limitations of the Raman technique have been discussed by Stamm (*3*).

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Spectrophotometric Titration of Telluric Acid

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As no direct, simple, and precise volumetric methods are available for the determination of telluric acid alone or in the presence of other acids, the possibility of a spectrophotometric titration was investigated. The tellurate ion absorbs at a longer wave length in the ultraviolet than does telluric acid. Therefore, the production of the tellurate ion during an acid-base titration can be followed spectrophotometrically. A plot of absorbance *vs.* milliliters of titrant gives a smooth curve. The linear portions of the curve can be extrapolated to indicate the stoichiometric point of the titration. The spectrophotometric titration serves satisfactorily for the determination of telluric acid alone and in the presence of hydrochloric, sulfuric, nitric, selenic, and acetic acids.

BECAUSE telluric acid is a very weak polyprotic acid, the usual acid-base titration with an internal indicator is not feasible. Rosenheim and Weinheber (*4*) suggested adding neutral glycerol to the telluric acid solution. The glycerol forms a complex with the telluric acid which behaves as a stronger monoprotic acid. This complex can then be titrated with a standard sodium hydroxide solution using phenolphthalein as the internal indicator. However this method gives results ranging from 96.87 to 103% for a single sample. Another modification also suggested by Rosenheim and Weinheber is the addition of barium chloride to a solution containing the telluric acid sample plus an excess of standard sodium hydroxide. Barium tellurate precipitates and the excess sodium hydroxide is back-titrated with a standard oxalic acid solution. This modification gives results ranging from 98.97 to 100.2%.

Of the oxidation-reduction techniques, the most widely accepted method is the procedure proposed by Gooch and Howland (*2*). Telluric acid is reduced to tellurous acid by bromide ion in a strongly acid medium. The resulting bromine is distilled into a solution of potassium iodide. The iodine is then titrated with a standard sodium thiosulfate solution, using starch solution as the internal indicator. Although this method is complicated, good results can be obtained.

Scott and Leonard (*5*) used the absorbance of the tellurate ion in the ultraviolet region for the spectrophotometric determination of telluric acid. Therefore the possibility of spectrophotometrically titrating telluric acid in the presence of other acids with a standard base was investigated.

REAGENTS AND EQUIPMENT

Commercial grade tellurium dioxide was purified by dissolving it in a sodium hydroxide solution, filtering, and reprecipitating the tellurium dioxide by the addition of nitric acid. The purified tellurium dioxide was oxidized with hydrogen peroxide in a dilute solution of sodium hydroxide. The telluric acid was precipitated by the addition of nitric acid, and purified by three recrystallizations from water solutions. Stock solutions were prepared from the purified telluric acid and standardized by the method of Gooch and Howland (*2*). Stock solutions of the other acids and bases were prepared and standardized. The normality of the ammonium hydroxide solution was checked frequently; no noticeable change was found in its concentration over a month's time. The Beckman Model DU spectrophotometer, equipped with a set of thermospacers, was used with 1-cm. quartz absorption cells for measuring the absorbance of the samples.

RECOMMENDED PROCEDURE

Place the sample of the telluric acid solution in a 250-ml. Erlenmeyer flask and add sufficient water to bring the volume to 50 ml. With an eyedropper transfer a portion of this solution to a quartz cell of 1-cm. light path. With water as a blank, determine the absorbance of the solution. Then return the sample of the acid to the titrating flask by the same method of transfer. Add a small amount of standardized ammonium hydroxide to the flask, stir the contents thoroughly, and transfer a sample to the quartz cell. After each addition of base, use some of the solution to rinse the cell, return it to the flask, again stir the contents, and then transfer a sample to the cell and determine the absorbance. Continue the process for the entire titration. If the volume of titrant added, after the absorbance begins to increase, is greater than 1% of the total volume just before the absorbance increase begins, the absorbance must be multiplied by the dilution factor, $(V + v)/V$.

The corrected absorbances are plotted against milliliters of base added. This type of titration gives a very smooth curve which is easily extrapolated to give the stoichiometric point of the reaction. Klingman Hooker and Banks (*3*) have shown recently a modification of the cell compartment of a Beckman Model DU spectrophotometer which would speed up the titration as used in this investigation. The cell compartment should be equipped with a set of thermospacers and maintained at the temperature of the solution being titrated.

EXPERIMENTAL AND DISCUSSION

In the ultraviolet region of the spectrum, sodium hydroxide and potassium hydroxide solutions, because of the presence of impurities such as carbonate, were found to have greater absorbances than corresponding solutions of ammonium hydroxide. Therefore ammonium hydroxide was selected as the standard solution in this investigation. The change in the absorption spectrum of telluric acid upon the addition of ammonium hydroxide is shown by curves I and II in Figure 1, while curves II and III show the change with concentration of tellurate ions.

Effect of Wave Length. The effect of wave length upon the ease of detecting the end point was studied. A series of samples, each consisting of 10 ml. of a 0.2*M* telluric acid solution, was transferred to 250-ml. Erlenmeyer flasks and 40 ml. of water was added. The samples were titrated with standard ammonium hydroxide solution and the absorption of the solution was measured after each addition of the titrant. The change in absorbance during the titration was observed at various wave lengths as shown in Figure 2.

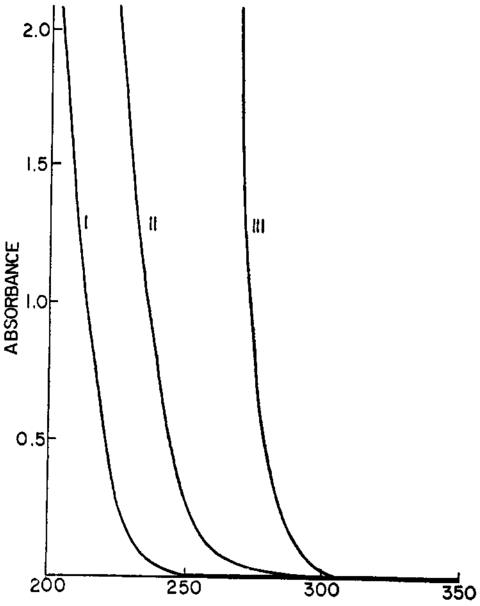

Figure 1. Absorption spectra

I. 20 mg. of telluric acid per 50 ml.
II. 20 mg. of telluric acid with stoichiometric amount of ammonium hydroxide per 50 ml.
III. 500 mg. of telluric acid with stoichiometric amount of ammonium hydroxide per 50 ml.

At the wave lengths studied the telluric acid solutions did not absorb, but upon the addition of the ammonium hydroxide the tellurate ions did absorb. A linear relationship between the absorbance and the milliliters of titrant added was observed. Therefore, as the ammonium hydroxide was added to the telluric acid sample there was a very rapid rise in the absorbance of the solution. Near the stoichiometric point there was a slight rounding off of the curve of absorbance *vs.* milliliters of ammonium hydroxide. However, after the stoichiometric point has been reached, once again the linear relationship of absorbance and milliliters of ammonium hydroxide was established, but this time very little rise in absorbance was observed. The two straight lines could easily be extrapolated to their intersection, thus giving the end point for the titration. At shorter wave lengths than 270 mμ, the molar absorptivity of the tellurate ions is so large that, at the concentrations of telluric acid used in this study, infinite absorbance was reached before the stoichiometric point. Therefore, 270 mμ was the lower wave length limit for this concentration; at longer wave lengths than 290 mμ the molar absorptivity was so small that there was not sufficient difference in the slopes of the lines before and after the stoichiometric point to justify extrapolation.

Optimum Wave Length for Various Concentrations of Telluric Acid. A study of the effect of concentration (Table I) revealed that by changing wave length the titration was made useful for a concentration range between 445 and 11 mg. of telluric acid per 50 ml. of solution. The results obtained for the concentration range showed that the best wave length was approximately 280 mμ for the 445-mg. samples. As the concentration of the acid decreased, lower wave lengths were necessary to assure adequate absorption. To simplify the selection of the proper wave length for an unknown telluric acid sample, the absorbances of a series of telluric acid samples were measured at 240 mμ. Then the samples were titrated at various wave lengths and the optimum wave length was selected for each concentration range (Table II). Thus by merely measuring the absorbance of the telluric acid sample at 240 mμ one can determine from Table II the optimum wave length for the titration.

Concentration of Base. The concentration of base with respect to the concentration of the acid should be in the range of at least 3 to 1, to minimize the dilution error. Excessive dilution of the sample by the addition of the ammonium hydroxide will cause a change in the slope of the curve for absorbance *vs.* milliliters of base. This dilution effect may be corrected by multiplying the observed absorbances by $(V + v)/V$, where V is the volume at the start of the titration and v is the volume added (*1*).

Accuracy and Precision. Analyses of ten separately prepared samples, each containing 96 mg. of telluric acid per 50 ml., gave an average value of 96.22 mg. and a standard deviation of 1.29 mg.

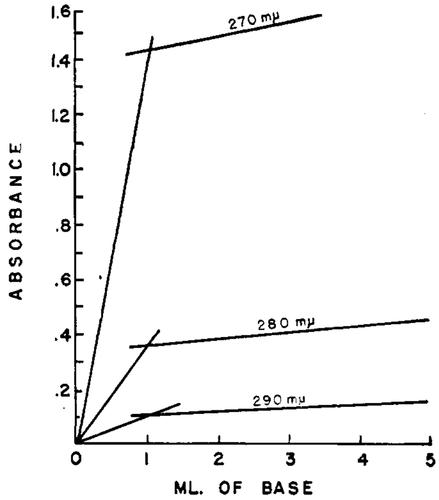

Figure 2. Effect of wave length upon photometric titration curve for 10 ml. of $0.2M$ telluric acid *vs.* $1.937N$ ammonium hydroxide

Table I. Effect of Concentration on Determination of Telluric Acid

Wave Length, Mμ	Acid, Ml./50 Ml. Solution Added	Found	Error, Mg.
280	445.5	445.5	0.00
270	222.5	223.5	+1.0
270	112.5	112.3	−0.2
260	31.23	31.12	−0.11
250	11.25	11.25	0.00

Table II. Selection of Optimum Wave Length for Titration

Absorbance Range for Telluric Acid Sample at 240 Mμ	Optimum Wave Length for Titration, Mμ
Less than 0.075	250
0.075 to 0.190	260
0.190 to 0.340	270
0.340 to 0.500	280

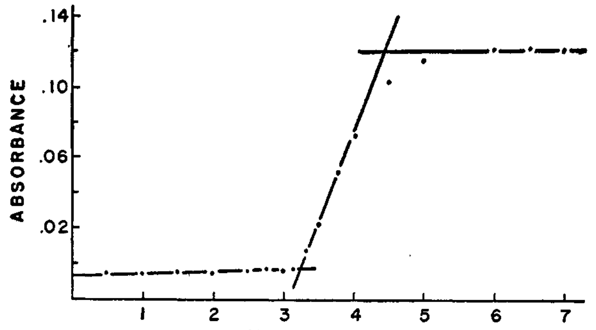

Figure 3. Titration of telluric acid in presence of sulfuric acid

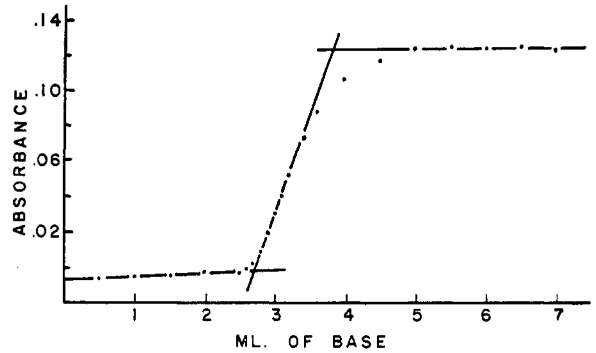

Figure 4. Titration of telluric acid in presence of acetic acid

Titration of Telluric Acid in Presence of Strong Acids. The titration of telluric acid in the presence of other strong or weak acids was studied at a wave length of 270 mμ. Figures 3 and 4 show the general type of curve obtained when telluric acid is titrated in the presence of other acids. There is little change in the absorbance until the stronger acid is titrated. As the telluric acid is titrated, there is a rapid rise in the curve up to the stoichiometric point of the telluric acid titration and then the curve levels off again as more ammonium hydroxide is added. By extrapolating the linear portions of the curve, two breaks are obtained. The first break represents the beginning of the telluric acid titration and the second represents the stoichiometric point. Therefore, the volume of base consumed between these two points corresponds to the volume necessary for the titration of the telluric acid. Table III shows the results of titrations of telluric acid in presence of other acids.

Table III. Titration of Telluric Acid in Presence of Other Acids[a]

Acid Present	Telluric Acid Found, Mg.	Error, Mg.
HCl	107.7	−0.2
HNO_3	107.1	−0.8
H_2SeO_4	107.9	0.0
H_2SO_4	108.6	+0.7
$HC_2H_3O_2$	108.5	+0.6

[a] Each sample contained 107.9 mg. of telluric acid and 5 ml. of a selected acid at approximately 0.3*N*.

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Identification of *S*-Benzylthiuronium Salts from X-Ray Powder Diffraction Patterns

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The advantages of S-benzylthiuronium salts for the analysis of organic acids have been extended by the application of x-ray powder diffraction data as a convenient and reliable means of identification. Several thiuronates, hitherto unreported, have been prepared and their x-ray data given. The use of x-ray analysis is offered as a valuable supplement for melting point determinations in qualitative organic analysis.

THIS paper outlines the results of an application of x-ray diffraction analysis for the identification of some acid derivatives. *S*-Benzylthiuronium chloride is a familiar reagent in the qualitative analysis of carboxylic and sulfonic acids (*10, 11*). The preparation of these derivatives has certain distinct advantages (*6*), which unfortunately are marred by several limitations. In general, the melting points of the derivatives lie within a narrow range (*12*). Moreover, there are marked discrepancies among the published melting points, owing to variations in the rate of heating (*1*) or to the presence of impurities (*7*). Although modifications have been suggested (*3, 5*), the facile accessibility of *S*-benzylthiuronium chloride makes it the more commonly used reagent.

During the course of an investigation relating to the elucidation of certain plant degradation products, this reagent was frequently employed for the identification of thermally sensitive acids in preference to the preparation of other derivatives such as the para-substituted phenylacyl esters, the anilides, or silver salts (*8*). In order to circumvent the disadvantages entailed in its use, the feasibility of adopting x-ray powder diffraction analysis for identification was investigated. The results described prompted this report.

EXPERIMENTAL

The thiuronium derivatives were prepared essentially by the method outlined by Vogel (*11*), except that in some instances it