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CHLOROBENZENE AS A DIFFERENTIATING SOLVENT FOR THE OSCILLOMETRIC TITRATION OF WEAK ORGANIC BASES

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by

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THIS THESIS IS DEDICATED TO

MY WIFE, SAVITRI

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K. Jagan Mohan Rao.

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ABSTRACT

CHLOROBENZENE AS A DIFFERENTIATING SOLVENT FOR THE OSCILLOMETRIC TITRATION OF WEAK ORGANIC BASES

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An oscillometric method has been developed for the determination of a number of weak organic bases ranging in pK_b from 8.84 (p-toluidine) to 14.44 (2-fluoropyridine) using chlorobenzene as a solvent. Mixtures of these bases, having a pK_b difference (ΔpK_b) of from 4.24 to 0.24, have also been analyzed. In these differential titrations, two inflections corresponding to the two bases present in the mixture have been obtained. The breaks are sharp and both the equivalence points are easy to evaluate accurately. A method has also been developed for the titration of diprotic bases, where two inflections corresponding to the two basic groups were obtained.

The excellent differentiating properties of chlorobenzene as a solvent have been demonstrated and the importance of precipitate formation in oscillometric titrations has been pointed out.

Finally it is shown that oscillometry is an excellent analytical technique for the quantitative determination of weak bases and their mixtures using chlorobenzene as a solvent.

INTRODUCTION

For a number of years there has been great interest in the development of analytical methods which will permit the accurate quantitative analysis of weak organic acids and bases - a problem of considerable importance in organic, biological and pharmaceutical chemistry, both from the standpoint of its use in research and in industry.

A variety of results have been reported in the literature in this area which have utilized non-aqueous solvent systems and have employed the potentiometric technique to monitor the titrations carried out.

It is the purpose of this investigation to extend the applicability of this type of analysis, not only to include the determination of weak bases but also to permit the analysis of mixtures of such bases.

The approach to solving this type of problem must involve at least two aspects: 1) screening solvents to obtain one superior in its differentiating properties to those presently found useful, and 2) to investigate experimental techniques not subject to certain limitations inherent in the potentiometric method when used in non-aqueous solvents.

The matter of obtaining an appropriate aprotic solvent will be considered in the part of this thesis entitled "Statement of the Problem".

As an experimental technique it is proposed to explore the applicability of high frequency conductimetry or oscillometry in spite of negative statements appearing in the literature as to the probable success.[1,2]

STATEMENT OF THE PROBLEM

In recent years considerable use has been made of such organic solvents as glacial acetic acid, acetonitrile, and others as media for conducting acid-base titrations, especially for the determination of weak organic bases.[3,4,5] Using the solvents mentioned above, it is possible to follow the reactions and to find the equivalence points potentiometrically utilizing the glass electrode-reference electrode system.

At the present time increasing attention is being given to chemical investigations of acid-base behavior in organic solvents of comparatively inert character. Such solvents include aliphatic and aromatic hydrocarbons and halogenated hydrocarbons which have very low dielectric constants and are characterized by being almost devoid of acidic and basic properties.

Having only feeble acid-base properties these solvents do not interact strongly with acidic solutes such as carboxylic acids, phenols and mineral acids or with basic solutes such as amines and derivatives of guanidine or pyridine. Consequently, they are not "leveling" or "masking" solvents like water and low molecular weight alcohols, but instead are "differentiating" solvents.

In media of such low dielectric constants it becomes impractical to follow acid-base titrations potentiometrically for the electrical resistance of the solutions is so high that it would be necessary to place the glass electrode and the reference electrode as close together as possible which because of uncertainty in the distance of separation would lead to poor reproducibility of results, but of even greater

importance in solvents of such low dielectric constants the products of the reaction are likely to precipitate, thus fouling the electrodes and rendering the results unsatisfactory for quantitative results.

In an attempt to extend the titration technique to the determination of weak bases and to the analysis of mixtures of weak bases, it was decided to seek a satisfactory aprotic solvent for such work and an experimental technique other than the traditional potentiometric method which would give analytically acceptable results.

An examination of the literature suggested the possibility of using chlorobenzene as a solvent. Chlorobenzene has been used as a solvent in potentiometric titrations of single base[5] (aniline, pyridine, etc.) and from a consideration of its properties, it was decided to investigate its use as a differentiating solvent. Olah and coworkers[8] from their own and published data on the shifts of infrared fundamental H - X stretching frequencies concluded that the relative order of decreasing basicity of halobenzenes is as follows:

$$C_6H_6 \rangle\ C_6H_5I \rangle\ C_6H_5Br \rangle\ C_6H_5Cl \rangle\ C_6H_5F$$

Thus chlorobenzene should be the least basic of the four convenient solvents. In addition, chlorobenzene is available in pure form at a reasonable price. Its solvating power is higher than that of benzene. The dielectric constant of chlorobenzene is 5.708; consequently the conductance of its solutions would be very low. It was decided to investigate the properties of this solvent for acid-base titrations.

The other aspect of the problem would be to find a suitable method for monitoring such titrations for the potentiometric method could not be used. As a method, it was decided to investigate the possible use of oscillometric

titrations, for these are well known to be suitable for non-aqueous systems, since a given change in the intrinsic conductivity causes a greater change in the related quantity measured (the impedance), the lower the dielectric constant of the medium.

A REVIEW OF CERTAIN ASPECTS RELATING THE SYSTEMS AND EQUIPMENT UNDER CONSIDERATION

In this section will be presented the following topics: 1) a brief review of acid-base titrations in aprotic solvents, and 2) an introduction to oscillometry and its applications.

ACID-BASE TITRATIONS IN APROTIC SOLVENTS:[9] On the whole, there has been a strong inclination to use mixed solvents in non-aqueous titrimetry. It has been comparatively rare for a single non-aqueous solvent to be used for titrations, especially an aprotic solvent. However, titrations in completely aprotic solvents are entirely feasible when a proper combination of reactants is selected. A brief survey of such titrations in which various indicator dyes or physical measurements were used for end-point location is given below.

Titrations with Indicator Dyes in Aprotic Solvents. Bromophthalein magenta E, tamarack green base, and victoria blue B anhydro-base are examples of indicators intended especially for aprotic solvents. The latter two are bases. p-Naphtholbenzein, an acid weaker than bromophthalein magenta E, is sometimes useful in benzene.

Instrumental Procedure for Detecting End Points in Aprotic Solvents. Aliphatic amines have been titrated with picric acid, trichloroacetic acid, etc., using conductometric end point methods. Bryant and Wardrop[10] have studied the acid-base interactions in acetone and acetonitrile by both conductometric and dielectrometric methods. They conducted dielectrometric titration of triethylamine with trichloroacetic acid in benzene and also in dioxane. The dielectric constant increased gradually until the equivalence point,

then became essentially constant. Ishidate[11] and co-workers have recently explored analytical dielectrometric titrations in dioxane.

What are in effect photometric titrations have been performed frequently in spectrophotometric investigations intended mainly to determine acid-base stoichiometry and relative strengths in solvents like benzene.[12,13]

Forman and Hume[14] titrated bases with hydrogen bromide in acetonitrile using thermometric methods. Mead[15] also performed thermometric titrations of bases with trichloroacetic acid in benzene. Mead's principal objective was to determine enthalpy changes and to correlate them, if possible, with relative strengths of bases.

Gur'yanoua and Beskina[16] performed cryoscopic titrations of benzoic acid in benzene with amines like Am_3N, Et_3N, and piperidine as an adjunct to dielectrometric titrations in studying the association of benzoic acid with amines. More recently, Bruckenstein and Vanderborgh[17] have titrated bases in benzene with trifluoroacetic and trichloroacetic acids, using an experimental apparatus for recording continuously the change in the freezing point depression during a titration.

It is only recently that much attention has been given to the investigation of acid-base properties in completely aprotic solvents and even now there are no established methods for the determination of very weak bases in aprotic solvents of low dielectric constant like chlorobenzene.

OSCILLOMETRY AND ITS APPLICATIONS: In 1946 Jensen[41] and Blake[42] independently published conductometric titration curves made with electrodes that had no physical contact with the solution being titrated. This method of performing measurements at high frequencies with electrodes outside the

cell is called oscillometry. The uniqueness of this technique lies in the fact that a chemical system absorbs electromagnetic energy of radio-frequency through the walls of the containing vessel and stores it. The resulting energy transformation is reflected in the operation of the generator that produces the electromagnetic field and, if some electrical parameter of the generator is measured, it is found to be a function of the magnitude of the energy absorption and hence of the composition of the chemical system. The advantage of this type of measurement over conventional conductometric measurements is that as the electromagnetic energy is transmitted through the walls of the container, there is no physical contact between the chemical system and the electrodes, and electrode polarization and fouling are avoided. When electromagnetic energy is transmitted through a cell and chemical system used in oscillometry both a resistance and reactance component are always present. There is no practical instrument which measures only the resistance, or the reactance of the chemical system. In every case, the measured parameter is a rather complex function of the total impedance of the chemical system.

$$Z\ (\text{impedance}) = \sqrt{R^2(\text{resistance}) + X^2(\text{reactance})}$$

The measured value is not a linear function of the impedance, but reflects a disproportionate amount of either the resistance or the reactive component of the impedance. The fact that the measured value does not indicate the magnitude of any single property of the chemical system does not destroy its utility as an analytical tool. By means of suitable circuits, the measured value does become a nearly linear function of the composition of the chemical system (over a relatively narrow concentration range) and can be used advantageously

as the indicator in titrimetry.

There are two major types of oscillometers. One is the resistance type and the other, the reactance type. The resistance type instrument measures predominantly the resistance of the chemical system, while the reactance type measures predominantly the reactance of the chemical system. E. H. Sargent Company, Oscillometer Model V, which is used in this work, is a reactance type instrument and all titration curves for a reactance type oscillometer will be "V" shaped, because the capacity of the cell system increases with the increase in conductance and exhibits no maximum; however, the slope of the sides of the "V" will show considerable curvature if the titration is carried out in the region of maximum curvature of the instrument response curve, or the slope will be very flat if the titration is conducted at a point beyond the region of maximum curvature.

An excellent discussion of the principles of oscillometry is given by Burkhalter.[43]

Oscillometry has found wide applications in analytical chemistry. Numerous titrations of inorganic ions and organic compounds have been found to yield good end point detection by the oscillometric method, some of which do not lend themselves to accurate titration by other common electrometric or indicator procedures. Typical of these are the determination of thorium[18], fluoride[19], calcium, magnesium[20], and different metal ions with disodium EDTA.[21] It has been used in the studies of composition of complex compounds[22], in titrations involving chelation[23], and also in argentometric[24] and other precipitation titrations. It has also found use in the quantitative evaluation of paper chromatograms[25], in determining the induction period in gold-sol formation[26], in the measurement of dielectric constants[27],

in the analysis of water-benzene-methyl ethyl ketone system[28] and in the study of saponification rate of ethyl acetate.[29]

By far the largest number of applications have been in the determination of organic compounds. Wagner and Kauffman[3] and also Lippincott and Timnick[4] have studied the oscillometric determination of nitrogen containing bases. Mixtures of nitrogen containing bases have also been studied. The substances were dissolved in glacial acetic acid and a glacial acetic acid solution of perchloric acid was used as the titrant. Oscillometry has also been used for the titration of alkaloids[30], organic salts[31], phenols[32], acids[33] and amino-acids.[34] It has found wide application in pharmaceutical analysis.

EXPERIMENTAL WORK

REAGENTS

SOLVENT: Certified monochlorobenzene was obtained from Fisher Scientific Co., Cat. No. B-255; b.p. 131.4° - 131.9°C. This was used without further purification.

TITRANT: The titrant used was approximately 0.1 N perchloric acid in glacial acetic acid containing a little acetic-anhydride. All the work reported here has been performed using perchloric acid mixture "A" obtained from G. Frederick Smith Chemical Co., Columbus, Ohio, Item No. 71. This solution is approximately 0.1 N perchloric acid in glacial acetic acid with a little acetic-anhydride.

GLACIAL ACETIC ACID: Reagent grade from Fisher Scientific Co., Cat. No. A-38-C.

PERCHLORIC ACID: Baker analyzed; Cat. No. 9652. Perchloric acid assay 71.0% from J. T. Baker Chemical Co.

POTASSIUM HYDROGEN PHTHALATE: Fisher primary standard grade, Cat. No. P-243 from Fisher Scientific Co.

DRIERITE (Anhydrous $CaSO_4$): Size 8 mesh, from W. H. Hammond Drierite Co., Xenia, Ohio.

WEAK ORGANIC BASES: Unless otherwise specified all were used as obtained from the manufacturer without any further purification.

p-Toluidine: Eastman Organic Chemicals, Cat. No. 254.

Aniline: Fisher Certified, Cat. No. A-740 from Fisher Scientific Co.

o-Toluidine: K & K Laboratories Inc., Cat. No. 18668.

6-Nitroquinoline: Aldrich Chemical Co., Inc., Cat. No. N2400. This was twice recrystallized from "hot" ethanol.

Pyrazole: Aldrich Chemical Co., Inc., Cat. No. P5660.

4-Nitroaniline: Aldrich Chemical Co., Inc., Cat. No. N985.

2-Nitroaniline: Technical grade of unknown origin. This was twice recrystallized from hot ethanol.

2-Fluoropyridine: K & K Laboratories Inc., Cat. No. 1891.

8-Hydroxyquinoline: Reagent grade obtained from G. Frederick Smith Chemical Co., Columbus, Ohio, Item No. 142.

Nicotine: K & K Laboratories Inc., Cat. No. 13741.

p-Aminobenzoic Acid: K & K Laboratories Inc., Cat. No. 1435.

Table 1[35]

pK_b Values of the Bases[a]

Name of the Compound	pK_{b1}	pK_{b2}
p-Toluidine	8.84	-
Aniline	9.31	-
o-Toluidine	9.48	-
6-Nitroquinoline	11.28	-
Pyrazole	11.52	-
4-Nitroaniline	12.96	-
2-Nitroanailine	14.24	-
2-Fluoropyridine	14.44	-
8-Hydroxyquinoline	4.09	8.89
p-Aminobenzoic Acid	9.13	11.50
Nicotine	6.0	10.90

[a]Aqueous values

EQUIPMENT

pH METER: Corning pH meter, Model 7, distributed by Fisher Scientific Co.

ELECTRODES: Combination Glass-Ag/AgCl electrodes, Sargent S-30070-10.

BURET: The buret used was obtained from Kontes Glass Co., Cat. No. K-351790 (class A). It is a 50 ml. Teflon stoppered buret to which an 8" long glass tip was attached.

STIRRER: For potentiometric titrations a magnetic stirrer was used. For oscillometric titrations a motor-driven, paddle-type stirrer was used.

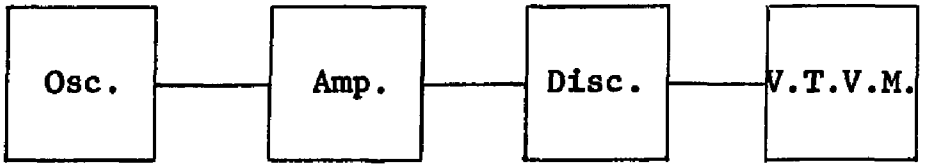
HUMIDITY INDICATOR: Air Guide Humidity Indicator, No. 605. The hygrometer was used to monitor the relative humidity in the room.

DEHUMIDIFIER: Signature Automatic Dehumidifier 25. It was run with the humidity control set at extra dry and the air flow meter set at constant high.

OSCILLOMETRIC CELL: Sargent & Co., No. S-29222. A 230 ml. capacity cell with female ground glass cover.

SARGENT MODEL V OSCILLOMETER: The circuit arrangements of a reactance type of oscillometer are rather more complex than those of resistance type. The mechanical lay out and design must be carefully planned to prevent the interaction of the tuned circuits; the stability and sensitivity of a soundly constructed instrument of this type exceed, however, those of other types of instruments. The E. H. Sargent and Co.

Oscillometer Model V, a well designed instrument of reactance type with excellent performance, was used in this work. It has a single oscillator, an amplifier stage, a frequency discriminator circuit, and a capacitor re-tune measuring device as shown in the block diagram below. The cell is connected



Block Diagram of Sargent Oscillometer Model V.

Osc. = Oscillator Disc. = Discriminator

Amp. = Amplifier V.T.V.M. = Vacuum tube volt meter

in parallel with the tank circuit of the oscillator, whose output is amplified and fed into the discriminator, which is permanently tuned to 5 MC/Sec. The discriminator is so designed that its voltage output is essentially zero when the oscillator frequency corresponds exactly to that of the tuned discriminator. The voltage output of the discriminator is directionally sensitive and rises sharply when the oscillator frequency deviates from the reference frequency of 5 MC/Sec. When the frequency of the oscillator is altered by changes in composition of the chemical system, the deviation is indicated by the vacuum tube volt meter, and the oscillator is returned to the reference frequency by means of a variable precision condenser in parallel with the cell; the number of scale divisions of capacitance necessary to re-tune the oscillator is used as the sensible indicator. The details of the circuit and the method of operation are well described in the instrument manual and need not be included here.

TEMPERATURE AND HUMIDITY CONTROL: Experience with the titrations demonstrated the importance of temperature and humidity control on the results obtainable. All the titrations were done in an "air conditioned" room maintained at constant temperature of within $\pm$ 1°C. The relative humidity in the room was monitored with an Air Guide Humidity Indicator. At one time during the titration of a mixture of pyrazole and 4-nitroaniline the relative humidity in the room was above 80%. The high humidity appeared to interfere with the titration and the breaks obtained in the titration curve were not sharp. It was difficult to locate the equivalence point. The second equivalence point could be located easily but uncertainty in the location of the first equivalence point made the whole titration useless. Although relative humidity up to 65% could be tolerated and had no appreciable effect on the titrations, it is important to keep the humidity in the room as low as possible. During the summer months of May, June and July the relative humidity in the room was very high, so a dehumidifier was used.

PROCEDURES

STANDARDIZATION OF PERCHLORIC ACID IN GLACIAL ACETIC ACID WITH POTASSIUM HYDROGEN PHTHALATE

Potassium hydrogen phthalate when dissolved in glacial acetic acid behaves as a base, so it is an excellent substance for standardizing perchloric acid in glacial acetic acid solution.

Primary standard grade potassium hydrogen phthalate was dried at 110°C for two hours and then stored in a desiccator over "Drierite". About 0.5 gm. of the potassium hydrogen phthalate was accurately weighed into a beaker type cell of 200 ml. capacity. After about 100 ml. of glacial acetic acid was added, the solution was stirred by means of a magnetic stirrer. The cell was covered with a rubber stopper having two holes. A glass-Ag/AgCl combination electrode (which was soaked in glacial acetic acid for about two hours) was then inserted through one of the holes and the buret tip through the other. The pH meter was switched to the millivolt scale and the potential recorded. Perchloric acid in glacial acetic acid was then added from the buret in small increments to the cell, and the change in potential was recorded after each addition. A "large" change in potential was obtained at the equivalence point. The potential in millivolts was plotted against the volume of the perchloric acid added and the equivalence point volume read from the graph from which the normality of the perchloric acid solution was calculated.

GENERAL PROCEDURE FOR THE DETERMINATION OF WEAK BASES

All the bases were stored in a desiccator which contained Drierite as the desiccant.

About two milliequivalents of the base were weighed accurately into a dry oscillometric cell and covered with the ground glass lid. To this was added about 100 ml. of chlorobenzene. This was enough to bring the upper level of the chlorobenzene solution more than 1 cm. above the electrodes. (It is necessary to fill the cell 1 cm. above the electrodes to include all the fringing capacitances in the total capacitance value so that any change in volume alone will not change the capacitance value).

The cell was kept in the cell holder and then fitted with a polyethylene cover with two holes, one for the buret tip and one for the stirrer. The stirrer and the buret tip were inserted into their respective holes. The stirring was started and the oscillometer was adjusted to read zero on the meter: i.e., brought to resonance by means of the variable precision capacitor. In about two minutes a steady reading was obtained. Then the initial reading of the oscillometer was recorded and 0.1 N perchloric acid in glacial acetic acid (standard titrant) was added in small increments (about 1 to 2 ml. at a time) from the buret. The perchloric acid reacts with the base forming a salt and consequently the composition of the chemical system changes. This brings about a change in the oscillator frequency; this deviation was indicated by the vacuum tube voltmeter. The oscillator was returned to the reference frequency by means of the variable precision capacitor in parallel with the cell; the number of scale divisions of capacitance necessary to retune the oscillator after each addition of the titrant was recorded. These values

were then plotted against the volume of the titrant added. A sharp break was obtained at the equivalence point. The titration was continued well beyond the equivalence point to obtain the final portion of the curve. The time to attain equilibrium after each addition of the titrant and the sharpness of the break at the equivalence point depended upon the nature and strength of the base being titrated. This will be considered in more detail in the discussion.

GENERAL PROCEDURE FOR THE DETERMINATION OF MIXTURE OF BASES

About 1.5 milliequivalents of each of the two selected bases were weighed accurately into the dry oscillometric cell and approximately 100 ml. of chlorobenzene were added to it. (General procedure was the same as when a single base was titrated). The stronger of the two bases present in the solution reacted with the added perchloric acid first to form a salt. When all of the stronger base had been titrated, the weaker base reacted with any further additions of perchloric acid. The titration was continued well beyond the weaker base equivalence point to obtain the final portion of the curve. The scale divisions of capacitance change were plotted against the volume of the titrant added. Two breaks, corresponding to the equivalence point volumes of the two bases present, were obtained in the titration curve. Once again the shape and sharpness of the breaks depended upon the nature and strength of the two bases present. This will also be considered in more detail under discussion.

GENERAL PROCEDURE FOR THE TITRATION OF DIPROTIC SUBSTANCES

The procedure for the titration of diprotic substances was the same as given for monobasic substances. The only difference was that the titration in the case of a monobasic

substance was stopped when a few milliliters of the titrant were added beyond the stoichiometric equivalence point, whereas in the case of dibasic substances, it was continued until more than twice the stoichiometric amount of the titrant was added. As in the case of a monobasic substance, the scale divisions of capacitance were plotted against the volume of the titrant added. A curve with two breaks (only one break corresponding to the second pK_b in the case of nicotine) were obtained.

RESULTS AND DISCUSSION

A curve showing the instrument response on the addition of perchloric acid in glacial acetic acid to chlorobenzene is shown in Figure 1 and Table 17 in the appendix shows the data.

Carbon tetrachloride and fluorobenzene were also tried as solvents. Many of the bases selected for analysis were not soluble in carbon tetrachloride. Fluorobenzene is very expensive and seemed to offer no particular advantage over chlorobenzene. So it was decided to do all the work using chlorobenzene as solvent.

Sargent Oscillometer, Model V, is a reactance type oscillometer; therefore, as it was pointed out earlier, all titration curves should be "V" shaped. However, because the capacity of the cell system increases with increase in conductance and exhibits no maxima, the slope of the sides of "V" will show considerable curvature, if the titration is carried out in the region of maximum curvature, or the slopes will be very flat if the titration is conducted at a point beyond the region of maximum curvature. This fact should be kept in mind when considering the titration curves that follow.

p-TOLUIDINE

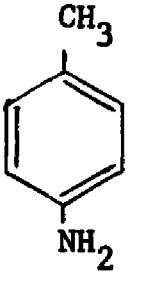
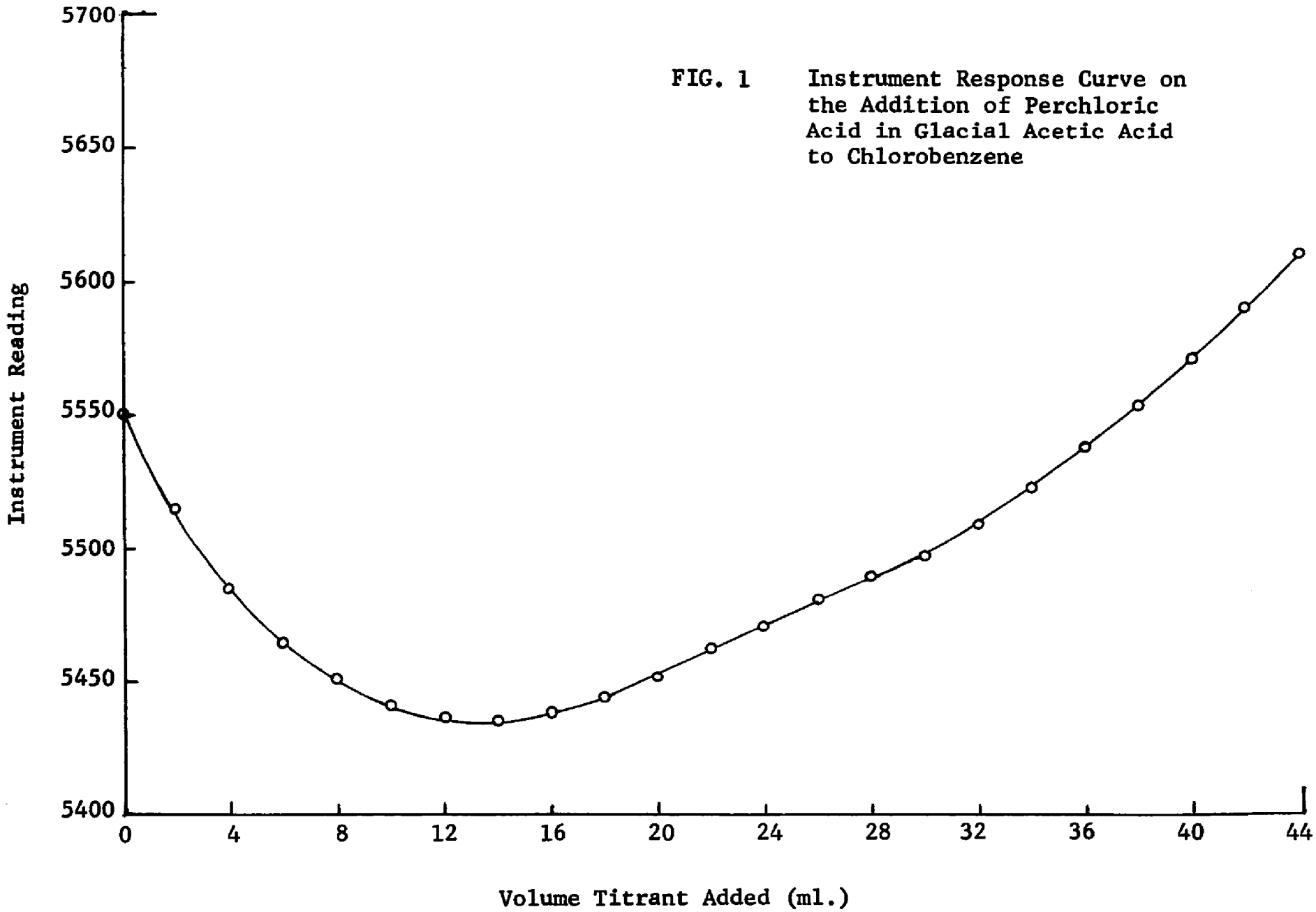


Figure 2 shows the titration curve of p-toluidine and Table 18 in the appendix shows the data. The equivalence

FIG. 1 Instrument Response Curve on the Addition of Perchloric Acid in Glacial Acetic Acid to Chlorobenzene



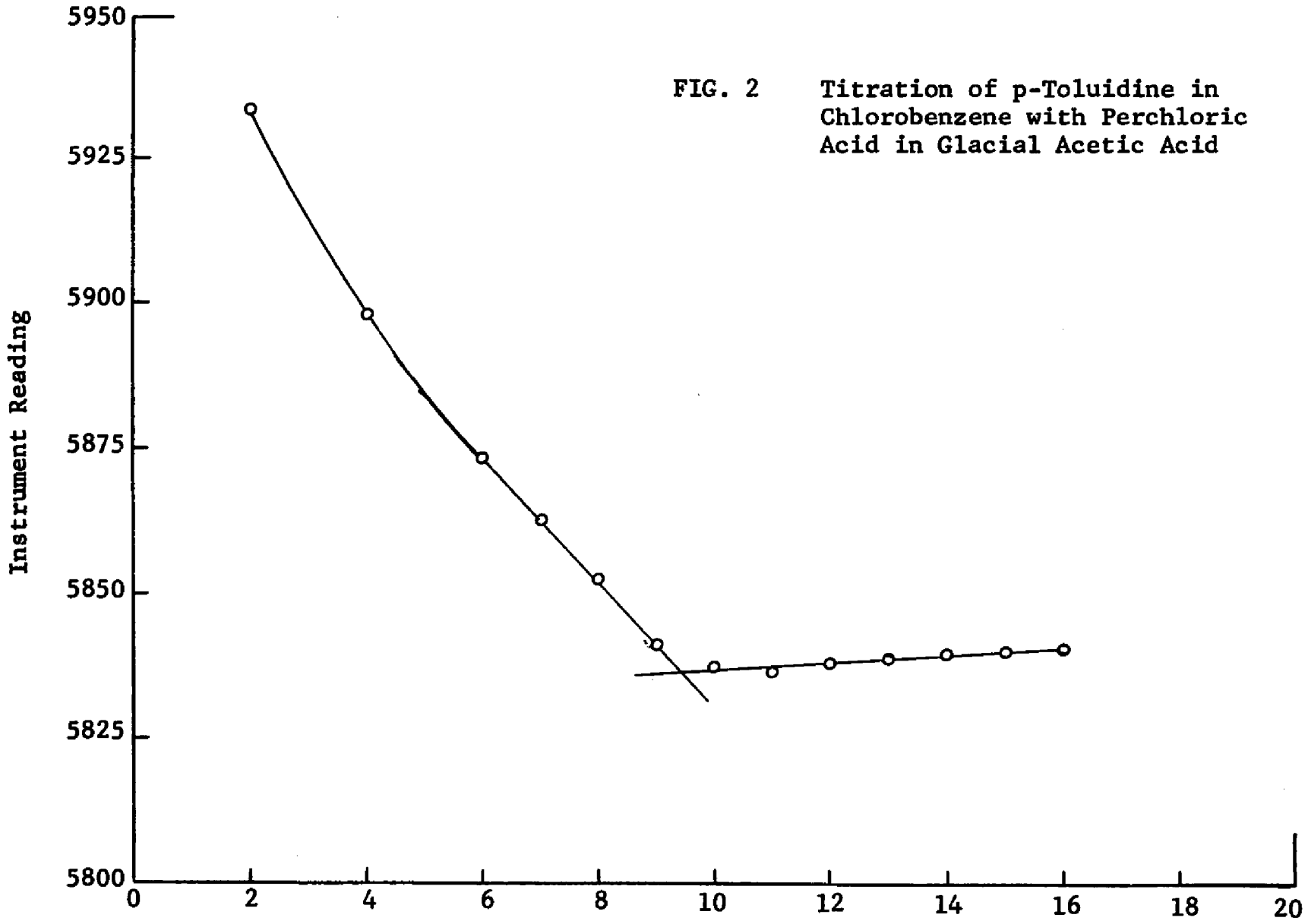


FIG. 2 Titration of p-Toluidine in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

point volume is 9.40 ml. and the shape of the titration curve obtained is " __ "; i.e., a deformed "V". Looking at the instrument response curve, this would be expected, for the equivalence point volume (9.40 ml.) falls on the fairly "flat" region of the response curve.

Figure 3 and Table 19 show another titration curve of p-toluidine. In this case the equivalence point volume is 21.27 ml. This falls on the steep portion of the instrument response curve, so a "V" shaped curve would be expected and such is the case. The shapes of the titration curves of all the weak bases titrated follow the same pattern. Depending upon where the equivalence point falls on the instrument response curve, the shape of the titration curve varies all the way from a deformed "V" (__) to a perfect "V".

Results of the quantitative determination of p-toluidine are given in Table 2. This was the strongest monoprotic base titrated. The reaction throughout the titration was fairly rapid; it took about 40 sec. to reach equilibrium after each addition of the titrant. The first 2 ml. of the titrant did not produce any precipitate (the solution was in a supersaturated state), but after about 3 ml. of the titrant had been added, a precipitate was obtained. As can be seen in the titration curve a discontinuity was obtained when precipitate formed. This change in the curve is due to the precipitation of the salt from the solution, which caused a decrease in the conductivity. As can be seen in the titration curves, the "breaks" are sharp.

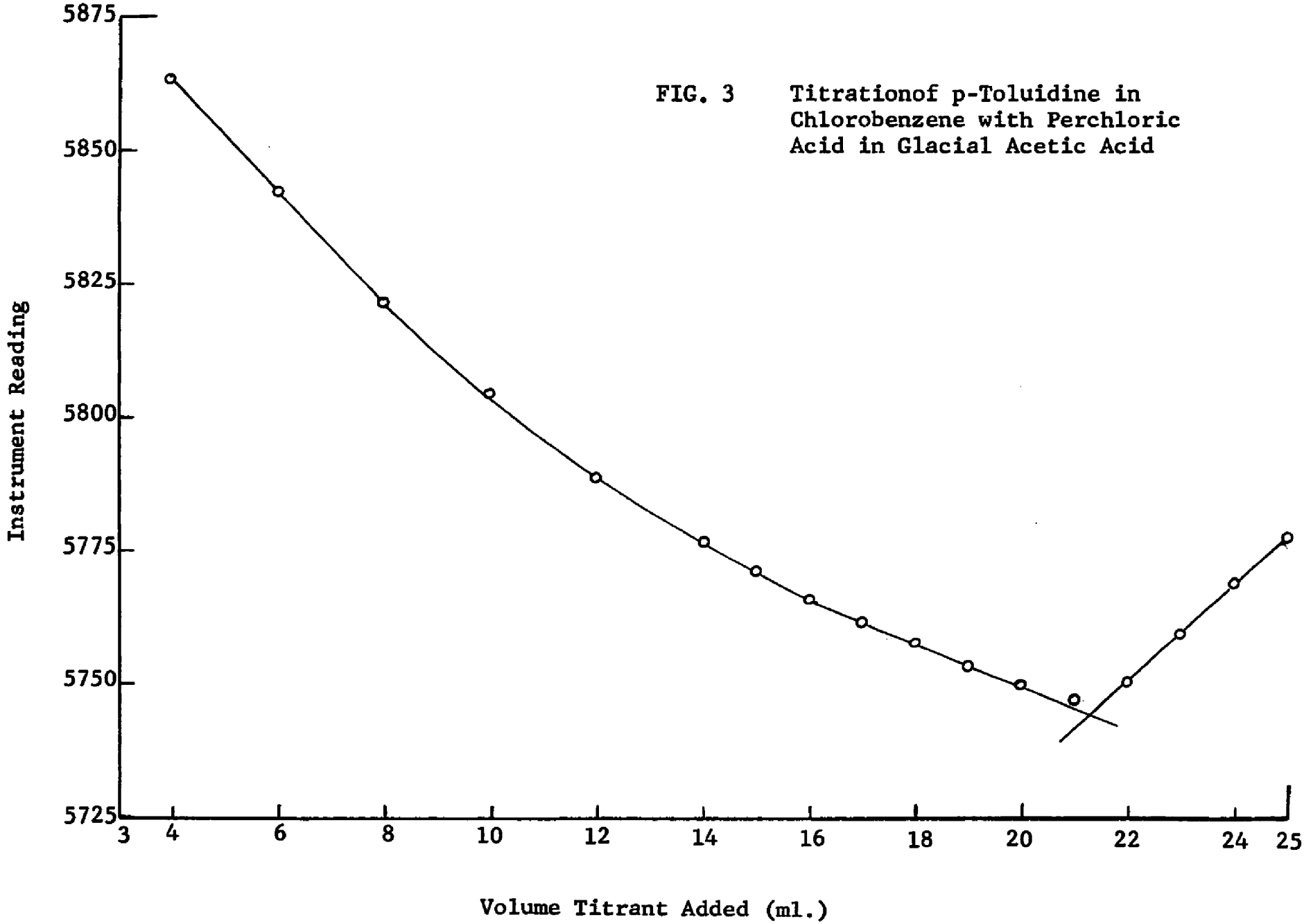


FIG. 3 Titrationof p-Toluidine in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Table 2

Determination of p-Toluidine

$pK_b = 8.84$

Sample	wt of the base taken	wt of the base found	Percent recovery
1.	0.1052 g.	0.1062 g.	100.9
2.	0.2032 g.	0.2045 g.	100.6
3.	0.2403 g.	0.2403 g.	100.0

Average percent recovery = 100.5

Percent standard deviation = 0.46

Table 3

Determination of Aniline

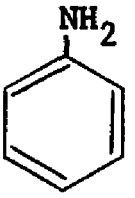
$pK_b = 9.31$

Sample	wt of the base taken	wt of the base found	Percent recovery
1.	0.1330 g.	0.1323 g.	99.5
2.	0.2716 g.	0.2714 g.	99.9
3.	0.2865 g.	0.2874 g.	100.3

Average percent recovery = 99.9

Percent standard deviation = 0.42

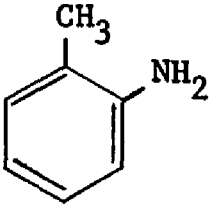
ANILINE



$pK_b = 9.31$

The titration curve of aniline is shown in Figure 4 and the data in Table 20. During the titration after each addition of the titrant 20 sec. was required to reach equilibrium. The shape of the titration curve follows the same pattern as described under p-toluidine. The "breaks" obtained at the equivalence point are sharp. The results are shown in Table 3.

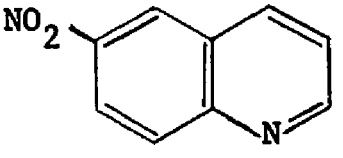
o-TOLUIDINE



$pK_b = 9.48$

The titration curve of o-toluidine, shown in Figure 5 and Table 21, follows the same general pattern of the other bases titrated and as usual the "breaks" are sharp. The results are shown in Table 4.

6-NITROQUINOLINE



$pK_b = 11.28$

The titration curve of 6-nitroquinoline is shown in Figure 6 and data in Table 22, and the results are given in Table 5. During the titration after each addition of the titrant, about 20 sec. was required to reach equilibrium. The salt precipitated after the addition of two milliliters of the titrant.

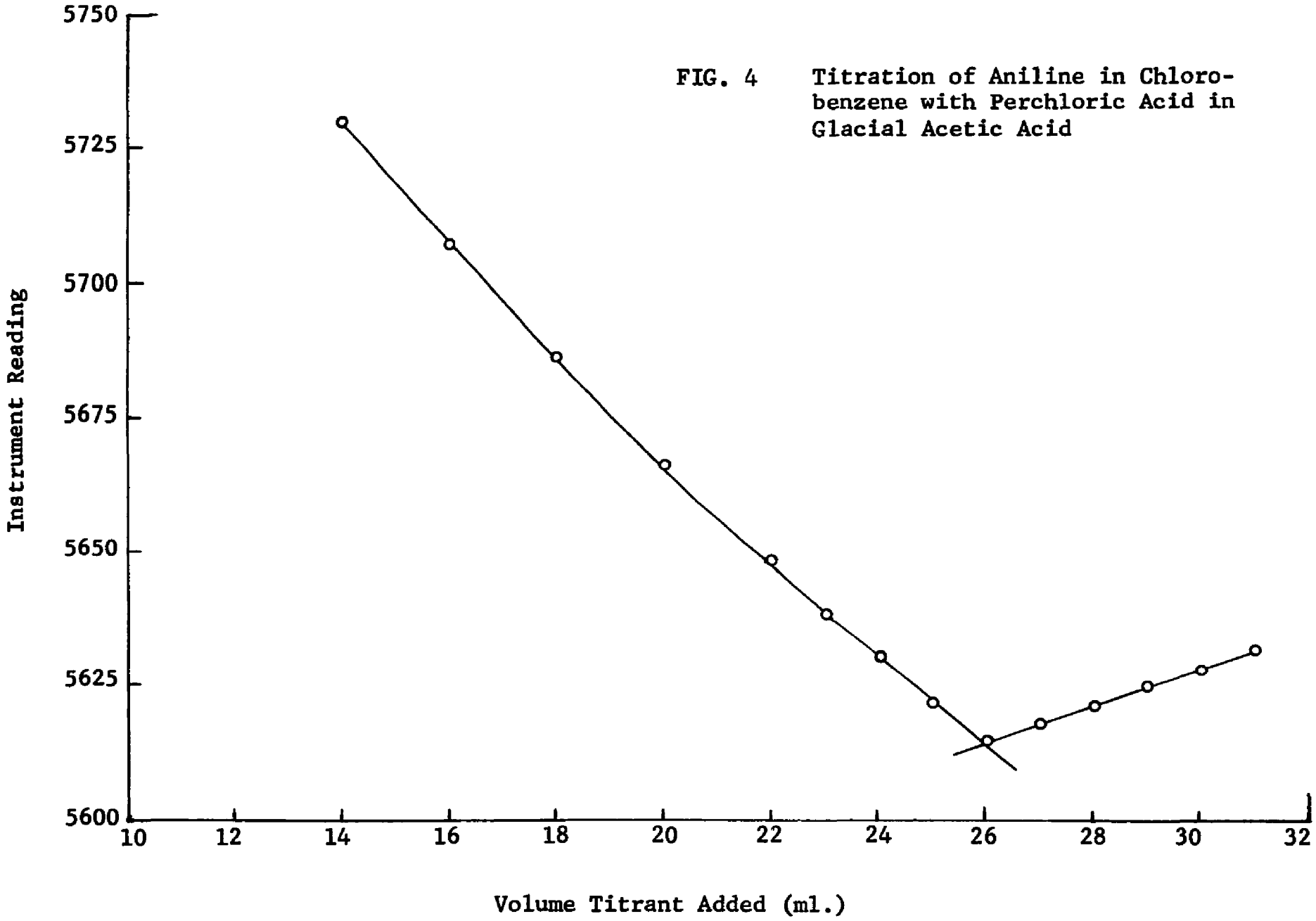


FIG. 4 Titration of Aniline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

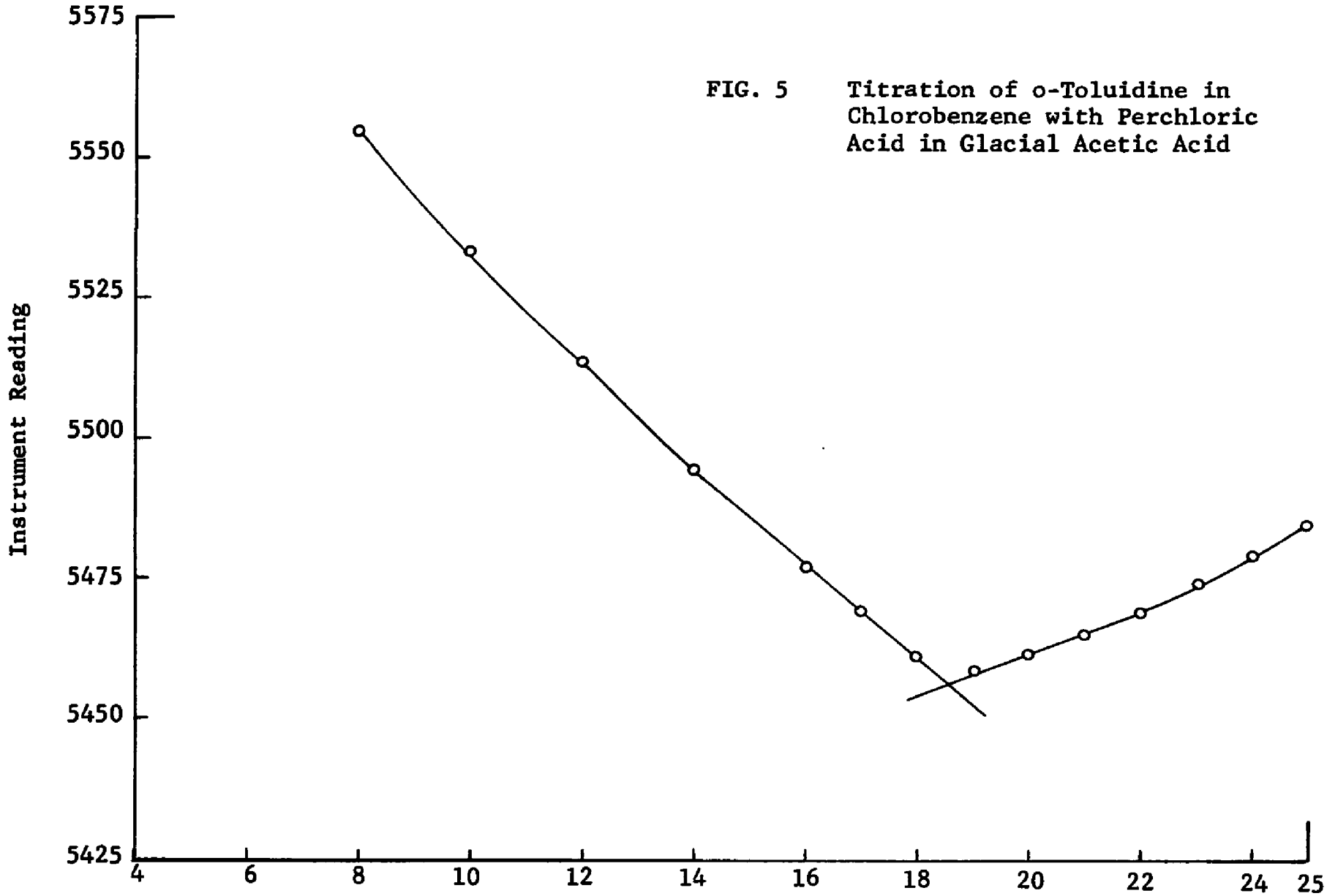


FIG. 5 Titration of o-Toluidine in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Table 4

Determination of o-Toluidine

$pK_b = 9.48$

Sample	wt of the base taken	wt of the base found	Percent recovery
1.	0.1376 g.	0.1359 g.	98.8
2.	0.2250 g.	0.2235 g.	99.3
3.	0.2849 g.	0.2846 g.	99.9

Average percent recovery = 99.3

Percent standard deviation = 0.55

Table 5

Determination of 6-Nitroquinoline

$pK_b = 11.28$

Sample	wt of the base taken	wt of the base found	Percent recovery
1.	0.3004 g.	0.3009 g.	100.2
2.	0.3426 g.	0.3444 g.	100.6
3.	0.3593 g.	0.3586 g.	99.8

Average percent recovery = 100.2

Percent standard deviation = 0.40

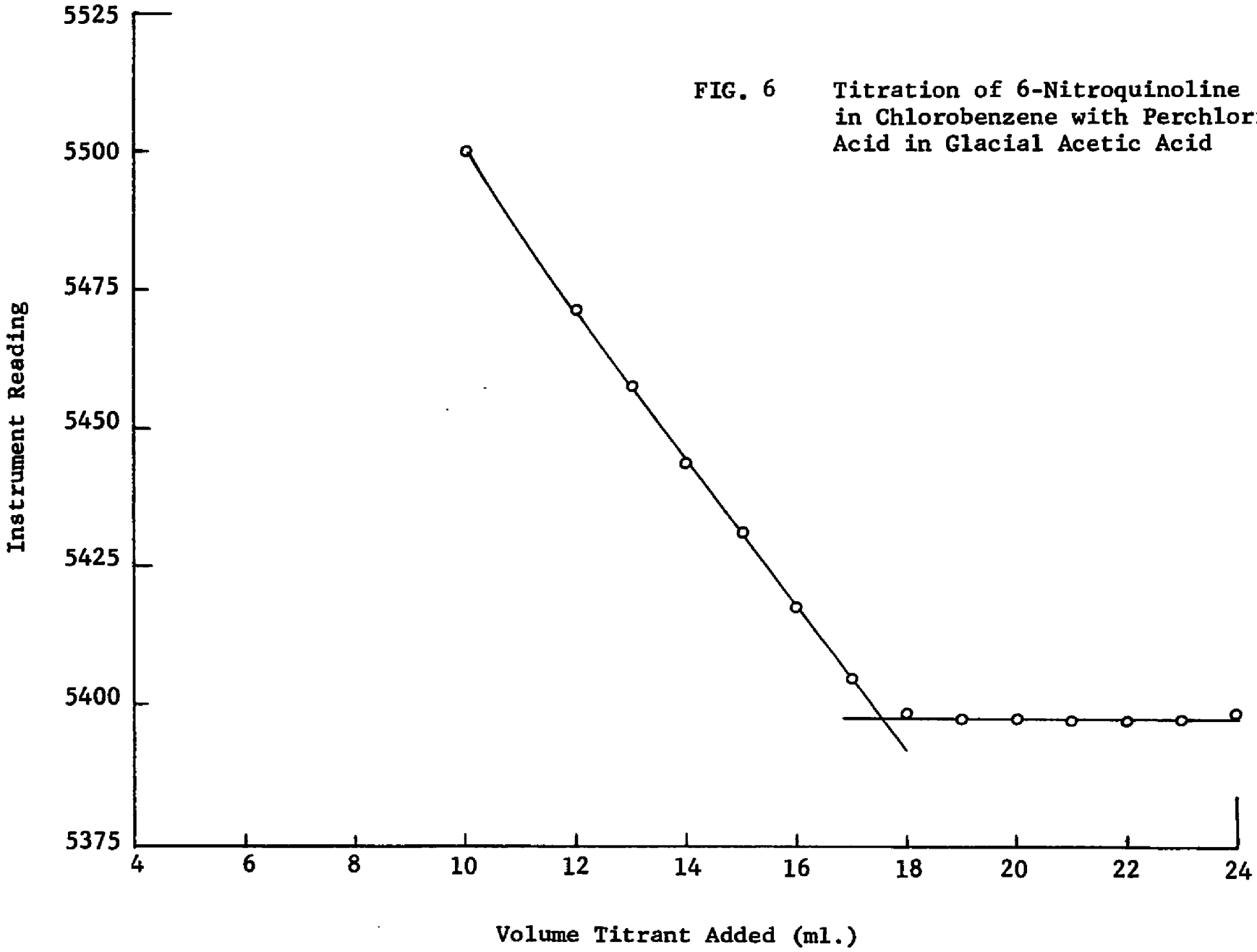
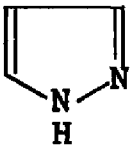


FIG. 6 Titration of 6-Nitroquinoline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

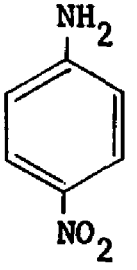
PYRAZOLE



$pK_b = 11.52$

Pyrazole is a weak base with a $pK_b = 11.52$. It was observed during the titrations that, as the bases became weaker, it usually took more time to reach equilibrium after each addition of the titrant. In the case of pyrazole it took about 1 1/2 minutes to reach equilibrium after each addition of the titrant. The titration curve is shown in Figure 7 and Table 23. As usual the "breaks" are sharp, and the equivalence point is easy to locate. The results are shown in Table 6.

4-NITROANILINE



$pK_b = 12.96$

4-Nitroaniline when dissolved in chlorobenzene gives a light yellow solution. On adding the first 2 ml. of the titrant, the yellow color of the solution intensified, but there was no precipitate formation. When about 4 ml. of the titrant was added, precipitation of the salt took place; it took about 45 sec. to reach equilibrium after each addition of the titrant. As the titration was continued further, the yellow color of the solution started fading away, and, at the same time, the amount of the precipitate increased. After the equivalence point, the solution became almost colorless with a "bulky" white precipitate floating around in it. (The same type of behavior was exhibited by 2-nitroaniline.) The titration curve is shown in Figure 8 and data in Table 24. The "breaks" are sharp, and the equivalence point once again is

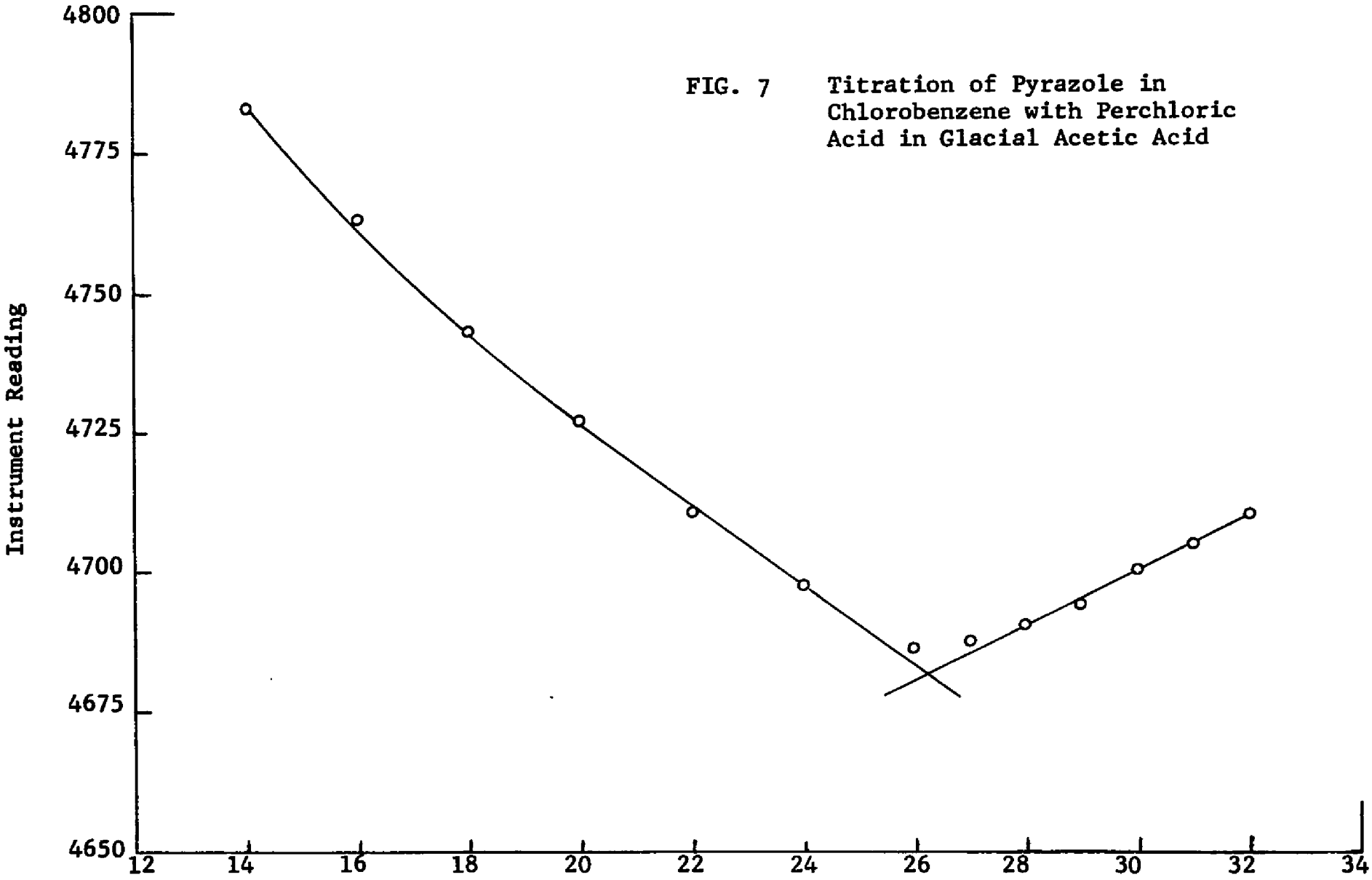


FIG. 7 Titration of Pyrazole in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Table 6

Determination of Pyrazole

pK_b = 11.52

Sample	wt of the base taken	wt of the base found	Percent recovery
1.	0.1641 g.	0.1644 g.	100.2
2.	0.1981 g.	0.1995 g.	100.7
3.	0.2201	0.2204 g.	100.1

Average percent recovery = 100.3

Percent standard deviation = 0.32

Table 7

Determination of 4-Nitroaniline

pK_b = 12.96

Sample	wt of the base taken	wt of the base found	Percent recovery
1.	0.2693 g.	0.2679 g.	99.5
2.	0.3124 g.	0.3113 g.	99.7
3.	0.4291 g.	0.4282 g.	99.8

Average percent recovery = 99.7

Percent standard deviation = 0.15

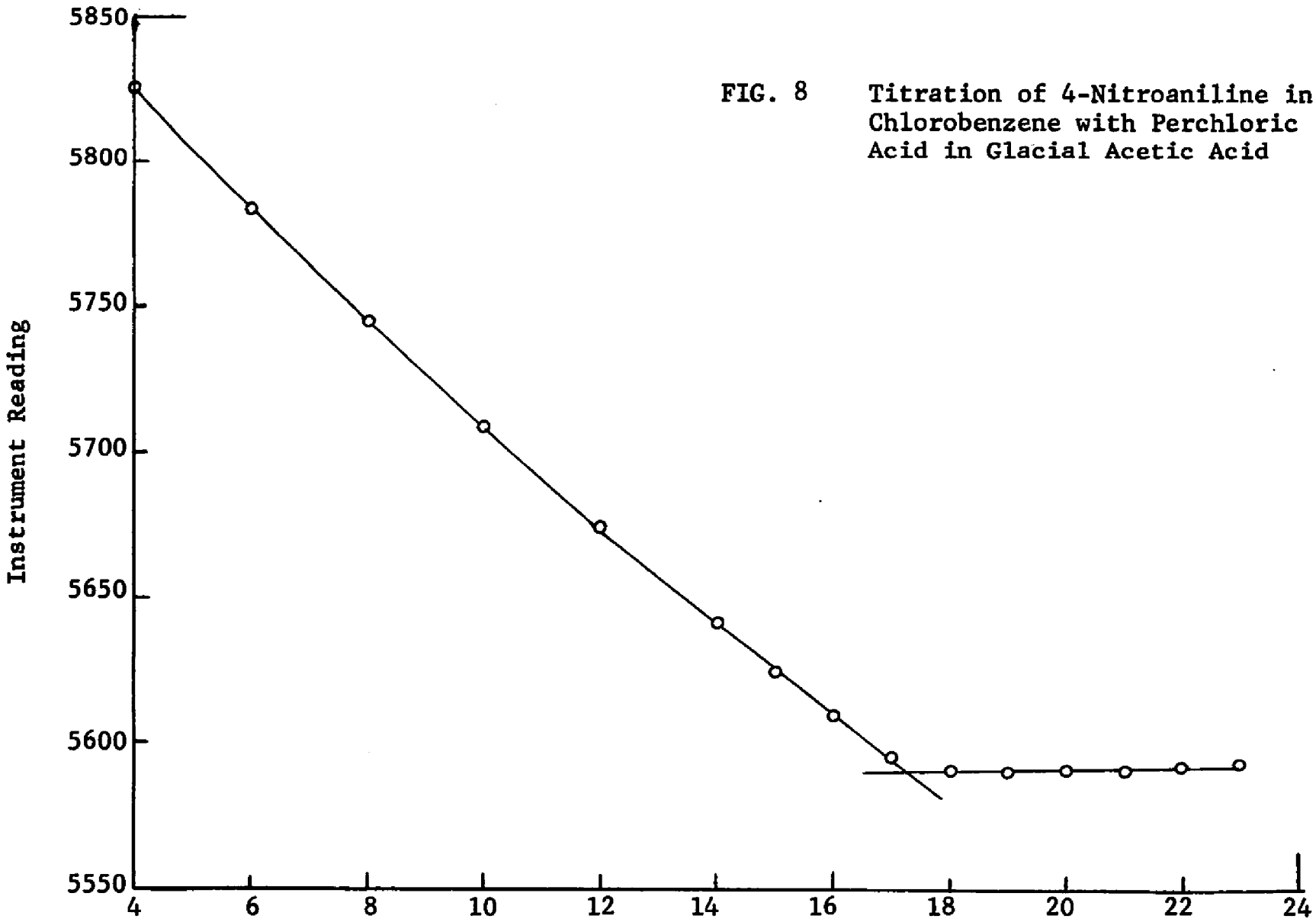
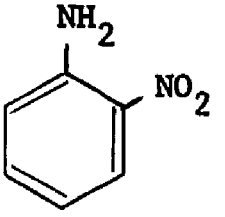


FIG. 8 Titration of 4-Nitroaniline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

easy to locate. The results are shown in Table 7.

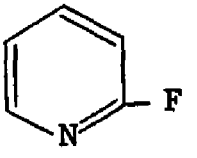
2-NITROANILINE



$pK_b = 14.24$

AND

2-FLUOROPYRIDINE



$pK_b = 14.44$

2-Nitroaniline and 2-fluoropyridine are very weak bases with $pK_{b's}$ of 14.24 and 14.44, respectively. In both cases the reaction was slow; it took about 2 min. to reach equilibrium after each addition of the titrant. In both cases a precipitate was obtained. The titration curves are shown in Figure 9 and Table 25 and in Figure 10 and Table 26. As can be seen in both cases there is curvature at the equivalence point. But this in no way interferes with "exact" location of the equivalence point. By extending the "straight" line portions of the curve near the equivalence point, the equivalence point, taken as the intersection of the two lines, can be located easily and accurately. The results are shown in Tables 8 and 9.

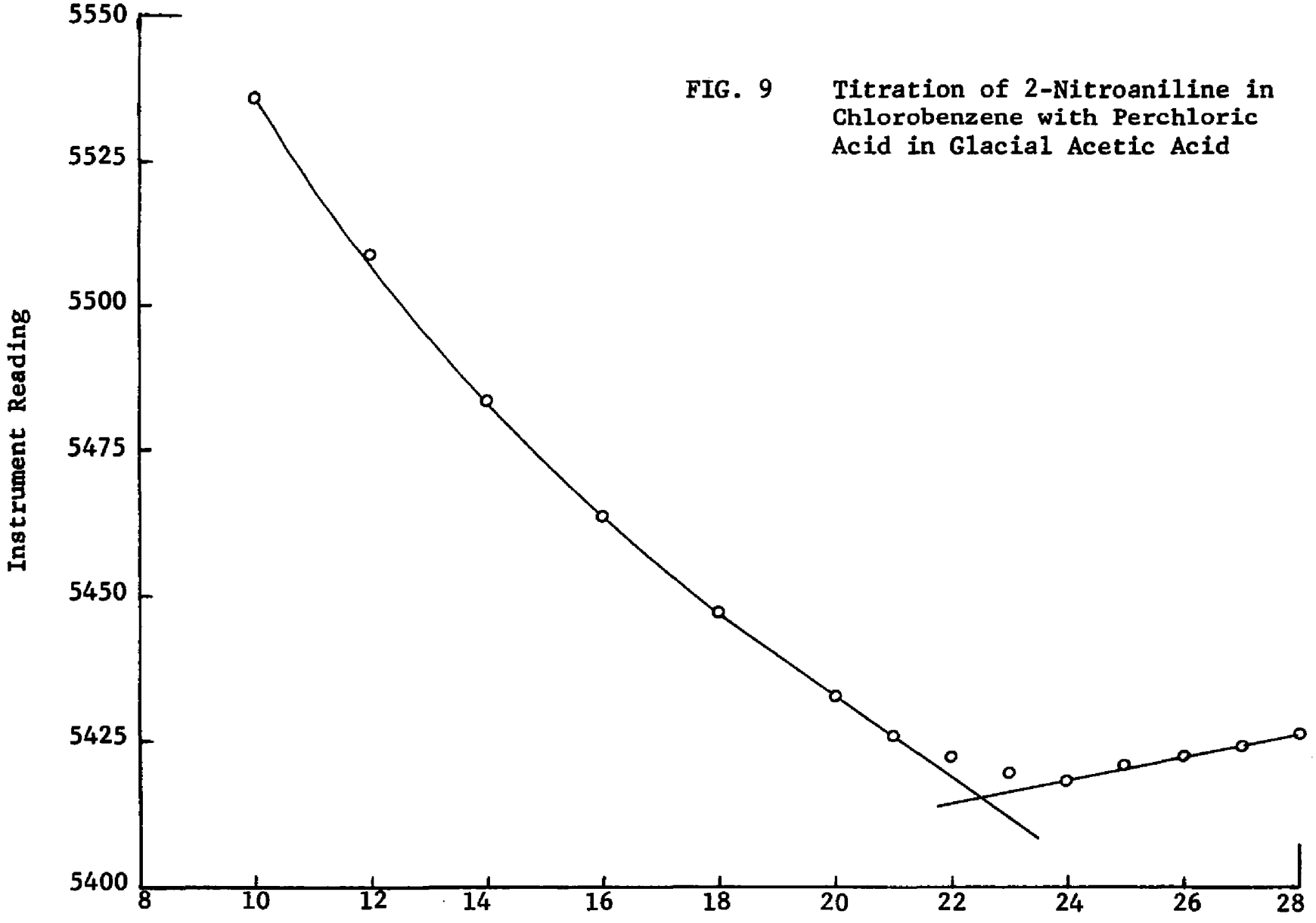


FIG. 9 Titration of 2-Nitroaniline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Table 8

Determination of 2-Nitroaniline

pK_b = 14.24

Sample	wt of the base taken	wt of the base found	Percent recovery
1.	0.2706 g.	0.2707 g.	100.0
2.	0.2960 g.	0.2948 g.	99.6
3.	0.3459 g.	0.3476 g.	100.5

Average percent recovery = 100.0

Percent standard deviation = 0.43

Table 9

Determination of 2-Fluoropyridine

pK_b = 14.44

Sample	wt of the base taken	wt of the base found	Percent recovery
1.	0.1874 g.	0.1881 g.	100.4
2.	0.2292 g.	0.2290 g.	100.0
3.	0.2485 g.	0.2491 g.	100.2

Average percent recovery = 100.2

Percent standard deviation = 0.26

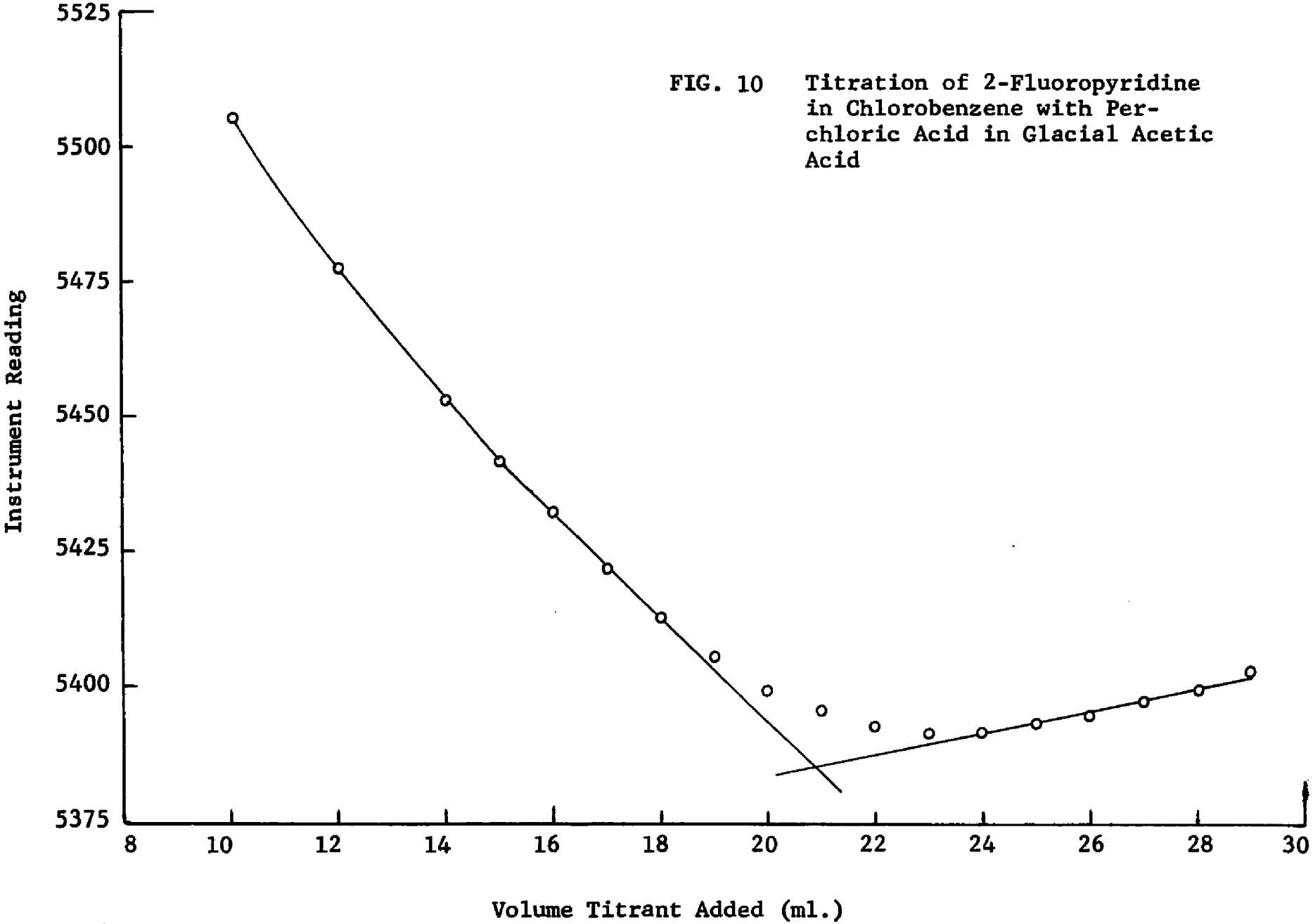


FIG. 10 Titration of 2-Fluoropyridine in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

THE ANALYSIS OF MIXTURE OF BASES

Having only feeble acid-base properties, chlorobenzene does not interact strongly with either acidic or basic substances. Consequently, chlorobenzene is not a "leveling" or "masking" solvent, but instead is a differentiating solvent. In other words, when two bases of different strengths are dissolved in chlorobenzene, they maintain this difference even in solution, so it should be possible to titrate them individually when they are present in a mixture.

A series of four two-component mixtures of weak bases were prepared. The difference in the pK_b values ($\Delta\ pK_b$) of the two bases present in the mixtures prepared progressively diminished from 4.12 to 0.24. It should be kept in mind that all these pK_b values are valid only in aqueous solutions. In chlorobenzene the actual strength of the bases must be different.

MIXTURE No. 1 -	p-toluidine	$pK_b = 8.84$	$\Delta\ pK_b = 4.12$
	and		
	4-nitroaniline	$pK_b = 12.96$	
No. 2 -	p-toluidine	$pK_b = 8.84$	$\Delta\ pK_b = 2.68$
	and		
	pyrazole	$pK_b = 11.52$	
No. 3 -	pyrazole	$pK_b = 11.52$	$\Delta\ pK_b = 1.44$
	and		
	4-nitroaniline	$pK_b = 12.96$	
No. 4 -	6-nitroquinoline	$pK_b = 11.28$	$\Delta\ pK_b = 0.24$
	and		
	pyrazole	$pK_b = 11.52$	

When two bases of different strengths are present in a solution, the stronger base reacts first with the added titrant. In aqueous solutions p-toluidine is a stronger base than 4-nitroaniline and the order of basic strength was found

to be the same in chlorobenzene; in fact, all the bases used to make the mixtures studied maintained their aqueous basic strength sequence in chlorobenzene.

It is of interest to consider the shape of the titration curve (see Fig. 11/12 and data in Table 27) for the mixture p-toluidine and 4-nitroaniline. On adding the standard perchloric acid solution to the solution of this mixture, p-toluidine being the stronger base reacted first forming a salt (which precipitated out); this continued until all the p-toluidine had been titrated. At that point the weaker base, 4-nitroaniline, started to react with the added acid. Since the composition of the two chemical systems were different, there was a change in the instrument response (change in impedance) curve after all the p-toluidine had been titrated and 4-nitroaniline started to react. 4-Nitroaniline did not form a precipitate immediately; it remained in a supersaturated state. When about 6 to 8 ml. of the titrant had been added beyond the first base equivalence point, the 4-nitroaniline salt began to precipitate and a "large" discontinuity occurred in the titration curve; again the slope of the curve changed. Finally, when all the 4-nitroaniline had been titrated, the curve rose steeply giving a sharp "V" shaped curve for the second base equivalence point.

All of the four mixtures followed the same pattern of titration. After the first base equivalence point was reached, in every case there was a supersaturated region followed by precipitation of the second base salt. In each case the formation of a precipitate was accompanied by a "large" discontinuity in the curve. This discontinuity arose from the fact that the ions, ion pairs, and triplets, etc., present in the supersaturated solution, were removed by precipitation, thus causing a large decrease in the impedance of the solution.

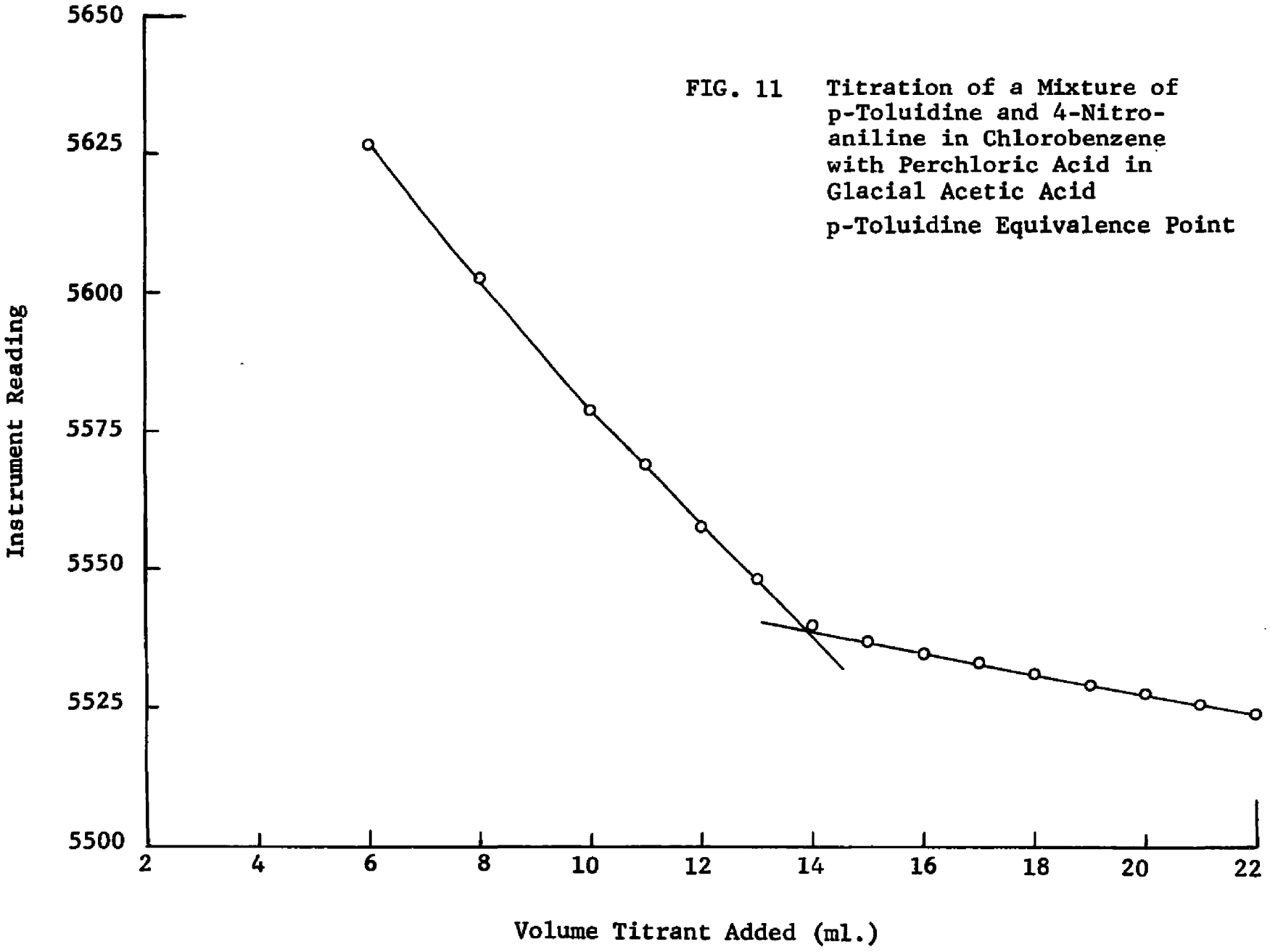


FIG. 11 Titration of a Mixture of p-Toluidine and 4-Nitro-aniline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

p-Toluidine Equivalence Point

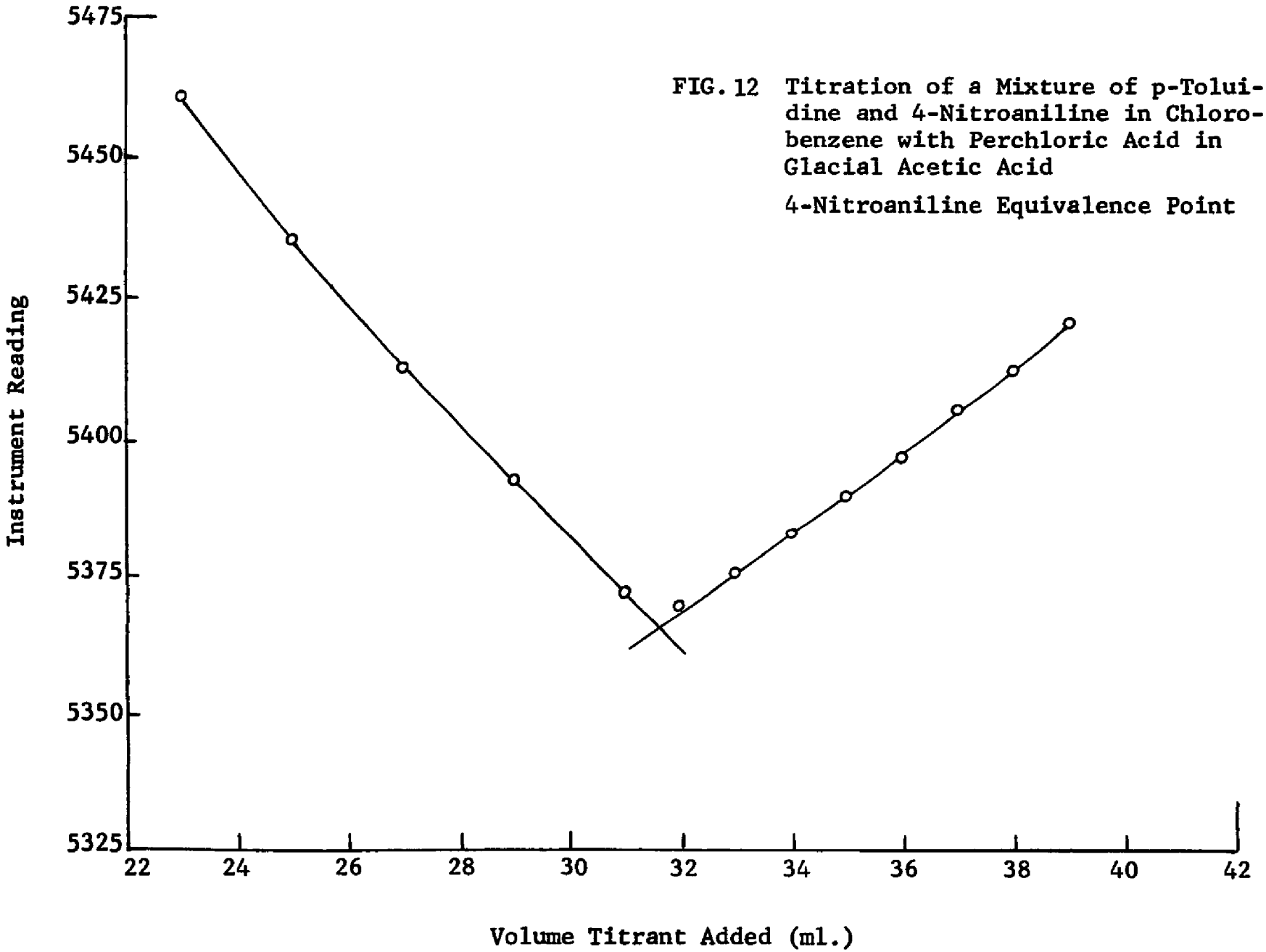


FIG. 12 Titration of a Mixture of p-Toluidine and 4-Nitroaniline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

4-Nitroaniline Equivalence Point

Table 10

Determination of a Mixture of p-Toluidine and 4-Nitroaniline

p-toluidine $pK_b = 8.84$
4-nitroaniline $pK_b = 12.96$
$\Delta\ pK_b = 4.12$

	Sample	wt of the base taken	wt of the base found	Percent recovery
1.	p-Toluidine	0.2283 g.	0.2257 g.	98.9
	4-Nitroaniline	0.2595 g.	0.2586 g.	99.6
2.	p-Toluidine	0.1669 g.	0.1668 g.	99.9
	4-Nitroaniline	0.2772 g.	0.2744 g.	99.0
3.	p-Toluidine	0.1379 g.	0.1368 g.	99.2
	4-Nitroaniline	0.2329 g.	0.2312 g.	99.3

Average percent recovery:	p-Toluidine	99.3
	4-Nitroaniline	99.3
Percent standard deviation:	p-Toluidine	0.54
	4-Nitroaniline	0.38

It was found that the precipitation of the second base salt made the detection of the second equivalence point easy and accurate. On occasions during the titration of a mixture of pyrazole and 4-nitroaniline, for some reason the second base salt did not precipitate out. Throughout the titration the system remained in a supersaturated state as evidenced by the fact that the color of the solution remained yellow. (When the salt precipitates out the solution at the equivalence point becomes almost colorless). The titration curve is shown in Figure 13 and in the data in Table 28. As can be seen, the second equivalence point break was not sharp and did not have a satisfactory "V" shape. When the salt did precipitate out, the break was sharp as is shown in Figure 14/15 and Table 29. In all the cases the stronger base salt precipitated. The titration curves and results of all the four mixtures are given below. In all four cases the two breaks corresponding to the two bases are sharp, and the location of the equivalence point easy and accurate. A typical titration takes about 2 1/2 hr. to complete.

TITRATION OF DIPROTIC BASES

In the previous section it was shown that chlorobenzene behaves as a differentiating solvent; consequently, it was possible to titrate individually two bases present in a mixture.

Next it was decided to investigate the titration of diprotic bases. Since chlorobenzene is a differentiating solvent, it should be possible to titrate these two basic groups individually; i.e., to obtain two breaks in the ratio of 1:1 in the titration of a diprotic base.

The following three diprotic bases were chosen to

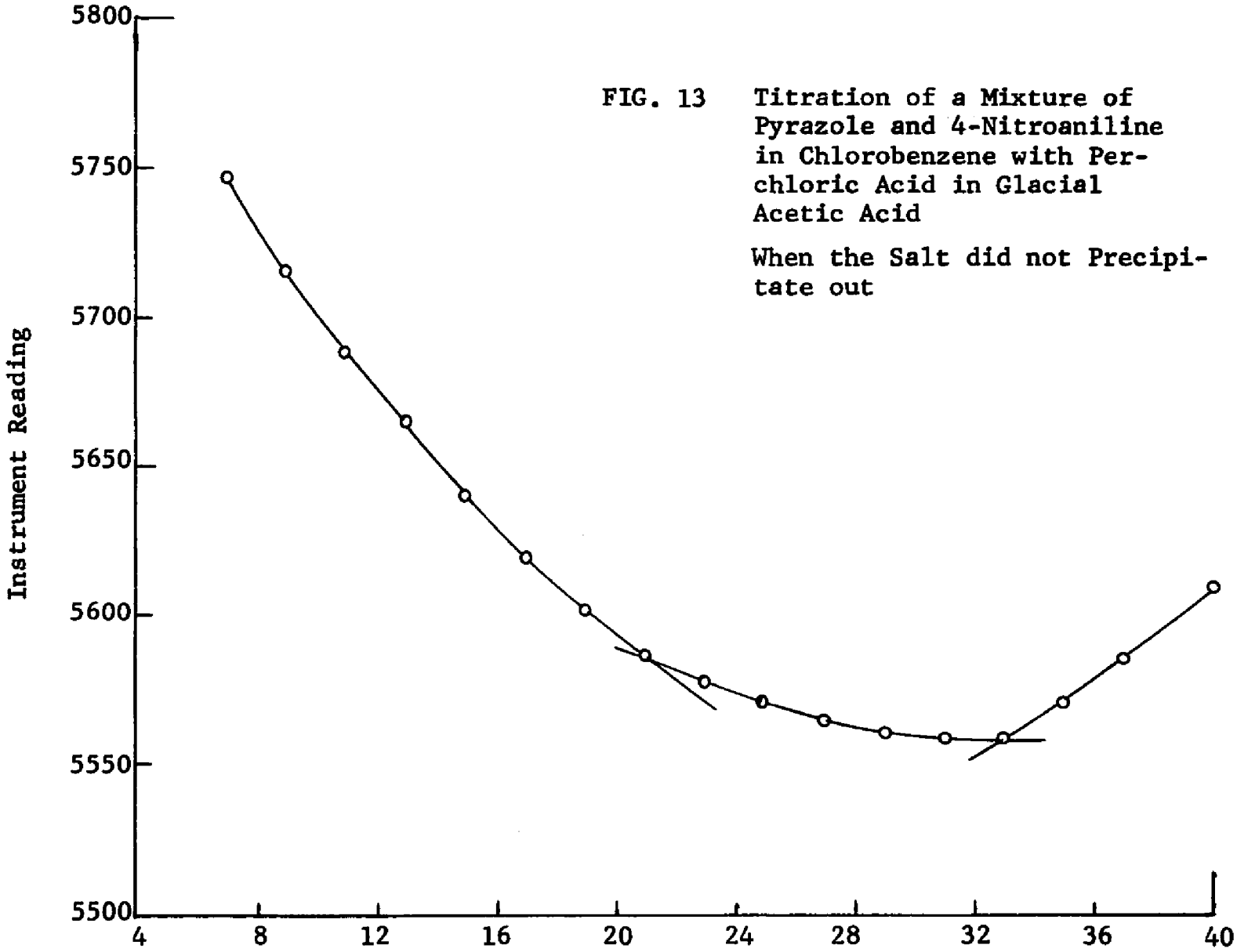


FIG. 13 Titration of a Mixture of Pyrazole and 4-Nitroaniline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

When the Salt did not Precipitate out

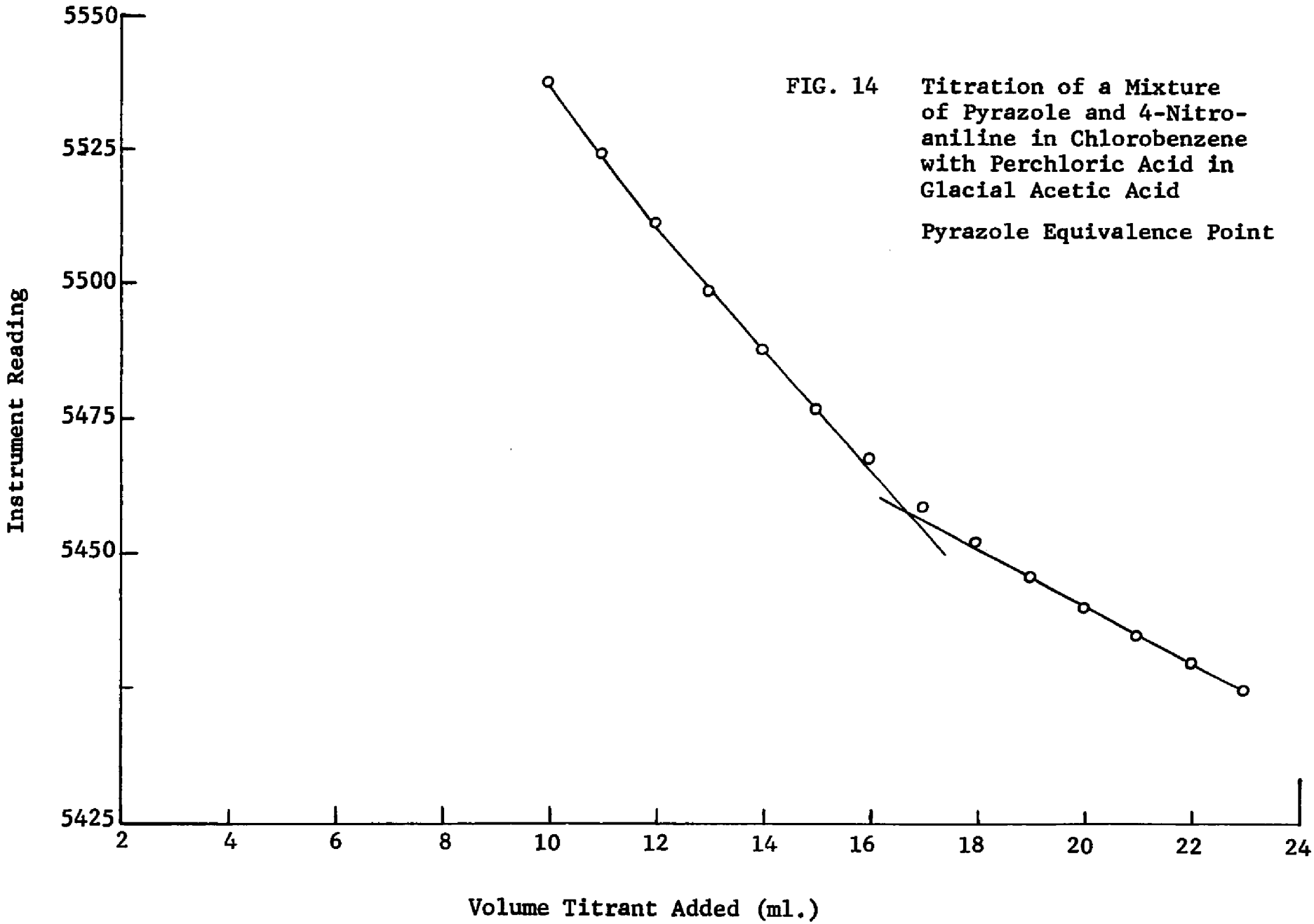


FIG. 14 Titration of a Mixture of Pyrazole and 4-Nitroaniline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Pyrazole Equivalence Point

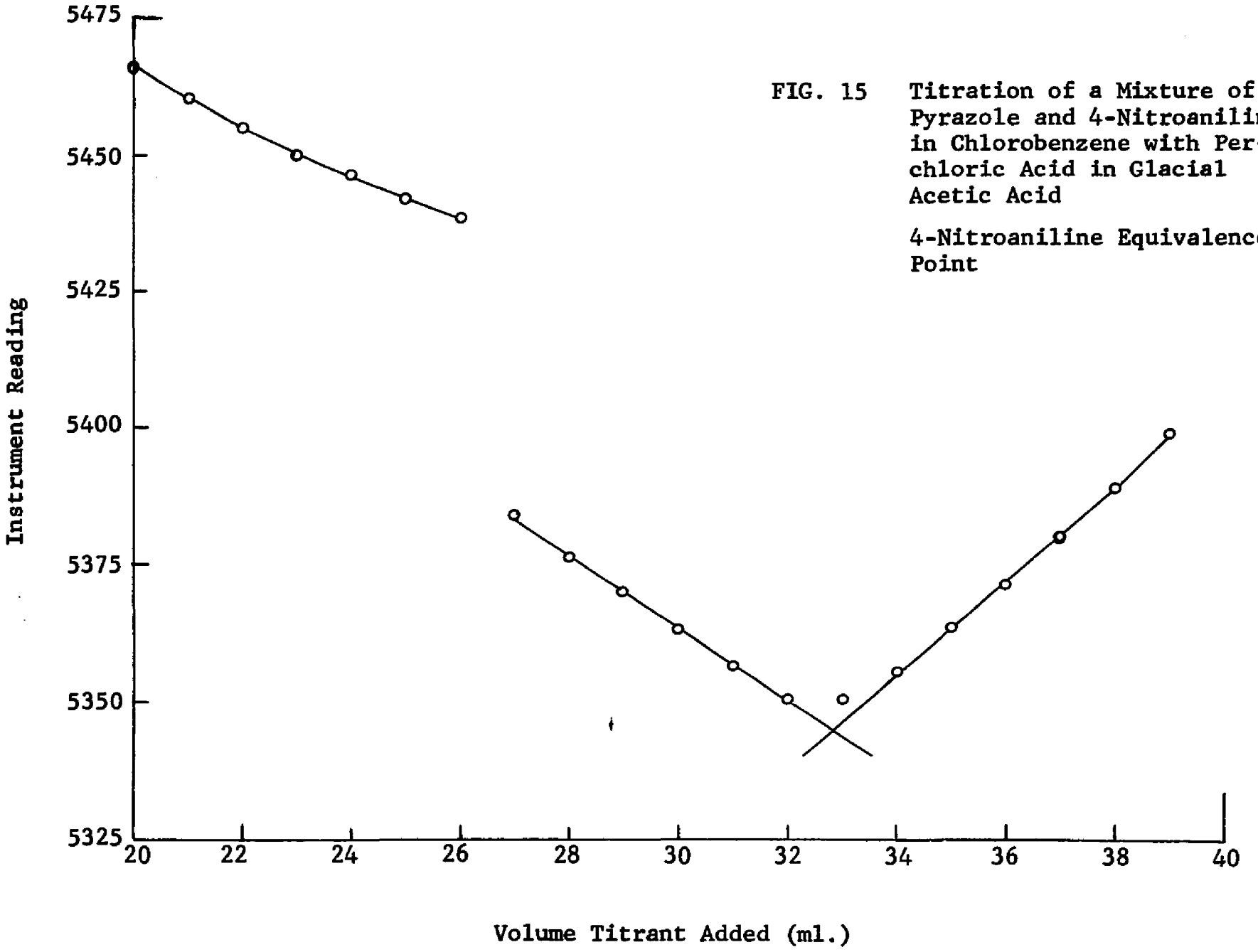


FIG. 15 Titration of a Mixture of Pyrazole and 4-Nitroaniline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

4-Nitroaniline Equivalence Point

Table 11

Determination of a Mixture of Pyrazole and 4-Nitroaniline

pyrazole $pK_b = 11.52$
4-nitroaniline $pK_b = 12.96$
$\Delta\ pK_b = 1.44$

	Sample	wt of the base taken	wt of the base found	Percent recovery
1.	Pyrazole	0.1269 g.	0.1278 g.	100.7
	4-Nitroaniline	0.2519 g.	0.2485 g.	98.7
2.	Pyrazole	0.1187 g.	0.1160 g.	97.7
	4-Nitroaniline	0.3030 g.	0.3010 g.	99.4
3.	Pyrazole	0.1273 g.	0.1259 g.	98.9
	4-Nitroaniline	0.4143 g.	0.4137 g.	99.9

Average percent recovery:	Pyrazole	99.1
	4-Nitroaniline	99.3
Percent standard deviation:	Pyrazole	1.5
	4-Nitroaniline	0.59

FIG. 16 Titration of a Mixture of p-Toluidine and Pyrazole in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

p-Toluidine Equivalence Point

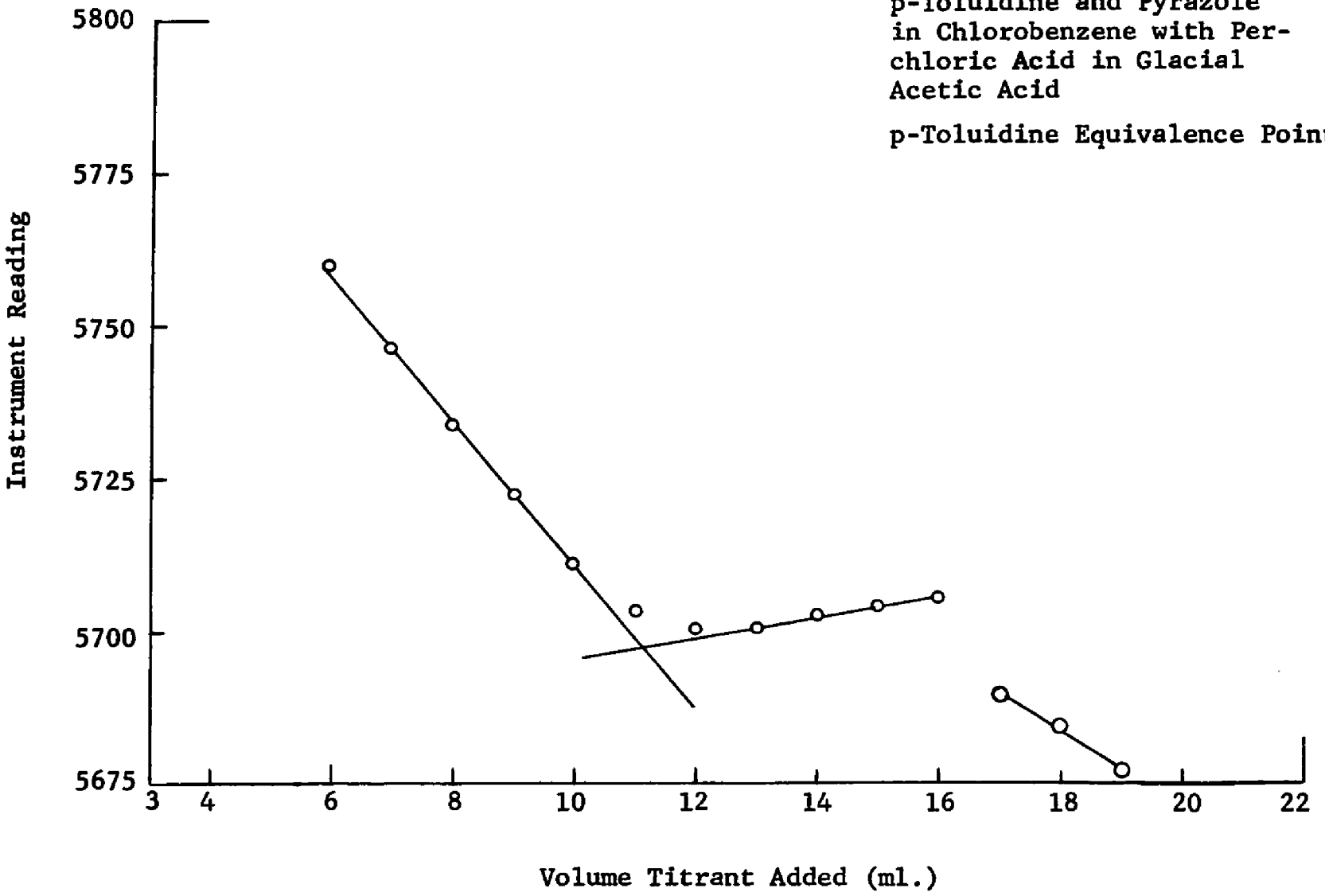


FIG. 17 Titration of a Mixture of p-Toluidine and Pyrazole in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

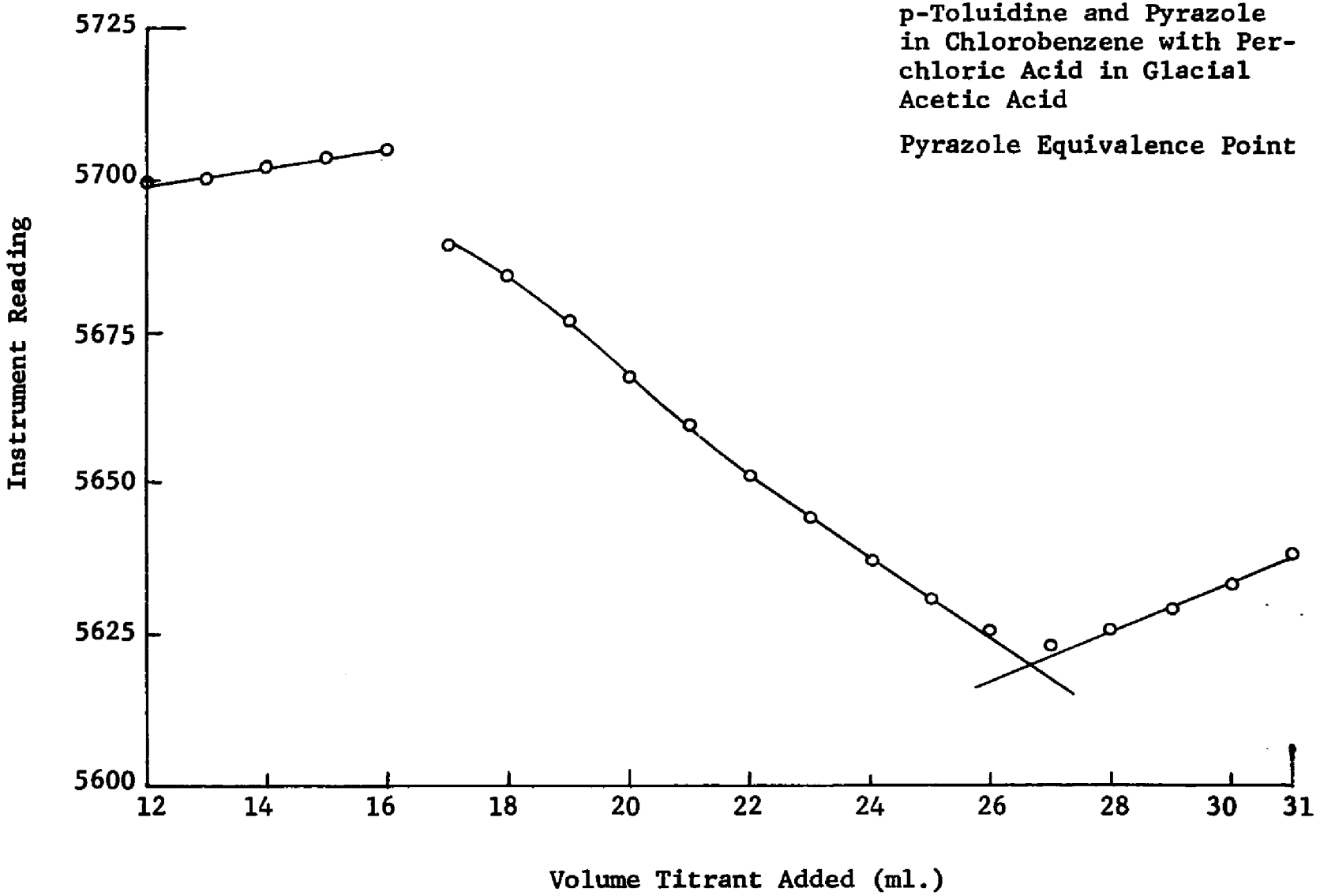


Table 12

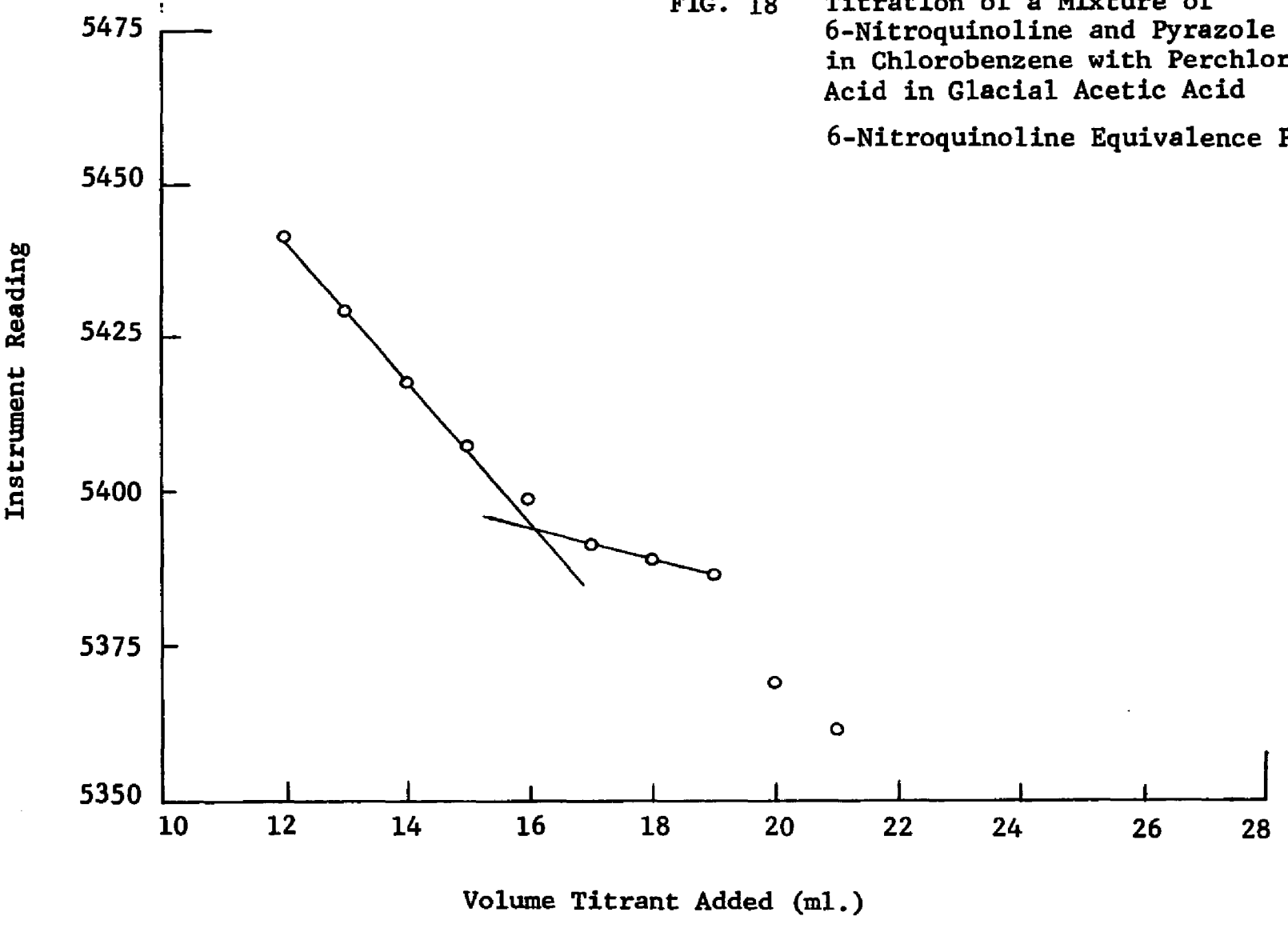
Determination of a Mixture of p-Toluidine and Pyrazole

p-toluidine $pK_b = 8.84$
pyrazole $pK_b = 11.52$
$\Delta\ pK_b = 2.68$

Samples		wt of the base taken	wt of the base found	Percent recovery
1.	p-Toluidine	0.1279 g.	0.1271 g.	99.4
	Pyrazole	0.1094 g.	0.1092 g.	99.8
2.	p-Toluidine	0.1257 g.	0.1254 g.	99.8
	Pyrazole	0.1127 g.	0.1116 g.	99.0
3.	p-Toluidine	0.1654 g.	0.1666 g.	100.7
	Pyrazole	0.1293 g.	0.1295 g.	100.2

Average percent recovery:	p-Toluidine	100.0
	Pyrazole	99.7
Percent standard deviation:	p-Toluidine	0.69
	Pyrazole	0.59

FIG. 18 Titration of a Mixture of 6-Nitroquinoline and Pyrazole in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid



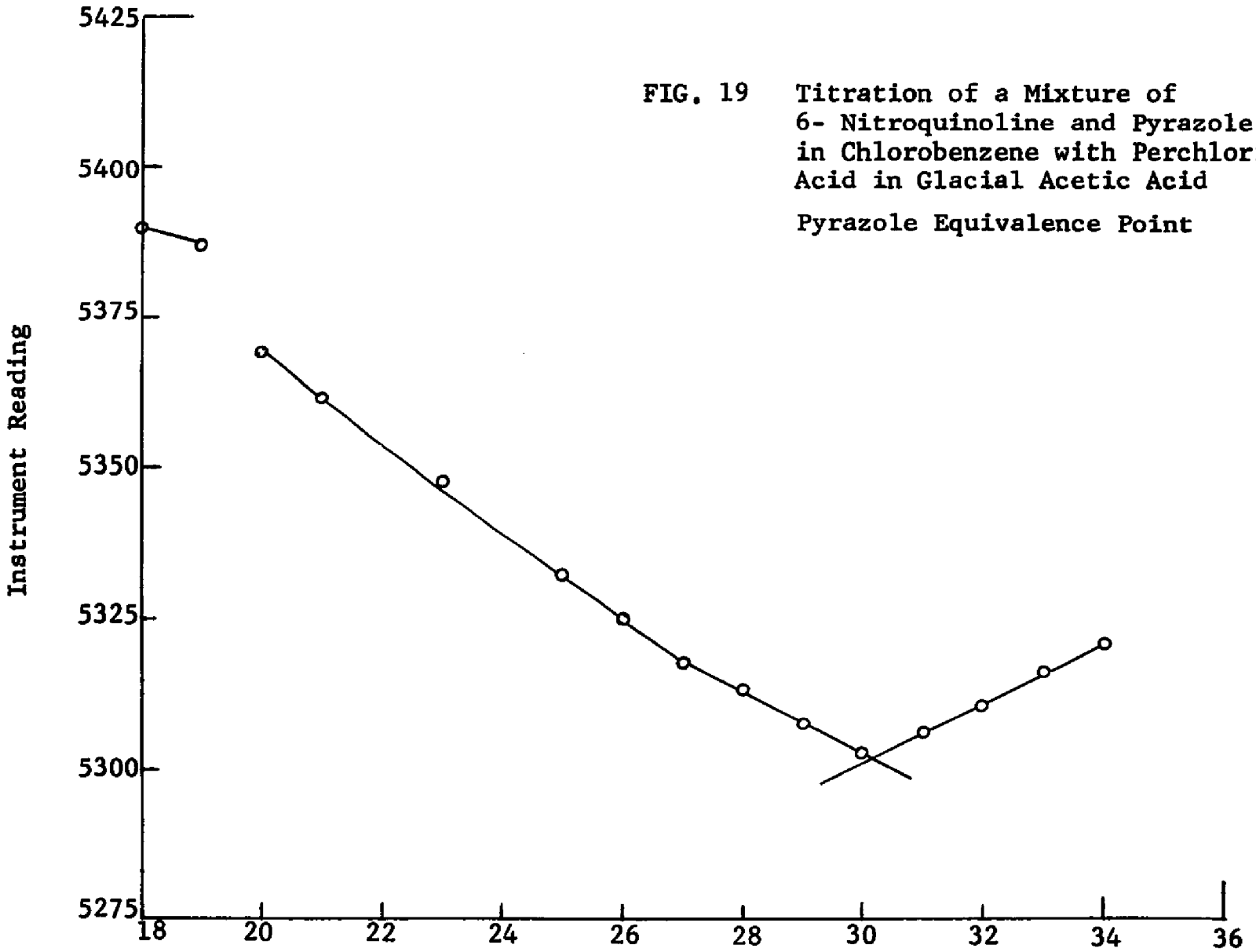


FIG. 19 Titration of a Mixture of 6- Nitroquinoline and Pyrazole in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Pyrazole Equivalence Point

Table 13

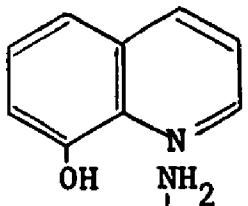
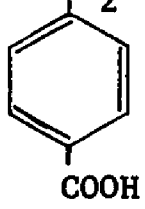
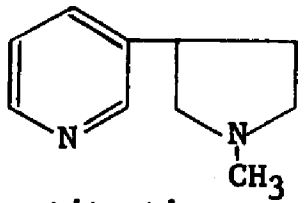
Determination of a Mixture of Pyrazole and 6-Nitroquinoline

6-nitroquinoline $pK_b = 11.28$
pyrazole $pK_b = 11.52$
$\Delta\ pK_b = 0.24$

	Sample	wt of the base taken	wt of the base found	Percent recovery
1.	6-Nitroquinoline	0.3168 g.	0.3127 g.	98.7
	Pyrazole	0.1064 g.	0.1074 g.	100.9
2.	6-Nitroquinoline	0.4407 g.	0.4407 g.	100.0
	Pyrazole	0.1162 g.	0.1158 g.	99.6
3.	6-Nitroquinoline	0.4652 g.	0.4636 g.	99.7
	Pyrazole	0.1069 g.	0.1075 g.	100.6

Average percent recovery:	6-Nitroquinoline	99.5
	Pyrazole	100.4
Percent standard deviation:	6-Nitroquinoline	0.65
	Pyrazole	0.66

test this possibility:

		pK_{b1}	pK_{b2}
1.	8-hydroxyquinoline 	4.09	8.89
2.	p-aminobenzoic acid 	9.13	11.50
3.	nicotine 	6.00	10.09

First the titration curve of 8-hydroxyquinoline was investigated. On adding the standard acid the stronger basic group reacted first accompanied by precipitation of the salt produced. After the stronger basic group had been titrated, the weaker basic group started reacting. Once again the composition of the two chemical systems being different, there should be a change in the instrument response curve. However, this portion of the titration curve seemed to be almost flat, probably due to the fact that there was no precipitate formation during the titration of the weaker basic group. After the second basic group had been titrated, the curve rose , but the rise was not sharp. The curve is shown in Figure 20 and data in Table 32. As can be seen, two breaks were obtained in the ratio of 1:1 (within experimental error), corresponding to the two pK_b values. The location of the two equivalence points was easy and accurate. The results are given in Table 14.

p-Aminobenzoic acid followed exactly the same pattern. The titration curve is shown in Figure 21 and Table 33, and the results are shown in Table 15. But nicotine behaved differently; although it has two pK_b values, it gave only one break in the titration curve as shown in Figure 22 and in the

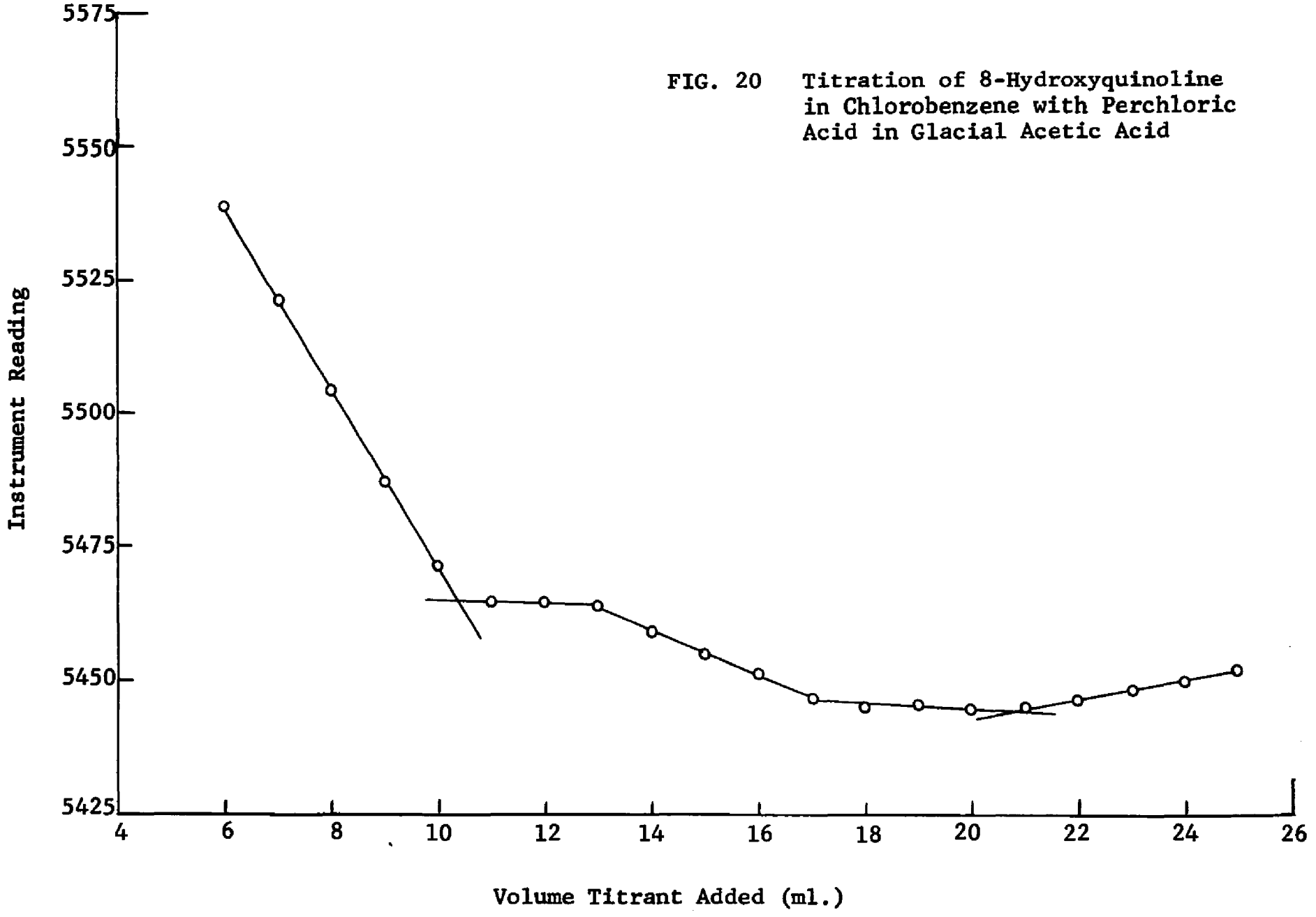


FIG. 20 Titration of 8-Hydroxyquinoline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Table 14

Determination of 8-Hydroxyquinoline

$pK_{b1} = 4.09$
$pK_{b2} = 8.89$
$\Delta\ pK_b = 4.80$

Sample	wt of the base taken	wt of the base found using primary proton	wt of the base found using secondary proton	Percent recovery using primary proton	Percent recovery using secondary proton
1.	0.1689 g.	0.1684 g.	0.1688 g.	99.7	99.9
2.	0.1710 g.	0.1714 g.	0.1713 g.	100.2	100.2
3.	0.2363 g.	0.2369 g.	0.2373 g.	100.2	100.4

Average percent recovery using:
primary proton = 100.0
secondary proton = 100.2

Percent standard deviation using:
primary proton = 0.29
secondary proton = 0.24

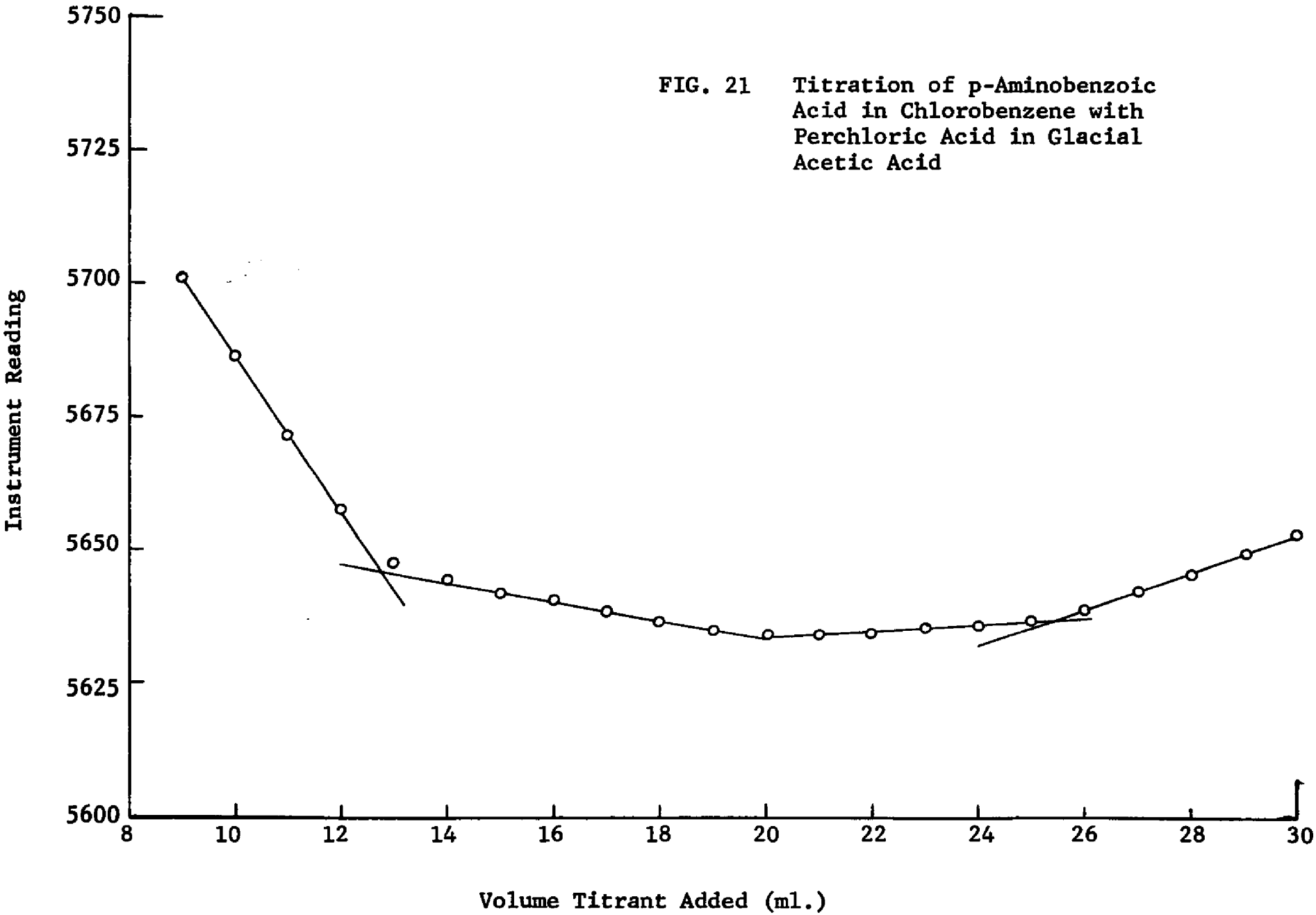


FIG. 21 Titration of p-Aminobenzoic Acid in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Table 15

Determination of p-Aminobenzoic Acid

$pK_{b1} = 9.13$
$pK_{b2} = 11.50$
$\Delta pK_b = 2.37$

Sample	wt of the base taken	wt of the base found using primary proton	wt of the base found using secondary proton	Percent recovery using primary proton	Percent recovery using secondary proton
1.	0.1961 g.	0.1948 g.	0.1954 g.	99.3	99.6
2.	0.2009 g.	0.2005 g.	0.2002 g.	99.8	99.7
3.	0.1850 g.	0.1845 g.	0.1844 g.	99.7	99.7

Average percent recovery using:
primary proton = 99.6
secondary proton = 99.7

Percent standard deviation using:
primary proton = 0.26
secondary proton = 0.024

FIG. 22 Titration of Nicotine in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

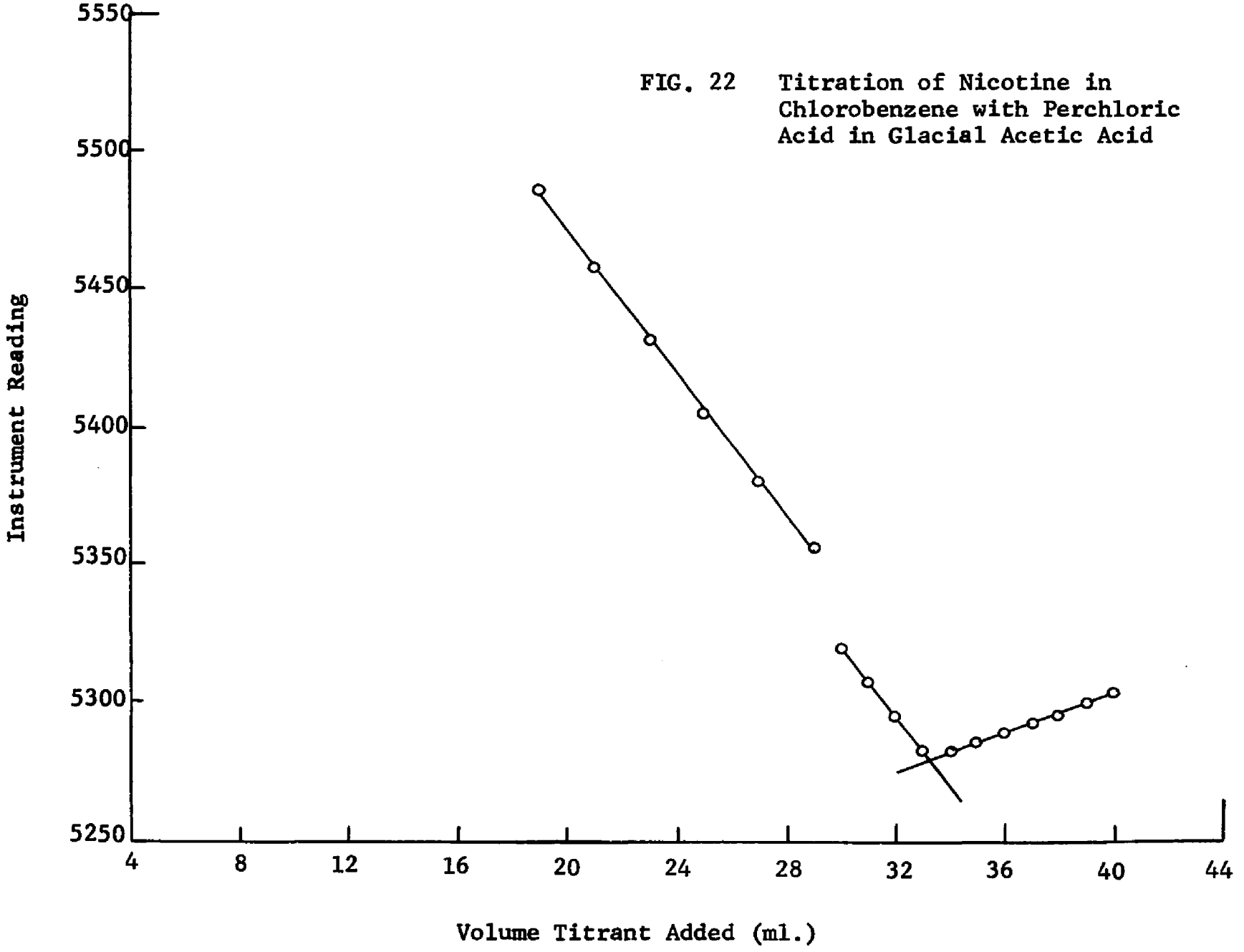


Table 16

Determination of Nicotine

$pK_{b1} = 6.0$
$pK_{b2} = 10.9$
$\Delta pK_b = 4.9$

Sample	wt of the base taken	wt of the base found using primary proton	wt of the base found using secondary proton	Percent recovery using primary proton	Percent recovery using secondary proton
1.	0.3089 g.	---	0.3021 g.	---	99.8
2.	0.2233 g.	---	0.2192 g.	---	99.8

Average percent recovery using:
primary proton = ----
secondary proton = 99.8

Percent standard deviation using:
primary proton = ----
secondary proton = 0.07

data in Table 34. This break corresponded to the second (i.e., weaker) pK_b value. In other words no break was obtained for the titration of pK_{b1} which is the stronger basic group. This can be explained as follows: on adding the standard acid as usual the stronger basic group (pK_{b1}) should react first. But during the titration of this group, there was no precipitate formation and consequently there was no sudden change in the impedance of the system at the first equivalence point, the change was gradual and therefore no break was obtained. But when the second basic group (weaker group) started reacting, a precipitate was obtained and consequently, a sharp break was obtained at the equivalence point. From the behavior of nicotine and the other example given (mixture of pyrazole and p-nitroaniline) it was concluded that precipitation is an essential step in the location of equivalence point in these oscillometric titrations.

The results of nicotine determination are given in Table 16. The 2% error may be due to impurities in the sample used. No attempt was made to purify it. It is included here only because it is a unique case and shows the importance of precipitate formation in oscillometric titrations.

CONCENTRATION RANGE APPLICABLE: The concentration range which could be determined by this method is from about 9×10^{-3} M to 4×10^{-2} M (i.e., 0.9 milliequivalents to about 4.0 milliequivalents of the base to be determined dissolved in 100 ml. of chlorobenzene). Solutions of less than 9×10^{-3} M were found to be too dilute to titrate satisfactorily; oscillometric end point detection became difficult, for this region lies on the very steep portion at the beginning of the instrument response curve where the break would not be sharp. Above 4×10^{-2} M the equivalence point region lies on the far side of the maximum of the response curve where the precision in locating the equivalence point is once again poor. Between the concentration limits, 9×10^{-3} M to 4×10^{-2} M, the location of the equivalence point is easy and accurate.

CONCLUSIONS

There are many methods for the determination of organic bases in acetic acid, dioxane, acetonitrile and other solvents.[5,6,7] These are good general methods, but do not serve to differentiate various types of amines. The use of acetic anhydride permits the determination of tertiary amines in the presence of primary and secondary amines.[36] Treatment of the mixture with salicylaldehyde, followed by titration in benzene-propanol[37] or in ethyleneglycol-2-propanol[38], has been used to determine the primary amines.

Fritz[39] was the first to do differential titrations to distinguish between amines of different basic strength. He carried out potentiometric titration of various bases in acetonitrile and was able to differentiate between aliphatic and aromatic amines in a mixture. The pK_b's of aliphatic amines generally lie around 4, and for aromatic amines, usually between 9 to 12. The pK_b difference between these two groups is about 4 units and was therefore sufficient to permit their stepwise titration in a mixture. Fritz also carried out potentiometric differential titration of a mixture of aromatic amines (examples: aniline and o-chloroaniline, pyridine and caffeine, etc.) in acetonitrile. Two inflections were obtained in the titration curve, but the breaks were not sharp and it was difficult to locate the equivalence point accurately.

Lippincott and Timnick[9] used oscillometric titrations in glacial acetic acid, and McCurdy and Galt[40] used conductrometric titrations in 1) a mixture of 1,4-dioxane + 34% formic acid and 2) glacial acetic acid for the differential titration

of various aromatic amines. Here, once again, the breaks in most cases were not sharp, and it was difficult to evaluate the inflections corresponding to individual bases.

Pungor[1] in his book writes that "the oscillometric or conductometric determination of a number of nitrogen bases in the presence of each other can only be carried out with difficulty. Determination of the total bases is simple, but the inflections corresponding to the individual bases can be located only vaguely....".

Here an oscillometric method has been developed for the quantitative determination of weak and very weak bases, singly and in two component mixtures using chlorobenzene as a solvent. A method has also been developed for the titration of diprotic bases whereby two inflection points have been obtained corresponding to the two basic groups (except in the case of nicotine, where only one break was obtained). In every case the perchlorate salt formed, being insoluble in chlorobenzene, precipitated out, but this did not in any way interfere with the titration. In fact, it is shown that the precipitation made the determination of equivalence points easier and more accurate. In contrast to other methods, the breaks obtained in every case are sharp and easy to evaluate. Also inflections corresponding to the individual bases (in a mixture) could be located easily and accurately.

McCurdy and Galt titrated a mixture of 8-hydroxyquinoline and o-aminobenzoic acid. Although these two bases are diprotic, only two inflections (not sharp) were obtained in the titration curve for the mixture. In the present work 8-hydroxyquinoline and p-aminobenzoic acid (which is closely related to o-aminobenzoic acid) were titrated individually

in chlorobenzene using oscillometry for end point detection. Two sharp breaks were obtained in the titration curve for each of these diprotic bases. In other words, using this technique, it was possible to differentiate between the two basic groups in the same molecule.

As mentioned earlier, a series of four, two-component mixtures of weak bases were analyzed in this work. The least difference in the pK_b values (all of these are aqueous pK_b values) was in the case of a mixture of 6-nitroquinoline and pyrazole, which differ by 0.24 pK_b units. Even here sharp breaks were obtained in the titration curve (see Fig. 18/19) and it was easy to evaluate the inflections corresponding to the individual bases present in the mixture. No cases have been reported in the literature for the differentiation of such a small difference in pK_b values (Δ pK_b 0.24) for such a weak base mixture.

It has been demonstrated that oscillometry is a useful and accurate analytical technique for the quantitative determination of weak bases and their mixtures using chlorobenzene as a solvent.

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APPENDIX

Table 17

Instrument Response Curve on the Addition of Perchloric Acid in Glacial Acetic Acid to Chlorobenzene

Normality of perchloric acid	0.1119
Weight of the base taken	Blank
Temperature	19.0°C
Relative humidity in the room	35%

Volume titrant added (ml.)	Instrument reading
0.00	5552.0
2.00	5515.0
4.00	5485.0
6.00	5465.0
8.00	5451.0
10.00	5441.0
12.00	5436.2
14.00	5435.5
16.00	5438.0
18.00	5444.0
20.00	5451.5
22.00	5462.0
24.00	5470.5
26.00	5480.5
28.00	5489.0
30.00	5497.0
32.00	5508.0
34.00	5522.0
36.00	5537.0
38.00	5553.0

Table 17 cont'd.

Volume titrant added (ml.)	Instrument reading
40.00	5569.5
42.00	5589.0
44.00	5609.0
46.00	5630.0
48.00	5651.5
50.00	5675.0

Table 18

Titration of p-Toluidine in Chlorobenzene
with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1054
Weight of the base taken	0.1052 g.
Temperature	28.0°C
Relative humidity in the room	71%

Volume titrant added (ml.)	Instrument reading
0.00	5956.0
2.00	5933.5
4.00	5898.0
5.00	5885.5
6.00	5873.0
7.00	5862.5
8.00	5852.0
9.00	5841.0
10.00	5837.5
11.00	5836.5
12.00	5837.0
13.00	5837.5
14.00	5838.5
15.00	5840.0
16.00	5840.5
18.00	5836.8
20.00	5836.0

Table 19

Titration of p-Toluidine in Chlorobenzene
with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1054
Weight of the base taken	0.2403 g.
Temperature	27.0°C
Relative humidity in the room	72%

Volume titrant added (ml.)	Instrument reading
0.00	5920.5
2.00	5897.0
4.00	5863.0
6.00	5842.0
8.00	5821.0
10.00	5804.0
12.00	5788.5
14.00	5776.0
15.00	5770.5
16.00	5765.0
17.00	5761.0
18.00	5757.2
19.00	5752.8
20.00	5749.5
21.00	5746.5
22.00	5750.0
23.00	5759.0
24.00	5768.3
25.00	5777.0
26.00	5780.6

Table 19 cont'd.

Volume titrant added (ml.)	Instrument reading
27.00	5783.0
28.00	5786.0
30.00	5792.0
32.00	5799.0
36.00	5819.0
40.00	5844.0

Table 20

Titration of Aniline in Chlorobenzene
with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1121
Weight of the base taken	0.2716 g.
Temperature	21.0°C
Relative humidity in the room	72%

Volume titrant added (ml.)	Instrument reading
0.00	5932.5
2.00	5898.0
4.00	5864.0
6.00	5833.0
8.00	5804.5
10.00	5778.0
12.00	5753.0
14.00	5730.0
16.00	5707.0
18.00	5686.0
20.00	5666.5
22.00	5648.0
23.00	5638.5
24.00	5630.0
25.00	5621.5
26.00	5619.5
27.00	5617.6
28.00	5621.0

Table 20 cont'd.

Volume titrant added (ml.)	Instrument reading
29.00	5624.5
30.00	5627.5
31.00	5631.0
33.00	5640.0
35.00	5650.00

Table 21

Titration of o-Toluidine in Chlorobenzene
with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1121
Weight of the base taken	0.2250 g.
Temperature	19.0°C
Relative humidity in the room	70%

Volume titrant added (ml.)	Instrument reading
0.00	5664.0
2.00	5635.0
4.00	5605.0
6.00	5578.5
8.00	5554.5
10.00	5533.5
12.00	5513.5
14.00	5494.5
16.00	5477.0
17.00	5469.5
18.00	5461.0
19.00	5458.5
20.00	5461.5
21.00	5465.1
22.00	5469.1
23.00	5474.0
24.00	5479.2
25.00	5484.5
26.00	5491.2
28.00	5504.5
30.00	5520.0

Table 22

Titration of 6-Nitroquinoline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1121
Weight of the base taken	0.3444 g.
Temperature	20.5°C
Relative humidity in the room	75%

Volume titrant added (ml.)	Instrument reading
0.00	5673.5
2.00	5638.5
4.00	5600.1
6.00	5565.2
8.00	5532.5
10.00	5500.0
12.00	5471.5
13.00	5457.3
14.00	5443.5
15.00	5431.1
16.00	5417.8
17.00	5404.8
18.00	5398.3
19.00	5397.6
20.00	5397.4
21.00	5396.8
22.00	5397.0
23.00	5397.1
24.00	5398.4
25.00	5400.0

Table 23

Titration of pyrazole in Chlorobenzene
with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1119
Weight of the base taken	0.1971 g.
Temperature	21.0°C
Relative humidity in the room	60%

Volume titrant added (ml.)	Instrument reading
0.00	4989.1
2.00	4962.2
4.00	4920.4
6.00	4888.0
8.00	4857.0
10.00	4830.3
12.00	4805.0
14.00	4783.0
16.00	4763.4
18.00	4743.5
20.00	4727.0
22.00	4711.1
24.00	4698.0
26.00	4687.0
26.50	4687.8
27.00	4688.0
28.00	4691.0
29.00	4694.5
30.00	4701.0
31.00	4705.7
32.00	4711.0

Table 24

Titration of 4-Nitroaniline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1121
Weight of the base taken	0.2693 g.
Temperature	20.0°C
Relative humidity in the room	74%

Volume titrant added (ml.)	Instrument reading
0.00	5913.5
2.00	5872.5
4.00	5824.5
6.00	5783.0
8.00	5744.5
10.00	5708.0
12.00	5674.0
14.00	5641.5
15.00	5623.7
16.00	5609.0
17.00	5594.3
18.00	5590.1
19.00	5589.7
20.00	5590.0
21.00	5590.0
22.00	5591.5
23.00	5593.0
24.00	5595.0

Table 24 cont'd.

Volume titrant added (ml.)	Instrument reading
25.00	5598.0
26.00	5600.5
28.00	5608.2
30.00	5617.2

Table 25

Titration of 2-Nitroaniline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1121
Weight of the base taken	0.3459 g.
Temperature	20.0°C
Relative humidity in the room	62%

Volume titrant added (ml.)	Instrument reading
0.00	5705.5
2.00	5668.0
4.00	5630.0
6.00	5596.0
8.00	5564.5
10.00	5535.5
12.00	5508.2
14.00	5483.5
16.00	5463.5
18.00	5447.0
20.00	5432.5
21.00	5425.8
22.00	5422.0
23.00	5919.0
24.00	5418.0
25.00	5420.5
26.00	5422.0
27.00	5423.5
28.00	5426.0
30.00	5434.5
32.00	5444.5

Table 26

Titration of 2-Fluoropyridine in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1118
Weight of the base taken	0.2292 g.
Temperature	24.0°C
Relative humidity in the room	54%

Volume titrant added (ml.)	Instrument reading
0.00	5653.0
2.00	5628.0
4.00	5601.5
6.00	5575.0
8.00	5534.5
10.00	5505.2
12.00	5477.4
14.00	5453.1
15.00	5441.9
16.00	5432.3
17.00	5422.0
18.00	5412.9
19.00	5405.4
20.00	5399.2
21.00	5395.5
22.00	5392.5
23.00	5391.5
24.00	5391.5

Table 26 cont'd.

Volume titrant added (ml.)	Instrument reading
25.00	5393.2
26.00	5394.7
27.00	5397.3
28.00	5399.6
29.00	5403.0
30.00	5407.8

Table 27

Titration of a Mixture of
p-Toluidine and 4-Nitroaniline in Chlorobenzene
with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1118
Weight of p-toluidine taken	0.1669 g.
Weight of 4-nitroaniline taken	0.2772 g.
Temperature	20.0°C
Relative humidity in the room	65%

Volume titrant added (ml.)	Instrument reading
0.00	5712.5
2.00	5690.0
4.00	5652.6
6.00	5626.5
8.00	5602.5
10.00	5578.6
11.00	5568.5
12.00	5557.6
13.00	5548.0
14.00	5539.8
15.00	5536.6
16.00	5534.5
17.00	5533.0
18.00	5531.2
19.00	5529.0
20.00	5527.5

Table 27 cont'd.

Volume titrant added (ml.)	Instrument reading
21.00	5525.0
22.00	5518.2
23.00	5460.0
25.00	5434.5
27.00	5411.0
29.00	5391.0
31.00	5371.0
32.00	5369.0
33.00	5374.2
34.00	5381.0
35.00	5388.0
36.00	5395.0
37.00	5403.3

Table 28

Titration of a Mixture of
Pyrazole and 4-Nitroaniline in Chlorobenzene
with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1054
Weight of pyrazole taken	0.1538 g.
Weight of 4-nitroaniline taken	0.1755 g.
Temperature	22.0°C
Relative humidity in the room	61%

Volume titrant added (ml.)	Instrument reading
0.00	5871.0
1.00	5856.5
2.00	5836.5
3.00	5815.0
4.00	5796.0
5.00	5778.0
6.00	5761.5
7.00	5746.5
8.00	5731.5
9.00	5715.7
10.00	5701.5
11.00	5687.5
12.00	5676.5
13.00	5664.5
14.00	5652.5
15.00	5639.5
16.00	5628.5
17.00	5618.8

Table 28 cont'd.

Volume titrant added (ml.)	Instrument reading
18.00	5609.6
19.00	5601.8
20.00	5594.0
21.00	5586.0
22.00	5581.5
23.00	5576.8
24.00	5574.0
25.00	5570.5
26.00	5567.2
27.00	5564.6
28.00	5563.5
29.00	5560.0
30.00	5559.5
31.00	5558.5
32.00	5558.0
33.00	5559.0
34.00	5564.5
35.00	5570.5
36.00	5578.0
37.00	5584.6
38.00	5592.0
40.00	5609.5

Table 29

Titration of a Mixture of
Pyrazole and 4-Nitroaniline in Chlorobenzene
with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1118
Weight of pyrazole taken	0.1269 g.
Weight of 4-nitroaniline taken	0.2519 g.
Temperature	22.0°C
Relative humidity in the room	44%

Volume titrant added (ml.)	Instrument reading
0.00	5720.5
4.00	5648.5
8.00	5587.0
9.00	5577.4
10.00	5563.0
11.00	5549.5
12.00	5536.8
13.00	5523.8
14.00	5513.2
15.00	5502.0
16.00	5493.0
17.00	5484.0
18.00	5477.3
19.00	5470.8
20.00	5465.5
21.00	5460.2
22.00	5455.0
23.00	5450.0

Table 29 cont'd.

Volume titrant added (ml.)	Instrument reading
24.00	5446.5
25.00	5442.0
26.00	5438.5
27.00	5384.5
28.00	5376.5
29.00	5370.0
30.00	5363.0
31.00	5356.5
32.00	5350.5
33.00	5350.5
34.00	5355.3

Table 30

Titration of a Mixture of
Pyrazole and p-Toluidine in Chlorobenzene
with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1054
Weight of p-Toluidine taken	0.1257 g.
Weight of pyrazole taken	0.1127 g.
Temperature	20.5°C
Relative humidity in the room	47%

Volume titrant added (ml.)	Instrument reading
0.00	5850.4
1.00	5836.0
2.00	5822.1
3.00	5809.0
4.00	5786.5
5.00	5772.0
6.00	5759.0
7.00	5745.8
8.00	5733.0
9.00	5721.5
10.00	5710.5
11.00	5703.0
12.00	5700.0
13.00	5700.0
14.00	5702.2
15.00	5703.6
16.00	5705.0
17.00	5689.0

Table 30 cont'd.

Volume titrant added (ml.)	Instrument reading
18.00	5684.0
19.00	5676.8
20.00	5667.5
21.00	5659.5
22.00	5650.8
23.00	5644.2
24.00	5637.0
25.00	5631.0
26.00	5625.5
27.00	5623.0
28.00	5625.6

Table 31

Titration of a Mixture of
6-Nitroquinoline and Pyrazole in Chlorobenzene
with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1121
Weight of 6-nitroquinoline taken	0.3168 g.
Weight of pyrazole taken	0.1064 g.
Temperature	19.5°C
Relative humidity in the room	61%

Volume titrant added (ml.)	Instrument reading
0.00	5647.0
2.00	5625.5
4.00	5571.1
6.00	5737.2
8.00	5503.5
10.00	5473.0
12.00	5442.0
13.00	5929.5
14.00	5418.0
15.00	5408.0
16.00	5399.0
17.00	5391.5
18.00	5389.5
19.00	5386.5
20.00	5369.0
21.00	5361.5
23.00	5347.6
25.00	5332.0

Table 31 cont'd.

Volume titrant added (ml.)	Instrument reading
26.00	5324.8
27.00	5317.6
28.00	5313.2
29.00	5307.3
30.00	5302.5
31.00	5306.0
32.00	5310.5
33.00	5316.5
34.00	5321.0
35.00	5329.0
36.00	5335.0
38.00	5348.0
40.00	5362.5

Table 32

Titration of 8-Hydroxyquinoline in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1118
Wieght of 8-hydroxyquinoline taken	0.1689 g.
Temperature	19.5°C
Relative humidity in the room	70%

Volume titrant added (ml.)	Instrument reading
0.00	5653.0
2.00	5614.5
4.00	5575.5
6.00	5538.5
7.00	5521.0
8.00	5504.0
9.00	5486.8
10.00	5471.3
11.00	5464.5
12.00	5464.7
13.00	5463.2
14.00	5458.4
15.00	5454.5
16.00	5451.0
17.00	5446.2
18.00	5444.8
19.00	5445.0
20.00	5444.0

Table 32 cont'd.

Volume titrant added (ml.)	Instrument reading
21.00	5444.5
22.00	5445.9
23.00	5447.5
24.00	5449.5
25.00	5451.8
26.00	5456.0
27.00	5458.0
28.00	5461.8
29.00	5466.8
30.00	5470.5

Table 33

Titration of p-Aminobenzoic Acid in Chlorobenzene with Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1119
Weight of p-aminobenzoic acid taken	0.1961 g.
Temperature	23.0°C
Relative humidity in the room	42%

Volume titrant added (ml.)	Instrument reading
0.00	5848.0
1.00	5839.5
2.00	5821.2
3.00	5802.0
4.00	5783.5
5.00	5766.5
6.00	5749.0
7.00	5732.5
8.00	5716.2
9.00	5701.0
10.00	5686.0
11.00	5671.0
12.00	5657.6
13.00	5647.5
14.00	5644.5
15.00	5641.6
16.00	5640.2
17.00	5638.5
18.00	5636.5

Table 33 cont'd.

Volume titrant added (ml.)	Instrument reading
19.00	5634.8
20.00	5634.0
21.00	5633.8
22.00	5634.3
23.00	5635.0
24.00	5635.7
25.00	5636.6
26.00	5638.7
27.00	5642.0
28.00	5645.0
29.00	5649.0
30.00	5652.7
31.00	5657.5
32.00	5662.2
33.00	5667.5
34.00	5671.9
35.00	5677.8

Table 34

Titration of Nicotine in Chlorobenzene
With Perchloric Acid in Glacial Acetic Acid

Normality of perchloric acid	0.1118
Weight of nicotine taken	0.3089 g.
Temperature	25.0°C
Relative humidity in the room	44%

Volume titrant added (ml.)	Instrument reading
0.00	5668.0
3.00	5681.0
5.00	5670.5
7.00	5656.0
8.00	5649.5
10.00	5622.0
11.00	5606.8
12.00	5592.0
13.00	5576.3
14.00	5560.5
15.00	5546.0
16.00	5530.8
17.00	5515.0
18.00	5500.5
19.00	5485.5
20.00	5471.3
21.00	5457.6
22.00	5444.0

Table 34 cont'd.

Volume titrant added (ml.)	Instrument reading
23.00	5430.5
24.00	5417.8
25.00	5404.8
26.00	5391.3
27.00	5379.3
28.00	5367.0
29.00	5355.5
30.00	5318.3
31.00	5306.5
32.00	5293.8
33.00	5281.0
34.00	5280.5
35.00	5284.1
36.00	5287.5
37.00	5291.1
38.00	5293.8
39.00	5298.5
40.00	5302.0

BIOGRAPHICAL DATA

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