vanishes in the tertiary amines. From this he deduces the conclusion that this band represents the first overtone frequency characteristic of the N—H bond, the fundamental band occurring near 6.1μ. He is led to this conclusion through the fact that ammonia has bands of absorption at 6.1μ and 2.96μ. Although the measurements by Bell on alkyl, benzyl- and phenylamines show a variation in absorption near 6μ as well as distinct bands near 3μ, thus supporting Salant's hypothesis, the hypothesis receives no support in the case of the anilines, for no detectable change in absorption occurs at 6μ.

The author plans to extend the investigation to a study of a number of alkyl amines, benzylamines, phenylamines and alkyl naphthylamines.

Summary

1. The infra-red absorption spectra below 2.8μ have been recorded for aniline and ten mono- and dialkyl anilines by means of a self-registering spectrograph.

2. Absorption bands occurring at 1.47μ and 1.04μ are associated with the presence of N—H bonds within the molecule, and these taken with a band found by Bell at 2.8μ are shown to form a three-membered, parabolic frequency series.

3. A possible identification of bands near 2.0μ and 1.2μ as combinations of N—H frequencies and a fundamental C—H frequency is suggested.

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[Contribution from the Department of Chemistry, University of Idaho]

DIPHENYLBENZIDINE AS AN INTERNAL INDICATOR FOR THE TITRATION OF ZINC WITH POTASSIUM FERROCYANIDE

By W. H. Cone and L. C. Cady

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At present there is no suitable internal indicator for the titration of zinc with potassium ferrocyanide. The authors have been able to find only one inside indicator suggested for this titration, namely, the use of ferrous sulfate by Scott.[1] This indicator had been suggested for use only in the titration of zinc ores prepared for analysis by the hydrogen sulfide method, in which case there are no oxidizing agents present.

Uranium nitrate, the indicator largely used at present, has the disadvantage of being an external indicator. Much time is required to determine the exact end-point and an error is introduced in removing portions of the solution for testing. At best, the titration must proceed slowly and a blank correction be applied to the volume of titrating solution required.

The use of diphenylamine or diphenylbenzidine as indicators depends

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[1] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1920, p. 484.

on the blue oxidation product which both form with potassium ferricyanide in the presence of zinc salts and the subsequent reduction of the blue compound by the first excess drop of potassium ferrocyanide. In the absence of zinc salts, no blue color is produced by a dilute solution of potassium ferricyanide with the above indicators. According to Marqueyrol and Muraour,[2] the blue coloration given with oxidizing agents is due to the formation of a quinone salt of diphenylbenzidine. The amount of potassium ferricyanide required for oxidation is small and a solution of potassium ferrocyanide which has been allowed to stand for a few weeks will usually contain sufficient potassium ferricyanide due to the oxidation of the ferrocyanide by oxygen dissolved in the water. However, the addition of a small amount of potassium ferricyanide to the standard ferrocyanide solution is desirable.

Solutions Required

1. A titrating solution containing 22 g. of potassium ferrocyanide and 0.3 g. of potassium ferricyanide per liter of solution.
2. A 30% solution of sulfuric acid.
3. An indicator made by dissolving 1 g. of diphenylamine or diphenylbenzidine in 100 cc. of concd. sulfuric acid.

Method

To show the effect of varying amounts of diphenylamine and diphenylbenzidine on the volume of titrating solution required, the following preliminary experiment was made. Two-tenths g. of zinc oxide was dissolved in 15 cc. of 30% sulfuric acid by heating, 100 cc. of water and 10 g. of ammonium chloride were added, the mixture was cooled, the indicator added and the resulting solution titrated cold. The indicator decomposes in hot solution. The results for diphenylamine are given in Table I and those for diphenylbenzidine in Table II.

TABLE I

EFFECT OF VARYING AMOUNTS OF DIPHENYLAMINE

ZnO, g.	0.2	0.2	0.2	0.2
Drops of indicator	4	6	12	24
$K_4Fe(CN)_6$, cc.	29.25	29.18	28.97	28.60

Table I shows an average decrease in the amount of potassium ferrocyanide used of about 0.03 cc. for each additional drop of indicator.

TABLE II

EFFECT OF VARYING AMOUNTS OF DIPHENYLBENZIDINE

ZnO, g.	0.2	0.2	0.2	0.2
Drops of indicator	2	4	6	12
$K_4Fe(CN)_6$, cc.	29.29	29.30	29.30	29.28

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[2] Marqueyrol and Muraour, *Ann. chim. anal., chim. appl.*, **19**, 174 (1914).

According to Table II, the amount of indicator added evidently had little or no effect on the titration. When twelve drops of indicator were used, the solution at the end of the titration was quite dark, which diminished the sharpness of the end-point; two to four drops of indicator are recommended. The fact that the amount of potassium ferrocyanide required in all cases was practically the same attests to the sharpness of the end-point. To test the indicator further, aliquot parts of a zinc chloride solution were titrated. No difficulty was found in determining the end-point and the results checked almost within the accuracy to which the buret could be read. Due to the effect of diphenylamine on the volume of titrating solution, diphenylbenzidine was chosen as the more suitable indicator and was used in all subsequent determinations in this investigation. A comparison of Tables I and II shows that diphenylamine may be used successfully if only three or four drops are taken and a small correction is made. The color change obtained with the two indicators is the same.

The blue coloration produced by the oxidation of the diphenylbenzidine appears after the addition of from 1 to 2 cc. of titrating solution. This color darkens as the titration proceeds, finally changing to purple within a few drops of the end-point if the addition of the titrating solution has been sufficiently slow. The purple color gives way to a pale green at the end-point. The change is permanent. The purple color is stable even within a drop or two of the end-point and may be left for hours without any noticeable change.

If the end-point is passed during the titration, the excess of ferrocyanide may be titrated back with a standard solution of zinc chloride, or a measured excess of the standardized zinc chloride may be added and the titration continued.

In order to test the value of the method for the determination of zinc in zinc ores, several typical ores were prepared for titration by means of the hydrogen sulfide method[3] and the method of von Schultz and Low.[4]

The hydrogen sulfide method was modified as follows. The zinc sulfide precipitate was washed back into the beaker in which it was precipitated by using 10 cc. of hydrochloric acid in 90 cc. of hot water. The sides of the beaker and the glass tube were rinsed with this solution, the hydrogen sulfide was boiled off and the solution just neutralized with ammonium hydroxide. Fifteen cc. of 30% sulfuric acid and 10 g. of ammonium chloride were added, the mixture was cooled, two to four drops of indicator were added and the solution was titrated cold.

The method of von Schultz and Low was modified in the following manner. Instead of adding hydrochloric acid to the filtrate, the ammoniacal

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[3] Ref. 1, p. 483.

[4] See Lord and Demorest, "Metallurgical Analysis," McGraw-Hill Book Co., New York, **1924**, p. 203.

solution was neutralized with 30% sulfuric acid and 15 cc. excess added. The solution was cooled, two to four drops of indicator were added and the titration made. If the ammoniacal solution is blue, copper is present and must be removed. This may be done by passing hydrogen sulfide into the acid solution and filtering off the copper sulfide. The hydrogen sulfide must be entirely removed by boiling. The copper may also be removed by boiling the acid solution with lead or aluminum, in which case it is not necessary to filter.

The ores used were: Sample D, U. S. Bureau of Standards[5] and Samples 1, 2 and 3, ores of known zinc content used in our own Analytical Laboratory. The results obtained with these ores are shown in Table III.

Table III

Titration of Zinc Ores

Sample	Method	Zn present, %	Zn found, %
D	Hydrogen sulfide	31.36–31.56	31.44 31.46
1	Hydrogen sulfide	14.20	14.31 14.18
2	Hydrogen sulfide	15.50	15.52 15.68
1	von Schultz and Low	14.20	14.04 14.18
3	von Schultz and Low	14.70	14.62 14.75

These results are seen to be well within the usual limits of error in routine quantitative analyses.

To compare the results obtained with diphenylbenzidine and uranium nitrate, eight samples of ore No. 3 were analyzed, four by the method of von Schultz and Low as modified above and four by the modified hydrogen sulfide method. Two samples prepared by each method were titrated, using diphenylbenzidine, and two by each method, using uranium nitrate as an indicator. Table IV gives the results of these determinations.

Table IV

Titration of Ore No. 3, Using Uranium Nitrate and Diphenylbenzidine

Method	Zn by uranium nitrate, %	Zn by diphenylbenzidine, %
von Schultz and Low	14.78	14.62
	14.50	14.61
Hydrogen sulfide	14.78	14.79
	14.74	14.78

It is to be noted that closer checks and more consistent results were obtained with diphenylbenzidine than with uranium nitrate. This is due to the greater sharpness of the diphenylbenzidine end-point. A comparison of the method of von Schultz and Low with the hydrogen sulfide

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[5] Stone and Waring, This Journal, 29, 262 (1907).

method shows that the former gives slightly lower results. This is largely due to the zinc which was carried down in the ferric hydroxide precipitate and was not subsequently recovered by reprecipitation.

Bromine and hydrogen sulfide must be completely removed by boiling, as they destroy the indicator. The use of sodium sulfite, sometimes recommended to remove the last traces of hydrogen sulfide, also affects the indicator. Our experience has been that the boiling alone is generally sufficient to remove the hydrogen sulfide. While small amounts of undecomposed potassium chlorate do not affect the blue color produced, its oxidizing action on the potassium ferrocyanide causes high results.

The authors wish to express their appreciation for the suggestions given by Professor C. L. von Ende and Professor J. A. Kostalek during the progress of this work.

Summary

1. Diphenylbenzidine, a new internal indicator for the titration of zinc by the ferrocyanide method, gives more satisfactory results than those obtained by the use of uranium nitrate.

2. The use of diphenylbenzidine permits back-titration.

3. No blank correction is required.

4. The time required for the titration is very much reduced.

5. Diphenylamine may also be used as the indicator, but it has the slight disadvantage that the amount of indicator affects the titration. This effect is slight and may be obviated by using a fixed amount of indicator.

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[Contribution from the Laboratory of Physical Chemistry, McGill University]

AN AUTOMATIC LOW-TEMPERATURE THERMOSTAT

By O. Maass and W. H. Barnes

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Introduction

In a previous paper[1] a method was described for maintaining cooling-baths at any low temperature between —78.5° and that of liquid air. Owing to the inconvenience of adding small amounts of liquid air by hand, an automatic device has been developed for regulating the temperature and is described in the present paper.

Description of Apparatus

The apparatus (not drawn to scale) is shown in Fig. 1. A current of air passes through a mercury pressure regulator A, two calcium chloride towers B and a large volume bottle C to a glass tap D. The head of this tap is mounted on the axle of a light metal wheel E of about 41 cm. radius.

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[1] Maass and Barnes, *Proc. Roy. Soc.*, **111A**, 227 (1926).