m-NITROPHENYLARSONIC ACID AS A POLAROGRAPHIC REAGENT FOR TITANIUM

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A Thesis
Submitted to the Faculty of Arts and Science
in Partial Fulfilment of the Requirements
for the Degree
Master of Science

McMaster University
May 1955

Master of Science (1955)
(Chemistry)

McMaster University,
Hamilton, Ontario.

Title: m-Nitrophenylarsonic Acid as a Polarographic Reagent for Titanium.

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Number of Pages: 54

Scope and Contents:

A study was made of the variables affecting the quantitative precipitation of titanium with m-nitrophenylarsonic acid. The precipitate formed in the presence of a large excess of reagent was found, by a polarographic method, to be the di-m-nitrophenylarsonate.

The precipitation was shown to be the basis for an accurate method for the polarographic determination of titanium. Several complex alloys of widely differing compositions were successfully analyzed for titanium by this new method.

The feasibility of an amperometric titration of titanium with m-nitrophenylarsonic acid was demonstrated. Under the conditions of an amperometric titration, the composition of the precipitate is apparently the mono-m-nitrophenylarsonate.

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Dr. R.P. Graham for his guidance and encouragement. Thanks are also extended to Mr. G.B. Larrabee for helpful suggestions. Grateful acknowledgement is made to the Research Council of Ontario for the award of a Scholarship, and to this body and the Defence Research Board of Canada for financial assistance during two summers.

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GENERAL INTRODUCTION

The need for precise and accurate analytical methods for titanium has grown with the growing industrial interest in titanium in recent years. A very important application of titanium is as a constituent of alloys that recently have been developed for applications at high temperatures. Although the element is present in only relatively low concentration in these alloys, it increases markedly their resistance to thermal and mechanical stresses.

Several methods for the determination of titanium are available, but none is well suited to the analysis of a material containing such a variety of elements as a modern high-temperature alloy.

The purpose of the present research was to develop new methods for the determination of titanium, making use of m-nitrophenylarsonic acid as a precipitant and as a polarographically reducible substance. Although attention was given to an amperometric method, emphasis was accorded the development of a new polarographic procedure. This polarographic method depends on the quantitative precipitation of titanium with m-nitrophenylarsonic acid, the dissolution of the precipitate, and the polarographic determination of the m-nitrophenylarsonic acid so obtained.

HISTORICAL INTRODUCTION

(a) High-Temperature Alloys

In the last few years an entirely new type of heat engine, the jet engine, has been developed. Severe operating conditions, especially high speeds of rotation at elevated temperatures, have made necessary the development of new alloys. Modern high-temperature alloys are characterized by exceptional strength and resistance to oxidation and carburization at temperatures up to 1050°C., high fatigue strength against thermal and mechanical stresses, and resistance to flow and creep under powerful centrifugal forces(1).

The new group of alloys that possess this imposing list of qualities are sometimes referred to as superalloys. The typical superalloy is a solid-solution matrix of iron and chromium, with sufficient nickel to provide a face-centered cubic lattice structure down to room temperature(2). Additional cobalt and nickel atoms in the positions that otherwise would be occupied by iron renders the matrix a very stable entity, resistant to oxidation(3).

The required hardness in the alloy is provided by one or more of the elements molybdenum, chromium, tungsten, niobium, aluminium, tantalum and titanium. These precipitate as hardening phases which act as anchoring structures in the solid-solution; thus these elements induce resistance to creep and flow and prevent coalescence of the matrix during service at high temperatures(3). The hardening phases produced by two or more of these elements are better than those produced by a single element. Consequently several of the elements listed above are used in many commercial alloys, the chemical compositions of which are given in Table I.

TABLE I

AVERAGE PERCENTAGE COMPOSITION OF ALLOYS

Element	Discaloy	K42B	Waspalloy	Inconel X*	A-286
Iron	53	13	3	7	53
Nickel	26	41	57	72	26
Chromium	14	19	19	15	15
Cobalt	-	22	14	-	-
Molybdenum	3.2	-	3.1	-	1.2
Titanium	1.8	2.5	2.3	2.4	1.9
Manganese	0.7	0.9	0.8	0.7	1.4
Silicon	0.8	0.7	0.6	0.4	0.9
Aluminium	0.1	0.5	1.1	1.0	0.2
Vanadium	0.08	0.05	-	-	0.3
Carbon	0.04	0.04	0.05	0.04	0.03

* Also contains Cu 0.1%; Nb 0.7%; and Ta 0.2%

(b) m-Nitrophenylarsonic Acid

A recent survey tabulates over twenty arsonic acids that have been proposed for the detection of cations(4). Studies of the effect of substituents on the analytical applications of these acids have shown that substituents may increase the sensitivity or the selectivity of the reagent. Substitution by nitro groups often increases the sensitivity by reducing the solubility of the precipitate. Titanium is precipitated by most of the arsonic acids referred to in the literature. Unfortunately, the conditions under which this element is precipitated have not been extensively studied. As a result, titanium is generally considered as an undesirable interference in the use of the reagent for the detection or determination of some other element. Only in the case of p-hydroxyphenylarsonic acid have the conditions for precipitation been defined sufficiently rigidly to make this acid a useful reagent for the detection and the gravimetric determination of titanium(5).

m-Nitrophenylarsonic acid has been little used as an analytical reagent. It was recommended some years ago for the detection of zirconium and tin(6,7), but its first application in quantitative analysis appears to be that proposed by Kolthoff and Johnson(8). These authors studied m-nitrophenylarsonic acid as a precipitant for amperometric titrations and showed that uranyl, thorium, zirconium and tin ions could be determined using this reagent.

(c) Earlier Methods for Titanium

Several gravimetric procedures for the determination of titanium are available. An early method involved the precipitation of titanium as the hydrous oxide from boiling acetic acid solution(9,10). Since a large number of other elements also precipitate under these conditions, the application of the method is severely limited.

More elegant gravimetric procedures, based on the use of organic precipitants, were developed later. Among the organic reagents may be included 8-hydroxyquinoline(11), tannin and antipyrine(12), p-hydroxyphenylarsonic acid(5), and cupferron(13,14). None of these is a specific reagent for titanium. They range in selectivity from cupferron and 8-hydroxyquinoline, which precipitate a substantial number of cations, to p-hydroxyphenylarsonic acid which, although not a truly specific precipitant, may be used as such under carefully controlled conditions.

In these methods, titanium is removed from interfering elements by preliminary separations usually involving precipitations. These separations are unattractive for several reasons. They are time consuming, complete removal of interferences is difficult, and there is the very real possibility, especially when working with low concentrations of titanium, of appreciable losses of titanium through sorption and co-precipitation.

Of the precipitates obtained with these organic reagents, only that given by 8-hydroxyquinoline can be dried to constant weight at 110°C; the others must be ignited to titanium dioxide before being weighed. This frequently involves a very unfavorable weight factor, since the amount of titanium that is required for accurate weighing as the dioxide produces a very bulky organic precipitate that is difficult both to filter and to wash.

Colorimetric methods for the determination of titanium have found considerable application. These are usually based on the color of the peroxo-titanyl ion, as in the hydrogen peroxide method, or of colored organic complexes formed with disodium-1,2-dihydroxybenzene-3,5-disulfonate(15). Other colorimetric reagents include chromotropic acid, thymol, gallic acid and resoflavine(16). In general these reagents have admirable sensitivity, but their use is subject to a considerable number of interferences. These interferences are due both to cations and anions. They include colored cations, such as nickel and copper, that do not react with the reagent, as well as colorless cations capable of reacting with the reagent to yield colored substances. Anions such as tartrate and fluoride also interfere by preventing or inhibiting the formation of the colored reaction product. As in the gravimetric methods, a preliminary separation of interferences is usually required before the colorimetric measurements are made.

Polarographic reductions of titanium complexes have been carried out in media containing one or other of oxalic, citric, tartaric or ethylenediaminetetraäcetic acids(17,18,19). Based on such reductions, mainly in tartaric acid media, there have been developed methods(20,21,22) for the direct polarographic determination of titanium in minerals, several alloys, and other substances posing fewer interference problems than modern high temperature alloys.

Titrimetric methods for the determination of titanium have also been developed. The earlier of these methods(23) is based on the reducing action of the titanium (III) ion. The titanium, usually the titanium (IV) ion as a result of dissolution and separation techniques, is first reduced by amalgamated zinc to titanium (III) ion. The titanium (III) ion is then either titrated directly with standard potassium permanganate solution, or allowed to reduce a known excess of iron (III) ion. In the latter case, the titanium is indirectly determined by titrating with standard potassium permanganate solution the iron (II) ion produced. This method is subject to many interferences.

Amperometric titrations are a relatively recent development in the field of titrimetric analysis. Kolthoff and Johnson(8) investigated m-nitrophenylarsonic acid as a reagent for titanium in amperometric titrations, but were unable to obtain analytically useful results. These authors did not make a detailed study of the reaction between titanium and m-nitrophenylarsonic acid. Their results did indicate, however, that the lack of constancy of composition of the precipitate was the major difficulty in perfecting a useful amperometric titration method for titanium.

APPARATUS

Most polarographic measurements were made using a Tinsley recording polarograph, type V722/13 (Tinsley Industrial Instruments, London, England). Some were carried out with a Sargent Model XX recording polarograph (E.H. Sargent and Company, Chicago, U.S.A.) operated at a sensitivity setting of 2/49 and a damping setting of 3.

All polarographic measurements were carried out at 25.0°C. ± 0.5° C., using a conventional "H" type of polarographic cell, electrolytic contact to the saturated calomel reference cell being made by a potassium chloride-agar bridge. The capillary for the dropping mercury electrode was constructed from a length of marine barometer tubing supplied by E.H. Sargent and Company.

The amperometric titrations were carried out using a Sargent Model XI photographically recording polarograph. The constant polarizing potential was obtained at an applied potential setting of 0.35 and a bridge potential setting of 2.00 volts. This supplied a potential of -0.70* volts to the dropping mercury electrode. The limiting diffusion current was registered on the galvanometer scale of the polarograph, with the galvanometer sensitivity shunt setting at 200, and was recorded in units of scale divisions.

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* Subsequent work indicated that -0.50 volts would have been a more suitable setting.

The dropping mercury electrode was constructed from a piece of marine barometer tubing. The titration cell was a 50 or 100 ml. Griffin beaker, into which was placed a glass bubbling tube, arranged so that the stream of nitrogen impinged on the bottom of the beaker, thoroughly stirring the contents of the titration cell. The reference cell was a saturated calomel electrode; electrolytic contact with the solution was made through a potassium chloride-agar bridge.

Measurements of pH were made with a Beckman Model G pH meter, (Beckman Instruments Inc., South Pasadena, U.S.A.) using either a G-1190-80 or 290 glass electrode, along with a saturated calomel reference electrode of appropriate size.

A Coleman spectrophotometer, Model 11 (Coleman Electric Company, Maywood, U.S.A.) was used for the colorimetric measurements.

The mercury cathode cell was constructed from a wide-mouthed, 250 ml. Erlenmayer flask(22). A three-way stopcock was attached to the bottom of the flask, which had previously been blown to resemble the bottom of a Kjeldahl flask. A levelling bulb to adjust the level of mercury in the cell and to facilitate the removal of spent mercury was attached to one outlet of the stopcock by means of rubber tubing. The second outlet was for the removal of the electrolyte from the cell after electrolysis. Through a two-holed rubber stopper was inserted a platinum anode, formed into a flat spiral which was parallel to the mercury surface.

An "Exax" 10 ml. buret, graduated in 0.05 ml. divisions was used for the amperometric titrations. All other glassware was "Exax" or "Normax" brand manufactured by the Kimble Glass Company (Toledo, U.S.A.).

REAGENTS

The m-nitrophenylarsonic acid was Eastman Grade obtained from Distillation Products Industries (Rochester, U.S.A.). This was dissolved in water to make a 0.8% solution. The solution was adjusted to a pH of 1.2 with 60% perchloric acid, and, after standing for 24 hours at room temperature, was filtered to remove any insoluble material.

Four stock solutions of titanium were used as sources of titanium during this research. Stock solution No. 1 was prepared by dissolving 0.83 g. of titanium dioxide (Standard No. 154 of the National Bureau of Standards, Washington, U.S.A.) in 5.0 ml. of boiling 18 M sulfuric acid containing 3 g. of ammonium sulfate. After cooling, the material was added to 300 ml. of 1.7 M perchloric acid. The sulfate was removed by precipitation with barium chloride and filtration. The filtrate was diluted to 500 ml. with a perchloric acid solution of pH 1.2, giving a solution with a titanium concentration of 1 mg. per ml.

Stock solution No. 2 was prepared by dissolving 4.99 g. of titanium dioxide in 28 ml. of boiling 18 M sulfuric acid containing 12 g. of ammonium sulfate. After cooling, the material was added to 400 ml. of 1.7 M perchloric acid containing 140 g. of barium chloride dihydrate. The mixture was digested on a hot plate for 4 hours, and then the barium sulfate was removed by filtration. The filtrate was diluted to 500 ml. This solution was analyzed for titanium according to the method of Kolthoff and Sandell(24) and found to contain 5.22 mg. titanium per ml.

Stock solution No. 3 was prepared by dissolving 12 g. of a Discaloy alloy in perchloric acid in a way similar to that described under "Polarographic Method" (vide infra). Small samples were then electrolyzed in the mercury cathode cell until a spot test for iron with thiocyanate was negative. The electrolyzed samples were combined to make 250 ml. of solution, the concentration of which was 0.8 mg. of titanium per ml.

A solution of titanium chloride was prepared from C.P. grade titanium chloride (Fisher Scientific Company, Pittsburg, U.S.A.) by diluting a 3.0 ml. sample to 100 ml. with 1.2 M hydrochloric acid. Stock solution No. 4 was prepared by diluting 10.00 ml. of this solution to a total volume of 100 ml. with 1.2 M hydrochloric acid. The concentration of titanium in this solution was approximately 1.3 mg. per ml.

A 1% gelatin solution, used to suppress polarographic maxima when methyl red was not present in solution, was prepared from Eastman Kodak Pigskin Gelatin (Eastman Kodak Company, Rochester, U.S.A.).

The mercury used for the mercury cathode cell and the dropping mercury electrode was purified by bubbling for at least 10 hours with 10-15% nitric acid, washed several times with water, and distilled twice in vacuo.

Nitrogen to de-aerate and stir the solutions was purified by passing the commercial product through an alkaline solution of potassium pyrogallate and washing with water.

Tiron (disodium -1,2-dihydroxybenzene-3,5-disulfonate) used in the colorimetric work was supplied by the LaMotte Chemical Products Company (Baltimore, U.S.A.) The reagent solution was prepared by dissolving 4 g. of the salt in 100 ml. of water.

All other chemicals used in this work were of analyzed grade.

"Tartrate solution" was prepared by making a 0.5 M solution of tartaric acid strongly alkaline with 8 M sodium hydroxide. The final tartrate concentration in this solution was approximately 0.35 M.

"Wash liquid" was an aqueous solution of perchloric acid of pH 1.2.

The acetic acid-sodium acetate buffer required in the colorimetric work was 0.5 M in acetic acid and 0.5 M in sodium acetate.

The "supporting electrolyte" used in the amperometric titrations was a 2 M aqueous solution of sodium perchlorate, adjusted to pH 1.2 with perchloric acid. The solution contained 50 ml. per l. of a methyl red solution (20 mg. of methyl red dissolved in 100 ml. of 95% ethanol).

EXPERIMENTAL RESULTS

(a) Variables Influencing Precipitation of Titanium m-Nitrophenylarsonate

A careful study was made of variables that were found to influence the quantitative precipitation of titanium with m-nitrophenylarsonic acid:pH and anion concentration, concentration of titanium, concentration of reagent, heating of the precipitate, and rate of the reaction.

(i) pH and Anion Concentration

During the early work on this problem it became clear that the degree of completeness and the nature of the precipitation of titanium by m-nitrophenylarsonic acid depends on the pH of the medium. At low pH values, no precipitation occurs, whereas at relatively high pH values a mixed precipitate, probably in part hydrous oxide, is obtained. Only at intermediate pH values, hereafter referred to as the "optimum pH", is the precipitation of titanium as the m-nitrophenylarsonate accomplished quantitatively.

The position of the optimum pH is dependent on the concentration of any anion capable of complexing with the titanium, as the following paragraphs having to do with the sulfate ion will show.

Curves relating the extent of precipitation to the pH of precipitation were constructed as shown in Figure I. Each point on these curves was obtained by adding to 5.00 ml. of stock solution No. 1

CAPTION FOR FIGURE I

Nature and Degree of Precipitation as a Function of pH of Precipitation, for Solutions Containing Sulfate

In the experiments represented by Curve A, the concentration of sulfate was 1.1×10^{-3} M; by Curve B, 4.1×10^{-3} M; and by Curve C, 3.6×10^{-2} M.

(to follow page 15)

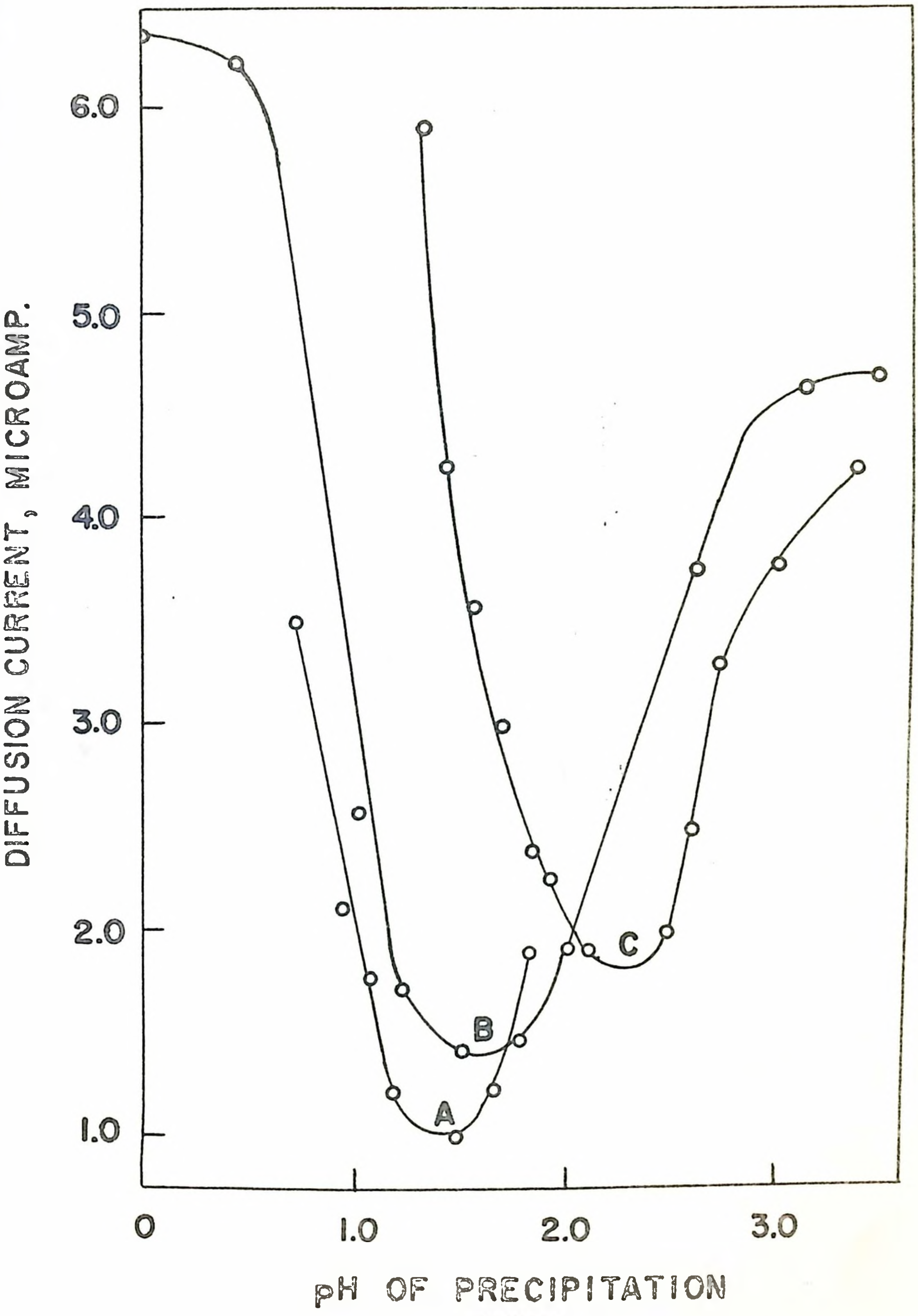
DIFFUSION CURRENT, MICROAMP.
6.0
5.0
4.0
3.0
2.0
1.0
0
1.0
2.0
3.0
pH OF PRECIPITATION
A
B
C

FIGURE I

sufficient sulfuric acid to give (in the final volume of 110 ml.) the sulfate concentration stated in the caption of the Figure, then water to give a volume of 100 ml., and then 10.00 ml. of 0.8% m-nitrophenylarsonic acid solution. Both the m-nitrophenylarsonic acid solution and the diluted titanium solution were separately adjusted to the same desired pH, using 7.5 M ammonia or 2.5 M perchloric acid, before being brought together. The white precipitate produced on mixing was digested for one hour at room temperature and the pH of the mixture then determined. The pH values plotted are, in each case, the mean of the two values, which differed by 0.1 pH units or less. The precipitate was filtered, washed with "wash liquid", and the filtrate and washings together adjusted to a pH of 4.0 with 7.5 M ammonia. The solution was then buffered with 50 ml. of a 0.50 M solution of potassium hydrogen phthalate, brought to a total volume of 250 ml. with water, and polarographed. The diffusion current corresponded to the concentration of unreacted m-nitrophenylarsonic acid, and thus was an indication of the composition of the precipitate.

The lowest points on the curves correspond to the pH values at which titanium is precipitated essentially completely as the m-nitrophenylarsonate*. These points are, by definition, the optimum pH. Points on the curves at lower pH values correspond to incomplete precipitation of titanium; at pH values higher than the optimum, the

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* See Appendix I.

precipitation is quantitative, but, in all probability, hydrous oxide as well as titanium m-nitrophenylarsonate is precipitating.

Although, at the optimum pH, the titanium was "quantitatively" precipitated* in the experiments summarized in Figure I, it is evident that the lower the concentration of sulfate, the more complete is the precipitation and the lower is the pH value at which it occurs. The position of the optimum pH as a function of sulfate concentration is shown in Table II.

Tests showed that while diluted solutions of perchloric acid did not dissolve high-temperature alloys, hot 72% perchloric acid was a satisfactory dissolving medium. The use of this acid made it possible to precipitate titanium from a perchloric acid solution during the analysis of the alloys.

The optimum pH of precipitation for a perchloric acid solution was determined from a new curve, Figure II, relating the extent and nature of the precipitation to the pH of precipitation. Each point on this curve was obtained by adding to 5.00 ml. of stock solution No. 3 sufficient water to give a volume of 100 ml., and then 50 ml. of 0.8% m-nitrophenylarsonic acid solution. Both the m-nitrophenylarsonic acid solution and the diluted titanium solution were separately adjusted to the same desired pH, using 7.5 M ammonia or 2.5 M perchloric acid, before being brought together. The precipitates were digested for one hour at room temperature, and the pH of the mixture was then determined.

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* See Appendix I.

TABLE II

EFFECT OF SULFATE ION ON OPTIMUM pH FOR PRECIPITATION

Sulfate Concentration	Optimum pH
0 ($HClO_4$)	0.80 - 1.50
0 (HCl)	1.20
1.1×10^{-3} M	1.20 - 1.50
4.1×10^{-3} M	1.62 - 1.80
36.0×10^{-3} M	2.25 - 2.35

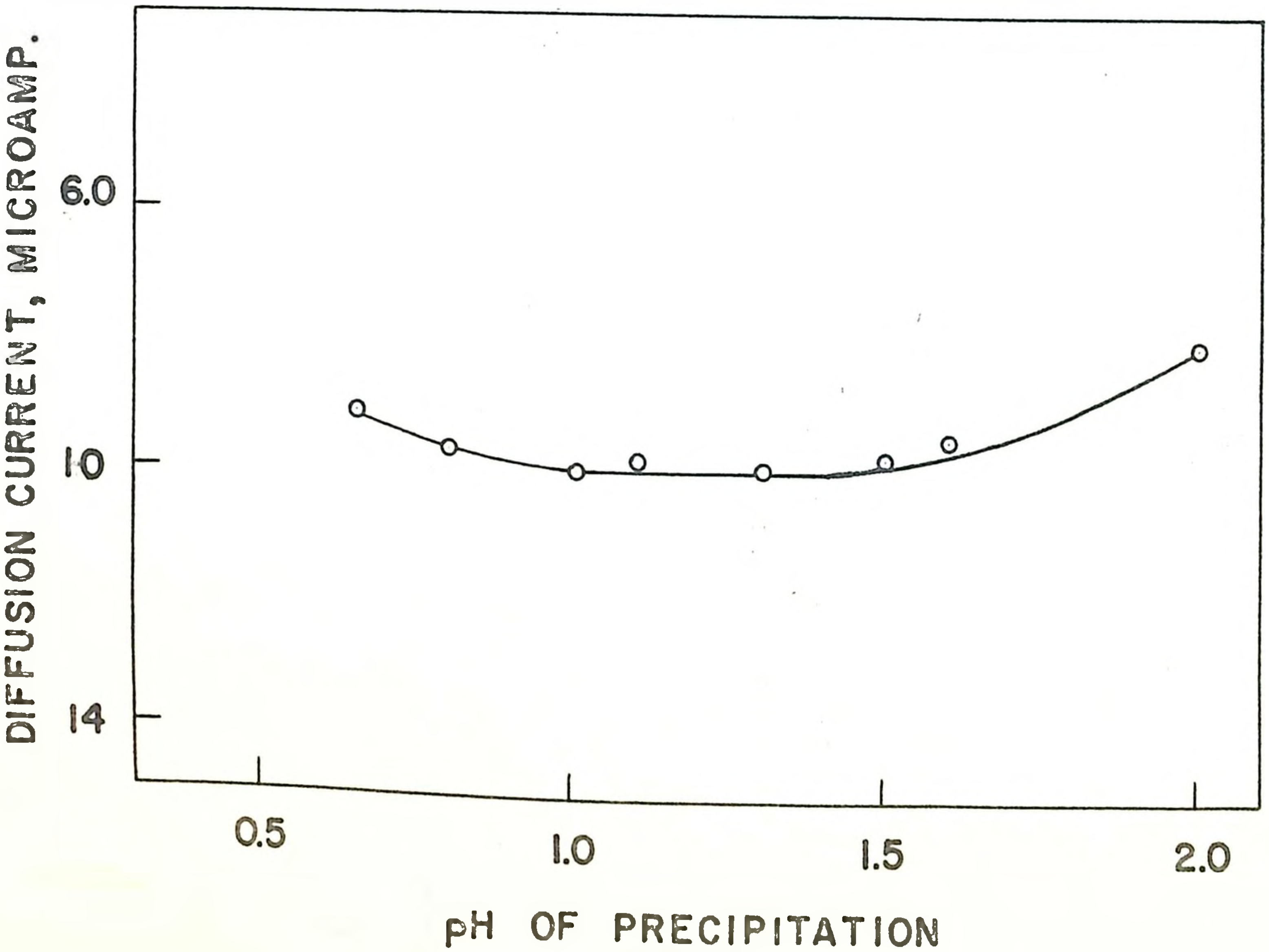

FIGURE II
Nature and Degree of Precipitation as a Function of pH of Precipitation; for Solutions of Perchloric Acid.

As before, the pH values plotted are the mean of the two values, which differed by 0.1 pH unit or less. The precipitate was filtered, washed, and dissolved in "tartrate solution", as described in the section on "Polarographic Method" (vide infra). The concentration of m-nitrophenylarsonic acid was determined polarographically.

The polarographic diffusion currents correspond to the amount of reacted m-nitrophenylarsonic acid (rather than to the unreacted m-nitrophenylarsonic acid, as in the experiments involving sulfate ion) and therefore are directly related to the composition of the precipitate. In Figure II the diffusion current has been plotted as a function of the pH of precipitation. The lowest points correspond to essentially complete (at least 99.9%) precipitation of the titanium as shown by colorimetric examination of the filtrates*. The higher points indicate, on the left, incomplete precipitation and, on the right, the probable precipitation of some of the titanium as the hydrous oxide. The curve shows that the optimum pH for precipitation in such a perchloric acid solution is in the range 0.8 to 1.5, with the midpoint at pH 1.2.

The optimum pH of precipitation for a hydrochloric acid solution was determined from another curve relating the extent and nature of precipitation to the pH of precipitation. This curve was constructed in the same manner as was the curve for the perchloric acid solutions. Four milliliters of stock solution No. 4 was precipitated at various pH values, 6 M hydrochloric acid being used to adjust the solutions to the

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* See Appendix I.

desired pH. The titanium was precipitated with 50 ml. of 0.8% m-nitrophenylarsonic acid solution that had been adjusted to the same pH with hydrochloric acid.

This curve showed that for a hydrochloric acid solution there was no range of optimum pH, the "range" being reduced to a point at pH 1.2.

(ii) Concentration of Reagent

The validity of a method for titanium based on the polarographic determination of m-nitrophenylarsonic acid precipitated by titanium depends not only on the quantitative precipitation of titanium but also on the constancy of the composition of the precipitate. Precipitations must be carried out under conditions that permit the formation of a precipitate of reproducible composition.

It was therefore necessary to establish the experimental conditions which allow a precipitate of constant composition to be produced. The results of the work on the effect of pH on precipitation had indicated that, although a modest excess (i.e., 10 ml. of 0.8% reagent solution for 5 mg. of titanium) of m-nitrophenylarsonic acid would quantitatively precipitate titanium, a substantial excess appeared to be necessary to produce a precipitate of constant composition.

The magnitude of this excess was determined from a curve relating the amount of m-nitrophenylarsonic acid present in the precipitate to the volume of reagent made available during precipitation. Each point on the curve was obtained by precipitating, at pH 1.2, 4.0 mg. of titanium (stock solution No. 3) in a total volume of 100 ml., with increasing amounts of m-nitrophenylarsonic acid (from 5 to 75 ml. of reagent) so that in these experiments the ratio of the moles of reagent to moles of titanium varied from 2:1 to 30:1. The amount of organic reagent was found by polarographing the dissolved precipitate. The polarographic diffusion current, which was related to the amount of m-nitrophenylarsonic acid arising from the precipitate, was plotted as a function of the volume of reagent.

The curve rose until 30 ml. of reagent had been added, and then became horizontal, presumably because the precipitate had become constant in composition. It was concluded that in a total volume of 150 ml., for every 4 mg. of titanium present a minimum of 30 ml. of reagent solution must be present for satisfactory precipitation. This is in the ratio of about 10 moles of reagent to one mole of titanium. In all subsequent precipitations involving up to 5 mg. of titanium, 50 ml. of the reagent solution were used. Colorimetric tests* on the filtrate showed that 99.9% or more of the titanium had been precipitated; in fact, the precipitation of titanium was "quantitative" when the excess of reagent was much less than that required to give a precipitate of constant composition.

(iii) Concentration of Titanium

The amount of m-nitrophenylarsonic acid associated with abou 4.0 mg. of titanium is quite large relative to the potential sensitivity

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* See Appendix I.

of polarographic measurements. After dissolution, this amount of m-nitrophenylarsonic acid can be detected readily at a polarograph setting that is only 1/200th of the maximum sensitivity of the instrument. It appeared desirable therefore, to conduct subsequent analyses in solutions only one-tenth as concentrated as those used in the experiments so far described. Unfortunately the analyses obtained with the more dilute solutions were very erratic. The discrepancies appeared to be due to solubility losses that become relatively more significant in the more dilute solutions.

A study was made of the minimum concentration of titanium that could be readily determined. Twenty-five milliliters of stock solution No. 3 were diluted to 100 ml. with 1.6 M perchloric acid. Various sized aliquot samples of this solution, along with aliquot samples of undiluted No. 3 stock solution, were then diluted to 80 ml. so that a series of solutions containing from 0.5 to 50 mg. of titanium per liter was available. The titanium in these solutions was precipitated at pH 1.2 with graduated amounts of m-nitrophenylarsonic acid solution so that from a twelve to thirty-six fold excess of reagent was present. The titanium in the precipitate was assessed from the polarographic diffusion current given by the m-nitrophenylarsonic acid after dissolution of the precipitate in the manner described earlier (page 21).

The diffusion current given by the m-nitrophenylarsonic acid was plotted as a function of the original titanium concentration. This plot produced a straight line through the origin, but there was scattering of the points in the region of low titanium concentrations. The scattering of the points for concentrations of titanium up to 10 mg. per l. is very likely due to solubility losses which prevent the quantitative recovery of titanium. Beyond 10 mg. per l., the solubility losses become, relatively, sufficiently low that quantitative recovery is possible.

If the solution contains much above 4.0 mg. of titanium the bulk of the precipitate is such that it is not readily handled. In the polarographic method, as finally developed, from 2.3 to 3.7 mg. of titanium were precipitated in a total volume of about 150 ml. In the amperometric titration, where there is no need to filter the precipitate, an upper limit to the amount of titanium is not of such consequence. A lower limit of titanium concentrations in amperometric titrations was not determined, but titrations were not attempted for titanium concentrations lower than 120 mg. per l.

Losses may also be experienced due to the ease with which titanium is hydrolyzed and with which the m-nitrophenylarsonate precipitate is peptized. For these reasons all washing operations were carried out using an acid solution (a solution of perchloric acid of pH 1.2).

(iv) Heating of the Precipitate

The addition of the reagent to a solution containing titanium resulted in the immediate production of a finely divided precipitate. It was found that the precipitate coagulated nicely within one hour on digestion at room temperature, but much more rapidly at 90°C.

Unfortunately, the composition of the precipitate digested at the higher temperature was not constant, even in the presence of a thirty-six fold excess of reagent.

The effect of heating on the composition of the precipitate was investigated by precipitating 5.00 ml. of stock solution No. 1 at pH 1.2 with 50, 60, 100 and 150 ml. of reagent solution. These precipitates were digested on a hot plate at 90°C., until the precipitates had coagulated to an easily filterable form, which usually occurred within five minutes. The amount of m-nitrophenylarsonic acid in each precipitate was assessed polarographically.

The composition of the precipitate, as indicated by the diffusion current, was plotted as a function of the volume of reagent added. This plot showed that the composition of the precipitate, after heating, was not constant, even in the presence of 150 ml. of reagent. The advantage of rapid coagulation on digestion at 90°C. was more than offset by the disadvantage that such a digestion produces a precipitate of variable composition. The idea of facilitating coagulation by digestion at an elevated temperature was therefore abandoned.

(v) Speed of Precipitation

The ideal amperometric titration involves an almost instantaneous precipitation. The reaction of titanium and m-nitrophenylarsonic acid is, unfortunately, not of this type.

The time required for the reaction to become "complete" for purposes of amperometric titrations was determined from curves, obtained during an amperometric titration, relating the concentration of reagent to the time of reaction. The concentration of the reagent, which is proportional to the limiting diffusion current, was plotted continuously by a Tinsley recording polarograph maintained at a constant polarizing potential of -0.7 volts, a sensitivity of 50 microamperes per full-scale deflection, and a damping setting of 2. Since the chart flowed past the pen at a known constant speed, it was possible to convert any linear chart distance into an interval of time. The tracing obtained in this way was in effect a plot of the reagent concentration as a function of time.

The rate of precipitation was followed at three different regions of the titration curve: when titanium was present in considerable excess, near the equivalence point, and when the reagent was present in considerable excess.

The curves showed that after each addition of reagent there was a small, steady decrease in reagent concentration. Some minutes after the addition of reagent, this rate of decrease became slower; eventually it was so slow that the concentration of reagent was, for purposes of an amperometric titration, constant. The initial decrease was assumed to be due to the relatively rapid removal of reagent by precipitation. To be significant, points on the titration curve must refer to essentially complete reaction of titanium and m-nitrophenylarsonic acid. The time necessary for the reaction to proceed to the state where reproducible results could be obtained was deduced by analyzing the curves in the following way.

Two straight lines were drawn through the curves, the first in the region of initial drop, and the second in the region of apparently constant reagent concentration. The point of intersection of these lines corresponded to the time when the reaction had reached the point where the concentration could be measured with reproducible accuracy.

This study showed that before the equivalence point, the concentration may not be measured until three minutes after the addition of reagent, whereas around the equivalence point the concentration may be measured within two minutes. During the titration in this region, therefore, galvanometer deflections may not be recorded until three minutes have elapsed after the addition of reagent. Beyond the equivalence point, an equivalent amount of reagent has reacted with the titanium, and further addition of m-nitrophenylarsonic acid is not expected to react rapidly. This was reflected by the almost constant concentration of the reagent at any given time in this region, even within one minute after addition of reagent. In this region, galvanometer deflections were therefore recorded immediately after addition of the reagent.

The effect of the stirring by the bubbling of nitrogen during the titration was also investigated. The stirring action was found to destroy the quiet solution conditions necessary for accurate diffusion current measurements. Diffusion current measurements were accordingly not made until one minute after stirring ceased.

(b) Composition of the Precipitate

During this work, the titanium m-nitrophenylarsonate was produced under two widely differing conditions, each of which produced a precipitate of a distinctive composition. There were investigated the compositions of the precipitate produced under the polarographic conditions, involving a large excess of reagent, and under the conditions of amperometric titration, involving nearly equivalent amounts of reagent.

(i) Amperometric Titration

Previous work had shown that 2.00 ml. of stock titanium solution No. 2 required approximately 6 ml. of m-nitrophenylarsonic acid for titration. Accordingly, 2.00 ml. of stock solution No. 2, containing 10 mg. of titanium, was precipitated under the conditions of an amperometric titration (vide infra) with 6 and 12 ml. of m-nitrophenylarsonic acid. These precipitates were filtered on Whatman No. 42 filter paper and washed thoroughly with either a 5% aqueous solution of tartaric acid or with "wash liquid".

The precipitates were dissolved in 10 ml. of "tartrate solution", and the filter papers thoroughly washed with water. Both the dissolved precipitate and washings were caught in 100 ml. volumetric flask, and diluted to the mark with water. The solutions of dissolved precipitate were polarographically analyzed for m-nitrophenylarsonic acid, and colorimetrically analyzed for titanium using hydrogen peroxide.

In the polarographic analyses for m-nitrophenylarsonic acid, 25.00 ml. aliquot samples of the solution of dissolved precipitate were pipetted into 100 ml. volumetric flasks. The samples were adjusted to the methyl red end point using 5 M perchloric acid. Thirty ml. of 0.50 M potassium hydrogen phthalate were added, the solution diluted to the mark with water, and polarographed using the Sargent XX polarograph.

The m-nitrophenylarsonic acid required for the calibration curve was purified by the method given in Organic Syntheses(25), starting with the commercial product referred to earlier.

In the colorimetric analyses for titanium, 10.00 ml. aliquot samples of the solution of dissolved precipitate were pipetted into 50 ml. volumetric flasks. Then were added 20 ml. of water, 10 ml. of 72% perchloric acid, and 5 ml. of 3% hydrogen peroxide, and finally sufficient water to dilute to the mark. The intensity of the color was measured with the Coleman spectrophotometer at a setting of 425 mμ, using matched cylindrical cuvettes.

The calibration curve for this colorimetric analysis was prepared by diluting 10.00 ml. of stock solution No. 2 to 100.0 ml. with 10 ml. of 72% perchloric acid and water. Into 100 ml. volumetric flasks there were pipetted 1.00, 2.00, 3.00, 4.00, 5.00 and 6.00 ml. aliquot samples of this diluted titanium solution. Twenty ml. of 72% perchloric acid, 2.00 ml. of "tartrate solution", and 10 ml. of 3% hydrogen peroxide were added, and then water to bring the solution to the mark. The color intensity was measured with the Coleman spectrophotometer.

The results of these analyses are summarized in Table III. The precipitate produced under the conditions of an amperometric titration

TABLE III

COMPOSITION OF PRECIPITATE PRODUCED UNDER CONDITIONS OF AN AMPEROMETRIC TITRATION

Precipitate No.*	Volume of Reagent Added, ml.	Moles of Titanium x 10^4	Moles of m-Nitrophenylarsonic Acid x 10^4	Moles of Reagent per Mole of Titanium
1	6.0	0.16	0.26	1.61**
2	6.0	1.66	1.40	0.84
3	6.0	1.48	1.37	0.93
4	12.0	2.07	1.88	0.91
5	12.0	2.15	1.96	0.91
6	7.0	1.93	1.63	0.85
7	7.0	1.81	1.75	0.97
8	12.0	2.18	2.37	1.09
9	12.0	2.25	2.34	1.04

* Precipitates 1 to 5 inclusive were washed with a 5% aqueous solution of tartaric acid; precipitates 6 to 9 inclusive were washed with "wash liquid".

** For discussion of this apparent anomolous value, see page 45.

appears to be a monoarsonate, although the results, for precipitates 2 to 9 inclusive, are not as precise as one might wish.

(ii) Polarographic Method

Precipitates that had been produced during the work with high-temperature alloys were analyzed to determine their composition. Values for the titanium content of these alloys, and hence of the precipitates, were available from both polarographic analyses and the manufacturer. For the determination of the amount of m-nitrophenylarsonate in these precipitates, a second calibration curve was constructed using the purified m-nitrophenylarsonic acid described earlier. For all alloys, the ratio of titanium to m-nitrophenylarsonic acid was calculated from the polarographic analyses for titanium. The calculations are summarized in Table IV.

In Table IV two values for the ratio of titanium to m-nitrophenylarsonic acid are given for each of the alloys K42B 131 and K42B 601. In the case of each of these alloys, the unbracketed ratio is based on the titanium content of the alloy as found by polarographic analyses dependent on a calibration using a standard sample of Inconel W. The other ratio (Value given in brackets) is based on the titanium content of the alloy as given by the manufacturer. There are good reasons for believing that the titanium values of Company D are in error (see "Discussion", page 46). If the bracketed values are ignored, the results show that a di-m-nitrophenylarsonate is produced in the polarographic method, i.e., under conditions in which there is present a great excess of m-nitrophenylarsonic acid.

(c) Polarography of m-Nitrophenylarsonic Acid

Low concentrations of m-nitrophenylarsonic acid are easily detec

TABLE IV

COMPOSITION OF PRECIPITATE PRODUCED UNDER CONDITIONS OF THE POLAROGRAPHIC METHOD

Alloy	Moles m-Nitrophenyl-arsonic Acid x 10^5	Moles Titanium x 10^5	Moles of Reagent per Mole of Titanium
Company A			
A-286	14.0	6.65	2.10
Waspalloy	14.7	7.40	1.98
Discaloy No. 1	13.2	6.64	1.98
Company B			
Discaloy No. 2	14.3	7.05	2.03
Discaloy No. 3	12.8	6.30	2.03
Company C			
Inconel X	13.7	7.10	1.93
Company D			
K42B 131	12.4	6.22 (7.16)	2.00 (1.73)
K42B 601	13.9	6.87 (8.00)	2.02 (1.74)

polarographically. The height of the wave, or the diffusion current, can be easily measured with good precision. The wave used in this work corresponds to the reduction of the nitro group$^{(26)}$ at the dropping mercury electrode in a solution buffered at pH 4.0 with 0.15 M potassium hydrogen phthalate. Although m-nitrophenylarsonic acid can give three reduction waves, only one appears at a pH of 4.0. This probably corresponds to the reduction of the nitro compound to the phenylhydroxylamine. Because the diffusion current given by the organic reagent was found to vary with changes in pH, as had been previously reported$^{(27)}$, a good buffer is required to ensure analytically useful results. Potassium hydrogen phthalate at a concentration of 0.15 M serves well both as a buffer and as a supporting electrolyte. When methyl red is also present in solution, as it is in the recommended procedures, polarographic maxima are not observed. The diffusion current given by the m-nitrophenylarsonic acid is linearly related to the amount of titanium in the original solution, as shown in Figure III.

(d) Procedures and Results

(i) Amperometric Titrations

Aliquot samples of No. 2 stock solution of titanium in amounts from 1.00 to 4.00 ml., were pipetted into the titration cell. Approximately 30 ml. of water were added, and the pH of the solution was adjusted to 1.2 by carefully adding 2.5 M ammonia. The pH of the solution during this operation was followed with a Model G pH meter equipped with a No. 290 glass electrode. Five ml. of "supporting electrolyte" were

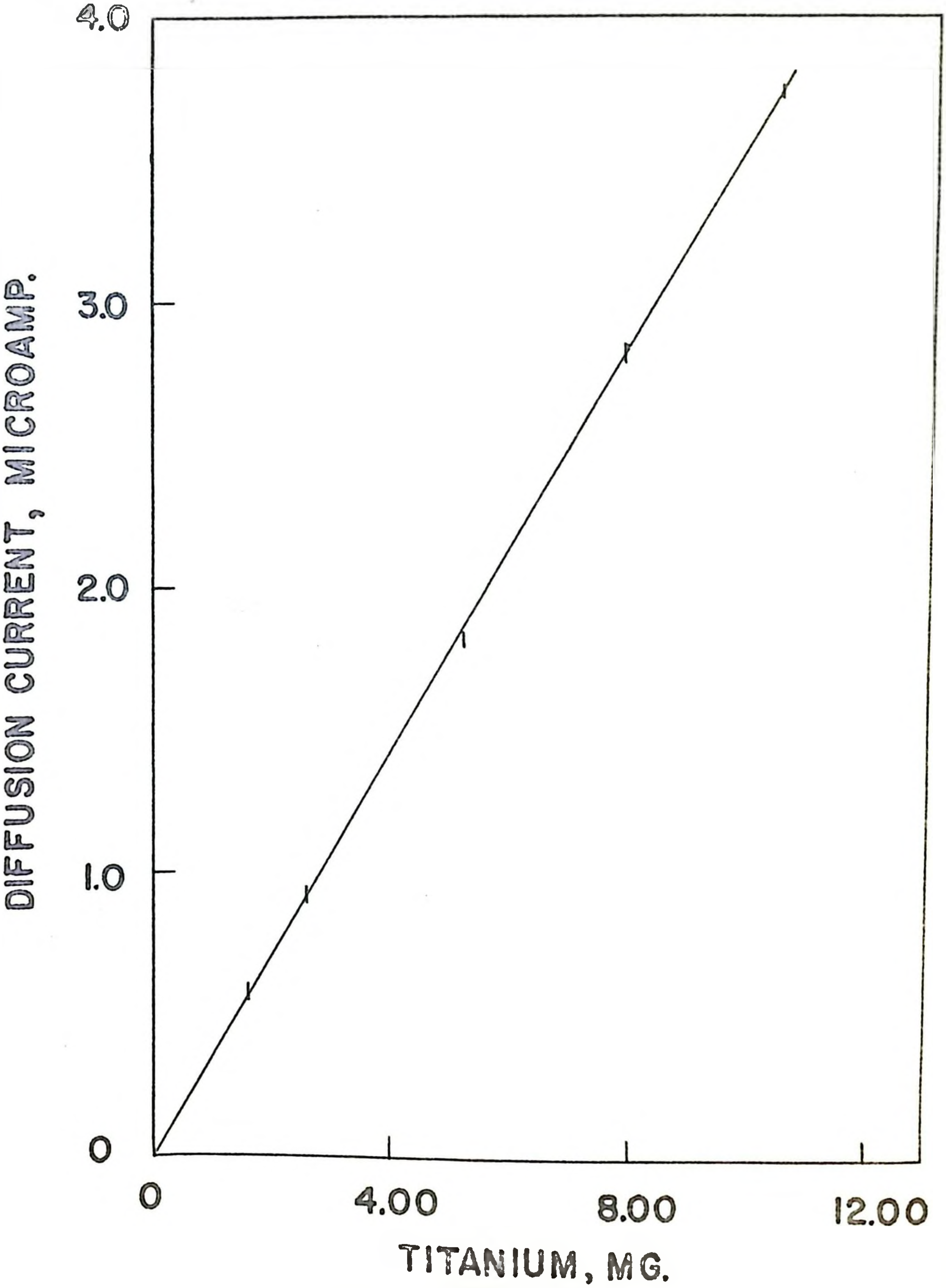

FIGURE III
Calibration Curve for Titanium

added, bringing the total volume of the solution to approximately 50 ml.

Before recording the first galvanometer deflection, purified nitrogen was bubbled through the solution for five minutes. In the titration, four points before and after the equivalence point were determined. The reagent was added in 0.5 and 1.0 ml. increments, followed by stirring for three or one minutes (depending on whether the point being determined was before or after the equivalence point). A one-minute waiting period for the restoration of quiet solution conditions was observed before the galvanometer deflection was recorded.

The galvanometer deflections were corrected for the dilution effect, and then plotted as a function of the volume of reagent added. The equivalence point was taken as the intersection of the two lines drawn through the experimentally found points. A typical titration curve is reproduced in Figure IV. The results of these titrations are tabulated in Table V.

(ii) Polarographic Method

A 1.2 to 2.0 g. sample of alloy turnings (containing about 2% titanium) was accurately weighed, placed in a 250 ml. round-bottomed standard taper flask, and covered with 40 ml. of 72% perchloric acid. A reflux condenser was attached to the flask, and the whole inclined at an angle 60° to the horizontal. The contents of the flask were heated to boiling, whereupon the alloy was readily attacked. Heating was continued until all of the metal had dissolved, leaving only a white siliceous residue.

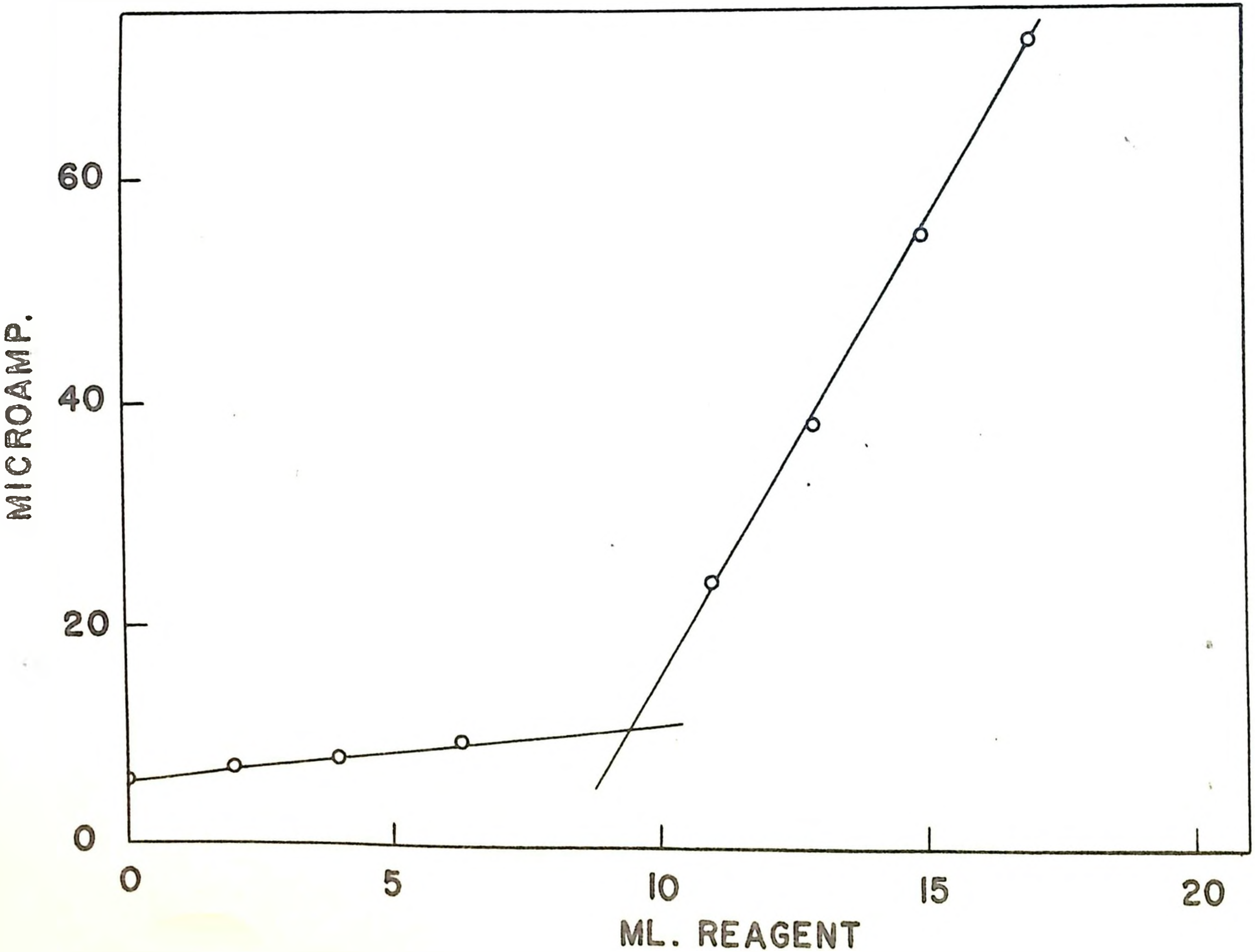

FIGURE IV
Amperometric Titration Curve

TABLE V

RESULTS OF AMPEROMETRIC TITRATIONS

Volume of Sample, ml.	Volume of Titrant Used, ml.	Average Volume of Titrant, ml.	Ratio of $\frac{\text{Volume of Titrant}}{\text{Volume of Sample}}$
3.00	9.48	9.47 ± 0.05	3.16
3.00	9.42		
3.00	9.50		
3.00	9.43		
2.00	6.35	6.34 ± 0.06	3.17
2.00	6.28		
2.00	6.35		
4.00	12.75	12.75	3.19
1.00	3.20	3.20	3.20

The contents of the flask were quantitatively transferred to a 250 ml. volumetric flask, and made up to the mark with "wash liquid". A 25 ml. aliquot sample of the solution was transferred to the mercury cathode cell, diluted to about 70 ml. with "wash liquid", and electrolyzed (at a current density of 0.15 amp./cm.^{2} and 5 volts) until a negative spot test for iron using thiocyanate was obtained. (This, in general, required about half an hour). The solution was transferred to a 250 ml. beaker and adjusted to the optimum pH of 1.2 ± 0.4 with 7.5 M ammonia. At this point the total volume of solution was about 150 ml. Fifty ml. of the 0.8% aqueous solution of m-nitrophenylarsonic acid were then added, resulting in the formation of a precipitate.

The precipitate was digested at room temperature for one hour, and was then filtered on Whatman No. 42 paper, washed three times with "wash liquid" and dissolved by adding dropwise 6 ml. of near boiling "tartrate solution". The solution was caught in a 100 ml. volumetric flask and adjusted to the methyl red end point with 5 M perchloric acid. Thirty ml. of 0.50 M potassium hydrogen phthalate were added, and the solution was brought up to the mark with water. The solution was deaerated by bubbling with purified nitrogen, and was polarographed at a countercurrent setting of 0, a galvanometer sensitivity of 20 microamperes per fullscale deflection, and a damping setting of 2. Four waves were recorded for each solution and the average wave height, measured by the slope intercept method, was calculated.

For calibration purposes a standard alloy sample (Inconel W) was analyzed with each batch of alloy samples under test. The titanium content of the standard alloy (2.32%) had been established by analyses of umpire grade carried out by the manufacturer, and subsequently satisfactorily confirmed by an independent polarographic method(22). The titanium contents of the original solutions of alloys under test were assessed by comparing the diffusion currents with that given by the solution from the standard alloy. This procedure eliminated any effect due to day-to-day variations in instrumentation.

The method was applied to several different high-temperature alloys, with the results shown in Table VI.

TABLE VI

RESULTS OF POLAROGRAPHIC ANALYSES

Alloy*	Polarographic Value		Standard Value %
	Individual %	Average %	
Company A			
A-286	1.94, 1.92, 1.93	1.93	1.92
Waspalloy	2.26, 2.26, 2.21	2.24	2.27
Discaloy No. 1	2.15, 2.08, 2.12	2.12	2.09
Company B			
Discaloy No. 2	1.74, 1.71, 1.67	1.71	1.71
Discaloy No. 3	1.67, 1.65, 1.66	1.66	1.66
Company C			
Inconel X	2.36, 2.36, 2.36	2.36	2.43
Company D			
K42B 131	2.81, 2.86, 2.91	2.86**	2.85
K42B 601	2.22, 2.22, 2.20	2.21**	2.23

* For the gross composition of these alloys, see Table I, page 4.

** In these analyses a standard Discaloy sample supplied by Company D was used for calibration purposes. For all the other analyses a standard sample of Inconel W was used.

DISCUSSION

This work has shown that titanium can be quantitatively precipitated by m-nitrophenylarsonic acid and that this precipitation can be made the basis of an accurate method for the polarographic determination of titanium. It was also demonstrated that titanium can be titrated amperometrically by means of m-nitrophenylarsonic acid. The composition of the precipitate under conditions of an amperometric titration is apparently the mono-m-nitrophenylarsonate, and under conditions of the polarographic method, in which a large excess of reagent is used, the composition of the precipitate has been established as the di-m-nitrophenylarsonate. The polarographic method, in conjunction with a separational procedure using a mercury cathode cell, has been adapted to the analysis of high-temperature alloys. The titanium contents of several such complex alloys of widely different compositions have been successfully determined with good precision by the new method.

For the quantitative precipitation of titanium by means of m-nitrophenylarsonic acid, several variables must be controlled. The [illegible] important of these is the pH of the medium in which precipitation is carried out. The precipitation of titanium was found to be quantitative only over a rather narrow range of pH values. The position of the appropriate range of pH values depends on the nature and concentration of anions that complex with titanium. The effect of sulfate ion, a complexing anion, on the precipitation has been studied.

It has been shown that the lower the concentration of sulfate ion, the more complete is the precipitation of titanium, and the lower is the pH at which it is achieved. Both these observations are consistent with the fact that sulfate ion is known to complex with titanium. In the presence of perchlorate, rather than sulfate ion, titanium is precipitated by m-nitrophenylarsonic acid without difficulty, and the appropriate range of pH values is wider than when sulfate ion is present. The conditions recommended under "Procedures and Results" (*vide supra*) apply to perchloric acid solutions and permit a variation of ± 0.4 pH units from the optimum value of 1.2 while still achieving a quantitative precipitation of titanium.

For quantitative precipitation the concentration of titanium must not fall below a minimum level. Although very low concentrations of titanium yield a precipitate with m-nitrophenylarsonic acid under controlled conditions of pH, solubility losses make difficult the quantitative recovery of titanium from solutions containing less than 10 mg. per liter. In the polarographic method it is convenient to work with solutions containing not more than 4 mg. of titanium, for reasons connected with the bulk of precipitate. Although the amperometric method was not studied as extensively as the polarographic method, it was shown that amperometric titrations can be carried out in solutions containing from 120 to 450 mg. of titanium per liter.

The determination of titanium by the polarographic method depends on the formation of a titanium m-nitrophenylarsonate precipitate of constant composition. The obtaining of such a precipitate requires an appreciable excess of reagent. The excess used, somewhat larger than necessary, was about 18 moles of reagent to one mole of titanium.

The composition of the precipitate is affected by the temperature of digestion. Digestion at elevated temperatures promotes rapid coagulation of the precipitate, but this advantage is more than offset by the fact that a precipitate of variable composition is produced.

The reaction between titanium and m-nitrophenylarsonic acid requires several minutes to reach completion. The polarographic method automatically affords this time on account of the digestion period for the coagulation of the precipitate. In amperometric titrations, a waiting period of up to four minutes must be allowed between addition of reagent and measurement of the diffusion current. Such a delay is not unusual in amperometric titrations.

In summary, the variables of pH and anion concentrations, concentration of titanium, concentration of m-nitrophenylarsonic acid, heating of the precipitate and the speed of the reaction all have a bearing on the quantitative precipitation of titanium by means of m-nitrophenylarsonic acid.

In this work two types of titanium m-nitrophenylarsonate precipitate were encountered. The data of Tables III and IV show that the conditions of precipitation dictate whether a mono- or di-m-nitrophenylarsonate precipitate is produced. When the titanium is precipitated in the presence of a large excess of reagent, as in the polarographic method, a di-m-nitrophenylarsonate precipitate is formed. Under the conditions of an amperometric titration, where m-nitrophenylarsonic acid is never present in great excess, a mono-m-nitrophenylarsonate apparently results. This precipitate is unstable, in the sense that it can react with additional m-nitrophenylarsonic acid to form the di-m-nitrophenylarsonate. The composition of the precipitate produced in the presence of a small excess of reagent (Table III) is intermediate between that of the mono- and di-m-nitrophenylarsonate, and reflects this tendency of the mono-m-nitrophenylarsonate to change to the di-m-nitrophenylarsonate. This observation is consistent with the work of Kolthoff and Johnson who found, under their conditions, compositions varying between one and one and one-half moles of m-nitrophenylarsonic acid per mole of titanium(8).

The amperometric titration method is capable of giving reproducible results as shown in Table V. In comparison with some amperometric titrations, the precision of this method is only fair. Lack of better precision is probably due to the slow hydrolysis of titanium at pH 1.2.

This amperometric titration differs from that carried out by Kolthoff and Johnson in the type of anion present in the solution during the precipitation. The amperometric titrations reported in this work were performed in a perchloric acid solution of pH 1.2. Although Johnson(28) was able to obtain titration curves in a hydrochloric acid solution of pH 1.3 and 0.96, the end points were not accurate and the precision was very poor. He found that titanium m-nitrophenylarsonate was too soluble for successful titrations in a solution 0.2 M in hydrochloric acid (a pH of

0.7) and in a solution 0.2 M in perchloric acid and 0.05 M in hydrochloric acid, a pH of 0.6(28). Kolthoff and Johnson(8) do not appear to have carried out any amperometric titrations in perchloric acid solution. Their inability to titrate titanium successfully with m-nitrophenylarsonic acid may be attributed to failure to remove from solution anions capable of complexing with titanium and failure to study the optimum pH condition for the precipitation.

The determination of titanium by amperometric titration with m-nitrophenylarsonic acid is not of much practical significance, for it rather time-consuming and subject to more rigid control of conditions than is desirable. The work is of interest, however, in establishing that titanium can be amperometrically titrated with this reagent.

The results obtained in applying the newly developed polarographic method for titanium to the analysis of alloys of complex composition are summarized in Table VI. The "standard values" listed in this table were obtained in the laboratories of the companies that kindly supplied the samples, by colorimetric and gravimetric methods of an umpire grade. The accuracy of the polarographic method in all but one case is very good, and the precision is as good or better than can be expected when applying a polarographic method at the two percent level.

In the analyses of the two samples of K42B alloy and a sample of Discaloy of Company D, the results were all distinctly low in comparison with the value given by the manufacturer (but "correct" relative to one another) when the standard Inconel W alloy was used for calibration.

When the samples of K42B alloy were analyzed using the sample of Discal from the same company as a standard, the polarographic values were in very good agreement with the company's "standard" values, as shown in Table VI. It is believed that there is a systematic error in the analyses of Company D. Not only have Discaloy samples from two other companies been successfully analyzed by the polarographic method but also, as noted in Table IV, the composition of the precipitate would be anomolous if the analyses of Company D were accepted. In this table, based on the values given by companies other than Company D, the number of moles of reagent associated in the precipitate with one mole of titanium is 2.0, indicating that the precipitate is a di-m-nitrophenylarsonate. The standard values of Company D led, as shown by the numbers given in brackets in Table IV, to the curious molar ratio of 1.7, whereas the values for the alloys of Company D, based on a calibration using Inconel W, yielded the reasonable ratio of 2.0.

In Table I (page 4) is shown the complexity of the alloys and the widely differing compositions to which the method is applicable. In most of these alloys, nickel, chromium, and cobalt, although present as major constituents, would not be expected to interfere with the polarographic method. Iron, present in widely varying concentrations, is an interference, but is conveniently removed (as are nickel, chromium and cobalt) by electrolysis of the perchloric acid solution of the alloy in a mercury cathode cell.

The determination of titanium by this method is very convenient when the concentration of the solution to which the reagent solution is added is about 20 mg./l., or 20 p.p.m., but it can be used with concentrations only half this without significant solubility losses. This sensitivity compares favourably with that of the well known colorimetric method using hydrogen peroxide(29,30,16). The polarographic method appears to be less subject to interferences than either this colorimetric method or the one using Tiron(15). In general, Fe^{+++}, Sn^{++++}, Zr^{++++}, Th^{++++}, Bi^{+++}, and UO_2^{++} are precipitated by m-nitrophenylarsonic acid. Although tin and bismuth are not present in the high-temperature alloys analyzed in this work, these can be removed with iron by electrolysis in a mercury cathode cell.

m-Nitrophenylarsonic acid is not attractive as a reagent for the gravimetric determination of titanium. With amounts of titanium that are sufficiently large for ordinary gravimetric work, it has been found in this work that the precipitate is bulky and difficult to wash. Drying of the precipitate at 105-110°C. yields a hygroscopic substance*, and ignition is likely to involve losses due to explosion of the arsenic compound, as has been found by Duval(31) for titanium p-hydroxyphenylarsonate.

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* See Appendix II.

APPENDIX I

DETERMINATION OF COMPLETENESS OF PRECIPITATION OF TITANIUM m-NITROPHENYLARSONATE

The completeness of the precipitation of titanium with m-nitrophenylarsonic acid was assessed by colorimetric determinations using Tiron, following the method of Yoe and Armstrong(15).

The combined filtrate and washings from the filtration of the precipitate were collected in 250 ml. beakers containing 25 ml. of 0.6 M tartaric acid. The solutions were adjusted to pH 4.0 with 7.5 M ammonia and then diluted to 250 ml. with an aqueous solution of perchloric acid of pH 4.0.

Twenty-five milliliter aliquot samples of this solution were pipetted into 100 ml. volumetric flasks, and 5.0 ml. of Tiron reagent solution and 5.0 ml. of the sodium acetate-acetic acid buffer were added. The solutions were mixed and diluted to volume with water. The intensity of the color was measured on the Coleman spectrophotometer at a wavelength setting of 380 mμ.

Two calibration curves were constructed using aliquot samples of stock solutions No. 1 and No. 3 that were diluted with a solution of hydrochloric acid of pH 4.0 to give a series of solutions, diluted by factors ranging from 800 to 1200. These solutions were then prepared for colorimetric measurement in exactly the same way as the unknowns. The calibration curves were obtained by plotting percentage transmittance against the dilution factor.

The completeness of precipitation could be assessed by reference to the appropriate calibration curve, a dilution factor of 1000 corresponding to a precipitation that was 99.9% complete.

APPENDIX II

HYGROSCOPIC NATURE OF TITANIUM m-NITROPHENYLARSONATE

Titanium m-nitrophenylarsonate was precipitated from solutions of various alloys according to the method outlined under "Polarographic Method" (page 36). A Gooch crucible, containing a glass fiber filter mat (No. X-934-AH obtained from H. Reeve Angel and Co., New York, U.S.A.) was used to separate the precipitate from the solution. After thorough washing, the precipitate and crucible were dried for one hour at 110-120°C., and then allowed to cool in a desiccator containing phosphorus pentoxide. The cold crucible was removed from the desiccator and quickly weighed, a previous rough weighing having made it possible to have most of the required weights in position. The crucible and precipitate were then reweighed at frequent intervals. Data obtained are shown in Table VII.

Extrapolation of the data indicated that the original weight of the precipitate was 0.0358 g. The hygroscopic nature of the precipitate is revealed by the fact that it gained 0.0018 g. in the nine minutes following the first weighing. This represents a gain of 5%.

TABLE VII

HYGROSCOPIC NATURE OF TITANIUM m-NITROPHENYLARSONATE

Elapsed Time, in Minutes	Weight of Precipitate, in g.
0	0.0358
4	0.0370
9	0.0376
25	0.0381
32	0.0382
47	0.0384

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