partial oxidation

¹ Volume of hydrogen peroxide varied.

² 25.00 ml of concentrated ammonium hydroxide used in each trial.

From these results it was concluded that 2 ml of 30 percent hydrogen peroxide was sufficient to oxidize one gram of tellurium dioxide. As this was still a four fold excess it was decided to increase the size of the sample of tellurium dioxide to ascertain if the ratio of hydrogen peroxide to tellurium dioxide could be decreased.

The results obtained when five gram samples of tellurium dioxide were used are shown in Table 4. The amount of tellurium dioxide oxidized by varying amounts of hydrogen peroxide is also tabulated. In these trials no heat was applied and the mixtures were permitted to stand for 24 hours.

Table 4. The oxidation of tellurium dioxide by 30 percent hydrogen peroxide¹ in the presence of concentrated ammonium hydroxide² and in the absence of heat.

Trial	:	H ₂ O ₂ (ml)	:	TeO ₂ oxidized (g)
1		4.00		1.88
2		4.50		2.63
3		5.00		3.17
4		5.50		4.26
5		6.00		5.00

¹ Volume of hydrogen peroxide varied.

² 40.00 ml of concentrated ammonium hydroxide used in each trial.

Table 4 shows that 6.00 ml of 30 percent hydrogen peroxide are necessary to completely oxidize a five gram sample of tellurium dioxide to telluric acid.

In the next series, 10 gram samples of tellurium dioxide were combined with varied volumes of 30 percent hydrogen peroxide. The results are shown in Table 5.

Table 5. The oxidation of tellurium dioxide by 30 percent hydrogen peroxide¹ in the presence of concentrated ammonium hydroxide² and in the absence of heat.

Trial	:	H ₂ O ₂ (ml)	:	TeO ₂ oxidized (g)
1		8.00		7.94
2		9.00		9.32
3		9.50		9.79
4		10.00		10.00
5		10.00		10.00
6		10.00		10.00

¹ Volume of hydrogen peroxide varied.

² 75.00 ml of concentrated ammonium hydroxide used in each trial.

The optimum conditions appear to be achieved when a 10 gram sample of tellurium dioxide is reacted with a mixture of 75.00 ml of concentrated ammonium hydroxide and 10.00 ml of 30 percent hydrogen peroxide.

Procedure. A 10 gram sample of tellurium dioxide, purified and oven-dried, was placed in a 250 ml Erlenmeyer flask fitted with a rubber stopper. To the flask was added a mixed solution of 10.00 ml of 30 percent hydrogen peroxide and 75 ml concentrated ammonium hydroxide. This mixture was added with shaking and after the pressure generated by the initial reaction had subsided the flask was stoppered, set aside and frequently agitated.

After the elapse of 24 hours the stopper was removed and the mixture heated for 15 minutes to decompose excess hydrogen

peroxide and lower the concentration of ammonium hydroxide. At the end of this period of heating 100 ml of water was added and a solution of 2M nitric acid was added also until the mixture tested acid to litmus. At this point the ammonium salt of the acid disappeared.

The resulting solution was concentrated to 60 ml and then 10 ml of concentrated nitric acid were added. After 24 hours the supernatant liquid was removed from the crystals of telluric acid which had formed, and the liquid was further concentrated to 25 ml. Another 10 ml of concentrated nitric acid were added and after an additional 24 hours a second crop of crystals was obtained and combined with the first.

Further purification was accomplished by recrystallizing twice from distilled water. This method produces telluric acid of 100 percent purity and in yields of 75-80 percent.

Determination of the Purity of Telluric Acid

When telluric acid is combined with glycerol it forms a compound that acts like a monobasic acid and can be titrated with standard sodium hydroxide in the presence of phenolphthalein as indicator.

Approximately 0.2 gram samples of the purified telluric acid were accurately weighed and dissolved in 20 ml of water. An equivalent amount of glycerol was added and the resulting

mixture titrated with 0.1N sodium hydroxide until the characteristic end point with phenolphthalein was obtained.

The Determination of Barium by Homogeneous Precipitation as Barium Tellurate

Aliquot portions of a standard barium chloride solution were added to solutions of telluric acid and urea. The resulting mixtures were heated in a boiling water bath until a pH of approximately 7.1 was attained. This method produced results very similar in accuracy and precision to a series of determinations by the barium sulfate method. Since the time of analysis is approximately the same in both procedures, the precipitation of barium as the tellurate has no advantage over the barium sulfate method for the analysis of barium if interfering ions are absent.

To ascertain if the precipitation of barium tellurate could be used to advantage in the presence of ions which normally interfere with the sulfate method for determining barium, a series of comparison analyses were made. Three aliquots of standard barium solution were precipitated as barium tellurate and three as barium sulfate. A known amount of potassium chloride in increasing concentration was added to each of the three aliquots to be precipitated as the tellurate. Identical concentrations were added to the aliquots to be precipitated as sulfates.

In the aliquots precipitated as tellurates, the results of the initial precipitation were very high. This was due to the coprecipitation of potassium and possibly chloride ions. However, as barium tellurate can be dissolved quite readily by a few drops of concentrated nitric acid, it was possible to reprecipitate the tellurate and thereby eliminate the contaminating ions. Constant weights were obtained after four precipitations. Table 1 shows the percent barium found in each precipitation.

Table 1. The determination of barium by precipitation as barium tellurate in the presence of potassium chloride.

Trial	KCl added (moles)	:	Percent barium ¹			
			1	2	3	4
1	0.25	131.23	100.41	99.62	99.63	
2	0.50	132.93	100.70	99.87	99.86	
3	1.00	138.02	100.99	99.88	99.84	

¹ Each value is a mean of two independent determinations.

The results obtained from the aliquots precipitated as barium sulfate are shown in Table 2.

Table 2. The determination of barium by the sulfate method in the presence of potassium chloride.

Trial	:	KCl added (moles)	:	Percent barium
1		0.25		104.31
2		0.50		104.73
3		1.00		106.02

It is evident from these results that the presence of potassium chloride, in the concentrations tabulated, effect very marked errors.

The results given in Table 1, compared with those of the sulfate method for the determination of barium in the presence of potassium chloride, would appear to demonstrate that the tellurate method is decidedly advantageous. This is due primarily to the fact that the tellurate can be dissolved, thereby enabling any contaminating ions present due to adsorption to be removed.

To conclude this study on homogeneous precipitation an investigation was conducted with a number of ions which are known to interfere with the determination of barium as the sulfate. These ions were placed in a solution containing telluric acid and urea, and heated in a boiling water bath as in previous experiments. The results of this experimentation are shown in Table 3.

Table 3. The influence of certain ions in the determination of barium as the tellurate.

Ion	:	Type of precipitate
Aluminum		Gelatinous
Ferric		Flocculent
Chromic		Flocculent
Cadmium		Dense
Manganous		Dense
Calcium		Dense
Strontium		Dense
Potassium		None
Sodium		None

These results reveal that numerous ions would have to be removed before precipitating barium as the tellurate. Those ions that precipitate in the presence of telluric acid and urea could not be excluded through the process of reprecipitation as were those that interfere only through coprecipitation.

During previous studies it became apparent that in the presence of anions such as chloride and nitrate, the barium could be successfully determined as the tellurate.

Procedure. Fifty ml aliquots of a standard barium chloride solution were placed in 400 ml beakers. To each beaker was added 20 ml of 0.4M telluric acid solution and 10-12 grams of urea. This solution was diluted to 150 ml, and the beakers were covered with watch glasses and placed in a boiling water bath.

At intervals of one-half hour, portions of the solutions were removed, cooled in running water, and the pH determined with a Beckman pH meter. When a pH of 7.1-7.2 was attained the samples were removed from the water bath and filtered through previously weighed, fine sintered-glass crucibles. After being washed with hot water the precipitates of barium tellurate were dried in an oven at 125° C. for three to four hours. The precipitates were then weighed and the percent barium calculated.

When there were interfering ions, the first precipitates were dissolved with a few drops of nitric acid, and then reprecipitated as described in the above paragraphs.

DISCUSSION

In determining the purity of tellurium dioxide, it was ascertained that if Mn^{II} were used as a catalyst with ceric sulfate as the oxidizing agent, results with a precision of 0.3 part per thousand could be achieved on samples of known composition. Results obtained by this procedure were considered to be sufficiently reproducible for the purpose to which they were applied. As the oxidation of the tellurium dioxide by the ceric ion does not occur in the absence of Mn^{II} , it was concluded that the presence of the latter ion induces the reaction in a step-wise manner, and permits the surmounting of the potential hump as described by Remick (6).

During the course of experimentation it became apparent that tellurium dioxide which was air dried, after undergoing purification, did not give the same results when titrated with ceric sulfate or when used in the telluric acid preparation as the oven dried dioxide.

When titrated with ceric sulfate the air dried tellurium dioxide was found to be 8-10 percent less pure than the oven dried samples. In the preparation of telluric acid, the air dried dioxide formed a gum which appeared to inhibit oxidation. If the air dried samples were placed in an oven for several hours the dioxide would then react like those which had been originally oven dried. From these observations it was reasoned

that adsorbed moisture was responsible for the observed results. In the titration this moisture was weighed as tellurium dioxide and caused the low results. The oxidation of the air dried tellurium dioxide by 30 percent hydrogen peroxide, in the presence of ammonium hydroxide, was inhibited by the formation of a gum which excluded the penetration of the oxidizing agent.

The method of preparing telluric acid developed during this work appears to have certain advantages over previous procedures. Although the yield does not surpass that achieved by others, the simplicity of recovery is decidedly advantageous. The ammonium salt of the acid which precipitated as the oxidation proceeded was readily dissolved by the addition of dilute nitric acid. When the solution is evaporated to a specified volume and concentrated nitric acid is added, telluric acid crystals separate upon standing. To purify, it is necessary only to recrystallize from hot water. If allowed to recrystallize from a fairly large volume, the telluric acid separates as large cube shaped crystals. When separated from a concentrated solution the acid has the appearance of a fine meal. The ionization constants of telluric acid are:

$$K_1 = 6 \times 10^{-7} \text{ and } K_2 = 4 \times 10^{-11}.$$

The work reported in this thesis concerning homogeneous precipitation discloses that in the presence of interfering ions, such as the alkali metals, the tellurate method is advantageous. This advantage stems primarily from the fact that the

tellurate is capable of being dissolved and reprecipitated numerous times if necessary to remove extraneous material.

An additional study revealed that a number of ions which interfere in the precipitation of barium as the sulfate would interfere also in the determination of barium as the tellurate. These ions form precipitates from a solution of telluric acid and urea upon heating, and could not be separated by reprecipitation.

SUMMARY

1. A study of the potassium permanganate method for determining tellurium dioxide revealed that reproducible results could not be obtained due to catalytic decomposition of permanganate by manganese dioxide which was formed.

2. A method for the volumetric determination of tellurium dioxide was established using ceric sulfate as the oxidizing agent and manganous sulfate as a catalyst.

3. Optimum conditions were found for the preparation of telluric acid in a concentrated ammonium hydroxide media. A 10 gram sample of tellurium dioxide was oxidized by 10 ml of hydrogen peroxide in 75 ml of ammonium hydroxide. The mixture was permitted to stand for 24 hours with frequent agitation.

4. Barium can be determined as barium tellurate in the presence of some ions which interfere by coprecipitation in the precipitation of barium as the sulfate. This is true in

the case of the alkali metals, chloride, and nitrate ions.

5. Many of the ions which interfere in the sulfate method would also interfere in the precipitation of barium as the tellurate. These ions precipitate from a solution of telluric acid and urea and could not be separated by reprecipitation.

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LITERATURE CITED

- (1) Brauner, B.
Volumetric estimation of tellurium. Jour. Chem. Soc. 59: 238-253. 1891.
- (2) Krepelka, J. H. and L. Kubik.
Preparation and determination of pure orthotelluric acid from metallic tellurium. Chem. Listy, 42: 28-30. 1948. Original not seen. Abstract in Chem. Abs. 44-9290. 1950.
- (3) Mathers, F. C., C. M. Rice, H. Broderick, and R. Forney.
Preparation of telluric acid from tellurium dioxide by oxidation with potassium permanganate. Proc. Ind. Acad. Sci., 52: 114-116. 1942.
- (4) Meyer, J. and W. Franke.
Preparation of telluric acid. Zeit. Anorg. allgem. Chem. 193: 191-192. 1930. Original not seen. Abstract in Chem. Abs. 25-657. 1931.
- (5) Pauling, L.
The formulas of antimononic acid and the antimonates. Amer. Chem. Soc. Jour. 55: 1895-1900. 1933.
- (6) Remick, A. E.
Studies on oxidation-reduction mechanisms. I. Potential humps and the equivalent-change principle. Amer. Chem. Soc. Jour., 69: 94-95. 1947.
- (7) Rosenheim, A., and M. Weinheber.
Alkalimetric determination of telluric acid. Zeit. Anorg. chem., 69: 266-269. 1910. Original not seen. Abstract in Chem. Abs. 5-1378. 1911.
- (8) Schrenk, W. T., and B. L. Browning.
The electrometric determination of tellurium in the presence of ferric iron, selenium, and copper. Amer. Chem. Soc. Jour., 48: 139-140. 1926.
- (9) Staundenmaier, C.
The preparation of telluric acid. Zeit. Anorg. Chem. 10: 189-191. 1896. Original not seen. Reviewed by Mathers, F. C., and G. M. Bradbury. Amer. Chem. Soc. Jour., 51: 3229-3232. 1929.

- (10) Watson, J. P.
Manganese sulfate as a catalyst in ceric sulfate titrations. *Analyst*, 76: 177. 1951.
- (11) Willard, H. H., and N. K. Tang.
A study of the precipitation of aluminum basic sulfate by urea. *Amer. Chem. Soc. Jour.*, 59: 1190-1197. 1937.
- (12) Willard, H. H., and Philena Young.
Ceric sulfate as a volumetric oxidizing agent.
XII. Determination of tellurous acid. *Amer. Chem. Soc. Jour.*, 52: 553-556. 1930.
- (13) Willard, H. H., and H. C. Fogg.
The precipitation of basic gallium sulfate by means of urea. I. A study of the precipitate produced. *Amer. Chem. Soc. Jour.*, 59: 1197-1199. 1937.

A STUDY OF THE PREPARATION OF TELLURIC
ACID AND ITS APPLICATION IN ANALYTICAL CHEMISTRY

by

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During the development of a method for the preparation of telluric acid it became necessary to determine the purity of the tellurium dioxide used. At first a procedure previously developed was used. This utilized an excess of potassium permanganate in a sulfuric acid media for oxidation, and subsequent back titration with oxalic acid. The method proved very erratic and further investigation disclosed that the potassium permanganate was catalytically decomposed by the manganese dioxide formed during the titration.

When ceric sulfate was used as the oxidizing agent in a 1N sulfuric acid media with manganous sulfate as a catalyst, results of fairly high precision were obtained. On tellurium dioxide of known composition a precision of 0.3 part per thousand was achieved.

Although many previous methods for the preparation of telluric acid have been developed, all of them involve slow and complex recovery of the product. The objective of this investigation was to prepare telluric acid through the oxidation of tellurium dioxide by 30 percent hydrogen peroxide in the presence of concentrated ammonium hydroxide. Preliminary studies of the solubilities of telluric acid and tellurium dioxide in concentrated ammonium hydroxide disclosed that this proposed method should prove practical.

Optimum conditions for the oxidation were established. A ten gram sample of tellurium dioxide could be oxidized by

a mixture of 10 ml of 30 percent hydrogen peroxide and 75 ml of concentrated ammonium hydroxide. The mixture was contained in a stoppered flask for 24 hours with frequent agitation. The insoluble ammonium tellurate salt which formed as the oxidation proceeded was easily dissolved with dilute nitric acid. Telluric acid was obtained by evaporating the solution to a specified volume and then adding concentrated nitric acid. Upon standing the acid separated from the solution. Purification was effected by recrystallization from distilled water. A yield of 75-80 percent was achieved.

Another phase of this research was concerned with the homogeneous precipitation of barium as the tellurate. Results very similar in accuracy and precision to the sulfate method of determining barium were found. Since both methods involve approximately the same amount of time, the tellurate method offers no advantages over the sulfate method in the absence of interfering ions.

In the presence of known concentrations of potassium chloride the tellurate was found to be advantageous. Although the first precipitation gave very high results, due to the coprecipitation of potassium chloride, it was possible to dissolve the tellurate precipitate in nitric acid and remove the interfering ions through a series of reprecipitations.

A final study revealed that a number of ions which interfere in the determination of barium as the sulfate would also

interfere in the precipitation of barium as the tellurate. These ions form precipitates from a solution of telluric acid and urea upon heating, and could not be separated by reprecipitation.