A NEW SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF MANGANESE WITH N,N,N'N'-TETRAKIS(2-HYDROXYPROPYL)ETHYLENEDIAMINE

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Master of Arts

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by

Jerry Wellons McKenzie

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DEDICATION

This thesis is dedicated to my daughter, Sumer Shea, and my wife, Brenda, whose hard work and understanding allowed the attainment of this goal.

ACKNOWLEDGEMENT

I wish to extend my sincere appreciation to Dr. LeRoy Pike for his advice and guidance throughout this research.

I am indebted to Mr. Bill Varner for his assistance in the reproduction of the figures in this paper.

I also wish to convey my sincere gratitude to my mother, who started me toward an education.

Jerry W. McKenzie

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INTRODUCTION

In 1959 Keyworth (11) reported the stability constants and colors for the chelates of copper, nickel, zinc, lead, cobalt, mercury and silver with N,N,N',N',tetrakis(2-hydroxypropyl)ethylenediamine (THPED). This investigation suggested the possibility of using THPED as a spectrophotometric reagent in trace metal analysis. Preliminary work, however, indicated that the absorption of the mentioned metal chelates was too low for their use in trace analysis.

Pike, using the semi-micro technique of Yoe (27) for studies of new organic analytical reagents, revealed a soluble yellow manganese chelate of N,N,N',N',tetrakis (2-hydroxypropyl)ethylenediamine in basic solution. This led to the development of a spectrophotometric method for the determination of manganese based on an absorbance maximum of the manganese-THPED chelate at 506mu (17). During the course of this work another absorbance maximum near 276mu was noted which appeared to be much more sensitive for manganese. This thesis contains an account of an investigation into the possibility of using this absorbance maximum (near 276mu) for the determination of manganese. The results have been successful. Optimum conditions for a determination have been established, as well as the tolerance to a number of foreign ions. The procedure has been

successfully applied to two samples supplied by the National Bureau of Standards.

HISTORICAL

The most important use of manganese is in the production of special steels. It is added to the steel either as ferro-manganese or as spiegeleisen (mirror-iron). Spiegeleisen is 20 to 32 per cent manganese. Ferro-manganese is about 80 per cent manganese and is used in producing manganese steel (14).

The dioxide of manganese is used in the manufacture of chlorine and iodine and as a depolarizer for dry cells. Permanganate is used as a disinfectant and as an oxidizing agent in analytical chemistry.

In addition to these uses, manganese in trace amounts is essential to both plant and animal life and to reproduction in animals.

Keboe (10) determined that manganese was mainly found in the body tissues and not in the plasma. Studies done with rats and mice (21) produced clear evidence that manganese plays an important part in normal reproduction, bone formation, growth and the activity of certain ensymes in animals. Non-viable young were produced by female rats whose diet was deficient in manganese. The young rats were characterized by loss of both equilibrium and coordination.

Perosis, an anatomical deformity of the tibial-metarsal joint of young chickens, can be prevented by the addition of manganese to the diet (25).

The role which manganese plays in the nutrition of man has not yet been determined.

From the previous paragraphs it is obvious that analytical methods for quantitative measurement of manganese are welcomed. Manganese may now be determined by a wide variety of methods based on different principles and techniques. Since this research is in the field of colorimetry and spectrophotometry only these methods are cited.

The most commonly used method for low concentrations of manganese is that of oxidizing it to the permanganate and comparing the color produced with that of known standards. Many procedures exist differing only in the method of oxidation. Among the earliest is the method of oxidizing with lead dioxide which was suggested by Crum (4) in 1845 and developed by Prichard (16) in 1872.

Reddrop and Ramage (18) proposed the use of sodium bismuthate as the oxidizing agent in 1895 and Dufty (7) gave the details of a method for the use of this reagent in 1901.

The persulfate method was originated in 1901 by Marshall (13) and developed by Walters (22) the same year.

In 1917 Willard and Greathouse (23) developed a procedure using periodate as the oxidizing agent. This procedure was adapted to the determination of low concentrations by Richards (19).

Today the most commonly used colorimetric methods are the persulfate and periodate. Both are standard methods for the determination of manganese in water, sewage and industrial waste (1).

The Official Association of Agricultural Chemists (2) lists the periodate method as official for the determination of manganese in fertilizer, foods, plants, grain and stock feeds. However, the persulfate method is official for the determination of manganese in mineral waters and the bismuthate method is official for manganese in soils.

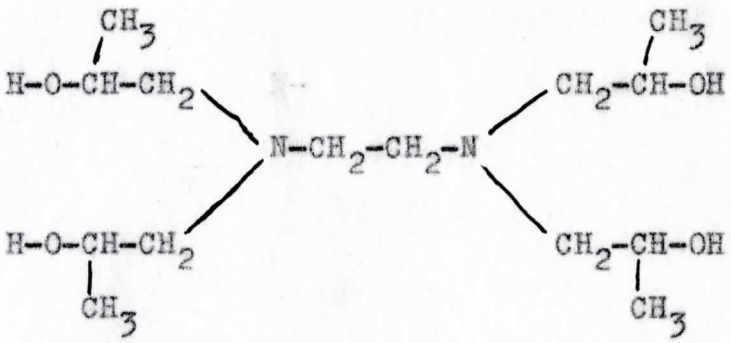
Several other methods of oxidation are available but are used less often. Heslinga (8) accomplished the oxidation in an alkaline solution with bromine and a trace of copper as a catalyst. He made the resulting solution acidic to convert the manganate to permanganate. Later Deniges (6) effected the oxidation with sodium hypochlorite in the presence of copper ions. Willard and Merritt (24) used ozone in perchloric acid to carry out the oxidation.

Deniges introduced the formaldoxime method in 1932 (5). Jaffe (9) reported a manganese complex with triethanolamine in basic solution which was shown to contain manganese(III). This was developed into a colorimetric method by Bruno (3) in 1953, and further modified by Nightingale in 1959 (19). Pike and Yoe (17) developed a

spectrophotometric method for the determination of manganese based on the manganese-THPED chelate's maximum absorbance at 506mu.

DESCRIPTION AND PROPERTIES OF THE REAGENT

N,N,N',N',tetrakis(2-hydroxypropyl)ethylenediamine (THPED)



The Wyandotte Chemicals Corporation, Wyandotte, Michigan holds a production patent (U.S. number 2,697,118) on this compound and markets it under the trade name "Quadrol." The diamine is a very viscous, watery white liquid at room temperature. It is 99.2% pure by tertiary amine assay, has a specific gravity of 1.033 at 25°C and a refractive index of 1.478 at 25°C. THPED is infinitely soluble in water and has a solubility greater than 10 gms. per 100 ml. of solvent in ethanol, toluene, ethylene, glycol, and perchloroethylene. It has a solubility of approximately one gm. per 100 ml. of solvent in kerosene, mineral oil and vegetable oil.

As would be expected from the presence of the two tertiary amine groups in the molecule, aqueous solutions of THPED exhibit basic properties. The pH of aqueous solutions

range from 8.1 for a 0.001% solution to 10.9 for a 10.0% solution.

THPED is exceptionally stable to heat. Observations have shown that this material can be heated in a stainless steel container in the absence of air to around 225°C for a period of 15 hours with only a slight discoloration. It can be vacuum distilled without decomposition from 190°C-240°C. Solutions of the compound can be standardized volumetrically with standard hydrochloric acid solutions using either a potentiometric end point or an acid-base indicator (17).

The reagent has a relatively low order of toxicity. In oral, vision and skin tests, little effects were exhibited.

THPED has proven to be an excellent cross-linking agent and catalyst for use in rigid type polyurethane forms. As an intermediate, the unique structure and physical properties of the reagent suggest possible use in the preparation of various resins, emulsifying agents, surface-active agents, pharmaceuticals, herbicides, fungicides, insecticides, adhesives and plasticiziers (26). Its structure certainly suggests its use as a chelating agent though little effort has been made to use it in this way.

PRELIMINARY STUDIES OF THE MANGANESE-THPED CHELATE

Spectra of Reagent and Chelate

The spectrum of the manganese-THPED chelate in a basic solution is shown in Curve II of Figure 1. As the pH is gradually lowered, a family of curves is obtained between Curve II and Curve III. At approximately pH 6.0 a distinctive pink color is formed and the chelate has maximum absorbance at 276mu. Below pH values of 5.5 rapid dissociation occurs which inhibits accuracy. Curve I of Figure 1 shows that the reagent does not absorb strongly near 276mu, thus it does not interfere with the absorbance of the manganese-THPED chelate.

Rate of Chelate Formation and Its Stability

The formation of the manganese-THPED chelate is limited entirely to strongly basic solutions. There is no formation at pH 8.5 and very slow formation between pH's of 9.0 and 10.0. The rate of chelate formation also depends upon the availability of oxygen. Any method of introducing oxygen to the reaction will increase the rate of formation. However, many oxidizing agents cause interference. Hydrogen peroxide appears to increase the rate of chelate formation but changes the shape of the absorption spectrum (17). Similarities were observed by Nightingale (15) while working with manganese-triethanolamine chelates and are

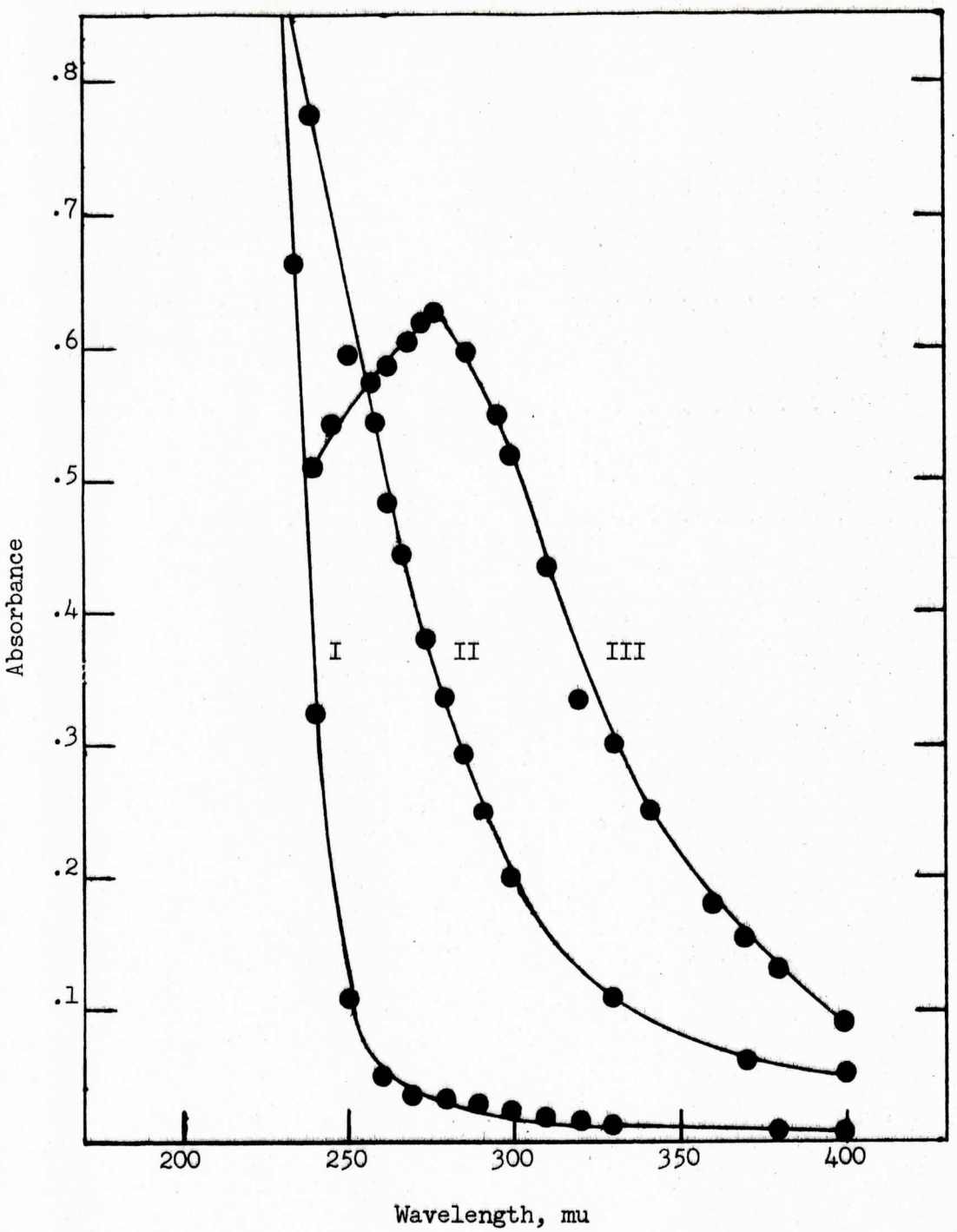


FIGURE 1

ABSORBANCE SPECTRA OF THPED (CURVE I) AND ITS MANGANESE CHELATE IN EXCESS REAGENT AT pH 12.2 (CURVE II) AND AT pH 6 (CURVE III)

TABLE I FIGURE 1

ABSORBANCE SPECTRA OF THPED (CURVE I) AND ITS MANGANESE CHELATE IN EXCESS REAGENT AT pH 12.2 (CURVE II) AND AT pH 6.2 (CURVE III)

CURVE I		CURVE II		CURVE III	
Wavelength (mu)	Absorbance	Wavelength (mu)	Absorbance	Wavelength (mu)	Absorbance
230	.900	240	.775	240	.508
240	.325	250	.595	246	.543
250	.113	258	.542	258	.572
260	.050	262	.483	262	.586
270	.035	266	.441	268	.606
280	.032	272	.380	272	.621
290	.027	278	.336	276	.626
300	.024	284	.292	284	.598
310	.021	292	.250	296	.552
320	.019	298	.202	300	.520
330	.017	330	.112	310	.431
380	.010	370	.065	320	.336
400	.007	400	.052	330	.302
				340	.250
				360	.178
				370	.155
				380	.129
				400	.090

believed to be due to manganese peroxide complexes. Reproducible results were obtained by shaking the reaction mixture rapidly in air for thirty seconds. For high concentrations of manganese (above 5 p.p.m.) it was also noted that an additional shaking of five seconds near the end of the reaction would aid the reproducibility.

The effect of pH on the rate of chelate formation was studied by preparing solutions containing the reagent, manganese and sufficient sodium hydroxide to obtain the desired pH, shaking rapidly for thirty seconds and, after various time intervals, adjusting the pH to 6.0 with acetic acid followed by measuring the absorbance at 276mu. The rate curves are shown in Figure 2. The rate of chelate formation and the maximum absorbance increase with pH up to 12.2, above which there is no significant change. Figure 2 shows that absorbance is nearly constant between ten and twenty minutes. From thirteen to fifteen minutes was chosen as the ideal time to measure the absorbance of the chelate.

After twenty minutes there is a definite increase in absorbance. This increase was not studied because of the reproducibility and convenience of absorbance values obtained between 10 and 20 minutes.

The chelate is reasonably stable at a pH of 6 or greater. Below this there is rapid dissociation. A small

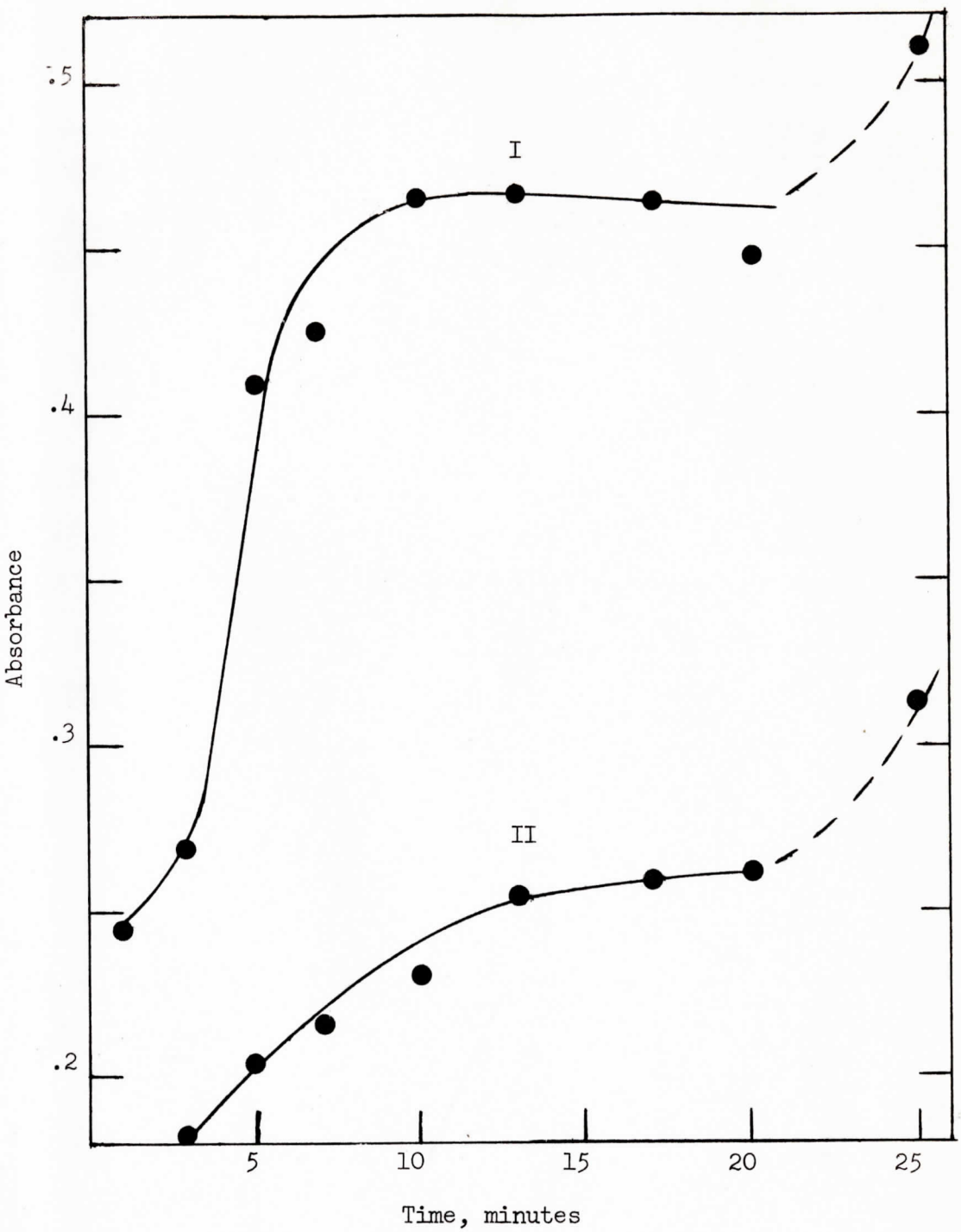


FIGURE 2

EFFECT OF pH UPON THE RATE OF FORMATION OF THE MANGANESE - THPED CHELATE. CURVE I,pH 12.2 CURVE II, pH 10.

TABLE II FIGURE 2

EFFECT OF pH UPON THE RATE OF FORMATION OF THE MANGANESE-THPED CHELATE

CURVE I		CURVE II	
Time (minutes)	Absorbance at 276mu	Time (minutes)	Absorbance at 276mu
1.0	.245	1.0	.156
3.0	.268	3.0	.183
4.0	.411	4.0	.203
7.0	.425	7.0	.216
10.0	.466	10.0	.230
13.0	.468	13.0	.254
17.0	.464	17.0	.259
20.0	.448	20.0	.262
25.0	.510	25.0	.313

but abrupt decrease in absorbance occurs after five minutes followed by a gradual decrease during the next forty-five minutes as shown in Figure 3. Longer periods of time were not investigated.

Effect of pH After Chelate Formation

Maximum absorbance of the chelate occurs at 276mu, thus the effects of changes in pH after formation were studied at this wavelength. The chelate was formed at a pH of 12.2 and after thirteen minutes the pH was lowered with acetic acid and the absorbance was determined. The changes in absorbance with changes in pH are shown in Figure 4. The acid used has no effect, but the rate of fading increases as the pH decreases. Rapid fading occurs below pH 5.5.

Excess Reagent Required to Yield Constant Absorbance

The method used to determine the amount of reagent required to yield a constant absorbance was that of Yoe and Jones (28). This method is complicated when optical approaches are used because the manganese precipitates and interferes when it is in excess in a basic solution. Filtration was used which did not effect the reproducibility of the absorbance of the chelate.

Solutions were prepared containing a constant concentration of manganese (9.0×10^{-5}M) and increasing amounts of reagent. The pH was lowered to 6.2 and the

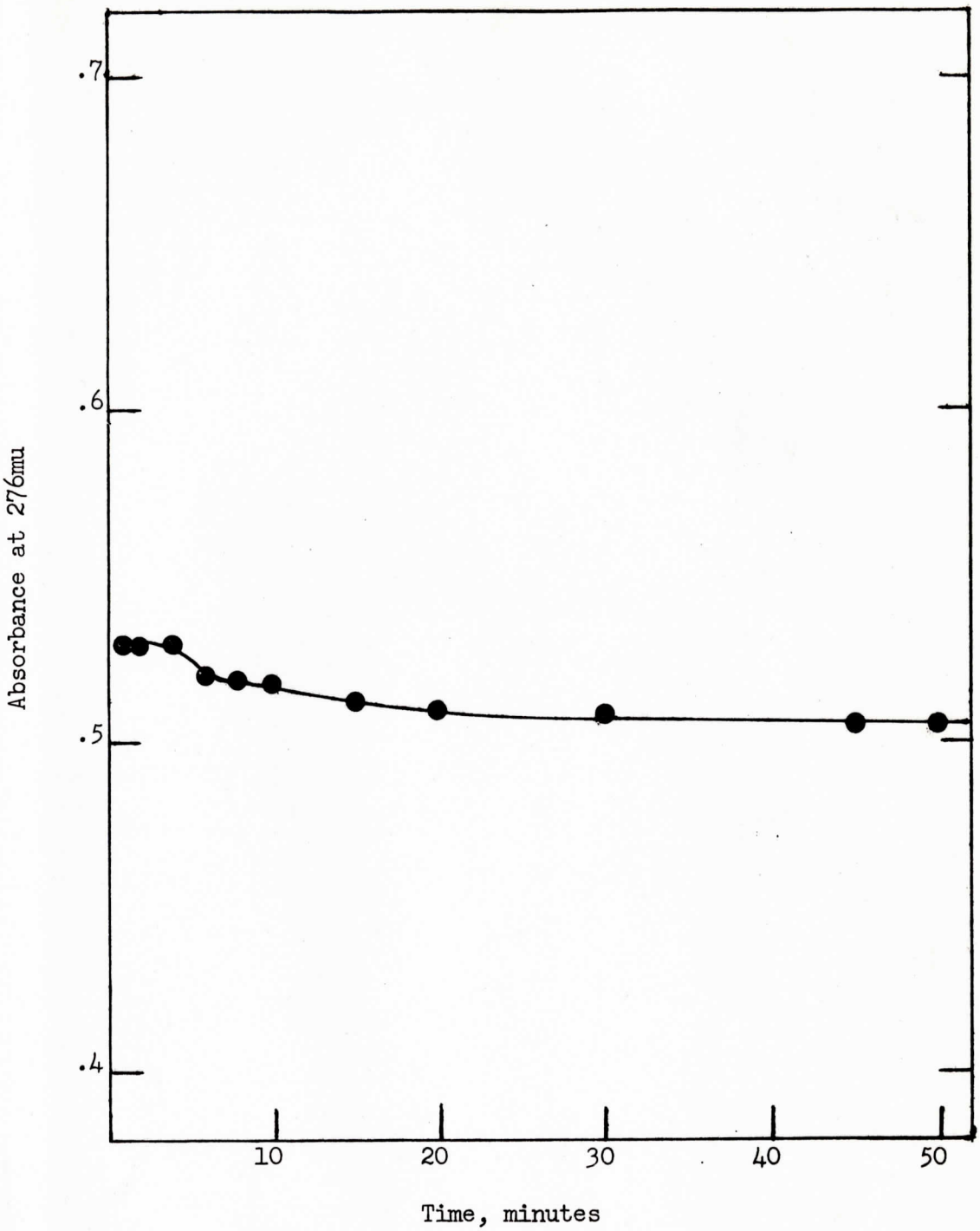


FIGURE 3

RATE OF DECOMPOSITION OF THE MANGANESE - THPED CHELATE AT pH 6.2

TABLE III FIGURE 3

RATE OF DECOMPOSITION OF THE MANGANESE -THPED CHELATE AT pH 6.2

Time (minutes)	Absorbance at 276mu
0	.530
.5	.530
2.0	.530
4.0	.530
6.0	.520
8.0	.519
10.0	.518
15.0	.513
20.0	.510
30.0	.509
45.0	.506
50.0	.506

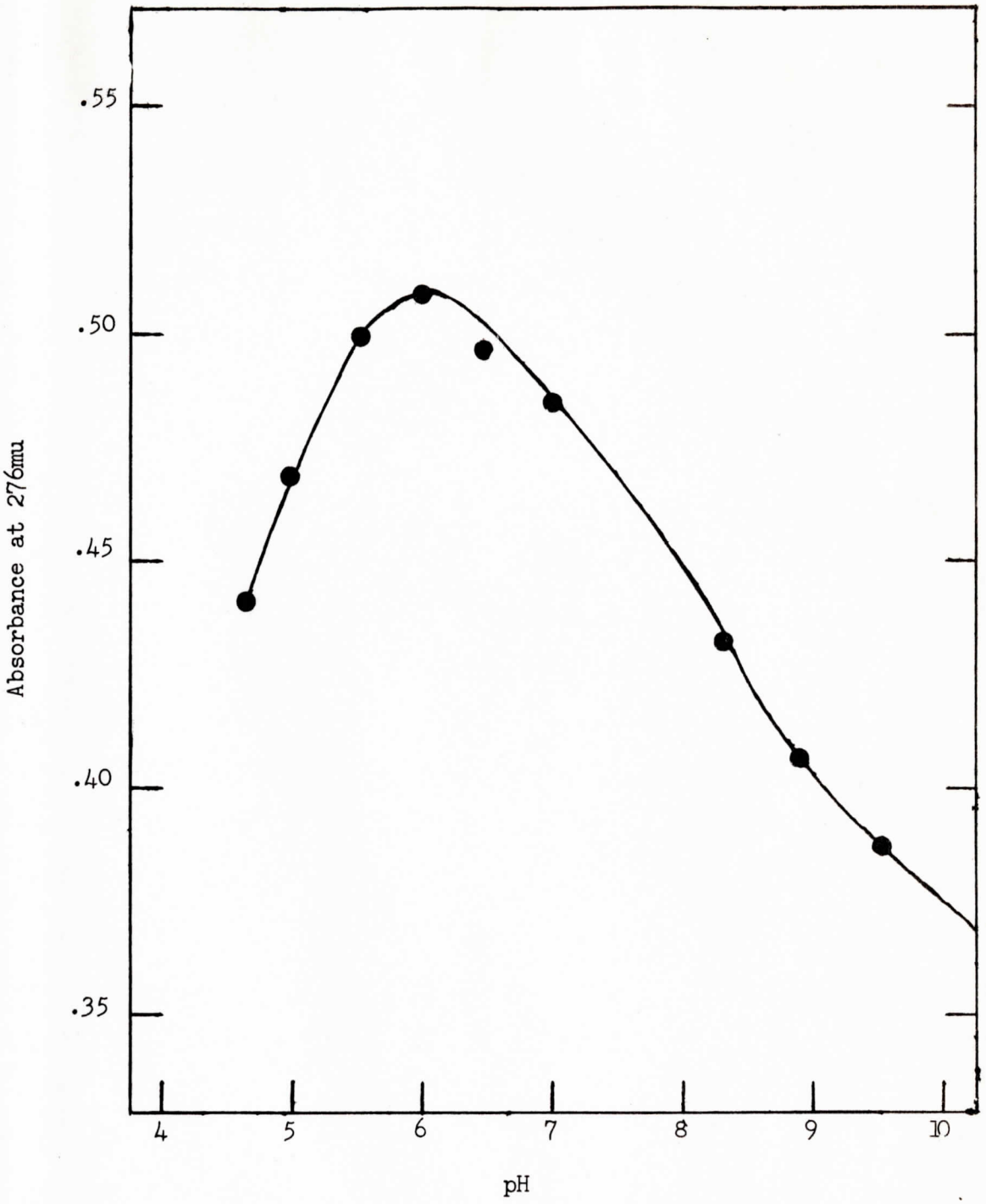


FIGURE 4

EFFECT OF pH ON THE ABSORBANCE OF THE
MANGANESE - THPED CHELATE
IN EXCESS REAGENT

TABLE IV FIGURE 4

EFFECT OF pH ON THE ABSORBANCE OF THE MANGANESE -THPED CHELATE AFTER FORMATION

pH	Absorbance at 276 mu
4.6	.442
5.0	.471
5.6	.496
6.0	.512
6.4	.492
7.1	.478
8.3	.435
8.8	.414
9.6	.385

absorbance measured. Figure 5 showsthat a mole-ratio of 1 to 2 is indicated, i.e. MnR_2.

The concentration of the reagent should be controlled so that only the necessary excess is present. Figure 6 shows that concentrations of reagent less than 1 milliliter of 10% THPED solution per 100 milliliters have little absorption at 276mu. Large concentrations, however, absorb appreciably.

Effect of Order of Addition of Reagents

The reagent must be added to the manganese before the solution is made alkaline in order to prevent the precipitation of hydrous oxides of manganese. The base or the manganese may be mixed with the reagent before the addition of the other with no effect on the absorbance of the chelate.

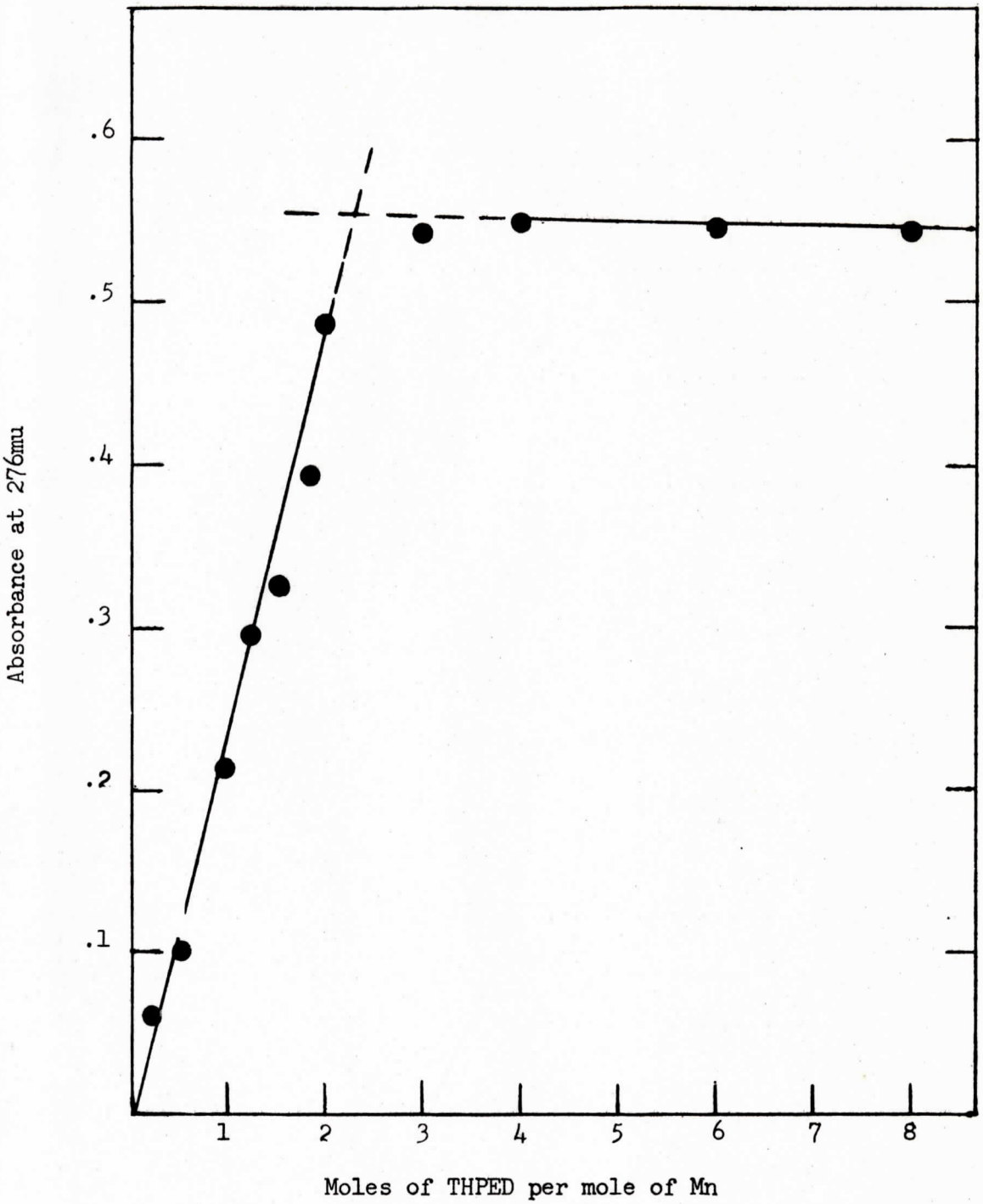


FIGURE 5

MOLE RATIO STUDIES OF THE MANGANESE - THPED CHELATE AT pH 6.2

TABLE V FIGURE 5

EXCESS REAGENT REQUIRED TO YIELD CONSTANT ABSORBANCE

Moles of THPED per Mole of Mn	Absorbance at 276 mu
0.25	.062
0.50	.102
1.00	.216
1.25	.295
1.50	.324
1.75	.396
2.00	.488
3.00	.542
4.00	.548
6.00	.546
8.00	.545

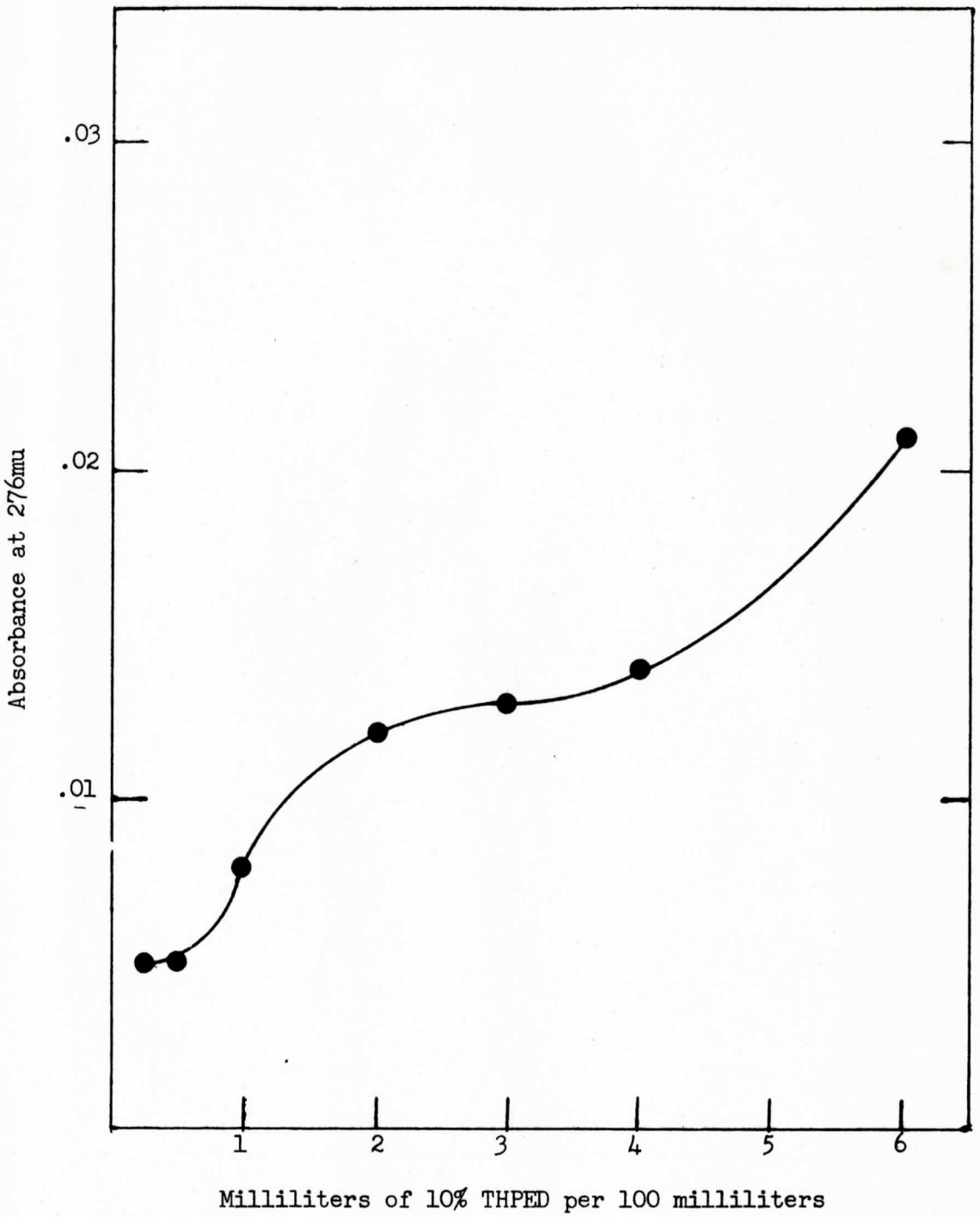


FIGURE 6

EFFECT OF INCREASING THPED CONCENTRATION
ON ABSORBANCE AT 276mu

TABLE VI FIGURE 6

EFFECT OF INCREASING THPED CONCENTRATION ON ABSORBANCE AT 276 mu

ml 10% THPED/100ml	Absorbance at 276mu
0.25	.005
0.50	.005
1.0	.008
2.0	.012
3.0	.013
4.0	.014
6.0	.021

THE MANGANESE DETERMINATION

Calibration Procedure

The following technique and conditions were selected from the preceding investigation and are recommended for obtaining a calibration curve (Beer's Law plot).

(1) Using a standard manganese solution (100 p.p.m.) transfer 0.25, 0.50, 1.00, 2.00, 4.00, 6.00 ml., respectively, to 100 ml. volumetric flasks and dilute to 50 ml. with distilled water. The series will contain 0.25, 0.50, 1.00, 2.00, 4.00, and 6.00 p.p.m. of manganese when diluted to 100 ml.

(2) Add 2 ml. of a 2.5% reagent solution.

(3) Add 0.5 ml. of 6N sodium hydroxide.

(4) Shake the unstoppered flask rapidly for thirty seconds.

(5) Allow the unstoppered solutions to stand for thirteen minutes, then shake again for five seconds and add sufficient acetate buffer solution (about 1 ml.) to produce a pH of approximately 6.2.

(6) Complete the dilution (100 ml.) with distilled water, mix thoroughly and measure the absorbance at 276mu against a reagent blank. The averages of eight determinations at each concentration were used to plot the calibration curve shown in Figure 7. This graph was used for subsequent determinations.

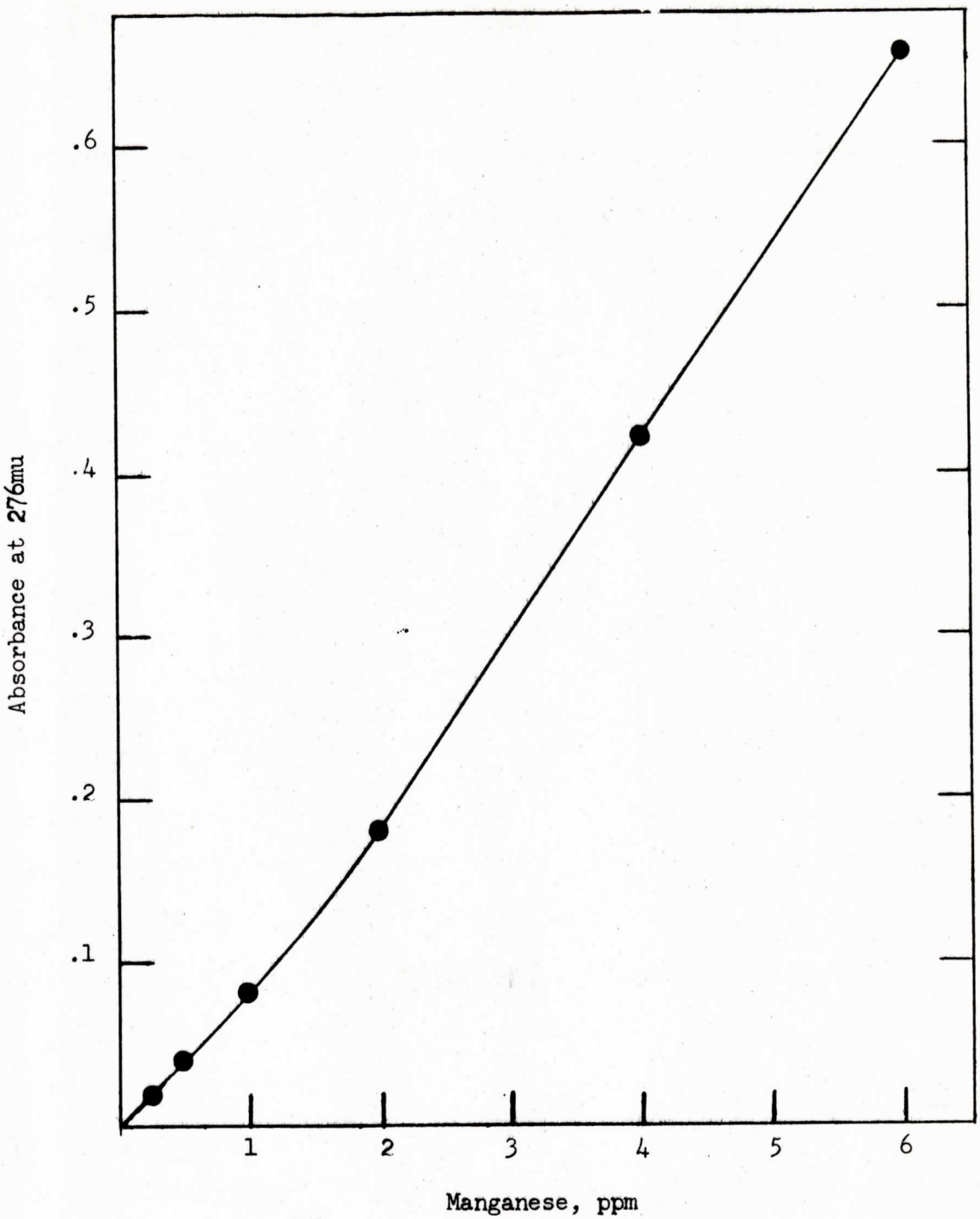


FIGURE 7

CALIBRATION CURVE FOR THE MANGANESE DETERMINATION

TABLE VII FIGURE 7

CALIBRATION CURVE (8 DETERMINATIONS)

p.p.m. Manganese	Average absorbance at 276 mu	Standard deviation
0.25	.020	.003
0.50	.040	.002
1.0	.082	.006
2.0	.181	.006
4.0	.422	.007
6.0	.656	.010

Reproducibility

Eight aliquots representing 4 p.p.m. of manganese at the final dilution were analyzed and the standard deviation was calculated. The results are given in Table VIII.

Discussion of the Determination

The absorbance system conforms very nearly to Beer's Law over the range of concentrations measured, that is, 0.25 to 6.0 p.p.m. If absorbance values between 0.2 and 0.6 are chosen as the optimum range, the values correspond to manganese concentrations between 2.0 and 5.5 p.p.m. The Sandell (20) sensitivity is 0.0095 ug of manganese per cm^2 for $\log \frac{I_o}{I} = 0.001$, i.e., about 1 part of manganese in 100,000,000 parts of solution. A more practical sensitivity, however, based on an absorbance of 0.005 is 1 part of manganese in 20,000,000 parts of solution. The molar absorptivity (molecular extinction coefficient) is 5800.

Figure 2 shows that a pH of 12 or higher must be used to obtain maximum intensity fairly quickly. One half milliliter of 6N sodium hydroxide solution yields a pH of about 12.5 with most samples. Larger amounts of alkali cause excessive heat when neutralized. Figure 5 shows that a threefold excess of reagent will produce maximum absorbance but since foreign ions may react with the reagent,

TABLE VIII

REPRODUCIBILITY OF MANGANESE DETERMINATION
(4 p.p.m. manganese)

Aliquot	Absorbance at 276 mu
1	.430
2	.422
3	.415
4	.415
5	.424
6	.417
7	.422
8	.430

Average = .422 σ = .007

two milliliters of 2.5% solution was used. This gives a concentration of 2.0×10^{-5} M which is about a thirtyfold excess for a 4 p.p.m. manganese concentration.

After the addition of the sodium hydroxide, it is necessary to thoroughly mix the 50 ml. of solution with air by vigorous shaking for thirty seconds. Pike and Yoe (17) have shown that the manganese is air oxidized from Mn(II) to Mn(III). A period of thirteen to fifteen minutes was alloted for maximum chelate formation.

An acetate buffer was quite satisfactory for adjustment of the pH to approximately 6.2. It is prepared so that 1 ml. will produce the required pH upon dilution and reaction.

Effect of Foreign Ions

The effect of foreign ions on the manganese determination was studied by carrying out the reactions in the presence of twenty-one separate ions. A manganese concentration of 4 p.p.m. which gave an absorbance of 0.422 was used in these tests.

A change in absorbance of 5% or less was arbitrarily considered as "no interference." The following ions caused no change in absorbance at the 4 p.p.m. manganese level when present at a 100 fold excess: Na^{+} K^{+}, Li^{+}, Bi^{+3}, $PO_4^{\equiv}$, I^{-}, Cl^{-}, $SO_4^{=}$, NO_3^{-}. Reducing ions, such as Sn^{+2},

NO_2^-, and $S^=$ must be absent. The ions listed in Table IX cause an interference no greater than 5% when present in the concentrations given.

TABLE IX

TOLERANCE OF MANGANESE DETERMINATION TO INTERFERING IONS (4 p.p.m. manganese)

Ion	Limiting concentration p.p.m.
Sn^{+4}	0.25 p.p.m.
Mg^{+2}	0.25 p.p.m.
Ca^{+2}	40 p.p.m.
Fe^{+3}	0.25
Co^{+2}	0.25
Cr^{+3}	0.1
Cu^{+2}	0.25
Ni^{+2}	20.
Zn^{+2}	100 p.p.m.
Al^{+3}	9.0
$CO_3^{=}$	200 p.p.m.

REAGENTS

N,N,N',N'-tetrakis(2-hydroxpropyl)ethylenediamine

This chemical was supplied by Wyandotte Chemical Company, Wyandotte, Michigan. Its properties are described in the body of the thesis. A 2.5 per cent by weight water solution was used for the determination.

Acetate Buffer

The acetate buffer solution was prepared by dissolving 165 grams of sodium acetate in 450 milliliters of distilled water. Enough glacial acetic acid (about 30 milliliters) was added to bring the pH to 5.3 and this was followed by dilution to 500 milliliters.

Manganese Standard

The manganese standard was prepared by dissolving one gram of spectrographically standardized "Matthey" manganese in concentrated hydrochloric acid. The excess hydrochloric acid was evaporated and the solution diluted to one liter. This gave a concentration of 1,000 p.p.m. manganese(II) ion. Aliquots of this standard solution were used to prepare desired concentration.

Other Chemicals

All other chemicals were reagent grade and were used without further purification. Regular laboratory distilled water was used throughout the work.

APPARATUS

Standard volumetric flasks and pipettes were used without further calibration. Also a 10 milliliter semi-micro burette, pH meter, spectrophotometer, power supply and an ion-exchange column was used.

Spectrophotometer

A Beckman Model DU Quartz Spectrophotometer with a Beckman DU A.C. Power Supply was used for all absorbance measurements. Beckman Type 2300 square silica absorption cells with a 1 centimeter light path were used.

pH Meter

A Beckman Zeromatic was used for all measurements of pH. It was carefully standardized with Fisher's Certified Buffers.

Ion-Exchange Columns

The columns used for the ion exchange separation consisted of a capillary stopcock attached to one end of a 20 cm. piece of 7 mm. (o.d.) pyrex tubing and a 10 cm. piece of 15 mm. (o.d.) pyrex tubing attached to the other end.

SOME PROPERTIES OF THE ORGANIC ION EXCHANGE RESINS

Resins composed of polystyrene-divinylbenzene copolymers are usually used in analytical work. Dowex-1, which was used in this work, is this type of resin. Thus, their properties are discussed in the following paragraphs.

Swelling

When ion-exchange resins are immersed in aqueous media, the considerable amount of water-pickup and swelling is strongly dependent on the degree of cross-linking of the exchangers. For the polystyrene-divinylbenzene resins, cross-linking is defined in terms of the per cent divinylbenzene added during polymerization. This is indicated by a number preceded by X in the name, e.g., Dowex-1 X 8 means the resin contains 8% divinylbenzene.

Swelling is relatively low with high cross-linking but may be enormous with low cross-linking. Salts decrease swelling as their concentrations increase. Swelling is also influenced by mobile ions in the exchangers.

Rates

Ion-exchange rates are principally diffusion controlled. They are clearly dependent on the degree of cross-linking of the resin, presumably because of the differences in the amount of swelling. At very low cross-linking, the diffusion rates within the exchanger appear to

approach those in aqueous solutions. At high cross-linking, diffusion coefficients may be several orders of magnitude smaller than at low cross-linking. These coefficients, however, are highly dependent on the charge of the ions for cation exchangers and less for anion exchangers.

Screening Effect

If an ion-exchange resin in an aqueous medium is visualized as being a three-dimensional organic network filled with water, an effective pore size may be visualized which would impose limits on the size of ions that can readily penetrate the exchanger. The pore size is dependent on the degree of cross-linking and the medium. Thus, it can be controlled to some extent. Advantages may be seen in the exclusion of large ions from the resin.

Selectivities

The selectivity of exchangers, i.e., the relative preference they show for one ion over another, is profoundly affected by the cross-linking.

For simple ions, such as the alkali metals or alkaline earths, selectivities increase at moderate cross-linking from lithium to cesium and from beryllium to barium. Further, the selectivities tend to increase with cross-linking.

Selectivities for anion exchangers have not been studied as thoroughly. For the halides, least adsorption is usually found for the fluorides and strongest adsorption for the iodides.

Capacity and Loading

The capacity of exchangers, C, may be defined in terms of the number of equivalents of exchange sites per unit weight or unit volume of exchanger. Organic exchangers in general have rather high capacities, usually in the order of 3 to 6 equivalents per kilogram of exchanger. Loading, L, is defined by the relationship $L=\frac{a\,(A^{\pm a})\,r}{C}$ where a is the charge on the ion A and ()r indicates concentration in the resin phase (29).

PREVENTION OF INTERFERENCE BY FOREIGN IONS

To prevent interference by foreign ions a method must be employed to either mask the interference or separate manganese. In this study the ion-exchange separation of Kraus and Moore (12) was used to isolate manganese. Kraus and Moore adsorbed the chloro complexes of manganese(II), copper(II), iron(III) and zinc on Dowex-1 anion exchange resin from 12M hydrochloric acid. Magnesium, aluminum, titanium(III), vanadium(IV), chromium(III), nickel(II) and many other ions are not adsorbed from 12M hydrochloric acid and may be eluted with it (29). Manganese is then eluted with 6M hydrochloric acid, followed by cobalt, copper, iron and zinc with 4, 2.5, 0.5 and 0.005 molar acid, respectively.

Preparation of Columns

The columns were packed by adding a water slurry of Dowex-1, 8X (50-100 mesh) and allowing it to settle. The resin bed was about 20 cm. in length and 5 mm. in diameter. A glass wool plug was used at each end of the resin beds.

Elution

Samples were placed on the conditioned columns in 1 ml. of 12M hydrochloric acid. If elution is continued with 12M hydrochloric acid, manganese appears in the fourth milliliter of effluent and tails over a considerable

volume. However, if the eluant is changed to 6M hydrochloric after rinsing the sample into the resin bed with 12M acid, manganese is eluted in a sharp band between the fourth and seventh or eighth milliliters of effluent. The elution curve in Figure 8 was obtained by collecting 1 ml. fractions, oxidizing the manganese to permanganate with periodate and measuring the absorbance at 520 mu.

Recommended Procedure

Dissolve the sample in a minimum of hydrochloric acid, or hydrochloric acid and nitric acid as required. Boil off the excess nitric acid and dilute the sample to volume with 12M hydrochloric acid. The weight of sample used should be such that 1 ml. will contain between 0.2 and 0.6 mg. of manganese, if 100 ml. volumetric flasks are used for the determination.

(1) Condition the resin bed with 12M hydrochloric acid.

(2) Transfer a 1 ml. aliquot of the sample to the bed and rinse in with two 1 ml. portions of 12M hydrochloric acid.

(3) Elute the manganese with 6M hydrochloric acid which is added in five 2 ml. portions.

(4) Discard the first two milliliters of effluent and collect the next 10 ml. which contain the manganese.

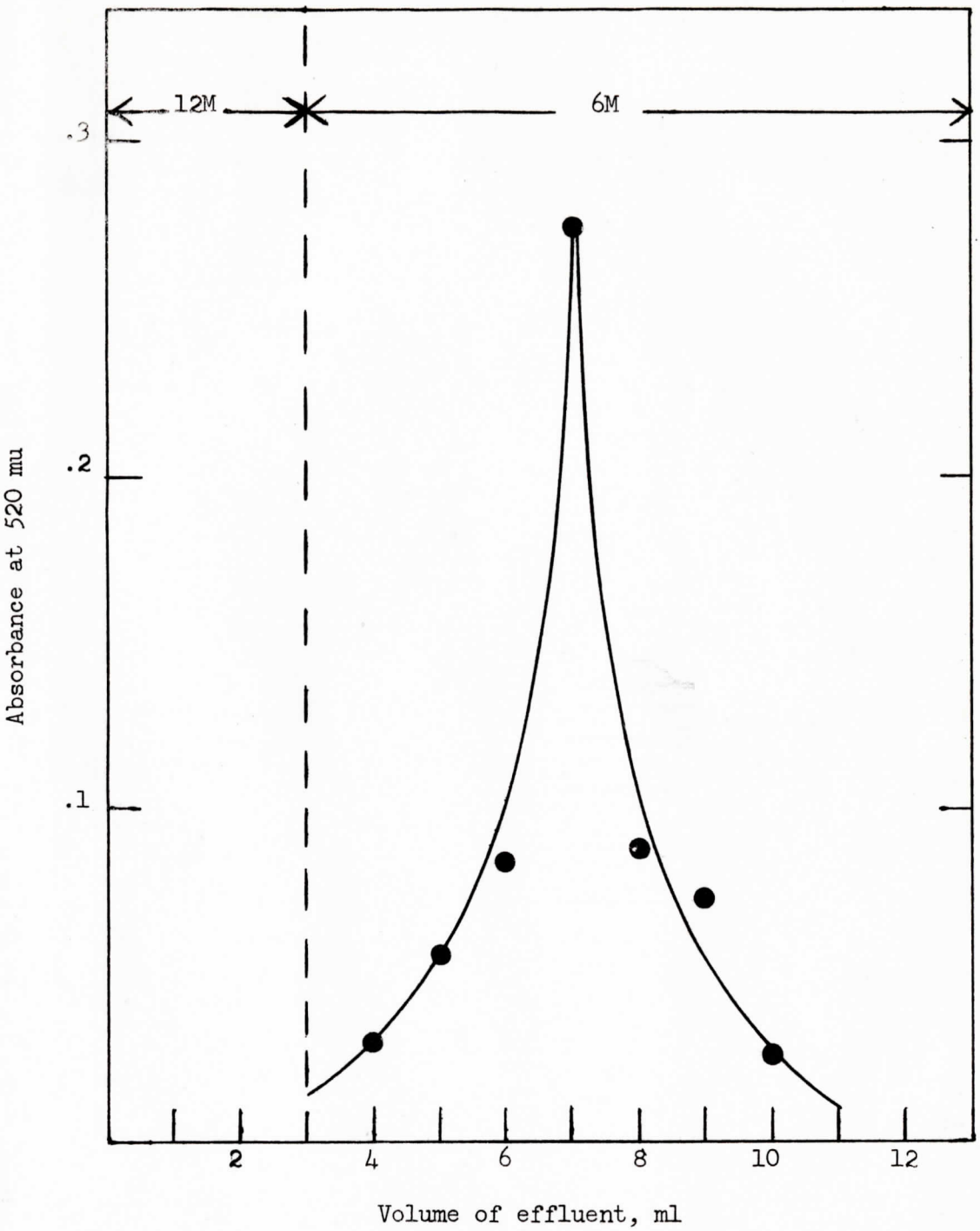


FIGURE 8

ELUTION OF MANGANESE (II) FROM DOWEX 1, 8X
WITH HYDROCHLORIC ACID

TABLE X FIGURE 8

ELUTION OF MANGANESE (II) FROM DOWEX-1, 8X WITH HYDROCHLORIC ACID

Volume of Effluent, ml	Absorbance at 520 mu
1	.028
2	.058
3	.084
4	.275
5	.071
6	.045
7	.027

(5) Evaporate almost to dryness, transfer to a 100 ml. volumetric flask and analyze for manganese as described in the calibration procedure.

Cobalt, copper, iron and zinc which remain on the column as their chloro complexes may be removed by the addition of 5 ml. of 0.05M hydrochloric acid followed by thirty to fifty milliliters of distilled water and the column reused.

The procedure gives a good separation of manganese from cobalt, copper, iron and zinc. Separation of manganese from unadsorbed ions, such as nickel and chromium would be difficult and may require longer columns because the distribution coefficient of manganese in 12M hydrochloric acid is only about 4. Such separations were not required for analysis of the samples used in this work.

The columns used have a capacity of about 4 meq. of adsorbable ions. This sets the lower manganese concentration at 0.2% if all the ions in the sample are adsorbed on the resin. This could be reduced to 0.02% by using 10 ml. volumetric flasks for the analysis. Of course, larger columns could be used.

ANALYSIS OF N.B.S. STANDARD SAMPLES

In order to evaluate the method, two National Bureau of Standards samples were analyzed for manganese by the recommended procedure. The results are summarized in Table XI. The samples were N.B.S. numbers 164 and 62.

N.B.S. Sample No. 62

This is a Mn-bronze having the following composition: 59.07% copper, 135.06% zinc, 1.59% manganese, 1.13% iron, 1.13% aluminum, 0.82% titanium, 0.64% nickel, and 0.56% lead. The sample tested the efficiency of the copper and iron separation. It also tested the efficiency of the removal of ions from the column, since zinc is the most difficult to remove.

Four samples were analyzed for manganese. The values ranged from 1.56% to 1.66% manganese, the average being 1.62% and the standard deviation 0.05. The Bureau's range is 1.53% to 1.64% manganese, the average being 1.59%.

N.B.S. Sample No. 164

This sample is a Mn-Al bronze; it contains more aluminum, copper and iron, and less zinc than N.B.S. Sample No. 62. Nine samples of No. 164 were analyzed for manganese. The values obtained ranged from 4.46% to 4.77%, the average being 4.62% and the standard deviation 0.12. The Bureau's

TABLE XI

DETERMINATION OF MANGANESE IN NBS STANDARD SAMPLES

NBS Sample	NBS Sample Range	%Mn Average	New Method		Standard Deviation
			Range	% Mn Average	
No. 62 Mn bronze	1.53-1.64	1.59	1.56-1.66	1.62	.05
No. 164 Mn-Al bronze	4.65-4.70	4.68	4.46-4.77	4.62	.12

range is 4.65% to 4.70%, the average being 4.68%. The results are given in Table XII.

TABLE XII

DETERMINATION OF MANGANESE IN N.B.S. SAMPLE NO. 164 (Mn-BRONZE)

Analysis	% Manganese	$dx\ 10^2$	$d^2 \times 10^4$
1	4.77	15	225
2	4.76	14	196
3	4.77	15	225
4	4.55	-7	49
5	4.55	-7	49
6	4.50	-12	144
7	4.51	-11	121
8	4.70	8	64
9	4.46	-16	256

Average = 4.62
N.B.S. Average = 4.68
Percent Deviation = 1.28%

$$\sum d^2 = 0.1329$$

$$\sigma = \sqrt{\frac{d^2}{n-1}} = \sqrt{\frac{0.1329}{8}}$$

$$\sigma = \pm 0.12\ \%\ Mn$$

CONCLUSION

A sensitive spectrophotometric method for the determination of manganese has been developed. The procedure is relatively rapid and simple. It is based on the absorbance of a manganese(III)-N,N,N',N'-tetrakis(2-hydroxypropyl) ethylenediamine chelate formed by air oxidation of manganese(II) in a basic solution in the presence of the reagent. Large quantities of substances such as chloride can be tolerated which the classical permanganate methods cannot tolerate. Several cations interfere, but a separation procedure based upon the adsorption of the metal-chloro complexes on Dowex-1 8X ion exchange resin was successfully applied.

Two National Bureau of Standards samples have been analyzed by the recommended procedure with good results and a standard deviation of about 3%.

SUMMARY

A new spectrophotometric method for the determination of manganese using N,N,N',N'-tetrakis(2-hydroxypropyl) ethylenediamine has been developed. The manganese(III) chelate is formed by air oxidation of Mn(II) to Mn(III) in sodium hydroxide solutions containing the reagent. After chelate formation, the pH is brought to 6.2 with an acetate buffer and the absorbance is measured at 276mu. Beer's law is obeyed between 0.25 and 6 p.p.m. manganese when using 1-cm. absorption cells. The sensitivity is 0.0095 ug. per cm^2 for an absorbance of 0.001, or about one part of manganese in one hundred million parts of solution. The optimum concentration range is between 2 and 5.5 p.p.m.

A study of 21 different foreign ions showed interference from transition metals, magnesium and aluminum.

A procedure based upon selective adsorption on Dowex-1 8 X from 12M hydrochloric acid proved to be satisfactory for the separation of the manganese from iron, cobalt, copper, and zinc. Two National Bureau of Standards samples were analyzed with good precision and accuracy. The standard deviation was about 3%.

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