

TRACE DETERMINATION OF MANGANESE AS THE TRIETHANOLAMINE COMPLEX  
USING LONG PATHLENGTH PHOTOMETRY

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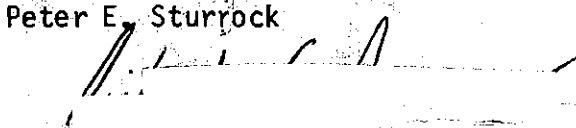
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## SUMMARY

Manganese and triethanolamine in the presence of base form a brilliant green complex. A spectrophotometric determination for manganese using this phenomenon was developed by Bruno and later modified by Nightingale. The procedures were investigated and it was found that the modifications to the method are neither advantageous nor necessary.

In order to determine the suitability of the procedure for trace analysis, it was necessary to use a long-path photometer developed by McKeithan. The photometer incorporates a 30 cm cell, a light emitting diode with a wavelength of 650 nm, a phototransistor, and appropriate electronic components.

When a 30 cm pathlength is used, the limit of detection for the method is 0.01 g/ml or 10 ppb, thus establishing its applicability as a method for trace analysis of manganese.

Only four metals, copper, chromium, nickel, and cobalt, form colored complexes which interfere with the determination of manganese. All the other metals tested either form colorless solutions or can be precipitated and removed from the sample solution. The tolerance limits for chromium(III) and cobalt(II) agree closely with those determined by Bruno; but Bruno allows a limit of twice as much copper(II) as the current investigation found acceptable, perhaps because Bruno makes his absorbance measurements at 625 nm rather than at 650 nm used in the present study.

Frequently in trace analysis the analyte is adsorbed onto the container walls. It was found that even at trace levels no detectable adsorption of analyte occurs with the present method if standard analytical procedures are followed.

## CHAPTER I

## INTRODUCTION

Manganese is a multivalent metallic element that is found world-wide, most commonly in the form of the mineral pyrolusite. It is added to steel to increase strength, hardness, and wear resistance. With copper it forms manganin, an alloy used in instruments for electrical measurements. Manganese dioxide is added to glass melts to negate the green color due to iron(II). The dioxide is also used as an oxidant in paints and as a depolarizing agent in dry cells. Potassium permanganate is employed as a disinfectant, deodorant, and germicide. This salt plays an important role as an oxidizing agent in various analytical procedures.

With such a wide variety of applications and the suggested role of manganese in the environment and in biological systems, it can readily be deduced that detection and determination of manganese is of great importance. Many methods have been developed over the years, but there is still room for improvement. In the present context, the determination of small amounts of manganese via photometry is the topic. The classical approach involves the oxidation of manganese to permanganate. The molar absorptivity of the permanganate ion is  $2500 \text{ l mole}^{-1} \text{ cm}^{-1}$  at 522 nm and, hence, relatively small amounts of manganese can be determined spectrophotometrically. Two methods are commonly employed to obtain the permanganate, oxidation with peroxydisulfate and with

periodate. Both methods work well in pure solutions but readily encounter difficulties when applied to actual samples. The reagents are strong oxidants and act upon many other compounds which may be present, including organic compounds and chloride. Therefore, special treatment of the sample is necessary, and the use of so common a reagent as hydrochloric acid is prohibited. Very small amounts of chloride can be tolerated, but only when extra steps are taken to cope with the interference. In the persulfate method silver ion is added as a catalyst; in the presence of chloride a precipitate forms which must be separated either by filtration or decantation before the optical measurement is made. In the periodate method, chloride is oxidized to chlorine which is then boiled off. Theoretically, large amounts of chloride can be taken care of in this manner, but the periodate is reduced to iodate, many of whose salts have rather limited solubility. Thus, in practise, the tolerable amount of chloride is restricted here also.

The persulfate method requires close control of acidity and boiling time in order to assure the complete transfer of all manganese to permanganate. Upon prolonged standing the permanganate color begins to fade, making impossible the storage of standard solutions containing manganese in the oxidized form. Such fading does not occur in the presence of periodate. This fact and the greater latitude permitted in other conditions makes the periodate method more and more the one preferred; still the persulfate procedures are by many workers, especially in the iron and steel industry, considered the standard methods (1).

The fact that, depending on the field of application, either or both methods are selected standard procedures should not detract from the severe drawbacks. When it comes to present day requirements of trace determination, field analysis, and routine handling of a multitude of samples, hopefully by automation, the situation is even worse. The molar absorptivity of  $2500 \text{ l mole}^{-1} \text{ cm}^{-1}$  is inadequate for trace analysis with ordinary photometric equipment; the necessity of having chlorides absent or face the task of their removal is severely restrictive; the requirement of boiling as a procedural step, possibly for sample treatment and definitely in the final oxidation to permanganate, is uncomfortable in automation and even more so in on-site field analysis. Thus, it is understandable that a search for more easily workable and adaptable methods has been initiated long ago. But so far no new method has been successful in eliminating the time-honored and firmly entrenched procedures.

There is, however, a method at hand which, after appropriate modification, may prove to be a formidable contender to the permanganate procedures; chlorides as well as many other compounds, especially organic ones, can be present that would be intolerable with the classical methods, and no heating is required for low manganese contents.

## CHAPTER II

## INVESTIGATION OF EARLIER PROCEDURES

The method for the determination of manganese described in this thesis is based on the work of Bruno (2), who used the reaction of manganese with triethanolamine as first described by Jaffe (3) in 1932. The latter author found that under certain conditions a distinctive emerald green color develops when manganese and triethanolamine are mixed. He attributed the color to the formation of a manganese-triethanolamine (Mn-TEA) complex and suggested it as a test for manganese. In 1951 Jaffe (4) reported on additional investigations, establishing the optimum conditions for and analytical sensitivity of the reaction. He found that pure triethanolamine and a 20% solution of potassium hydroxide initially produce not more than a slightly greenish color when added to a 1% manganese solution. The deep green color develops only when the mixture is agitated for about a minute. He also found that neither the presence of some organic acids nor ferrous or ferric salts impeded the reaction. He reports the limit of detection as  $1.6 \times 10^{-5}$  g of manganese, but does not state the concentration.

Bruno (2) in 1953 adapted Jaffe's (3,4) work for the quantitative determination of manganese. Although the exact nature of the Mn-TEA complex had not yet been elucidated, it was known that the reaction requires a pH above 11.5, and that the product possesses a color that is stable for several days and has an absorbance maximum at 625 nm.

Using the reagents and conditions recommended by Jaffe (4), Bruno found that the reaction proceeds stoichiometrically and that the Beer-Lambert law holds.

Bruno carried out his colorimetric analysis in the following manner. A reagent solution is prepared by mixing until homogeneous 70 ml of a 20% potassium hydroxide solution with 30 ml of pure triethanolamine. The acidic solution of  $Mn^{+2}$  is treated with the reagent solution, shaken for a few minutes to aerate, and then treated with 20% potassium hydroxide until pH 12 is reached. The solution thus obtained is shaken again, filtered if necessary, and brought to 100 ml with water. The absorbance is read at 625 nm.

Bruno found that the determination of manganese could be carried out in the presence of aluminum or iron if the interfering ions were below certain limits. Ions which did interfere with the determination were the following:  $Ni^{+2}$ ,  $Co^{+2}$ ,  $Cu^{+2}$ ,  $Mg^{+2}$ ,  $NH_4^+$ ,  $Cr^{+3}$ ,  $Cr_2O_4^{-2}$ ,  $CN^-$ ,  $SCN^-$ , citric ion, and tartaric ion.

In 1959 Nightingale (5) proposed a spectrophotometric determination of manganese using TEA that differs only slightly from that of Bruno. Several erroneous statements appear in the Nightingale paper. Initially, he claims that "Although the Mn(III)-TEA complex has been used for polarographic determinations of manganese, the complex has not been investigated previously for use in a spectrophotometric or colorimetric determination." Neither Bruno (2) nor Jaffe (4) are cited which is rather puzzling because one of Nightingale's polarographic references, Tettamanzi (6), clearly states that his work is based on Jaffe's (3) original investigation.

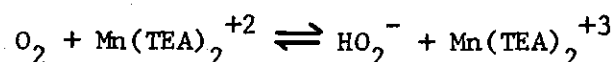
Portions of Nightingale's procedure, as well as some parts of his discussion are open to question. The procedure reads as follows:

Pipet an acid sample containing 0.02 to 0.2 mmole (0.001 to 0.01 gram) of manganese(II) into a 150-ml beaker. Evaporate, if necessary, to 25 ml and add 5 ml of triethanolamine. Add 10 ml of 9M sodium hydroxide and stir well to dissolve any manganese(II) hydroxide precipitated by a local excess of sodium hydroxide. If the sample contains more than 75 meg of acid, use additional sodium hydroxide. Add 1 ml of 0.1M potassium bromate, and heat the solution to boiling. Remove the sample from the hot plate, bubble air into the solution for 2 minutes, and cool to room temperature. Add 2 ml of 2M sodium sulfite. Transfer the solution to a 50-ml volumetric flask and dilute to volume. The final solution is 0.6M in TEA (80% solution) and approximately 0.6M in sodium hydroxide. Measure the absorbance at 438 m $\mu$  and determine the manganese concentration by comparison with standard samples.

Nightingale takes a sample of manganese (0.2 to 0.02 millimoles) in acid solution and adds 5 ml of 80% TEA (which is approximately 35 millimoles) and 10 ml of 9M sodium hydroxide (90 millimoles). If more than 75 milliequivalents of acid are present, he calls for additional base to be added, but there is no indication of the amount of base used. He says the final solution should be approximately 0.6M sodium hydroxide; but from the figures given, it may vary from 1.8 to 0.3M depending on the original acidity of the manganese solution. In comparison, Bruno also starts with an acidic sample solution; but he adds 5 ml of 30% TEA and then treats the solution with 20% potassium hydroxide until pH 12 is reached. In the present investigation it was found that the molarity of the hydroxide in the final solution is not critical.

Nightingale reports difficulties in achieving rapid, quantitative oxidation of manganese at room temperature; for this reason he recommends the addition of 1.0 ml of 0.1M potassium bromate and boiling the resulting solution. He postulates the formation of an unstable intermediate, a manganese(III)-peroxide complex which decomposes at elevated temperatures to form manganese(II) and liberated oxygen. The potassium bromate is added to supposedly hasten oxidation and prevent interference by the manganese(II)-peroxide complex. However, the bromate ion has no oxidizing power in Alkaline solutions as has been shown by other workers such as Prvbil (7). Air is bubbled through the solution for the same reason that potassium bromate is added, to hasten oxidation and make it quantitative. Sodium sulfite is added to remove any excess oxygen. However, this is not necessary as oxygen does not interfere. It would appear that Nightingale transferred the step directly from the procedures cited in his polarographic references (8,9,10,11) without understanding that free oxygen does interfere in the polarographic determination but has no effect in the spectrophotometric determination.

According to Nightingale, omission of the bromate and the sulfite is supposed to allow the formation of peroxides which lead to less precise results. He mentions that a manganese(II)-peroxide complex has not previously been reported in the literature. Yet, without any further explanation he states that the complex forms and bases his premise on the shape of the single spectral curve. For the formation of the Mn(III)-TEA complex he proposes the following equation:



which does not even balance. No explanation is offered for the formation of the peroxide ion and no definite proof is given for the existence of the Mn(II)-TEA complex. Jaffe (4) and Pirisi (12) examined the reaction mechanism for the formation of the green complex and simply state that the manganese(II) in alkaline conditions is oxidized to manganese(III) which complexes with two molecules of triethanolamine.

It should further be noted that Nightingale measures the absorbance of the colored species at the maximum which occurs at 438 nm. He never explains why he takes the readings there where the molar absorptivity is about 25% lower than at 625 nm, the wavelength used by both Bruno (2) and Jaffe (4). The present investigation proved the wavelength in the red region to be preferable.

It is difficult to deduce explanations for Nightingale's statements because of inconsistencies incorporated in the paper. For example, the two tables he gives do not agree in the absorbance data reported for solutions of 1 mM of manganese. In Table I the absorbance is given as 0.206, which according to our own measurements is correct; but in Table II the absorbance for a solution of the same concentration is twice as high, namely, 0.418. While many of the statements by Nightingale can be dismissed on grounds of conflicting with obvious chemical facts, it was still necessary to resolve the differences between the two existing papers on the application of TEA to the photometric determination of manganese.

## CHAPTER III

## PRELIMINARY EXPERIMENTS

The Nightingale (5) and Bruno (2) methods differ somewhat, and it was desirable to determine which, if any, of the modifications proposed by Nightingale are necessary. The four modifications to Bruno's procedure were tested individually. Nightingale's suggestions consisted of the following: (1) adding potassium bromate, (2) heating the sample to boiling, (3) bubbling oxygen through the sample for two minutes, and (4) adding sodium sulfite. All the solutions tested contained 100 ppm manganese, a concentration which is a factor of five greater than the minimum mentioned by Nightingale. Each modification was tested by making up a standard solution as specified by Nightingale and comparing it to a solution identical except for one modification deleted each time. All spectra in this portion were made using a Bausch and Lomb Spectronic 505.

The first test compares solutions with and without potassium bromate. The spectra were scanned from 400 nm to 700 nm. At 430 nm, where Nightingale measured absorbance, the solution containing no bromate has an absorbance approximately 8% higher than the solution with bromate. Thus the effect of the bromate is opposite to what Nightingale claims. At 650 nm, the curves differ by less than 0.01 absorbance units, indicating that the presence or absence of potassium bromate causes no significant difference in absorbance in the red region.

Next the second parameter, heating, was tested. The spectra differ throughout the scan by approximately 0.01 absorbance units. The absorbance of the heated solution is consistently 0.01 units greater than that of the unheated solution; however, this difference is within the limits of experimental uncertainty and is not considered significant.

The third variable tested is oxygenation. This time three solutions were made: one with air bubbled through it for two minutes, one shaken for one minute, and one merely made up and allowed to stand undisturbed. All three were then brought to volume, and the volumetric flasks inverted times to ensure thorough mixing. The spectra of the solution which was shaken and of that which was bubbled are essentially identical; the solution that was neither shaken nor bubbled has a markedly lower absorbance throughout the scan, approximately 38% lower at 438 nm and approximately 27% lower at 650 nm.

The fourth modification evaluated was the addition of sodium sulfite. At 438 nm the solution with sodium sulfite has an absorbance approximately 9% lower than the solution without it; at 650 nm there is no difference between the two solutions.

Finally two solutions, one made up with all the Nightingale (5) modifications and one made up according to the Bruno (2) procedure using none of the Nightingale modifications, were compared. At 438 nm the solution made using the modifications is approximately 9% lower than the solution made by the simpler method; at 650 nm there is again essentially no difference between the two.

Thus, it can be concluded that some of the Nightingale modifications investigated are not necessary and others are positively detrimental at the wavelength he employs. At 650 nm there is no

significant difference between the two methods. From these findings it was decided that further experimentation could be carried out using the Bruno procedure.

## CHAPTER IV

## LONG-PATH PHOTOMETRY

General

The basic philosophy of long-path photometry becomes clear from an inspection of the Lambert-Beer Law;  $A = \epsilon bc$ , where  $A$  is absorbance,  $\epsilon$  the absorptivity,  $b$  the pathlength of the cell, and  $c$  the concentration of the solution measured. In order to obtain good analytical results it is desirable to have reasonably high values of  $A$ , but this is difficult to achieve when dealing with trace analysis. Developments in the field of electronics have made it possible to amplify the output signal; but this works only up to a certain point, because the noise is amplified as well as the signal. Since the signal to noise ratio (S/N) is the ultimately critical parameter, a limit to useful amplification is reached all too soon. If the signal can be increased without simultaneously increasing the noise to the same degree, some improvement is possible. Such a signal increase for a given system and sample preparation, that is, for a given  $\epsilon$  and  $c$ , must result from an increase in the pathlength  $b$ . The pathlength in simple photometers is fixed at approximately one cm; more elaborate instruments are capable of accommodating cells of three to five cm or, in exceptional cases, as much as ten cm. Even when the longer cells are available, their usefulness is conditional. Commonly the increase in the pathlength necessitates a larger volume of solution to fill the cell. This is no disadvantage when an adequate

amount of solution is at hand. In the analysis for minor constituents, and especially for traces, the sample preparation is conducted in such a way that the final solution is as close to the tolerable minimum volume as possible in order to keep the effective concentration high. Thus the problem is to increase the pathlength without simultaneously increasing the volume. This can be achieved with a microcell. The common "microcell" needs very little liquid to fill it, but the pathlength is in the order of millimeters or fractions thereof. What is needed is a true microcell, one that requires a small volume for filling but without cutting the pathlength, desirably even permitting the increase of it. Such cells impose at least three major problems. One is appropriate and reproducible alignment of the cell in the light-path. The second is the difficulty of getting enough light into and through the cell if the conventional arrangement is employed. The third problem is constructing the cell in such a way that filling and emptying are not hampered by dead space between entrance and exit tubes and the respective correctly shaped and polished cell windows. Over the years, experimentation with various designs and components (13,14) has finally led to an instrument that, with the presently available commercial components, gives optimum results while being simple to operate. It has many features that are not always found in more expensive machines, such as extreme electrical and physical stability, ruggedness, portability, and very low power requirements.

The advantages derive mainly from the application of a light emitting diode (LED) as light source and a photodiode or a phototransistor as detector. The size of the optoelectronic devices allows them

to be attached to the end of the cell, thus solving the alignment problems and eliminating a great deal of the light loss which would occur using the conventional optical arrangement. Depending on the cell diameter and the purpose intended, the cell windows may be glued onto the end of an appropriately bent tube; or, suitable optoelectronic components can be placed directly onto the end of the cell in lieu of windows.

It should be noted that as cells get longer and narrower, they become increasingly fragile. The problem has been ingeniously handled by Coulter (15) who casts the whole cell with the attached LED and photodetector in a plastic block from which only filling arms and wires extrude. The casting also allows a modular design. Only the cell body, for example, is placed in the plastic. Side arms, cell windows, and optoelectronic devices are units that can interchangeably be screwed onto the block.

At present the choice of wavelengths is limited because only LED's emitting in the red, yellow, and green regions are commercially available. However, the great interest in the device and the speedy development in the field of semiconductors give hope that soon LED's of other wavelengths or else other equally simple devices may fill the gap. Reports of microlasers have already been released.

#### Description of the Photometer

The long path photometer used in the present study is the result of the combined efforts of Barnes (13) and McKeithen (14). The cell module itself is extremely simple (Figure 1). The cell has an actual

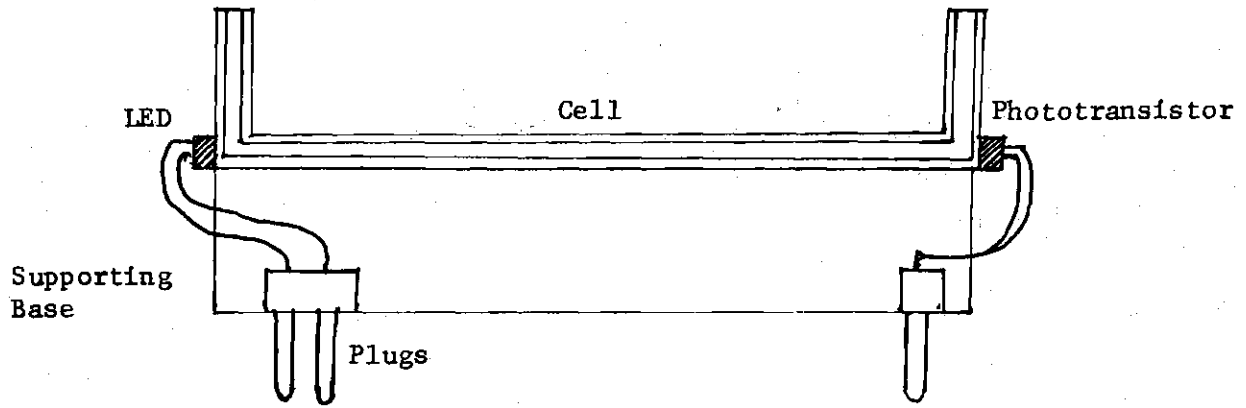


Figure 1. Cell Module

pathlength of 30 cm, an inner diameter of 4 cm, and requires only 4.2 ml of solution to fill it. It is made of 4 mm i.d. glass in the following way. Side arm inlet and exit ports of the same type tubing are fused to the cell body tube. The ends of the tube are cut off flush with the side arms, and the openings are sealed with a glass bead. The inner sides of the windows are flattened by blowing gently into the tube while the glass is still workable; the external surface of the windows are ground flat and polished. Since this cell is rather rugged, casting in plastic is not required. The cell is merely attached to a plexiglass strip to facilitate handling. The entire module is enclosed in a light-tight box.

The light source, a red LED (Monsanto 5054) with a wavelength of 650 nm and a bandwidth of 20 nm (16) is attached to one window of the sample cell using an optically clear cement. The LED is powered by two flashlight batteries which supply 3 volts. The circuit contains a fixed resistor to prevent burnout of the LED and a variable resistor to allow control of the intensity of emitted light (Figure 3).

The detector is a phototransistor (Fairchild FPT-136) glued to the other end of the cell. It, too, requires only a 3 volt power supply (Figure 4). An integrated circuit operational amplifier is included to boost the output from the phototransistor's 0.4 microamp maximum to the 250 microamps required for full scale deflection of the readout meter.

The meter is a simple moving coil panel meter (Assembly Products, Inc., Model 451), identical to that used in the Bausch and Lomb Spectronic 20 photometer; such a meter is rugged, portable, and

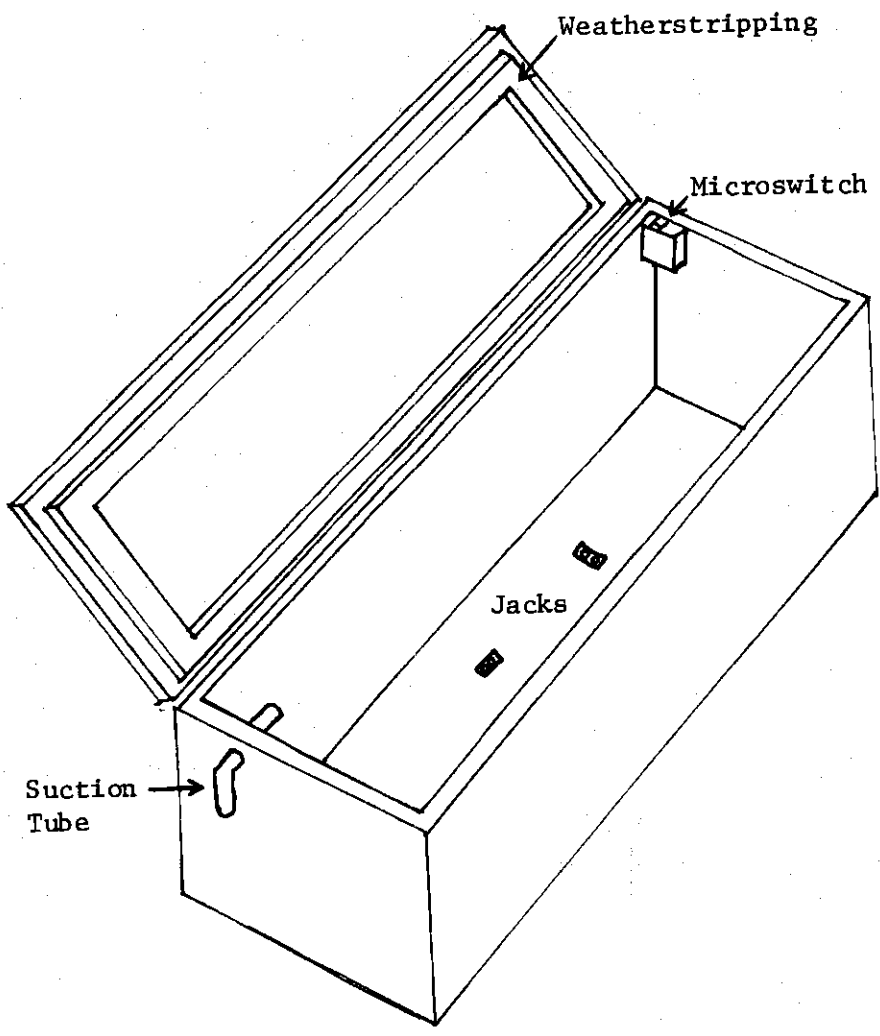


Figure 2. Cell Module Housing

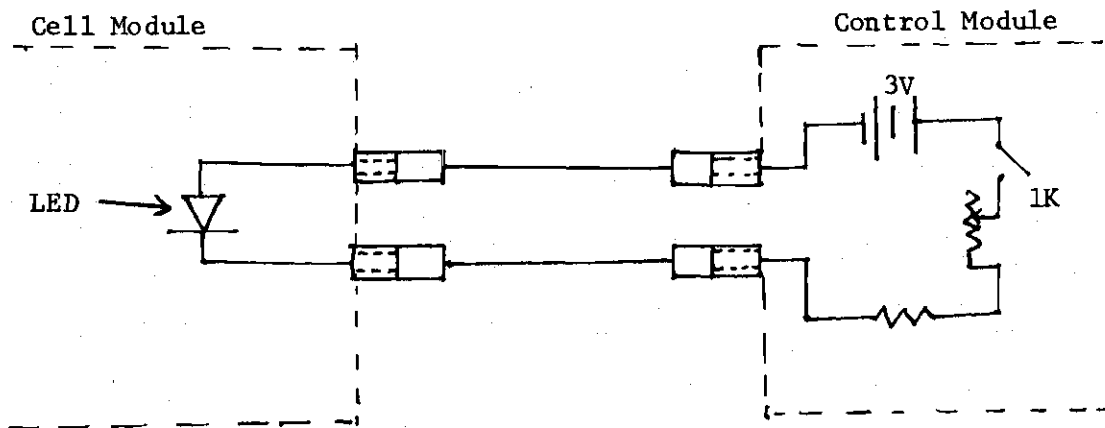


Figure 3. LED Circuit

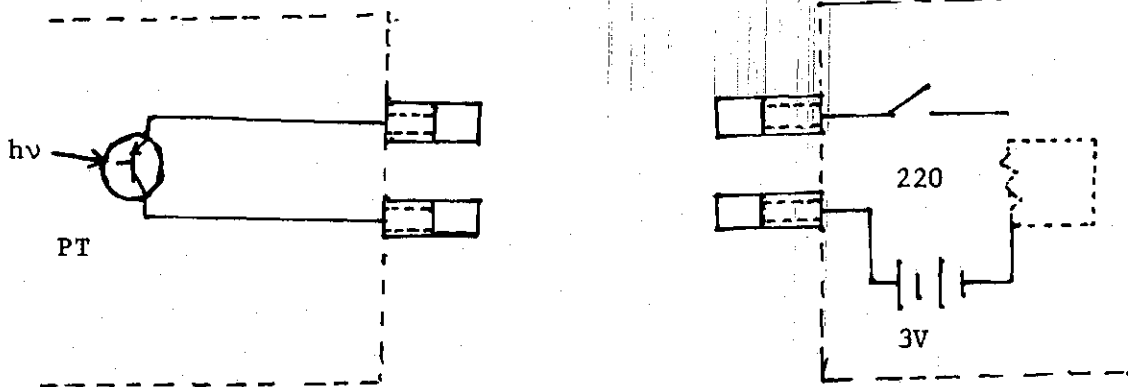


Figure 4. PT Circuit

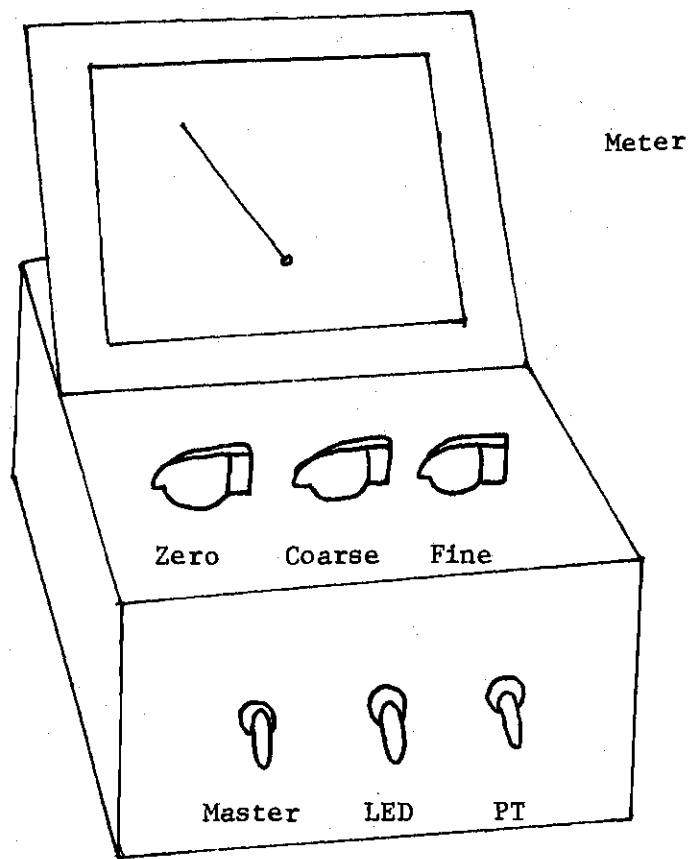


Figure 5. Control Module

inexpensive. The meter and all the circuitry are housed in a light weight aluminum box (3 1/2" x 6" x 8") (Figure 5). When portability and power supply are not important factors, a digital volt meter may replace the meter for more convenient readout.

## CHAPTER V

## PROCEDURE AND RESULTS

Experiments were carried out to test the suitability of the Bruno procedure for trace levels of manganese. The curve was read at 650 nm because an LED was not available at 625 nm. The difference in wavelength will not influence accuracy or precision, but it may have some bearing on Beer's Law, as well as the type and tolerance levels of interferences. Therefore, the investigation relates to something more than simply establishing the applicability of Bruno's method to a long-path photometric finish.

ExperimentalReagents and Solvents

J.T. Baker "Analyzed" metal salts were used throughout the work. The triethanolamine used was Fisher certified 99.8%. All acids, bases, and organic solvents were reagent grade. Distilled water, passed through a mixed bed deionizer column, was used exclusively.

Glassware

Common laboratory glassware, such as beakers and flasks, was employed as needed. Class A volumetric flasks were used without further calibration. Additionally, Class A Nalgene polypropylene volumetric flasks were employed in some phases of the work.

### Long-Path Photometer

The long-path photometer used is described in great detail in Chapter IV.

### Procedural Details

Manganese Standard Stock Solution, 10 mg/ml. Dissolve 9.0049 g  $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$  in 10 ml water and add 5 ml concentrated HCl. Make to the mark in a 250 ml volumetric flask. This solution contains 10.0 mg/ml manganese. Working solutions are prepared by appropriate dilution of the stock.

Sodium Hydroxide, 9 F. Dissolve 90 g NaOH in 250 ml water.

Triethanolamine. Use concentrated TEA directly from the bottle.

### Procedure

- 1) Place into a 50 ml volumetric flask a volume (up to 45 ml) of the sample preparation, chosen so that the final 50 ml contain between 0.01 and 2.0  $\mu\text{g/ml}$  manganese.
- 2) Add 0.5 ml TEA and 1 ml 9 F NaOH, stopper the flask, and shake for 1 minute. Make to the mark with water, stopper, and mix well.
- 3) Measure the absorbance of the solution at 650 nm against the reagent blank and read the result from the calibration curve.

### Calibration Curve

Carry exactly 1, 5, and 10 ml of the working standard solution containing 1  $\mu\text{g/ml}$  and 10 ml of working standard solution containing 10  $\mu\text{g/ml}$  manganese through the procedure and plot the absorbance versus the respective final concentrations of exactly 0.02, 0.1, 0.2, and 2.0  $\mu\text{g/ml}$  manganese.

## Results and Discussion

### Linearity

Bruno states that the curve is linear down to 2  $\mu\text{g/ml}$ . The present study found that the curve continues to be linear from the 2  $\mu\text{g/ml}$  described by Bruno down to 0.01  $\mu\text{g/ml}$ , the limit of detection. (See Figures 6 and 7).

### Accuracy and Precision

Accuracy and precision were determined using the data in Table 1, which includes solutions from 1.8  $\mu\text{g/ml}$  to 0.01  $\mu\text{g/ml}$ , that is, 90  $\mu\text{g}$  in the sample solution to 0.50  $\mu\text{g}$  in the sample solution. When subjecting the data to a linear regression analysis the line was found to have a degree of fit of 0.96, passing through the origin.

### Limit of Detection

The limit of detection was established in the same manner as the linearity of the curve. Figure 7 shows that the limit of detection under these conditions is 0.01  $\mu\text{g/ml}$  (10 ppb), the concentration below which no signal discernible from noise could be obtained. The 30 cm cell was the longest one used in the present study because of the limitations imposed by the size of the instrument. However, it appears that the limit of detection can be pushed even lower by using a longer cell. The limiting factor will probably be the radiant output from currently available commercial LED's.

### Interferences

Bruno (2), Jaffe (3), and Nightingale (5) conducted several interference studies which were confirmed by the present study. Several metals were found which do not interfere because they form a colorless

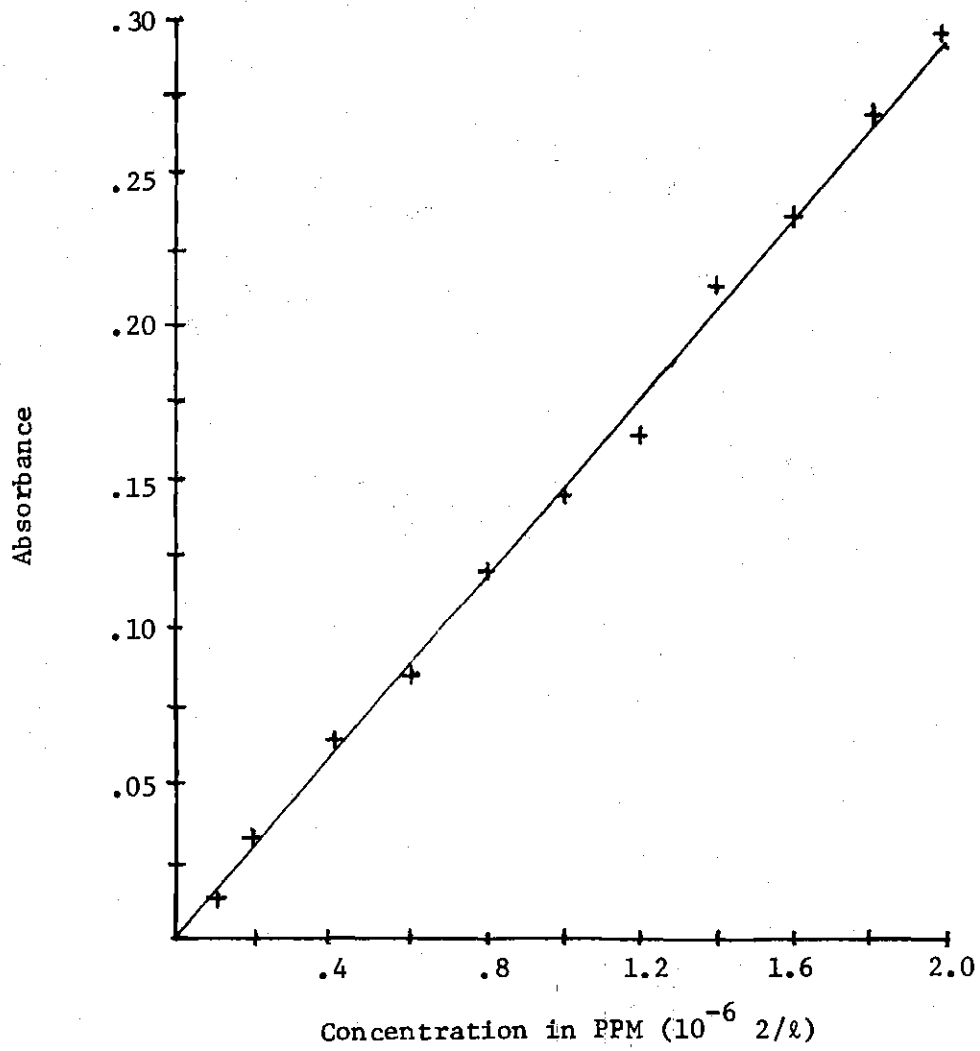


Figure 6. Linearity

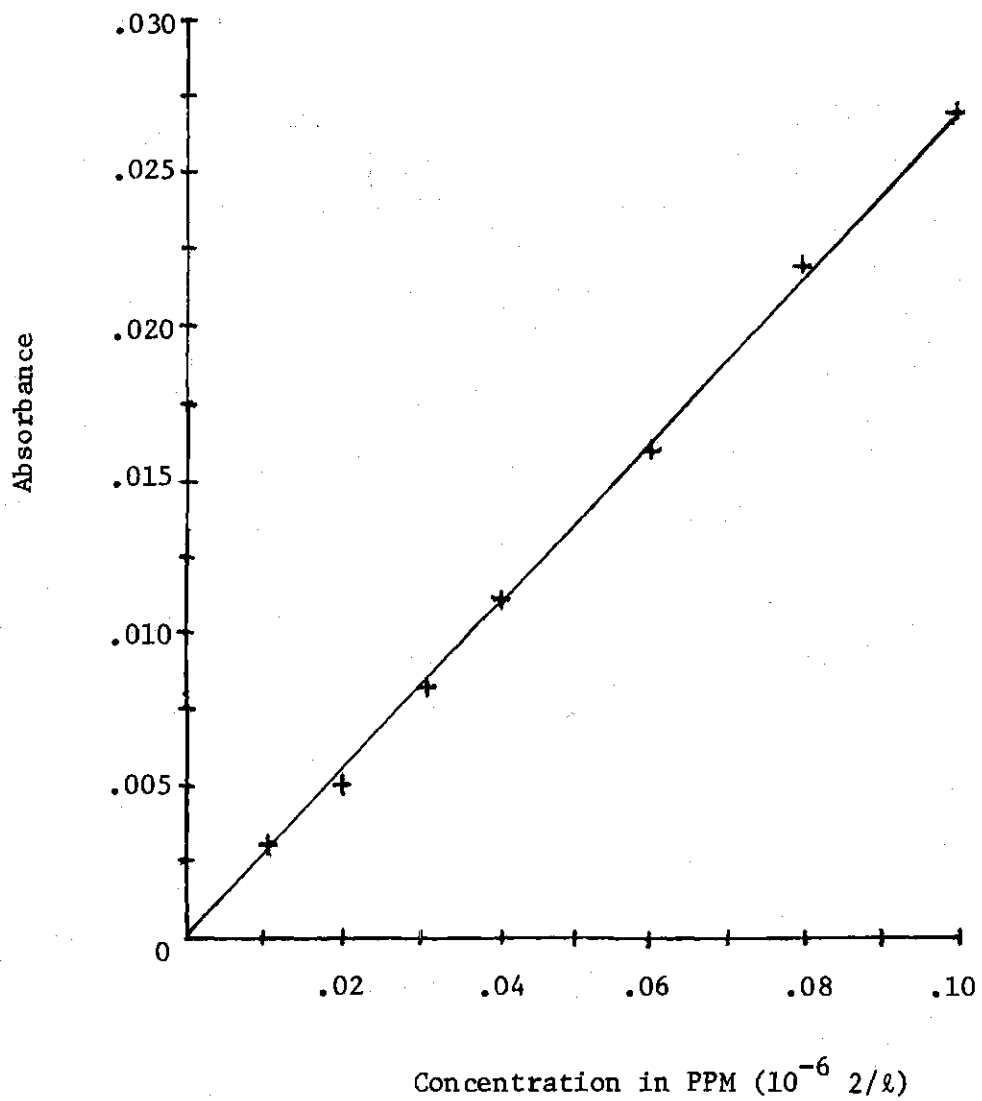


Figure 7. Limit of Detection

Table 1. Determination of Manganese with TEA

Taken	Found <sup>a</sup>	$\Delta$
90.0	92.2	+2.2
70.0	72.5	+2.5
50.0	47.2	-2.8
30.0	28.1	-1.9
10.0	10.50	+0.5
4.0	4.10	- .10
0.50	0.58	+ .08

<sup>a</sup>Average of 4 determinations.

solution in the presence of base and TEA. They are molybdenum(VI), tin(II), titanium(IV), tungsten(VI), zinc(II), and aluminum(III). Other metals do not form colored complexes, but do interfere by the formation of precipitates which must be removed by centrifugation or filtration. The procedure can then be carried out on the clear supernatant. These metals are antimony(III), bismuth(III), lead(II), mercury(I) and II, silver (I), and titanium(III).

Several ions exist which interfere because they complex or precipitate with manganese:  $\text{CN}^-$ ,  $\text{SCN}^-$ ,  $\text{PO}_4^{3-}$ , oxalic, citric, and tartaric ions.

Only a few metal ions form colored complexes and are the only ones which interfere significantly. They are copper(II), chromium(III), nickel(II), and cobalt(II). Iron(II) and (III) could cause problems if TEA is added before the base, but if one follows the procedure and makes the solution basic first, iron will precipitate and be filtered off.

An arbitrary tolerance limit was chosen and defined as the amount of interfering ion necessary to cause an error of 10% in the absorbance reading. Standard curves were established; then a series of solutions containing 1.0  $\mu\text{g}/\text{ml}$  Mn and various concentrations of interfering ions were prepared, the color developed, and the absorbances measured. The molar absorptivities of the TEA complexes, the concentration limits for each interfering metal ion, and the interference ratios are given in Table 2. The ratio is defined as  $C_{\text{M-TEA}}/C_{\text{Mn-TEA}}$  where the metal, M, causes the results to be high by 10%. Tolerable limits determined by Bruno are also listed. He, however, only states that certain concentrations of particular metals are unacceptable, without setting a percentage error.

Table 2. Comparison of Interference Data

Complex	$\epsilon$	Concentration Limit ( $\times 10^{-6}$ g/ml)	Molarity ( $\times 10^{-5}$ M)	$C_{M-TEA}/C_{Mn-TEA}$
Experimental Data				
Mn-TEA	250	1	1.82	1.0
Cu-TEA	62.5	0.5	0.78	0.43
Cr-TEA	40.0	6	11.5	6.3
Ni-TEA	12.5	0.5	0.85	0.47
Co-TEA	8.75	9	15.3	8.4
Bruno Data			( $\times 10^{-4}$ M)	
Mn-TEA		6	1.09	1.0
Cu-TEA		6	0.94	0.86
Cr-TEA		40	7.6	7.0
Ni-TEA		-	-	-
Co-TEA		50	8.4	7.7

The results for Cr(III)-TEA and Co(II)-TEA agree closely when molar ratios found in the two investigations are compared. However, the Bruno study indicates that twice as much Cu(II)-TEA can be tolerated than was found to be the case in this study. It is only fair to mention that copper does not pose a significant problem to Nightingale since the absorptivity of Cu(II)-TEA is negligible at 438 nm.

It is also interesting to note that nickel interferes almost as much as copper, yet the Cu(II)-TEA complex has a molar absorptivity five times as great as the Ni(II)-TEA complex. No truly adequate explanation readily presents itself for this peculiar phenomenon. Excess TEA was present in both solutions: there should have been little or no competition for complexing sites. Yet the two metals, which have different absorptivities when in solution with no other metals, behave almost identically in the presence of manganese.

## CHAPTER VI

## INVESTIGATION OF ADSORPTION PHENOMENA

Adsorption of the entities to be determined on the walls of vessels and apparatus takes place in many cases, and the loss of material thus incurred can readily lead to erroneous results when dealing with small amounts and concentrations as is the case in trace analysis. Examples can be cited from such diverse fields as metals analysis (17, 18), radiochemistry (19,20), clinical (21,22,23) and pharmaceutical chemistry (24).

When dealing with what may be termed "normal" concentrations as those involved in the studies by Bruno or Nightingale, the amount lost is negligible in comparison to the total amount present. But when operating at the lower levels involved in the present study the possibility of the losses becoming significant should not be overlooked. Therefore, an investigation into this matter was undertaken.

There have been several reasons suggested for the adsorptive properties of glass and plastic. Glass is a supercooled liquid and as such has distorted or broken bonds on its surface which enable the formation of linkages between the surface molecules and the ions in solution. Glass may also act as either an anionic or cationic exchanger. Plastics may degrade under the influence of heat, oxygen, or light to form carboxyl or carbonyl groups which provide active sites for adsorption. Plastics also contain catalysts and plasticizers which act in a similar manner.

There has been considerable study (20,25,26,27) devoted to the problem of preventing or minimizing adsorption onto the walls of storage vessels. Soft glass, borosilicate or Pyrex glass, "flint" glass, polyethylene, stainless steel, and other materials have all been investigated. The pH of the trace ion solution has been varied from very acidic to very alkaline, and various electrolytes have been added, all in order to retard the adsorptive process.

General conclusions are difficult to draw. West et al. (25) stored identical solutions in a series of borosilicate containers and found the adsorption to be highly erratic. In contrast the adsorption of ions from identical solutions onto the walls of polyethylene containers is much more uniform. Eichholz et al. (20) found borosilicate containers to be preferable to any others, but they were working with ions different from those used by West. The latter worker (25) also reports that the least amount of adsorption occurs between pH 4 and pH 8. Yet Rovivka (17) and others (20,27) state that only in acidic solutions is adsorption slowed. From the many studies in the literature and from the often conflicting data, it appears that the optimum combination of pH, electrolyte, and container material for minimal losses varies from ion to ion. Eichholz (20) believes that usually the combination of a low pH and borosilicate containers is best and most investigators agree on this as a general rule. Bahrgava (24), however, advocates the use of siliconized glassware. He claims the treatment to effectively block the active sites on the container walls from contact with the solution.

With regard to the present study the first point was to determine whether adsorption takes place during the time the sample solution is in the long-path cell, since the ratio of total surface area to volume is very large. The larger that ratio, the more pronounced one would expect adsorption to be. Fortunately, if one examines the relationship between surface area and volume the situation is not as bad as it seems. Neglecting the side arms, the surface,  $S$ , for the inner walls and the volume,  $V$ , are respectively given by

$$S = 2\pi r^2 + 2\pi r b$$

$$V = r^2 \pi b$$

where  $r$  is the radius and  $b$  is the length of the cell. Then the ratio,  $R$ , of surface area to volume is given by the following formula.

$$R = \frac{S}{V} = \frac{2 r(r+b)}{r^2 b} = \frac{2(r+b)}{rb}$$

In a long-path cell  $r$  is quite small in comparison to  $b$  and can be neglected in the numerator leading to the following approximation.

$$R \approx \frac{2b}{rb} \approx \frac{2}{r}$$

The ratio of total surface area to volume is inversely proportional to the cell radius and independent of the length of the cell. If one doubles the length of the cell one also doubles the volume and the ratio is unchanged.

In order to experimentally determine the true adsorption situation, a 30 cm cell and a solution containing 2.2  $\mu\text{g}/\text{ml}$  were used. Ordinarily, the cell can be flushed, filled with solution, and the absorbance read in less than a minute. This time the cell was filled, the sample allowed to stand in the cell, and the absorbance read at one minute intervals for ten minutes. For a solution with an absorbance around 0.340 the absorbance remained constant within  $\pm 0.002$  absorbance units, which is a normal and acceptable fluctuation. Thus, no adsorption at a detectable degree took place within the time period.

The second point was to determine whether significant loss of analyte occurs in the sample containers. Pyrex and Nalgene were chosen because they are the most commonly employed container materials. The test was carried out in the following manner. A 50 ml Pyrex and a 50 ml Nalgene volumetric flask were first thoroughly rinsed several times with concentrated nitric acid, then rinsed several times with distilled water. Both flasks were filled with 0.001 F Mn salt solution and allowed to stand. After the flasks containing the manganese solutions had equilibrated twenty-four hours each was emptied, the solutions were collected, the green color developed according to the procedure, and the absorbance measured. The absorbance of the solutions which had been allowed to stand were compared to the absorbance of a fresh solution of equal strength. There was no difference found beyond the usual uncertainty of the method. The empty containers were then washed with three portions of distilled water to remove any remaining solution

clinging to the walls. The walls of the vessels were leached with concentrated nitric acid, but no manganese could be found.

There is no noticeable adsorption at the 0.001 F level of manganese. This is not to say that adsorption does not take place. It is merely undetectable at the level at which the present study operates. It is, therefore, not possible to determine that either container material is superior in the present situation.

The entire process was repeated, substituting 0.001 F Mn-TEA for the Mn salt solution. The results are virtually identical to those for the  $MnCl_2$  solution. Whether the Mn-TEA complex is adsorbed as such, or as the manganese ion stemming from its decomposition cannot, of course, be deducted.

The final conclusion of the experiments described in this chapter are as follows. No significant adsorption takes place from the solutions within the period of time required for an analysis. Losses in containers can be avoided or minimized by applying normal, good analytical practice, namely, to prepare the dilute standard solutions as needed from more concentrated stock solution, and to process the samples as soon as they are drawn. When liquid samples or sample preparations low in manganese are to be stored for a prolonged time, however, problems with adsorption may arise.

## BIBLIOGRAPHY

1. H.H. Willard and L.H. Greathouse, J. Am. Chem. Soc., 39, 2366 (1917).
2. S. Bruno, Atti e Relazioni, 27, 409 (1953).
3. E. Jaffe, Ann. chim. appl., 22, 737 (1932).
4. E. Jaffe, Ann. chim. appl., 41, 397 (1951).
5. E.R. Nightingale, Anal. Chem., 31, 146 (1959).
6. A. Tettamanzi and B. Carli, Gazz. chim. ital., 63, 566 (1933).
7. R. Prvrbil, Collection Czechoslov. Chem. Comm., 19, 58 (1954).
8. I.M. Issa, R.M. Issa, J.F. Hewaidy and F.E. Omar, Anal. Chim. Acta, 17, 434 (1957).
9. J. Mojzic, Proc. Intern. Polarog. Congr. Prague, 1st Congr. 1951, Pt. I, p. 638.
10. J.V.A. Novak, J. Kuta and J. Riha, Chem. listy, 47, 649 (1953).
11. M. Pleva, Chem. listy, 49, 262 (1955).
12. R. Pirisi, Ann. chim., 44, 59 (1954).
13. H. Flaschka and R. Barnes, Microchem. J., 17, 588 (1972).
14. H. Flaschka, C. McKeithan and R. Barnes, Anal. Lett., 5, 585 (1973).
15. M. Coulter and H. Flaschka, Microchem. J., 21, 411 (1976).
16. Monsanto Corp., Catalog of Optoelectronic Products (1974).
17. J. Rovivka and J. Stary, Talanta, 8, 535 (1961).
18. D.E. Robertson, Anal. Chim. Acta, 42, 533 (1968).
19. F. Kepak, Chemical Reviews, 71, 357 (1971).
20. G. Eichholz, A. Nagel and R. Hughes, Anal. Chem., 37, 863 (1965).
21. R. Braman, D. Johnson, C. Foreback, J. Ammons and J. Bricker, Anal. Chem., 49, 621 (1977).

22. M. Andreae, Anal. Chem., 49, 820 (1977).
23. Y. Talmi and D. Bostick, J. Chromatogr. Sci., 13, 231 (1975).
24. H. Bhargava, J. Pharm. Sci., 66, 1044 (1977).
25. F. West, P. West and F. Iddings, Anal. Chem., 38, 1566 (1966).
26. A. Shendrikar and P. West, Anal. Chim. Acta, 72, 91 (1974).
27. P. Benes and I. Rajman, Collection Czechoslov. Chem. Comm., 34, 1360 (1969).