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BULLETIN 113

THE POLAROGRAPHIC DETERMINATION OF ALUMINUM IN ROCKS

Marilyn Levine

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By
Marilyn Levine

DEPARTMENT OF
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PREFACE

Aluminum is an important constituent of many rocks and minerals and yet the classical method of quantitative analysis is subject to serious error.

Various alternative methods have been proposed and two of these were tested by the author. One, after modification, was found to be both fast and accurate.

J. M. HARRISON,
Director, Geological Survey of Canada

OTTAWA, June 29, 1962

73458-2—2½

Bulletin 113—Der polarographische Nachweis von Aluminium in Gesteinen.
Von Marilyn Levine

Erörtert die Unvollkommenheiten zweier bekannter Verfahren der chemischen Analyse für Aluminium in Gesteinen und beschreibt ein modifiziertes Verfahren, wie es die Geological Survey of Canada anwendet.

Бюллетень 113 — Полярографическое определение алюминия в породах.
М. Левин.

Рассматривается недостатки двух хорошо известных методов химического анализа на алюминий в породах; описывается измененный метод, применяемый Геологической службой Канады.

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THE POLAROGRAPHIC DETERMINATION OF ALUMINUM IN ROCKS

Abstract

Three polarographic methods for the determination of aluminum, all involving complex formation with organic reagents, have been investigated for their application to the routine analysis of rocks. One method involving an aluminum-gluconate complex was found to be impractical because of a large hydrogen ion dependence, which would necessitate a too critical control of pH. A second method, based upon the reduction of an aluminum-di-ortho-hydroxyazo complex in acetate buffer of pH 4.7, could not be used for the determination of Al_2O_3 in amounts greater than 7 per cent because of the low solubility of the aluminum-dye complex. The third method, similar to the second, makes use of a more soluble analogue of the above organic compound, synthesized for the purpose, which permits the determination of aluminum in rocks over the range of about 1-20 per cent Al_2O_3 with a maximum error of 3 per cent. A study of possible interfering ions indicated that only titanium, iron, nickel, thorium, and uranium ions need be considered among the cations, and fluoride among the anions. A preliminary mercury cathode electrolysis removes iron and nickel, and thorium and uranium generally occur in negligible amounts. Titanium can be tolerated in amounts up to 3 per cent TiO_2 without serious interference, and in higher amounts if special precautions are taken. The effects of temperature and time of standing upon the complex were also studied.

Résumé

Trois procédés polarographiques de dosage de l'aluminium, qui comportent tous la formation de complexes avec des réactifs organiques, ont donné lieu à des investigations aux fins de déterminer s'ils pourraient servir à l'analyse régulière des roches. Un procédé faisant intervenir un complexe de gluconate d'aluminium s'est révélé inutilisable à cause de sa grande dépendance sur les ions d'hydrogène, ce qui nécessiterait un contrôle trop rigoureux du pH. Un deuxième procédé, fondé sur la réduction d'un complexe de di-ortho-hydroxyazo d'aluminium dans un tampon d'acétate de pH 4.7, ne peut pas être utilisé pour le dosage d'Al_2O_3 en quantités supérieures à 7 p. 100 à cause de la faible solubilité du complexe colorant d'aluminium. Le troisième procédé, qui ressemble au second, fait usage d'un composé organique analogue à celui susmentionné mais plus soluble; celui-ci a été synthétisé pour les besoins et permet de doser l'aluminium présent au sein des roches suivant une échelle qui varie d'environ 1 à 20 p. 100 d'Al_2O_3, avec erreur maximum de 3 p. 100. Une étude des ions qui pourraient intervenir dans la réaction a indiqué que seuls les ions de titane, de fer, de nickel, de thorium et d'uranium, doivent être considérés parmi les cations et que seuls les ions de fluorure, parmi les anions. Une électrolyse préliminaire à l'aide d'une cathode de mercure élimine le fer et le nickel. Quant au thorium et à l'uranium, ils n'existent ordinairement qu'en quantités négligeables. Des teneurs qui peuvent atteindre jusqu'à 3 p. 100 en TiO_2 n'entraînent ordinairement pas d'inconvénients sérieux, et même des teneurs plus élevées importent peu si l'on sait prendre certaines précautions. On a également étudié les effets de la température et de la durée de l'expérience sur le complexe.

PART I

ATTEMPT TO USE KNOWN POLAROGRAPHIC METHODS TO DETERMINE ALUMINUM IN ROCKS

In recent years the rapidly increasing interest in geochemistry has resulted in a simultaneously increasing demand for silicate rocks analyses. The two main groups of chemical methods by which these analyses are made are: 'classical', when results of high accuracy are wanted, and 'rapid' when accuracy is of less importance but when speed is required.

Both these methods, which are used by the Geological Survey, have serious disadvantages. In the 'classical' method the aluminum is determined gravimetrically by difference, and therefore errors of all other determinations accumulate in the final result. The 'rapid' method employs a spectrophotometric finish, based upon the formation of coloured lake resulting from the combination of the solution containing aluminum ion with the dye alizarin red S. The composition of this lake is uncertain, being either an aluminum complex which exists in colloidal solution, or colloidal aluminum hydroxide on which the organic compound is adsorbed. Spectrophotometric methods of this nature suffer serious interference from various other cations, such as iron and titanium, and also are affected by variations in the conditions of reaction, such as pH, ionic strength, and temperature. Consequently this method is generally less reliable than might be desired.

Because of the unsatisfactory nature of the existing techniques, work was undertaken to develop a method that would avoid both colorimetric lake methods and complicated chemical separations. Fluorimetric methods (White and Lowe, 1940; Davydov and Devekki, 1941; Weissler and White, 1946) are sensitive but unreliable because of interferences caused by various ion species. Spectrographic techniques, in general, are not very successful, owing to the refractory nature of aluminum oxide. It was therefore decided to investigate the possibility of applying a polarographic approach to the problem.

The polarographic determination of aluminum is one of the more difficult tasks in cation polarography. Aluminum salts in solutions of pH greater than 4 readily hydrolyse and the diffusion current obtained does not express the true concentration of aluminum ion. Aluminate ion, present in strongly alkaline solutions, does not give a polarographic reduction wave. Prajzler (1931) observed a fairly well developed wave for aluminum ion, with a half-wave potential of -1.75 v. vs. S.C.E. in 0.05 normal barium chloride as supporting electrolyte. The reduction of hydrogen ion, unfortunately, precedes that of aluminum ion, but when the concentration of hydrogen ion does not exceed that of aluminum ion the waves are well separated. Higher concentrations of hydrogen ion, however, completely mask the aluminum wave. It is evident, therefore, that the successful polarographic determination of aluminum by such a method is critically dependent upon the proper control of pH between narrow limits which vary with the concentration of aluminum ion. More-

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over, buffer solutions cannot be employed to fix the hydrogen ion concentration, because even though the pH is correctly adjusted to the neighbourhood of 3 to 4, the weak acid of the buffer can produce a large hydrogen wave which will completely obscure the aluminum wave. Because the half-wave potential of the aluminum wave is so highly negative, all ions present in appreciable concentrations with more positive half-wave potentials will interfere, as well as such ions as those of barium, sodium, and potassium, whose reduction waves follow closely after the -1.75 volt half-wave potential of aluminum ion. It is evident, therefore, that a method involving measurement of the diffusion current of the aluminum ion wave under such limited and critical conditions, conditions that are unlikely to be obtained with routine analytical procedures, would not fulfil the requirements for a reliable rapid method. However, by using the polarographic reduction wave of a complex aluminum species possessing different properties, some or all of these disadvantages may be overcome.

Two methods described in the literature, both involving complex formation with an organic reagent, looked promising. The Willard and Dean method (Willard and Dean, 1950; Perkins and Reynolds, 1958a) involves the modification by aluminum of the polarographic reduction of a 2,2′ - dihydroxyazo dye. The method of V.D. Bezuglyi (Bezuglyi, 1959) is based upon the formation of an aluminum gluconate complex species. The first part of this bulletin is concerned with an investigation into the application of one or other of these methods as a possible alternative to the methods presently in use for the determination of aluminum at the Geological Survey.

This work was done while the author occupied a term appointment with the Geological Survey of Canada. Thanks are due to J. A. Maxwell and staff of the Analytical Chemistry Section for their helpful assistance and advice.

Apparatus and Reagents

Polarograms were recorded on a Leeds and Northrup Electrochemograph type E at 25°C. Potentials were measured relative to the saturated calomel electrode (S.C.E.). The capillary had the following characteristics in distilled water:

$$m^{2/3} t^{1/6} = 2.06 \text{ mg}^{2/3} \text{ sec}^{-1/2},$$

with a drop time of 3.19 seconds and a 50 cm head of mercury.

Oxygen was removed from the solutions by purging with nitrogen, purified by passage through vanadous chloride solutions (Meites, 1955, p. 34) for 5 to 10 minutes. All pH measurements were made with a glass electrode and a Beckman Model G pH meter. An Eberbach Dyna-Cath magnetic mercury cathode electrolytic apparatus was used to remove iron and other heavy metals from the solutions.

Both constant temperature baths were controlled by means of mercury switch thermoregulators, in conjunction with Precision Scientific Co. Electronic Relays No. 62690. The thermoregulator in the polarographic bath was set at 24.7°C $\pm$ 0.2° and that in the bath used to heat the aluminum-dye solution was set at 54.0°C $\pm$ 0.5°.

A 0.01 M aluminum ion solution was prepared by dissolving 2.3719 grams of aluminum potassium sulphate dodecahydrate crystals in water acidified with 2 ml of 5 N perchloric acid to prevent precipitation of aluminum hydroxide, and diluting

to 500 ml in a volumetric flask. The solution was standardized gravimetrically with 8-hydroxyquinoline (Kolthoff and Sandell, 1952, p. 320) and duplicate determinations gave molarities of 0.01002 and 0.00998. Other concentrations of aluminum ion were prepared by appropriate dilutions of this standard in 50 ml volumetric flasks. These were further acidified with another 0.5 ml of 5 N perchloric acid.

The calcium gluconate solution was prepared by dissolving 10 grams of calcium gluconate and 8 grams of calcium chloride in 200 ml of water, to make a solution containing 5 per cent of calcium gluconate and 4 per cent of calcium chloride.

The solution of the dye, Pontachrome Violet SW[1] (colour index 169), which is the sodium salt of 1-(1-hydroxy-4-sulphonic acid-2-phenylazo)-2-naphthol, was prepared in an acetate buffer of pH 4.7 by dissolving 2.00 grams of Pontachrome Violet SW and 59.4 grams of sodium acetate trihydrate in water containing 25.0 ml of glacial acetic acid and diluting to 2500 ml. The solution so prepared was 0.175 normal in acetate ion and contained 0.08 per cent dye. The pH of the buffer solution was checked against a Beckman standard buffer solution of pH 4.00 $\pm$ 0.01 at 25°C.

Gluconate Method

The basic steps in the procedure suggested by Bezuglyi (1959) are: the pH of the solution containing aluminum ion is adjusted to the pK of bromophenol blue and this is added to an aqueous solution of calcium gluconate and calcium chloride. A polarogram is then run on the resulting solution. Bezuglyi reported that a wave appeared at -1.56 to -1.60 volts, whose diffusion current varied linearly with concentration of aluminum ion.

The present investigation was begun by testing the linearity of the relationship between diffusion current and concentration. To accomplish this, 5.0 ml of a standardized 0.01 M potassium aluminum sulphate solution, with no added perchloric acid, was diluted with increasing amounts of the 5 per cent calcium gluconate solution ranging from 5 ml to 25 ml. A polarogram was taken after each dilution step. Figure 1 shows a representative polarogram taken on a solution that was 0.005 M in aluminum ion, and contained 5 per cent of calcium gluconate and 4 per cent of calcium chloride. The pH of this solution was found to be 3.90. Figure 2 is a plot of the diffusion current versus concentration. As can be seen, the relationship is linear as reported by Bezuglyi. The next step was the consideration of the effects of such variables as diverse ions and pH.

To study the effects of various diverse ions upon this wave, differing amounts of solutions containing these ions were added to aluminum-gluconate solutions in which the final aluminum ion concentration remained constant.

Ferric and ferrous iron, divalent manganese and tetravalent titanium all increased the diffusion current. Sodium, potassium, and calcium ions had no observable effect. Fluoride ion tended to depress the wave height and in high concentrations almost eliminated the wave. It was noted that when an excess of sodium fluoride was added, the pH increased to around 6. Boric acid increased the diffusion current. The effects of fluoride ion and boric acid will be discussed below.

[1] This dye was obtained from the National Aniline Division of Allied Chemical Corporation under the trade name Superchrome Violet B.

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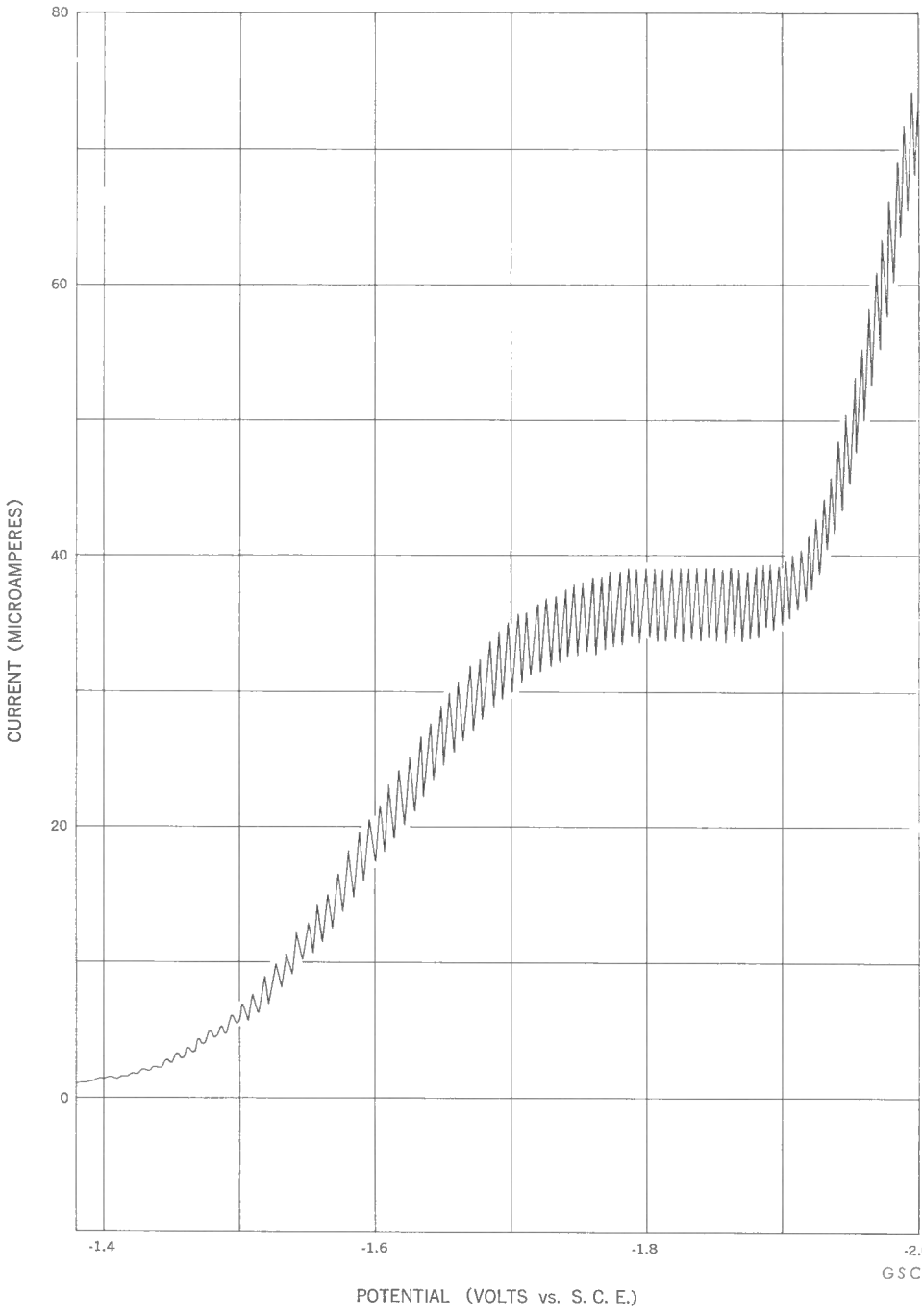


FIGURE 1. Polarogram of 5 millimolar aluminum potassium sulphate in 5 per cent calcium gluconate and 4 per cent calcium chloride solution. The pH of the solution was 3.90.

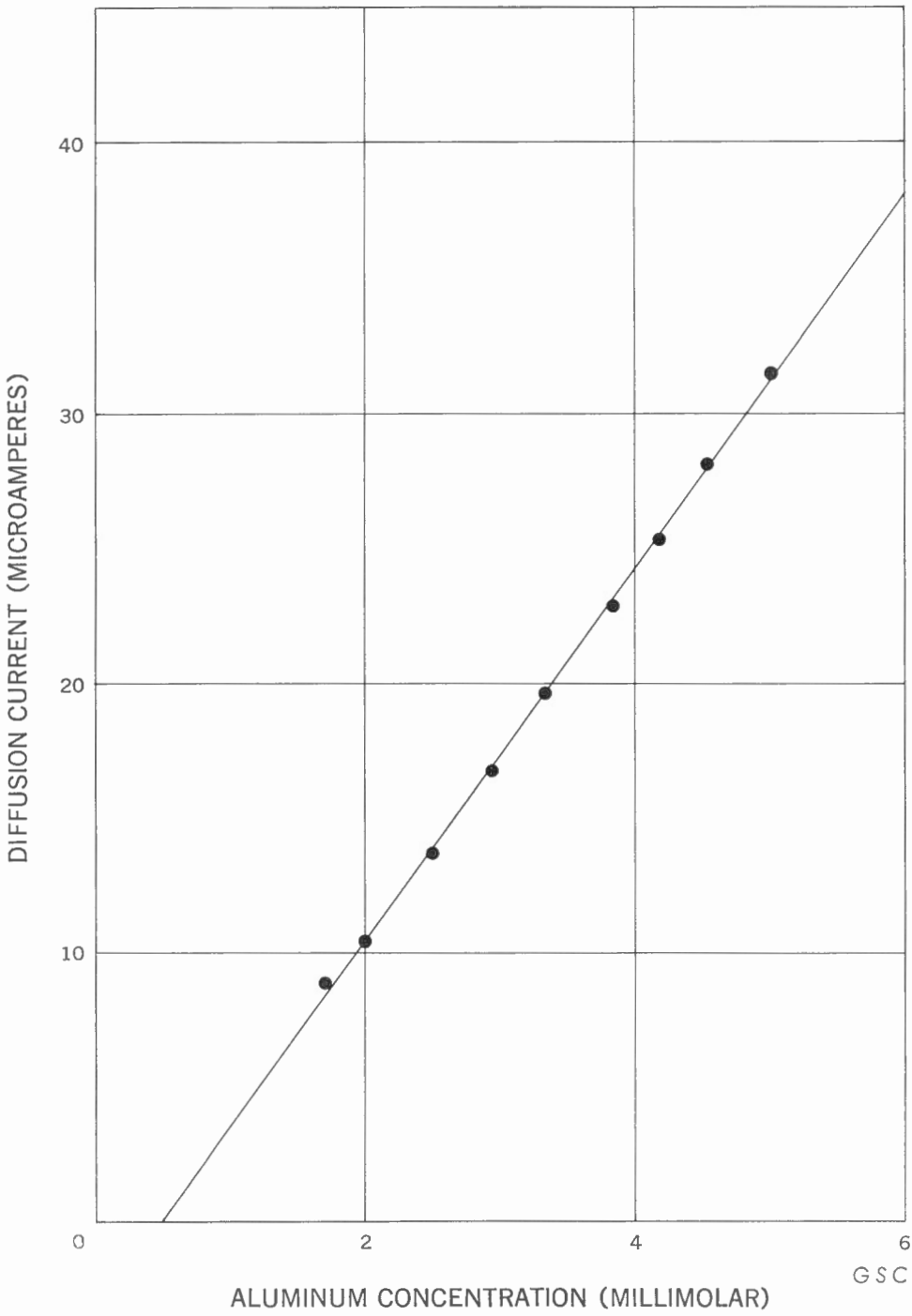


FIGURE 2. Variation of diffusion current of aluminum-gluconate solution with aluminum ion concentration.

To determine the effect of pH, a solution was made up to be 0.005 M in aluminum ion with 5 per cent of calcium gluconate, 4 per cent of calcium chloride, and 0.002 per cent of gelatin. Adjustments in pH were made with fractions of drops of concentrated hydrochloric acid and 40 per cent potassium hydroxide, such that the change in aluminum concentration would be negligible. After each addition of acid or base, the pH was read and a polarogram run.

The diffusion current was found to increase with a decrease in pH. The hydrogen ion concentration was calculated from the observed pH values, and the relationship between diffusion current and hydrogen ion concentration is shown in Figure 3.

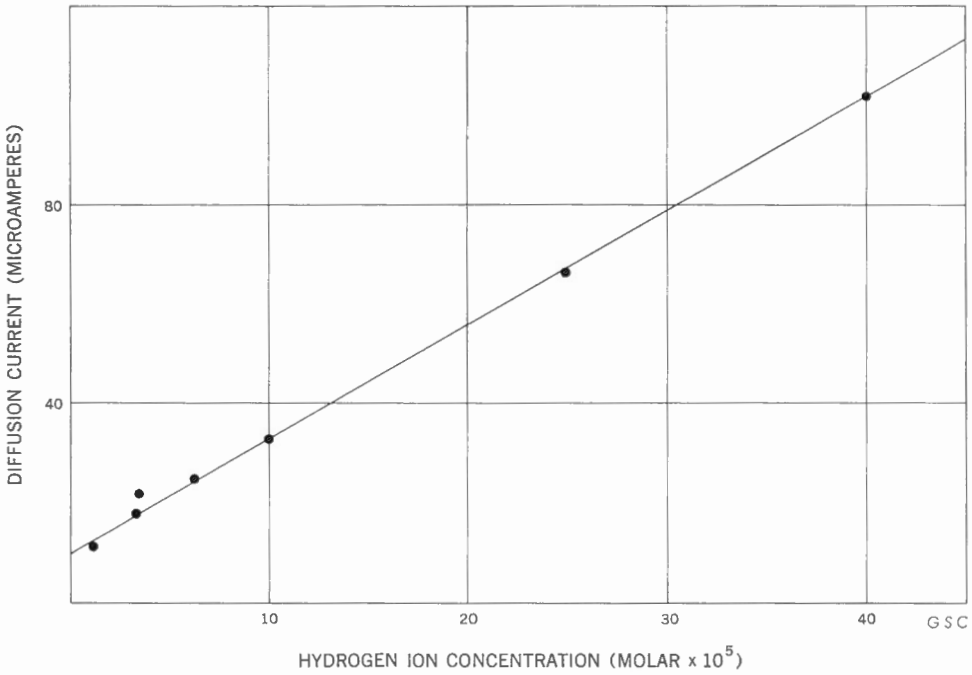


FIGURE 3. Variation of diffusion current of aluminum-gluconate solution with hydrogen ion concentration.

The fact that a linear variation was obtained suggests that perhaps the reduction of hydrogen ion is being measured rather than the reduction of the aluminum ion in the gluconate complex. To test this theory a blank solution was made containing 5 per cent of calcium gluconate and 4 per cent of calcium chloride, and then brought to a pH of 3.90 with 5 N perchloric acid. As less than one drop of perchloric acid was used to acidify 10 ml of the solution, there was no effective change in the calcium gluconate concentration. This solution was deoxygenated and polarographed, giving the polarogram shown in Figure 4. Comparison of the polarograms in Figures 1 and 4, the former representing a similar solution but containing 5 millimoles of aluminum ion, shows that although the former has a 0.04 volt more positive half-wave potential and a somewhat higher diffusion current than that in Figure 4, there is a striking resemblance between the two polarograms.

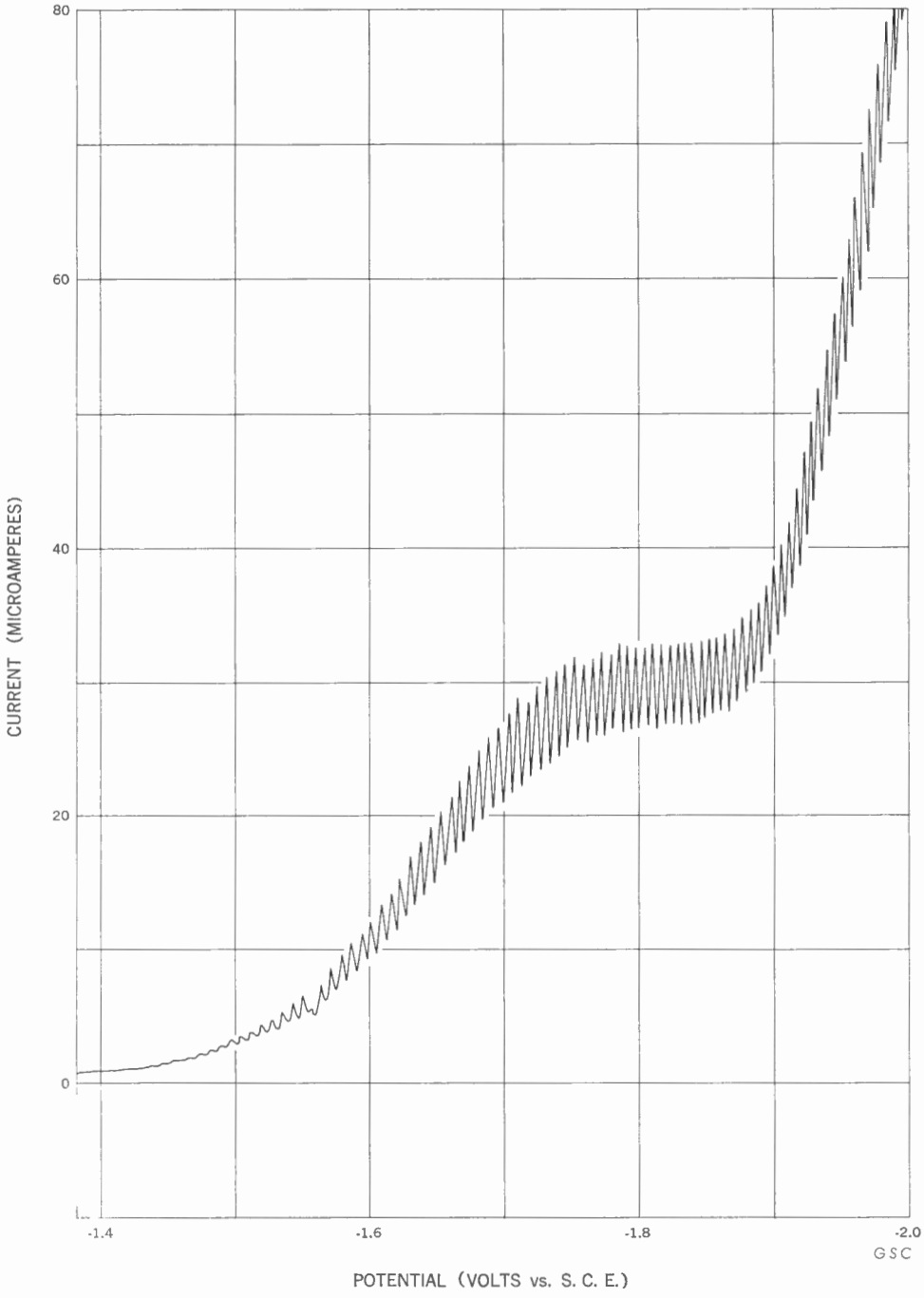


FIGURE 4. Polarogram of a solution containing 5 per cent calcium gluconate and 4 per cent calcium chloride brought to pH 3.90 with perchloric acid.

The polarographic waves shown in Figures 1 and 4 were analyzed for reversibility by plotting $\log \frac{i}{i_d - i}$ versus the potential, where i_d is the diffusion current and i is the current at any potential. The slopes of these plots, shown in Figure 5, were found to be 0.12 volts, which indicates that the reductions taking place are irreversible. Because hydrogen ion and aluminum ion would probably be reduced by different mechanisms, it is unlikely that the logarithmic plots for aluminum and hydrogen reductions would have the same slopes. From the results it therefore appears that it is the hydrogen ion that is being reduced in both cases.

To determine conclusively whether it was hydrogen ion or aluminum ion in the aluminum-gluconate solution which was being reduced, two identical solutions containing 5 per cent of calcium gluconate, 4 per cent of calcium chloride in a 0.005 molar solution of aluminum potassium sulphate were prepared. Both solutions were immersed in a constant temperature bath at 24.7°C and one of the solutions was reduced at the dropping mercury electrode for 22 hours at −1.85 volts vs. S.C.E. During this reduction the diffusion current dropped from 36.4 to 29.0 microamperes. Both solutions were then analyzed for aluminum by the 8-hydroxyquinoline procedure (Kolthoff and Sandell, 1952, p. 320). From the results of these analyses the concentration of the solution that had undergone the reduction step was calculated to be 5.03×10^{-3} molar, while that of the control solution was calculated to be 5.06×10^{-3} molar. As aluminum metal has a fairly high solubility in mercury (Sidgwick, 1950, p. 289) there is little possibility of it returning to the aqueous phase through reaction with the available hydrogen ion. Consequently, it is evident from these results that no reduction of the aluminum ion had taken place and it must, therefore, be the hydrogen ion in the solution that was reduced.

With these results in mind, it is obvious that the enhancing effect of boric acid on the diffusion current is due to the increase in the concentration of weak acid in solution.

Pecsoc and Sandera (1955) have determined that ferric ion forms a 1:1 complex with gluconate ion. It was thought that a polarographic study of this complex species might throw further light on the aluminum-gluconate problem. For this purpose a 0.005 molar solution of ferric ammonium sulphate was prepared which contained 5 per cent of calcium gluconate and 4 per cent of calcium chloride. The pH of this solution was 3.90, the same as that of the aluminum-gluconate solution of the same concentration. However, the polarogram of the ferric gluconate solution (Fig. 6) consists of two waves with half-wave potentials at about −1.4 volts and −1.65 volts. When the solution was acidified with perchloric acid to a pH of 3.62 the second wave increased in height from about 8 microamperes to about 24 microamperes, while the height of the first wave remained constant. This indicates that the first wave is the ferrous iron wave and the second the hydrogen ion wave. In contrast to this very small hydrogen wave, the wave that was thought to be due to hydrogen ion in the aluminum-gluconate solution had a diffusion current of about 35 microamperes.

Since the pH values of the aluminum-gluconate solution and the ferric gluconate solution were both 3.90, one would at first expect them to exhibit the same diffusion current due to hydrogen ion. However, on the basis of the proposed structures

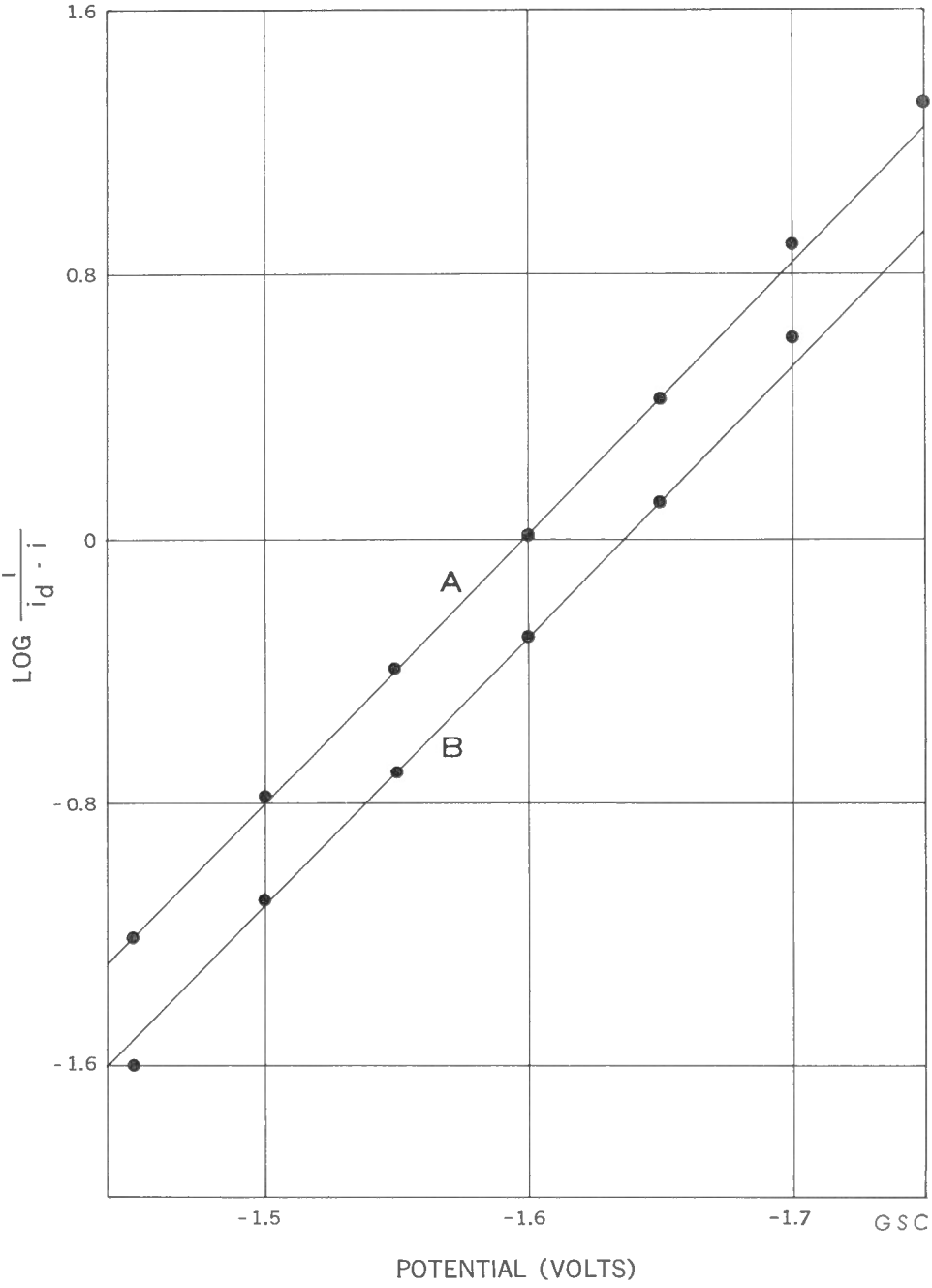
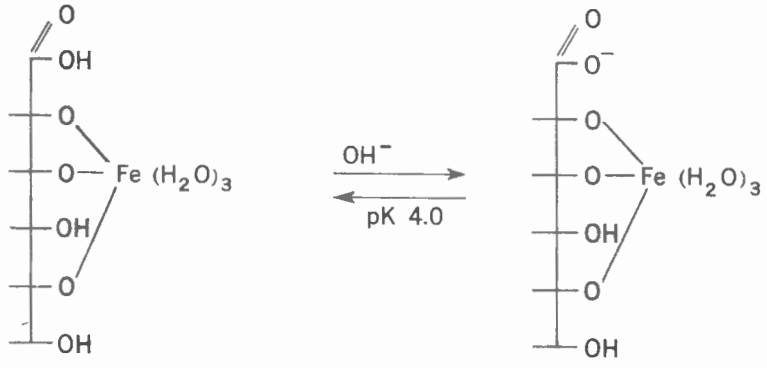
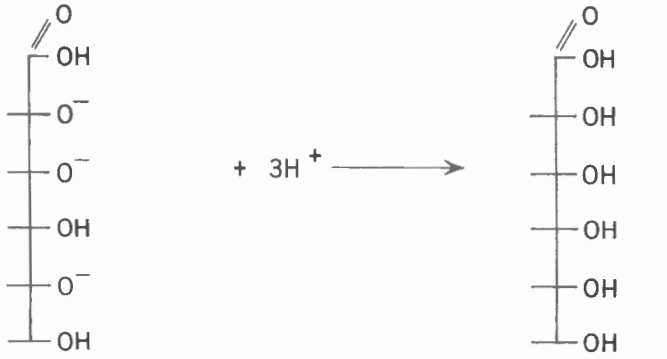


FIGURE 5. Plot of log $\frac{i}{i_d - i}$ vs. potential for polarograms of gluconate solutions at pH 3.90 containing aluminum ion (A) and no aluminum ion (B).

(equation 1) of Pecsoc and Sandera (1955) for the ferric gluconate complex in solution between pH 2.3 and 13.3, this low hydrogen wave is understandable when it is considered that the reduction of the ferric iron in the gluconate complex to metallic iron will liberate the very unstable gluconate species with three negatively charged oxygen atoms. The hydrogen ion diffusing up to the electrode surface will meet the outwardly diffusing gluconate anion species, and immediately react with it, as shown in equation (2).



(1)



(2)

If the hydrogen ion and the ferric gluconate complex had the same diffusion coefficients, then no hydrogen wave would appear in an unbuffered solution until the hydrogen ion concentration was three times that of the gluconate complex. The diffusion coefficient of the hydrogen ion at infinite dilution is 9.34×10^{-5} cm^2 sec^{-1}, whereas that of the ferricyanide complex anion (Parsons, 1959, p. 79) is only 0.89×10^{-5} cm^2 sec^{-1}. It would be expected that the diffusion coefficient of the ferric gluconate species would be even less because of the larger size of the ligand. Consequently, due to the very large diffusion coefficient of hydrogen ion and to the contribution of the weak acid, gluconic acid, in the solution, it is expected that a hydrogen wave will begin to appear when the measured hydrogen ion concentration is very much less than three times the gluconate concentration, as is so here.

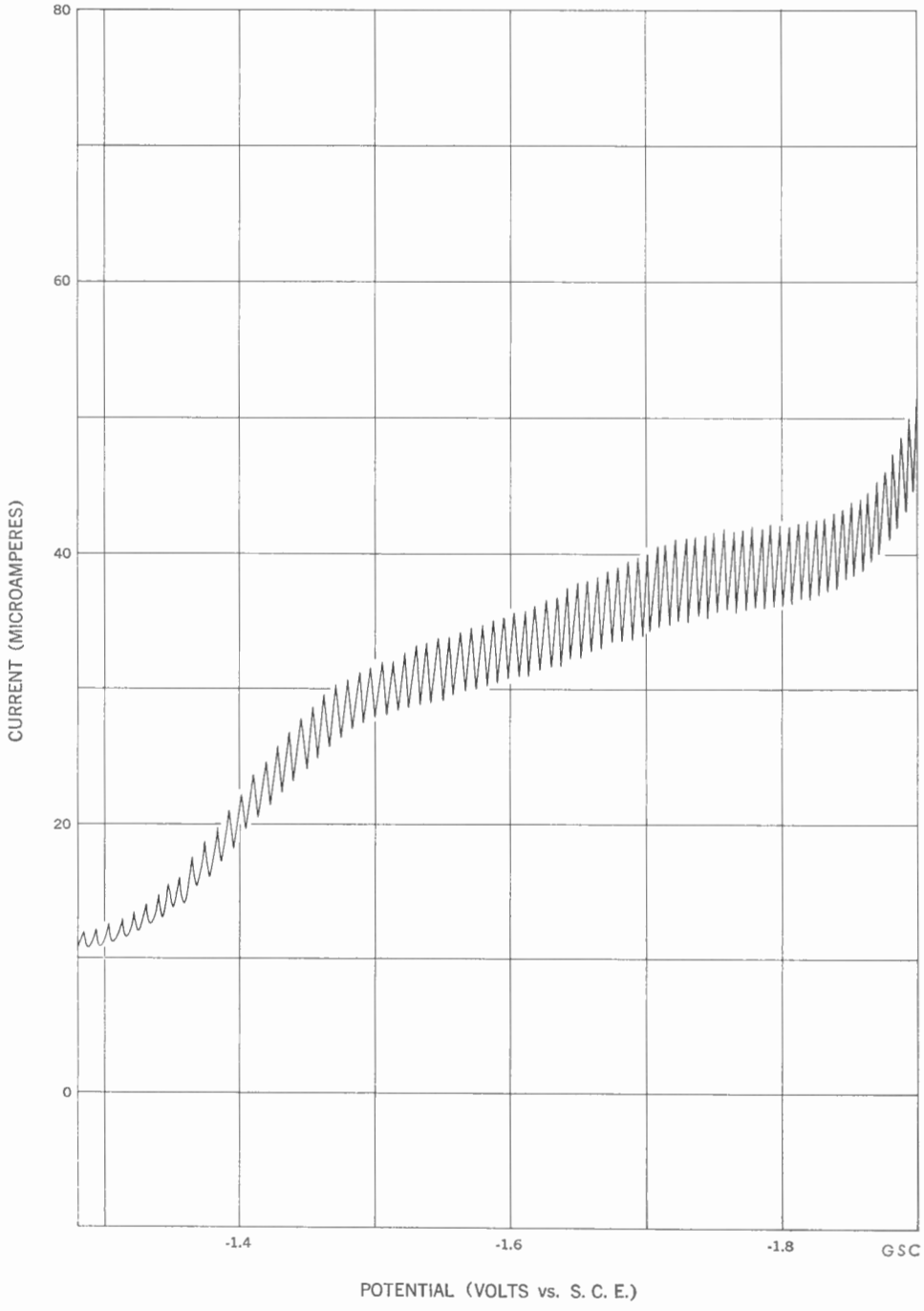


FIGURE 6. Polarogram of 5 millimolar ferric ammonium sulphate in 5 per cent calcium gluconate and 4 per cent calcium chloride solution. The pH of the solution was 3.90.

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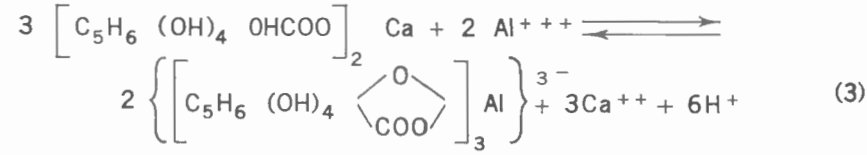
Certainly, these results show that the reduction of the ferric gluconate complex is not analogous to the reduction taking place in the aluminum-gluconate solution, and therefore no immediate conclusions can be drawn from a study of the former.

The reaction scheme proposed by Bezuglyi (1959) for the aluminum gluconate complex formation is shown in equation (3)[1].



$$3\left[C_5H_6(OH)_4\,OHCOO\right]_2 Ca + 2\,Al^{+++} \rightleftharpoons 2\left\{\left[C_5H_6(OH)_4\,\underset{COO}{\overset{O}{\diagdown\!\diagup}}\right]_3 Al\right\}^{3-} + 3Ca^{++} + 6H^{+} \qquad (3)$$

It can be seen that this differs from the ferric gluconate complex proposed by Pecsoc and Sandera (1955), in that Bezuglyi's complex contains three gluconate ligands per aluminum ion. Bezuglyi proposed this reaction on the evidence he obtained when titrating an aluminum sulphate solution with a calcium gluconate solution, and plotting the pH versus the volume of added gluconate. He designated the equivalence point as being the point where the second derivative of the plot becomes zero. This would mean that the equivalence point would be at the inflection point in the plot of pH versus volume. Although Bezuglyi does not indicate the volume of aluminum sulphate solution that he titrated (thus making it impossible to check his results) he says that his results confirmed that the species in solution was the aluminum trigluconate ion. The above reasoning leading to this conclusion is not, however, obvious. It is difficult to understand why Bezuglyi chose the inflection point of his plot as the equivalence point. In his proposed reaction hydrogen ion is released, and consequently the point at which the hydrogen ion concentration is a maximum would be the equivalence point.

The proposed reaction schemes of Bezuglyi, and Pecsoc and Sandera both involve the displacement of hydrogen ion from alcoholic hydroxyl groups upon complex formation. Assuming that alcoholic hydroxyl groups are thus involved the stoichiometric ratio of aluminum to gluconate can be determined by a titration similar to that done by Bezuglyi, but taking the point of lowest pH as the equivalence point rather than the inflection point of the plot. For this purpose, 50 ml of 0.002 molar potassium aluminum sulphate (0.100 millimoles) was titrated with 0.03 N calcium gluconate solution and the pH was read after each addition. In the plot of pH versus volume of added gluconate, shown in Figure 7, the minimum pH is at 3.38 ml, which is equivalent to 0.101 millimoles of gluconate ion. Therefore it may be concluded that the aluminum is present in a 1:1 complex with the gluconate ligand.

From the nature of the results depicted in Figure 7 it is evident that a strong complexing agent such as fluoride ion will lower the diffusion current by the removal of the aluminum ion from the gluconate complex, thus raising the pH of the solution.

[1] Bezuglyi had a total of seven carbon atoms in his gluconate ion. This is thought to be a misprint.

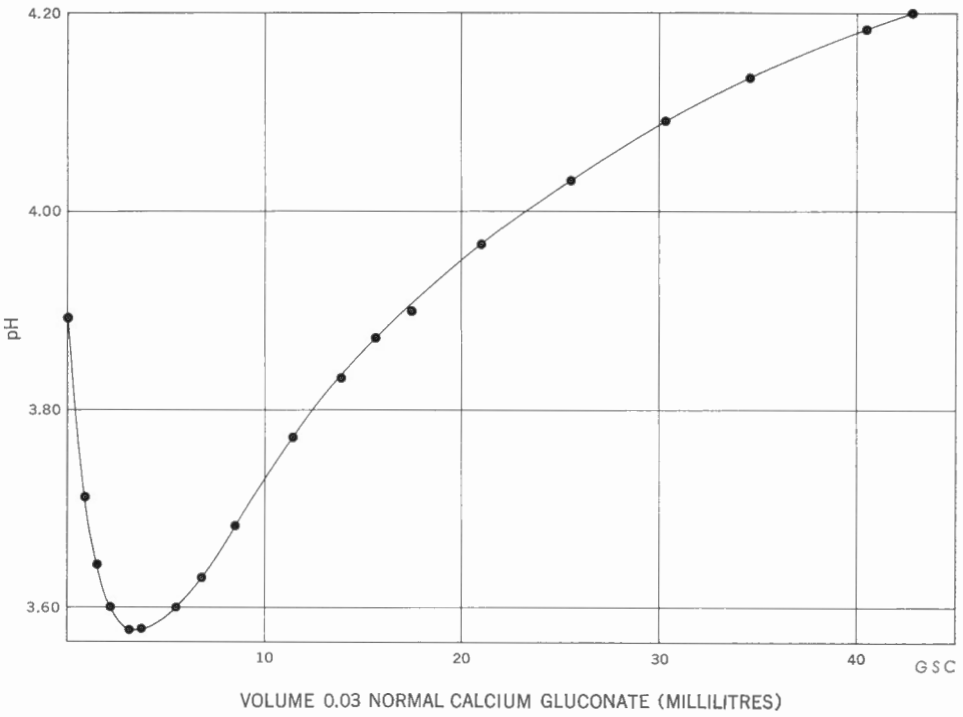


FIGURE 7. pH variation of 0.100 millimoles aluminum potassium sulphate solution with volume of added calcium gluconate solution.

The analytical application of this gluconate complex to the determination of aluminum would obviously be impractical because the polarographic wave obtained is the result of the reduction of hydrogen ion. The pH adjustment of the sample solution prior to the addition of calcium gluconate would be so critical that even the use of a glass electrode pH meter would not afford the necessary accuracy. Because of its logarithmic dependence, a relatively small pH variation will correspond to a significant change in hydrogen ion concentration and thus also in the magnitude of the diffusion current.

Willard and Dean Method

Experimental Results

Calibration Curve

The procedure used is a modification of that described by Willard and Dean (1950).

Three ml aliquots of each of the standard solutions, ranging from 2 to 7 millimolar in aluminum ion, and of a blank containing no aluminum ion, were transferred to 50 ml volumetric flasks and were made just basic to methyl red with 40 per cent

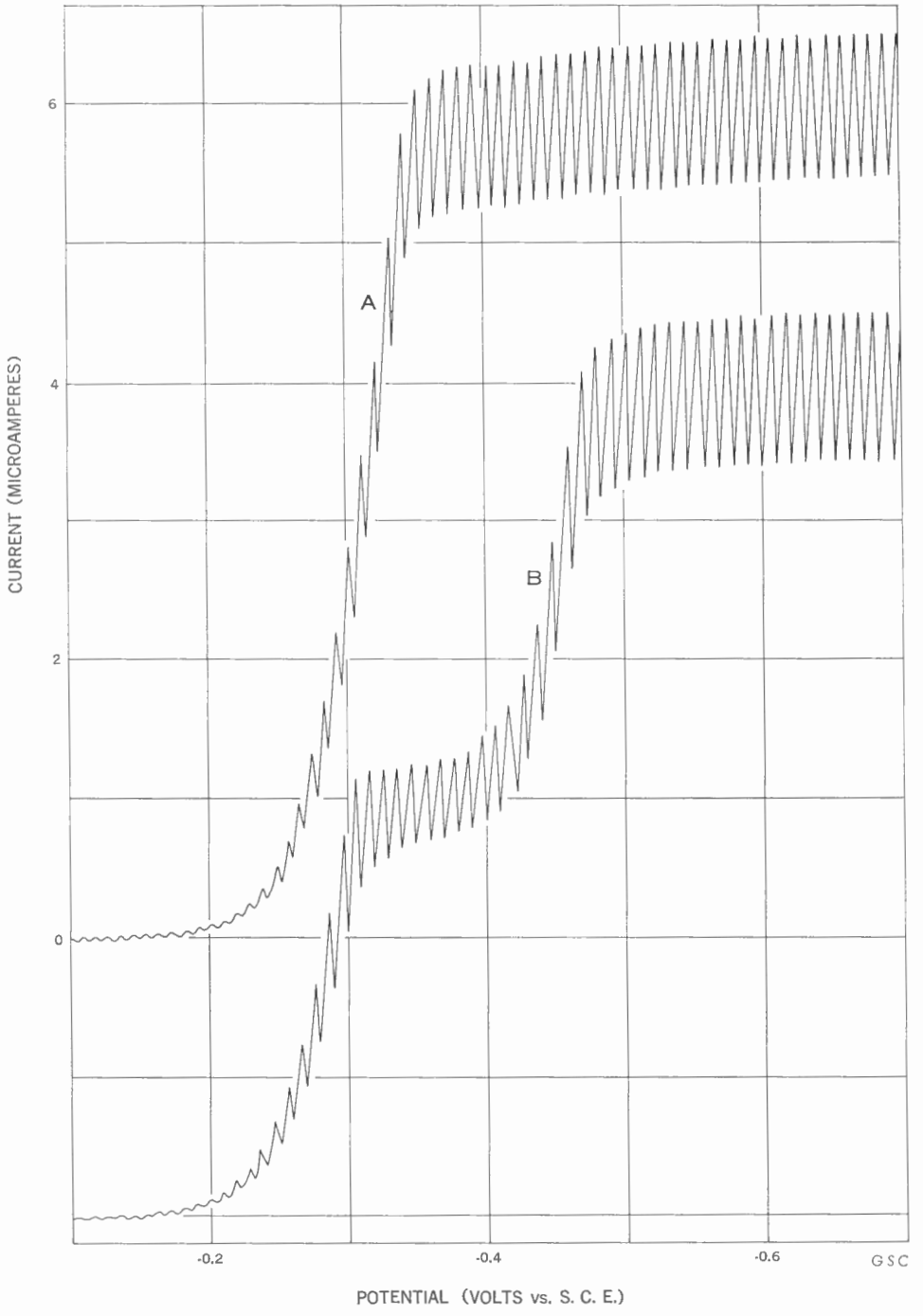


FIGURE 8. Polarograms of 0.04 per cent Pontachrome Violet SW in 0.09N acetate buffer solution pH 4.7, with and without added aluminum ion. A, dye solution alone; B, dye solution 0.24 mM in aluminum ion.

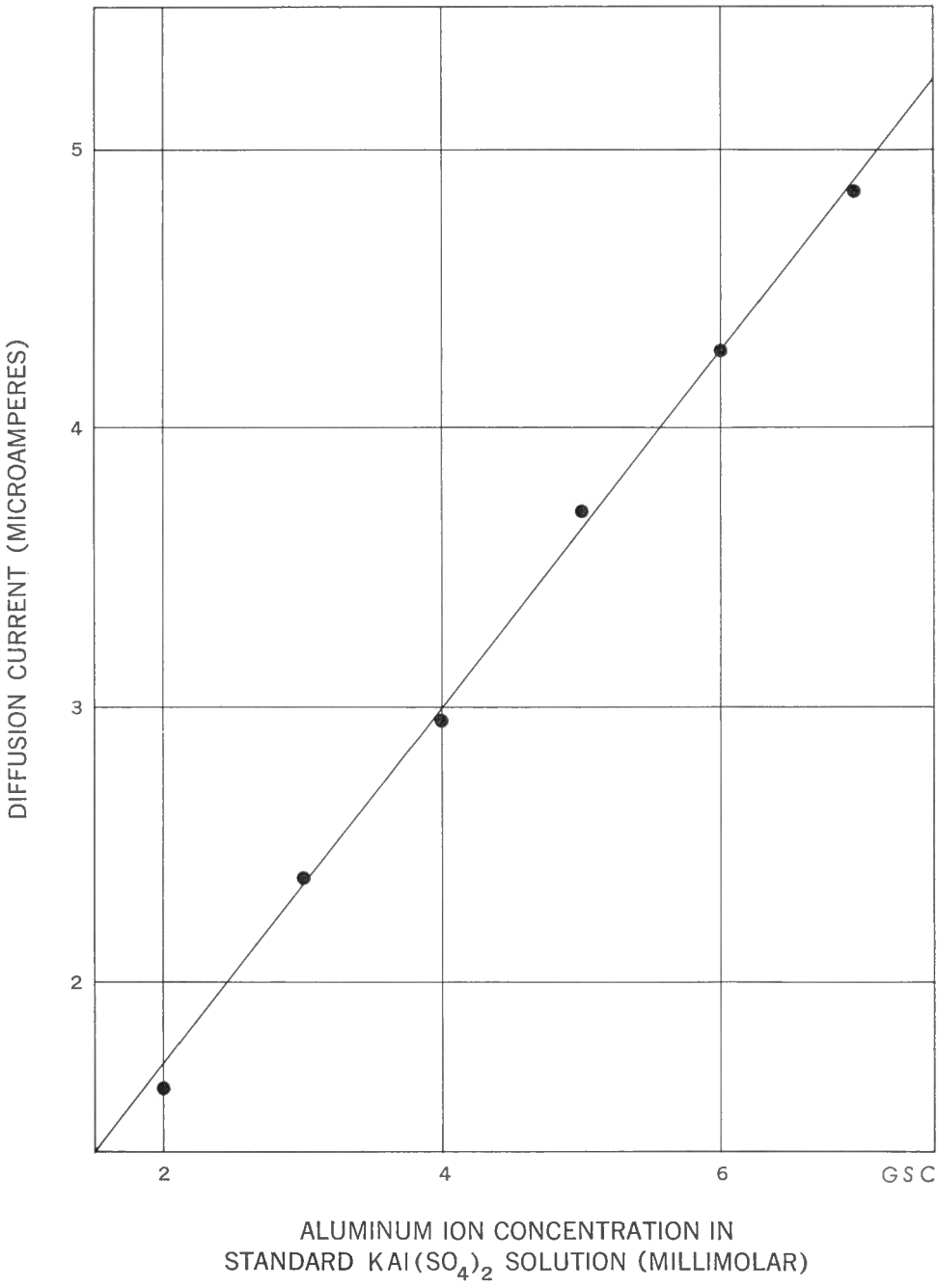


FIGURE 9. Variation of diffusion current of second wave with aluminum ion concentration.

sodium hydroxide. Perchloric acid (5N) was added dropwise until the solutions were just acid, 25.0 ml portions of the buffered 0.08 per cent Pontachrome Violet SW were added, and the solutions made up to volume with water. After immersion in a 54°C constant temperature bath for 15 to 20 minutes, the flasks were cooled in tap water and aliquots were transferred to polarographic cells (Harris, 1958), deoxygenated and polarographed.

The polarograms of the dye solution alone consisted of one wave for the reduction of the azo group with a half-wave potential of −0.31 volts to −0.32 volts vs. S.C.E. Polarograms of the aluminum-dye solutions consisted of two waves, the half-wave potentials were found to range from −0.28 volts to −0.26 volts for the first wave, and from −0.43 volts to −0.45 volts for the second wave, with increasing concentration of aluminum ion. The height of the first wave decreased with increasing concentration of aluminum ion and the height of the second wave increased correspondingly. Figure 8 shows current-voltage curves for the dye alone and in the presence of aluminum ion. If the measured diffusion currents of the second wave are plotted against the concentrations of the standard aluminum ion solutions used, as has been done in Figure 9, a linear relationship is obtained. However, the diffusion currents used for the calibration curve unfortunately were not as reproducible as might be desired. Diffusion currents of the same solution, taken on different days, varied inconsistently over a range as large as 0.3 microamperes. The same range of variations was observed for diffusion currents taken at the same time, but on different solutions, prepared by identical procedures. Average values for the diffusion current readings were used in Figure 9.

Effect of Other Ions

Both Willard and Dean (1950), and Perkins and Reynolds (1958a), have made rather extensive studies of the effect of many different ions. Their results are in general agreement with one another, so that no further study of this nature was undertaken here.

From the above studies it appears that, of the ions normally present in silicate rock samples, only ferric iron and titanium interfere appreciably. Titanium oxide normally does not exceed 0.5 per cent of the sample, and in this concentration its effect upon the diffusion current of the aluminum-dye wave will be negligible. Ferric iron, on the other hand, has a proportionately larger effect upon the diffusion current, and in general the amount of iron in the sample exceeds 1 per cent. Thus, it is generally necessary to remove iron from the sample solution prior to the addition of the dye. Because sulphate and potassium ions in amounts exceeding 5 mg per 50 ml cause precipitation of the dye, Willard and Dean suggest that only perchloric acid and sodium hydroxide should be used in preliminary steps requiring an acid or base. Fluoride ion forms a more stable complex with aluminum ion than does the dye, and therefore must be completely removed from the sample solution after sample decomposition with hydrofluoric acid.

Analysis of Laboratory Reference Rock Samples

Aluminum was determined in a series of analyzed rock samples by the following procedure:

A 0.400 gram sample of each rock was transferred quantitatively to a 90 ml platinum crucible and moistened with 1 to 2 ml of water. Ten ml of 48 per cent hydrofluoric acid was added cautiously, followed by 3 ml of concentrated sulphuric acid. The crucibles were covered and placed on a steam bath to digest overnight. The contents were then evaporated down to a volume of about 3 ml and 1 ml of concentrated nitric acid was added to complete the oxidation of any organic matter present. The evaporation was continued until copious white fumes of sulphur trioxide were evolved and the crucibles were then allowed to cool. The crucible contents were transferred quantitatively to 400 ml Vycor beakers and diluted to about 150 ml with water. The solutions were boiled gently for 15 to 20 minutes, cooled, and transferred quantitatively to 200 ml volumetric flasks, with filtration when necessary, and diluted to volume at room temperature.

About 50 ml of each of these solutions were electrolysed at the mercury cathode (Maxwell and Graham, 1950), with a current density of 0.13 amp cm^{-2} for about 40 minutes. Then 3.0 ml aliquots of the electrolysed solutions were transferred to 50 ml beakers and evaporated until sulphur trioxide fumes ceased to be evolved. Four to five ml of distilled water and about 5 drops of concentrated sulphuric acid were added, and the contents were again fumed to dryness. The sides of the beakers were washed down and the fuming procedure repeated. These repeated fumings were necessary to ensure the expulsion of all traces of fluoride ion.

The residues were taken up in 1 ml of 5 N perchloric acid, with heating, and the resulting solutions were transferred quantitatively to 50 ml volumetric flasks. Sodium hydroxide (40 per cent) was added until the solutions were just basic to methyl red. Perchloric acid (5N) was added dropwise until the solutions were just acid again and then 25.0 ml of the buffered 0.08 per cent Pontachrome Violet SW was added and the solutions made up to volume with water. After immersion in a 54°C constant temperature bath for 15 to 20 minutes, the flasks were cooled in tap water, and aliquots were transferred to polarographic cells (Harris, 1958), deoxygenated, and polarographed.

To convert the diffusion current reading into per cent Al_2O_3, the aluminum ion concentration in millimoles per liter, read from the calibration curve (Fig. 9), was multiplied by the factor $\frac{1}{1000} \times \frac{200}{1000} \times \frac{101.9}{2} \times \frac{100}{0.4}$, which reduces to 2.55.

Average results for the various samples, determined in duplicate by the above procedure, are listed in Table I. For comparison, the results obtained with the alizarin red S method and with the 'classical' gravimetric procedure are also listed.

Table I

Per Cent Al_2O_3 Found by Different Methods

Sample	Lab. Code Number	% Al_2O_3 Found		
		Pontachrome Violet SW	Alizarin Red S	Gravimetric
Gabbro	A 167	13.38	14.60	14.47
	"	13.65	15.31	
	"	14.55	14.20	
	"	14.12	13.82	
Granite	R 1873	13.36	14.22	13.61
	"	13.57		
Granite	A 138	15.69	14.76	14.81

Conclusions

The data obtained suggest that the Willard and Dean method in its present form is not suitable as an alternative method for the determination of aluminum in rocks with Al_2O_3 contents ranging from 8 to 20 per cent. The analytical results obtained with this method rarely showed any significant improvement over those obtained with the alizarin red S method and were indeed sometimes considerably worse. The relatively low solubility of Pontachrome Violet SW in water necessitated the use of large dilution factors in the preparation of the sample solution, and this is probably the chief source of inaccuracy in the results. A more soluble dye of similar structure might overcome this difficulty and Part II of this report is concerned with investigating this possibility.

PART II

A POLAROGRAPHIC METHOD INVOLVING THE REDUCTION OF AN ALUMINUM DI-ORTHO-HYDROXYAZO COMPLEX SPECIES

Part I of this report dealt with an investigation into the possible application of either of two polarographic methods for the determination of aluminum as an alternative to the colorimetric method now in use to determine aluminum in rocks and minerals in the laboratories of the Geological Survey. It was found that neither method afforded any significant improvement over the existing method involving the use of alizarin red S. The gluconate method (Bezuglyi, 1959), which involves the polarographic measurement of hydrogen ion released upon the formation of a complex between the aluminum ion and the gluconate ion, was found to be undesirable because of the necessity for critical adjustment of the pH of the sample before the addition of the calcium gluconate. The method of Willard and Dean (1950), which involves the modification by aluminum ion of the polarographic wave due to the reduction of the azo dye Pontachrome Violet SW, which is 1-(1-hydroxy-4-sulphonic acid-2-phenylazo)-2-naphthol, was found to be considerably better, but the low solubility of the dye prevented its application when the alumina concentration of the sample exceeded 7 per cent. Most samples coming to these laboratories for analysis contain from 8 to 20 per cent Al_2O_3, and the upper limit of 7 per cent for the use of this method is thus a serious disadvantage.

Despite this difficulty, the principle of the Willard and Dean method still looked promising. If a dye could be found that exhibits the same polarographic behaviour as Pontachrome Violet SW in the presence of aluminum ion but which has a greater solubility in water, then Al_2O_3 in the concentration range of 8 to 20 per cent might be determined with much greater accuracy.

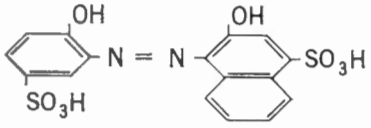
It is well known that the addition of a sulphonic acid group to an organic molecule generally increases its solubility in water. Therefore, as it is the azo group that is responsible for the polarographic reduction of the dye, and as only the azo group and the *ortho*-hydroxyl groups are likely to be involved in the complex formation with aluminum, it would seem reasonable to expect that a sulphonated analog of Pontachrome Violet SW would exhibit the desired characteristics as long as the large sulphonic acid groups were not in positions where they would sterically hinder the complexing reaction.

Part II of this report is therefore concerned with the synthesis of such a dye and with its application to the polarographic determination of aluminum in rocks.

Experimental Procedure

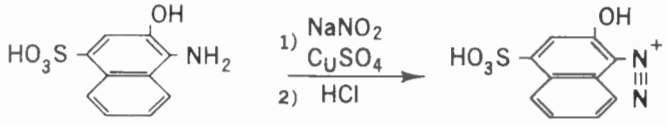
Preparation of the Dye

Attempted preparation of 1-(1-hydroxy-4-sulphonic acid-2-phenylazo)-2-naphthol-4-sulphonic acid (I)

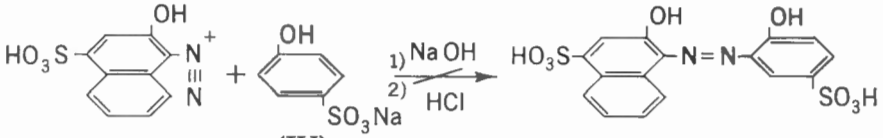


(I)

The method used was based upon that used by Lindstrom and Diehl (1960) for the preparation of Calmagite, which is 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulphonic acid. The reactions were expected to proceed by the following paths, but, as described later the second reaction did not proceed as planned.



(II) (III) (1)



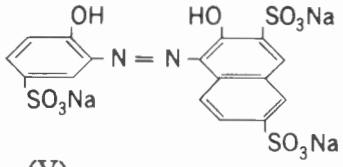
(IV) (2)

Sixty grams of 1-amino-2-naphthol-4-sulphonic acid (II) was suspended in 400 ml of water, the suspension cooled to 5°C and treated with 150 ml of an aqueous solution containing 5 grams of copper sulphate and 9 grams of sodium nitrite. After ten minutes the solution was filtered to remove impurities, and concentrated hydrochloric acid added to precipitate the yellow diazonium salt (III). This was filtered with suction, washed with dilute hydrochloric acid, and allowed to dry in air.

Fifty grams of the 1-diazo-2-naphthol-4-sulphonic acid (III) thus prepared was stirred in 100 ml of water until a creamy suspension formed. A second reagent, consisting of 40 grams of sodium-*p*-phenol sulphonate (IV), and 16 grams of sodium hydroxide dissolved in 100 ml of water to which was added 200 ml of a saturated solution of sodium hydroxide, was prepared. The suspension of the diazonium salt was added slowly over a period of 3 hours to the phenol sulphonate solution, with vigorous stirring. The mixture was then heated slowly to 60°C and maintained at that temperature until coupling was complete (Lindstrom and Diehl, 1960). Concentrated hydrochloric acid was added until the solution was strongly acidic, after which the mixture was cooled and the red precipitate filtered and washed twice with 100 ml portions of a solution containing 150 grams of sodium chloride and 50 ml of concentrated hydrochloric acid per liter. The product was allowed to dry in air.

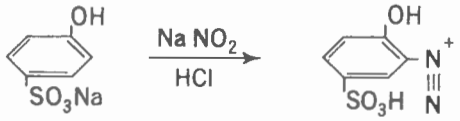
Both the colour and polarogram of the compound suggested that it was indeed an azo dye. There was, however, no evidence of a reaction between the dye and aluminum ion, indicating that the hydroxyl groups were not adjacent to the azo group or perhaps that some steric factor was unfavourable to complex formation. In order to test the assumption that this dye resulted from the coupling of the diazonium compound with itself, rather than with *p*-phenol sulphonic acid, the above procedure was repeated omitting the addition of the *p*-phenol sulphonic acid. A red compound resulted whose colour and polarographic behaviour were identical to the first compound prepared, indicating that the reaction that had occurred was either a dimerization or a polymerization of the diazonium molecule. This may be the same as the "reddish impurity" mentioned by Lindstrom and Diehl, in the report of their preparation of Calmagite. No further investigation of the nature of this dye was carried out.

Preparation of 1-(1-hydroxy-4-sulphonic acid-2-phenylazo)-2-naphthol-3,6-disulphonic acid, sodium salt (V)

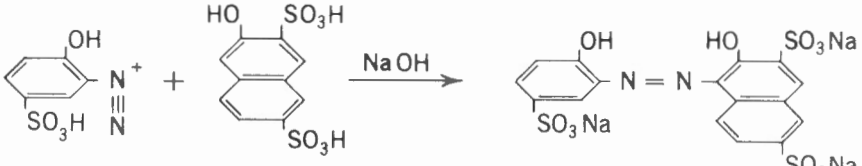


(V)

Sodium *p*-phenol sulphonate (IV) was diazotized by the procedure of Tedder and Theaker (1958) and then coupled with 2-naphthol-3, 6-disulphonic acid (VI).



(3)



(4)

(VI)

Twenty grams of sodium *p*-phenol sulphonate was treated with 1,500 ml of water, 100 grams of sodium nitrite, and 250 ml of 2N hydrochloric acid and allowed to stand for three days at 20°C. The solution was then treated with sulphamic acid to remove the excess nitrous acid, neutralized with sodium bicarbonate, and then brought to pH 8 with a saturated solution of sodium hydroxide. Thirty grams of 2-naphthol-3, 6-disulphonic acid was added and the mixture, after stirring for 2 hours, was acidified with concentrated hydrochloric acid to precipitate the dye.

The precipitate was filtered off with suction, transferred to a beaker, triturated with 200 ml of ethanol and again filtered. This trituration procedure was repeated two more times and the dye was allowed to dry in air. The product was then desiccated over potassium hydroxide in a vacuum desiccator for 4 days. The yield was 21.8 grams.

Analysis of the Product and Test of Polarographic Behaviour

The residual sodium chloride content was determined gravimetrically by precipitating the chloride from a slightly acidic solution with silver nitrate. Because there was considerable co-precipitation of organic matter the precipitate was filtered and redissolved in aqueous ammonia. After the excess ammonia was expelled by gentle boiling, the solution was reacidified, and a small excess of silver nitrate was added. After digestion the precipitate was collected in a fritted glass crucible, dried, and weighed. The NaCl found was 1.48 per cent.

A routine carbon and hydrogen analysis was made, with the following results:

Analysis

Calculated (for C_{16} H_9 N_2 O_{11} S_3 Na_3 and corrected for 1.48 per cent NaCl):
C, 33.18%; H, 1.57%; Ash, 38.28%.
Found: C, 33.40%; H, 2.22%; Ash, 38.41%.

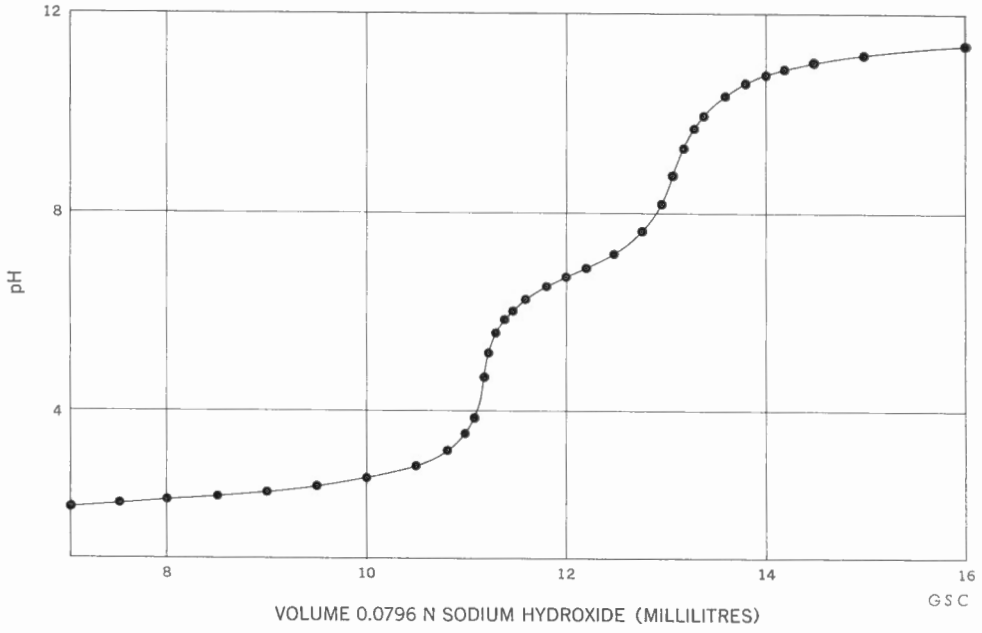


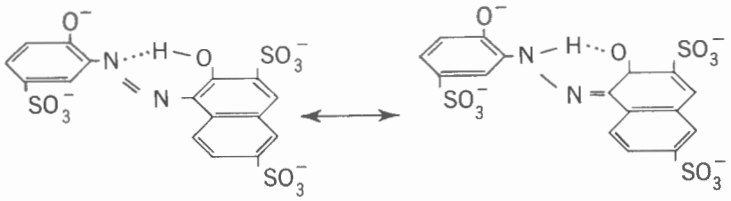
FIGURE 10. Titration curve for 0.0894 grams of 1-(1-hydroxy-4-sulphonic acid-2-phenylazo)-2-naphthol-3, 6-disulphonic acid dissolved in 9.00 ml of 0.1013 normal hydrochloric acid and 15 ml of water.

An acid-base titration of the dye was made in the following manner: a sample of the dye was dissolved in dilute standard hydrochloric acid and the solution was titrated with standard sodium hydroxide, the pH being read after each addition of base. Two distinct end points were observed, shown in Figure 10; the first is due to the neutralization of the three sulphonic acid groups and the second due to *ortho*-hydroxyl group neutralization. The number of milliequivalents of sodium hydroxide used to proceed from the first equivalence point to the second is equal to the number of milliequivalents of *ortho*-hydroxyl groups neutralized.

Analysis

Dye sample dissolved (corrected for 1.48 per cent NaCl):	0.154 meq
NaOH used to neutralize *ortho*-hydroxyl group:	0.155 meq

It can readily be seen from the above results that only one of the two *ortho*-hydroxyl groups present in the molecule can be neutralized by sodium hydroxide, which can be explained by considering the following facts. First, the dye probably exists in the *trans* configuration, due to the pronounced steric hindrance effects encountered in the *cis* configuration. In three of the four possible *trans* forms, the hydrogen of one of the hydroxyl groups lies adjacent to one of the nitrogen atoms of the azo group. Hydrogen bonding will occur between the hydrogen and nitrogen, thus forming a resonating six-membered ring, which will stabilize these structures.



The removal of the second *ortho*-hydroxyl hydrogen ion would interrupt this resonance stabilization and therefore would be very unfavourable.

Preliminary tests with the polarograph indicated that the dye, 1-(1-hydroxy-4-sulphonic acid-2-phenylazo)-2-naphthol-3,6-disulphonic acid (V), exhibited the desired characteristics towards aluminum ion. Two polarographic waves appeared in polarograms of buffered solutions containing both the dye and aluminum ion, the second wave displaced from the first by about 0.2 volts. The diffusion current of the first wave, unfortunately, was masked by a pronounced maximum, which could not be eliminated by any of the usual maximum suppressors. It was found, however, that the addition of 0.004 per cent methylene blue sufficiently suppressed the maximum to allow accurate readings of the diffusion current, probably due to the adsorption of the leuco base of this dye onto the dropping mercury electrode (Kolthoff and Lingane, 1952, p. 257).

Apparatus and Reagents

Except for the following solutions, the apparatus and reagents used have been described in Part I.

The dye solution for use in all the experiments except the pH, kinetic, and combining ratio studies, was prepared by dissolving 9.0 grams of the dye, [1-(1-hydroxy-4-sulphonic acid-2-phenylazo)-2-naphthol-3, 6-disulphonic acid, sodium salt (V)] and 60.0 grams of sodium acetate trihydrate in water containing 25.0 ml of glacial acetic acid and 8.0 ml of a 1 per cent (w/v) aqueous solution of methylene blue, and diluting the solution to 2 liters. The solution was therefore 8 millimolar in dye, 0.22 molar in sodium acetate, and at a pH of 4.7.

The dye solution, buffered at pH 5.7 for use in the pH studies, was prepared by dissolving 30.0 grams of sodium acetate trihydrate and 4.50 grams of the dye in water containing 25.0 ml of acetic acid (1:19) and 4.0 ml of 1 per cent methylene blue solution, and diluting the resulting solution to 1 liter. The solution was therefore 8 millimolar in dye and 0.22 molar in sodium acetate.

The dye solution used to determine the ratio of dye to aluminum in the complex and in the kinetic studies was prepared more precisely. The buffer was prepared separately by dissolving 60.0 grams of sodium acetate trihydrate in water containing 25.0 ml of glacial acetic acid and diluting to 2 liters. A sample of the dye was dried in a vacuum desiccator over potassium hydroxide for an additional 2 days and then 4.4945 grams of the desiccated dye was dissolved in the buffer, to which was added 4.0 ml of 1 per cent methylene blue solution, and the solution diluted to 1 liter with the buffer. Thus the resulting solution was 7.76 millimolar in dye, 0.22 molar in sodium acetate, and was at a pH of 4.7.

All the solutions used to determine the effects of different ions were prepared from either reagent grade chemicals or National Bureau of Standards samples.

Experimental Results

Calibration Curve

A series of solutions was prepared that contained different amounts of aluminum and excess dye. Twenty ml of each of the standard solutions, ranging from 1.0 to 9.0 millimolar in aluminum ion, and of a blank containing no aluminum ion, were transferred to ten 50 ml volumetric flasks and were made just basic to methyl red with a saturated solution of sodium hydroxide. Perchloric acid (5N) was added dropwise until the solutions were just acid, then 25.0 ml of the 8 millimolar dye solution buffered at pH 4.7 was added to each flask and the solutions made up to volume with water. After immersion in a 54°C constant temperature bath for 20 minutes, the flasks were cooled in tap water and aliquots were transferred to polarographic cells (Harris, 1958), deoxygenated, and polarographed.

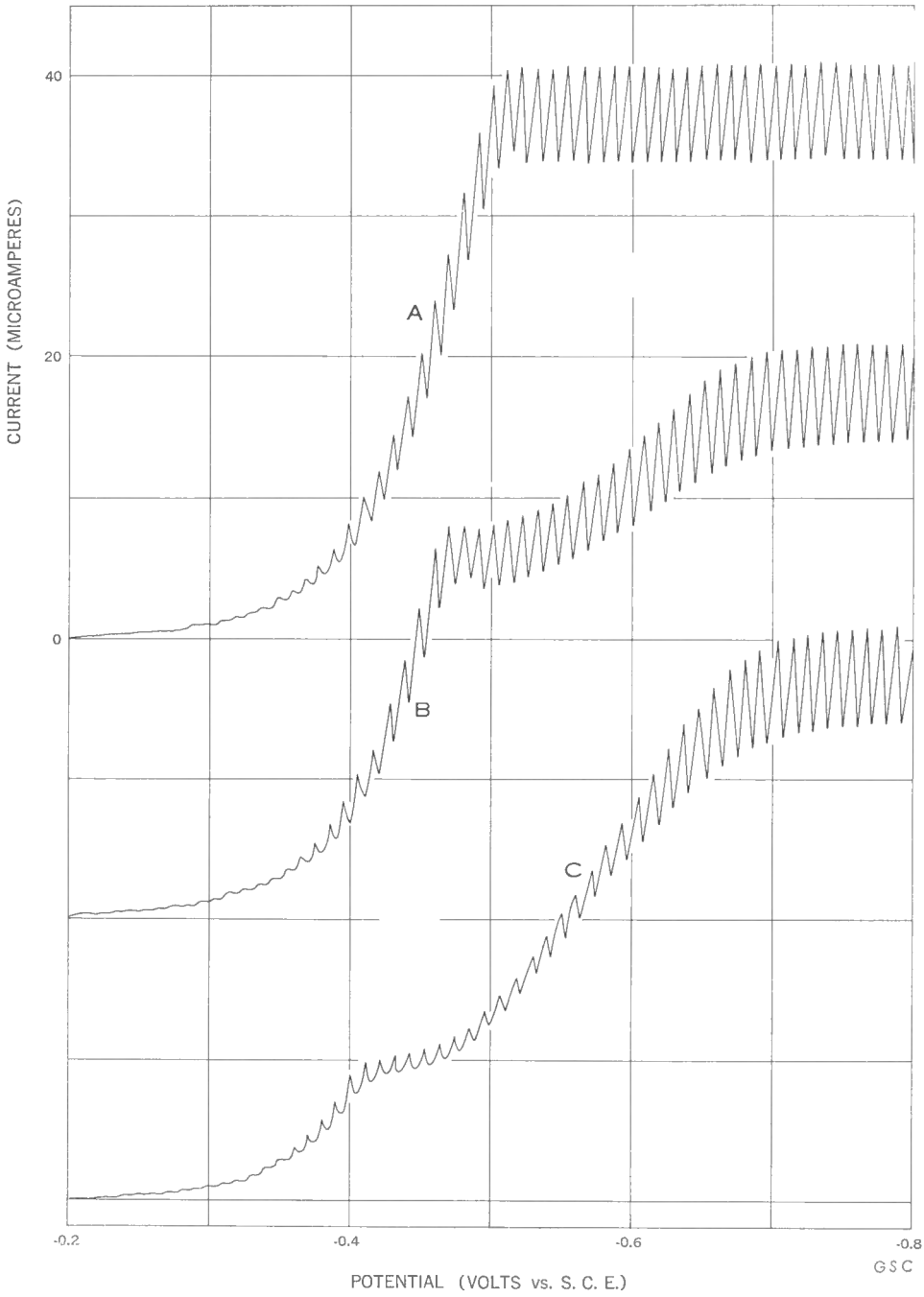


FIGURE 11. Polarograms of 1-(1-hydroxy-4-sulphonic acid-2-phenylazo)-2-naphthol-3,6-disulphonic acid in 0.11 normal acetate buffer solution pH 4.7, with and without added aluminum ion. A, dye solution alone; B, dye solution 1.2 mM in aluminum ion; C, dye solution 2.8mM in aluminum ion. All solutions contain 0.004 per cent methylene blue.

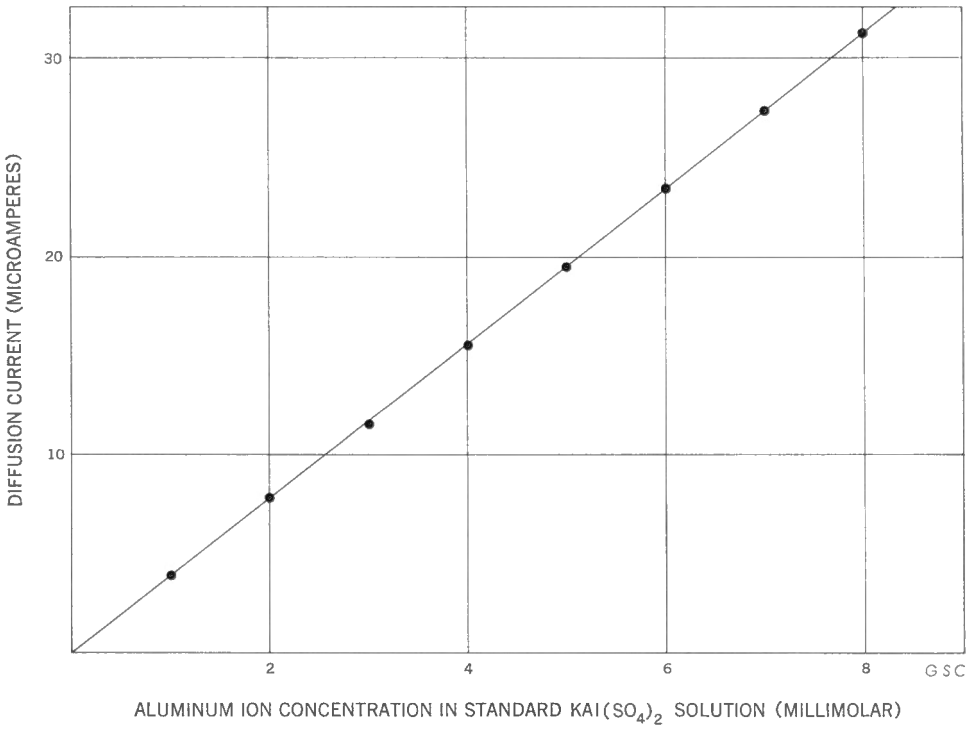


FIGURE 12. Variation of diffusion current of second wave with aluminum ion concentration.

The polarogram for the dye solution alone consisted of one wave for the reduction of the azo group having a half-wave potential of −0.45 volts vs. S.C.E. Polarograms of the aluminum-dye solution consisted of two waves, the height of the first wave decreasing with increasing aluminum ion concentration, and the height of the second wave increasing correspondingly. Figure 11 shows current-voltage curves for the dye alone and in the presence of aluminum ion, and Figure 12 is a plot of the measured diffusion currents of the second wave against the concentrations of the standard aluminum solution used. The plot is linear, as it is for Pontachrome Violet SW, but in contrast to the latter this plot passes through the origin. There is also a difference with regard to the observed half-wave potentials; the shifts with increasing aluminum ion concentration are considerably greater for the present dye than for Pontachrome Violet SW, and in the second wave the shift is in the opposite direction. Figure 13 is a plot of the half-wave potentials of the two waves against the aluminum ion concentration of the standard solution used. Because of this pronounced shift in half-wave potential with varying aluminum ion concentration it was impossible to read the diffusion current of the first wave at the same potential for each. For the sake of consistency the potential at which the first diffusion current was read was plotted against the wave height of the second wave, and the best straight line drawn through the points. This plot, shown in Figure 14, was used to determine the potential at which to read all future polarograms.

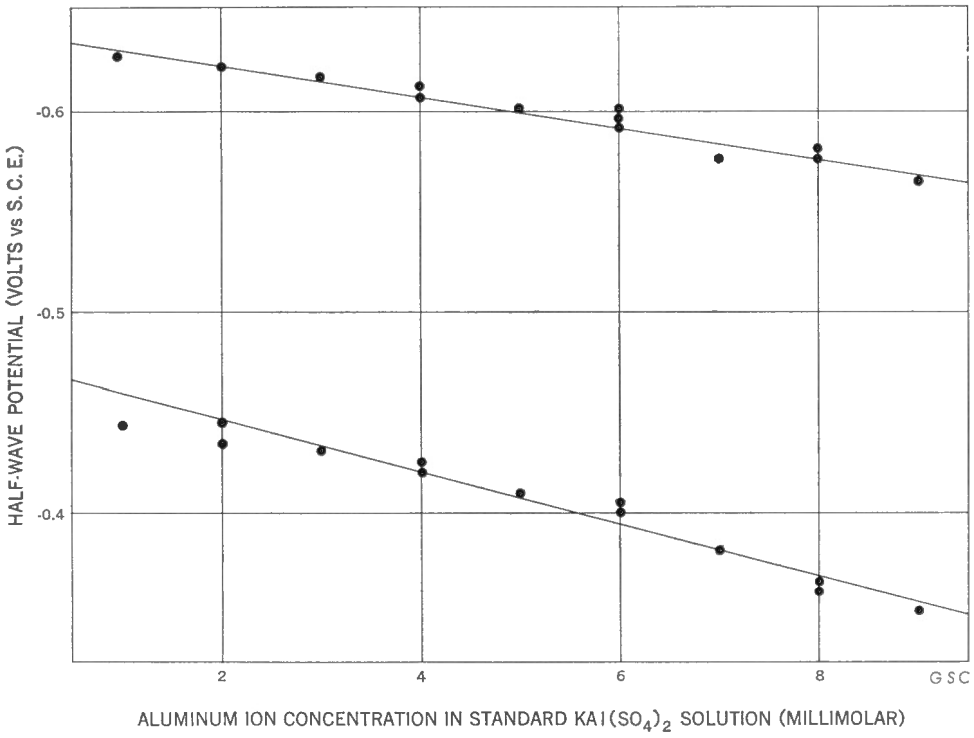


FIGURE 13. Variation of half-wave potentials of first and second azo dye waves with aluminum concentration.

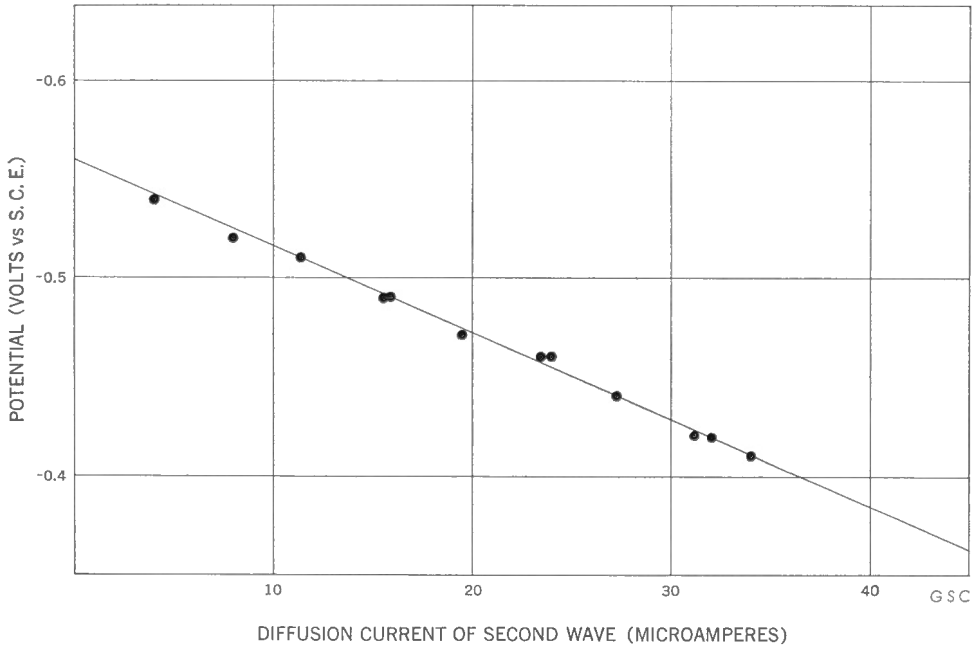


FIGURE 14. Plot of the potential at which the diffusion current of the first wave was read versus the diffusion current of the second wave.

Effect of pH

To determine the effect of pH a series of solutions, of different pH but containing constant amounts of aluminum ion and dye, was used. The standard aluminum-dye solution consisted of 120 ml of freshly prepared 0.020 molar aluminum solution containing no added perchloric acid, combined with 600 ml of the dye solution buffered at pH 5.7. Thirty ml aliquots of this aluminum-dye solution were transferred by pipette into each of twenty-two 50 ml volumetric flasks. Acetic acid was added to seventeen of the flasks in amounts calculated to give pH values ranging from 5.4 to 3.7, and sodium hydroxide to four of the flasks to give pH values up to 6.0; one flask was left with no added acetic acid or sodium hydroxide. Thus all the solutions would be at constant ionic strength except those four to which sodium hydroxide was added. The flasks were made up to volume with water and immersed in the constant temperature bath at 54°C for 20 minutes. After cooling under the tap, and purging with nitrogen gas, polarograms were run on aliquots. Immediately after taking the polarogram the pH of each sample was read.

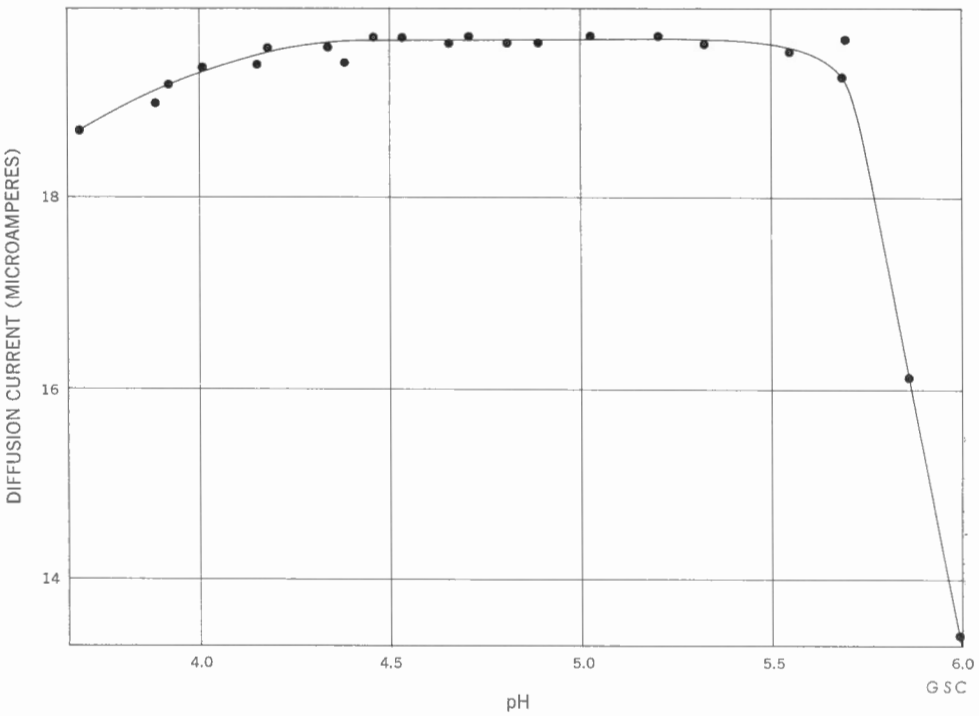


FIGURE 15. Variation of the diffusion current of the aluminum-dye wave (second wave) with pH.

The diffusion current data obtained are plotted in Figure 15. The diffusion current is constant over a pH range of about 4.4 to 5.4 and thus the optimum pH range for polarographic work is 4.9 $\pm$ 0.4. As in the results obtained by Willard and Dean (1950) and Perkins and Reynolds (1958b) with Pontachrome Violet SW, the diffusion

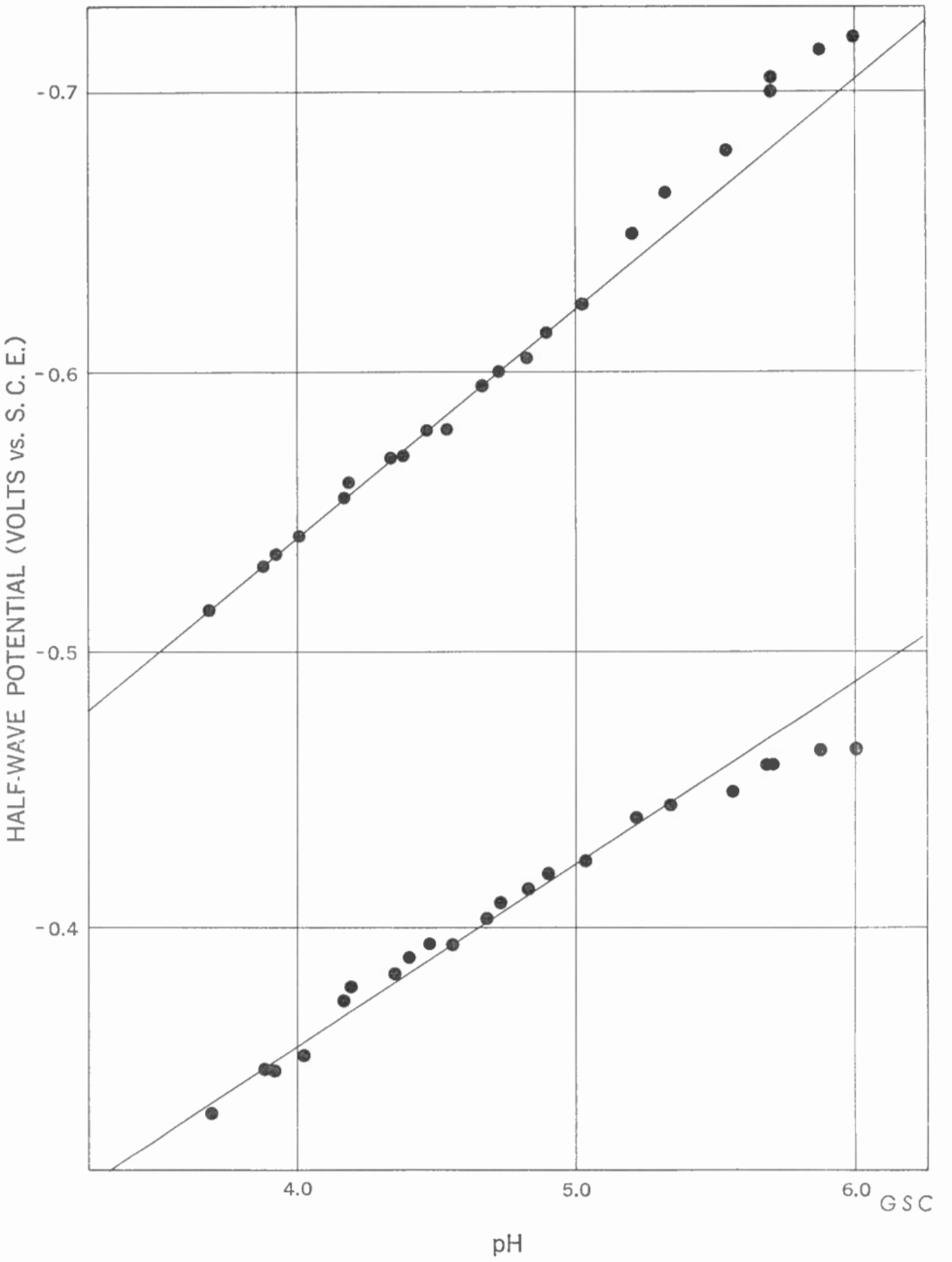


FIGURE 16. Variation of the half-wave potentials of the first and second waves with pH.

current decreases below pH 4. The drop-off above pH 5.5, however, is the opposite of the effect observed by the preceding workers for their dye, the diffusion current of which increased abruptly above pH 5.

When the diffusion currents of the free dye waves of this same series were plotted against the measured pH values, very similar results were obtained. That is, there was a similar decrease in the diffusion current below pH 4, with a levelling off between pH 4.4 and pH 5.4, followed by an abrupt drop-off above this pH.

The half-wave potentials of the two waves were plotted against the pH of the solutions, as shown in Figure 16. The half-wave potentials of both waves are a linear function of pH up to about pH 5, and can be represented by the following empirical equations: for the first wave due to unreacted dye, $E_{\frac{1}{2}} = -0.095\text{-}0.066$ pH; and for the second wave due to the aluminum-dye complex, $E_{\frac{1}{2}} = -0.212 - 0.082$ pH.

Effect of Other Ions

The interference of a number of common ion species was next studied. To each of a series of 50 ml volumetric flasks was added 0.100 millimoles of aluminum ion and various amounts of the ion species to be studied. The adjustment of the pH, the adding of the dye solution buffered at pH 4.7, and the heating of the solutions were done as described previously for the preparation of the calibration curve.

Table II

Effect of Other Ions

Ion added	Millimoles	Milligrams	Corresponding percentage in rock sample	Aluminum Found[1] (millimoles) (1)	(2)
Cl^-	12.1	430.		0.100	0.098
ClO_4^-	40.	3980.		0.100	0.100
NO_3^-	15.8	980.		0.100	0.100
$PO_4^{\equiv}$	0.003	0.284	0.53 as P_2O_5	0.101	
	0.03	2.84	5.33	0.086	0.100
	0.30	28.4	53.3	0.018	
$SO_4^{\equiv}$	1.8	173.		0.101	
	18.	1730.		0.094	0.094
Ba(II)	0.073	10.04	28.0 as BaO	0.099	
Ca(II)	0.125	5.0	17.5 as CaO	0.100	

Table II—(*cont.*)

Ion added	Millimoles	Milligrams	Corresponding percentage in rock sample	Aluminum Found[1] (millimoles) (1)	(2)
Fe(II), (III)	0.0018	0.1010	0.36 as Fe_2O_3	0.104	
	0.0181	1.0103	3.59	0.105	0.113
	0.181	10.103	35.9	0.116	
Mg(II)	0.125	3.04	12.6 as MgO	0.100	
Mn(II)	0.030	1.632	5.27 as MnO	0.103	
	0.089	4.896	15.8	0.100	
	0.297	16.32	52.7	0.098	0.101
Na(I)	30.	690.		0.100	0.100
Ni(II)	0.0003	0.0199	0.06 as NiO	0.102	
	0.0034	0.1990	0.64	0.104	0.106
	0.034	1.990	6.35	0.136	
Sr(II)	0.011	1.005	2.85 as SrO	0.100	
Th(IV)	0.0004	0.0996	0.28 as ThO_2	0.103	
	0.0043	0.996	2.84	0.106	0.106
	0.043	9.96	28.4	0.146	
Ti(IV)	0.0208	0.996	4.16 as TiO_2	0.103	
	0.1040	4.98	20.8	0.101	
	0.2496	11.95	49.8	0.105	0.135
U(VI)	0.0004	0.0998	0.88 as U_3O_8	0.103	
	0.0042	0.9984	8.84	0.106	0.106
	0.042	9.984	88.4	0.162	

[1] 0.100 millimoles, or 2.7 milligrams Al^{+++} present in each. This corresponds to 12.75% Al_2O_3 in the original rock. In column (1) are the results of readings taken the same day as the solution was prepared. In column (2) are readings taken 5 days later.

The results obtained are given in Table II. Permissible amounts of different ions were taken to be those amounts failing to cause more than 3 per cent error in the amount of aluminum found. Chloride and sulphate ions present in very large amounts interfere by causing precipitation of the dye, and therefore hydrochloric and sulphuric acids should be avoided in any preliminary solution preparation steps unless they can later be reduced in concentration. Perchlorate ion and nitrate ion seemed to cause no interference in the amounts tested. Fluoride ion forms a more stable complex with aluminum than does the dye, and must therefore be removed completely in the preliminary preparation of the sample. Phosphate ion also interferes by complexing

with aluminum; its presence is permissible, however, if the percentage of phosphorus pentoxide in the original sample does not exceed 0.5. Large amounts of sodium, magnesium, calcium, strontium, barium, and manganese ions are permissible. Titanium, iron, nickel, thorium, and uranium ions interfere by increasing the height of the dye-aluminum wave. For the nickel and thorium the number of millimoles added corresponds closely to the increase in the number of millimoles of aluminum found, indicating that these metals probably form complexes with the dye similar in nature to the aluminum-dye complex. Thorium and uranium are generally present in rock samples merely as traces, and in this concentration their interference will be negligible. Iron and nickel ions, on the other hand, should be removed from the sample solutions prior to the addition of the dye. This can be accomplished conveniently by electrolysis at the mercury cathode. Titanium, occasionally present in rocks in amounts over 1 per cent (calculated as TiO_2), is the only other cause of uncertainty. A more detailed study was therefore carried out to determine the extent of titanium ion interference.

For this purpose a sulphate-free 0.005 molar titanium ion solution was prepared by fusing National Bureau of Standards titanium dioxide with sodium carbonate, dissolving the fused material in hydrochloric acid, and diluting the solution to the desired volume with water. Into nine 50 ml volumetric flasks were put 0.100 millimoles of aluminum ion and amounts of the above titanium ion solution ranging from 0 to 8 ml. The solutions were then treated in the same manner as the aluminum-dye solutions used for the determination of the calibration curve. Polarograms were run on aliquots after they had been freed of dissolved oxygen. To determine the effect of time, the solutions were kept at 54°C for an additional 80 minutes, after which polarograms were run. Again, after 5 days standing at room temperature, polarograms were run. It can readily be seen from the results depicted in Table III that the magnitude of the effect of titanium ion increases with time. These data indicate that it is permissible to have up to 0.015 millimoles of titanium ion in the final solution, which corresponds to 3 per cent titanium dioxide in the original sample. If the polarograms are run immediately after the solution is prepared, the presence of much larger amounts of titanium dioxide is permissible.

To throw some light on the nature of the type of interference caused by titanium ion, such as the effect of aging, a series of solutions was prepared in which various amounts of a solution containing titanium ion were added to an aluminum-dye solution, which is reverse to the order used in the above samples. Twenty-five ml of a freshly prepared 0.02 M aluminum ion solution containing no added acid, and 125.0 ml of the 8 millimolar dye solution buffered at pH 4.7, were combined in a flask and thoroughly mixed. Fifteen ml aliquots of this solution were then pipetted into each of nine 25 ml volumetric flasks, and 2.5 millimolar titanium ion solution was added in amounts ranging from 0 to 8 ml. The flasks were diluted to volume with water and were heated to 54°C for 20 minutes. They were then quickly cooled under the tap and each solution was then kept below 5°C to inhibit any further reaction. Ten minutes before each polarogram was run, an aliquot was transferred from one of the cold solutions into a polarographic cell and immersed in the polarographic bath at 24.7°C for 5 minutes to allow it to come up to temperature. Nitrogen was bubbled through the solution for the next 5 minutes and then a polarogram was recorded.

Table III

Effect of Titanium

(Dye solution added to a solution containing 0.100 millimoles aluminum ion and varying amounts of titanium ion)

TITANIUM ADDED / 50 ml			ALUMINUM FOUND / 50 ml (millimoles)		
Milli-moles	Milligrams	Corre-sponding per cent TiO_2 in rock sample	Solutions at 54° for 20 min.	Solutions at 54° for 100 min.	Solutions at room temp. 5 days
0	0	0	0.100	0.100	0.100
0.005	0.240	1.00	0.101	0.101	0.101
0.010	0.479	2.00	0.100	0.101	0.102
0.015	0.719	3.00	0.100	0.102	0.103
0.020	0.958	4.00	0.101	0.102	0.104
0.025	1.198	5.00	0.100	0.102	0.104
0.030	1.437	6.00	0.100	0.103	0.107
0.035	1.677	7.00	0.101	0.105	0.107
0.040	1.916	8.00	0.102	0.106	0.108

Table IV

Effect of Titanium

(Titanium ion solution added to dye solution containing 0.100 millimoles aluminum ion)

TITANIUM ADDED / 50 ml			ALUMINUM FOUND / 50 ml (millimoles)	
Milli-moles	Milligrams	Corre-sponding per cent TiO_2 in rock sample	Solutions at 54°C for 20 min.	Solutions at room temp. for 2 weeks
0	0	0	0.099	0.101
0.005	0.240	1.00	0.099	0.100
0.010	0.479	2.00	0.100	0.101
0.015	0.719	3.00	0.102	0.103
0.020	0.958	4.00	0.103	0.104
0.025	1.198	5.00	0.105	0.106
0.030	1.437	6.00	0.106	0.108
0.035	1.677	7.00	0.110	0.111
0.040	1.916	8.00	0.114	0.114

The flasks were then allowed to stand at room temperature for 2 weeks and polarograms were run again on each sample to determine the effect of aging. From data given in Table IV, it can be seen that aging has little effect on the results. The interference was fairly pronounced from the beginning and did not take several days to develop as it had done in the previous experiment.

Effect of Temperature and Time of Standing

A solution that was 4 millimolar in both aluminum and dye, 0.11 molar in acetate ion, and at a pH of 4.7, was polarographed every few minutes for a period of 3 hours and was found to take about 120 minutes to reach final equilibrium at 24.7°C. To determine the time required for reaction at a higher temperature, a solution, buffered at pH 4.7, was prepared in a 50 ml volumetric flask in the usual manner, with a final aluminum ion concentration of 2 millimolar and a dye concentration of 4 millimolar. This was immediately immersed in a constant temperature bath at 54°C. Five ml aliquots were removed at timed intervals and transferred to cold polarographic cells in an ice bath to inhibit further reaction. Each sample was left in the ice bath until 6 minutes before polarographing the solution, at which time the cell was transferred to the polarographic constant temperature bath and allowed to remain there for 3 minutes to equilibrate the solution temperature. Nitrogen was then bubbled rapidly through the sample for the next 3 minutes, after which a polarogram was recorded. The results indicated that the solutions had reached equilibrium after being in the 54°C constant temperature bath for 14 minutes.

To determine whether the complex was stable at elevated temperatures, solutions prepared in the usual way were allowed to attain equilibrium in the constant temperature bath at 54°C and were then polarographed. They were then immersed in a boiling water bath for 20 minutes, cooled under the tap, deoxygenated, and polarographed again. No change was observed in any of the polarograms from those taken before the flasks were immersed in boiling water, indicating that the complex is stable at elevated temperatures. Therefore the solutions may be equilibrated at any temperature between 20°C and 100°C.

Ratio of Dye to Aluminum in the Complex

To determine the ratio of aluminum to dye in the complex at pH 4.7, Job's method of continuous variations (Perkins and Reynolds, 1958b) was used. A series of aliquots, ranging from 1 to 9 ml, of a solution 8.00 millimolar in aluminum ion were pipetted into nine 25 ml volumetric flasks. The pH was adjusted as usual and then 7.76 millimolar buffered dye solution was added to the flasks in amounts ranging from 9 to 1 ml, thus giving a series of flasks in which the ratio of dye to aluminum ranged from 1:9 to 9:1. In order to keep the buffer concentration constant in all the solutions, an acetate buffer solution of the same pH and concentration was added in amounts to give a total buffer volume of 10.0 ml in each flask, including the buffer of the dye solution itself. The solutions were made up to volume, heated as usual, and an aliquot of each was deoxygenated and polarographed.

The heights of the dye-aluminum waves were plotted against the ratio of dye to aluminum ion in the solutions to give the plot shown in Figure 17. The intersection of the straight lines occurs at a point representing 5.11 ml of 7.76 millimolar dye solution and 4.89 ml of 8.00 millimolar aluminum solution, which is equivalent to 39.6 millimoles of dye and 39.8 millimoles of aluminum ion. It was therefore concluded that the ratio of aluminum to dye in the species existing at pH 4.7 was one to one.

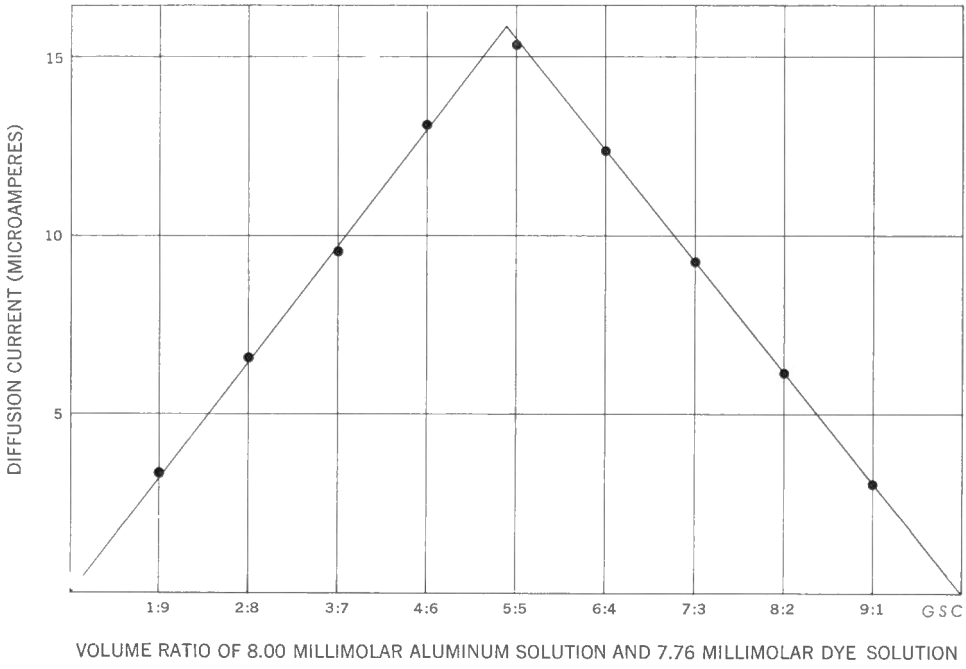


FIGURE 17. Determination of dye to aluminum ratio in complex at pH 4.7.

Measurement of Rate Constants

An investigation into the kinetics of the reaction between the dye and aluminum ion was started, with typical determinations proceeding as follows. Five ml of a 7.76 millimolar aluminum ion solution at pH 4.5, previously freed of dissolved oxygen, was added to 5 ml of a 7.76 millimolar dye solution buffered at pH 4.7, which had also previously been freed of dissolved oxygen. Nitrogen was then bubbled through the solution for one minute to remove the last traces of oxygen and a polarogram was recorded immediately. Polarograms of the same solution were then taken at timed intervals for a period of 2 hours. The same procedure was repeated for another more dilute solution, which was prepared from 1.0 ml of 7.76 millimolar dye solution, 1.0 ml of 7.76 millimolar aluminum ion solution, 4.0 ml of an acetate buffer solution of the same concentration as that in the dye solution, and 4.0 ml of water.

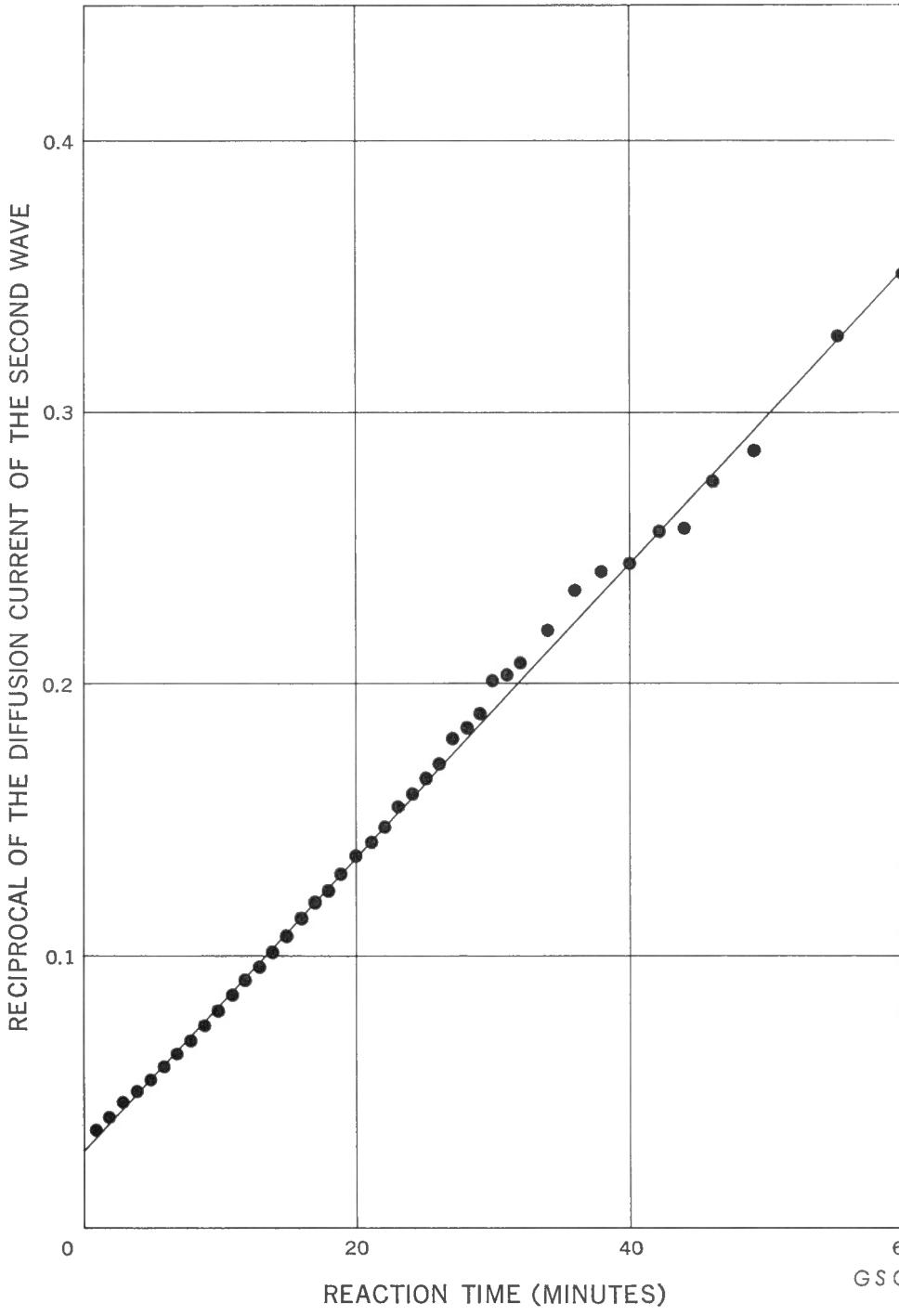


FIGURE 18. Variation of the reciprocal of the diffusion current (microamperes^{-1}) of the aluminum-dye wave with time.

Thus the ionic strength and hydrogen ion concentration were the same in both solutions but in the latter the aluminum ion and dye concentrations had been reduced by a factor of five.

In both experiments a plot of the reciprocal of the diffusion current of the dye wave against reaction time yielded straight lines for the greater part of the reaction. For a typical rate plot see Figure 18. However, after the reaction had proceeded beyond 92 per cent completion ($>$ 60 minutes) in the first instance and beyond 80 per cent completion ($>$ 40 minutes) for the more dilute solution, there was considerable scatter of the points. No significance can be assigned to this effect because of the large relative error involved in reading the small diffusion currents near the completion of the reaction, and because of the progressively increasing change in the ratio of the concentrations of the two reactants if their initial concentrations were not identical. The latter point is important, because the type of rate plot used in Figure 18 applies only when the concentrations of the reactants are identical at all times.

Second order rate constants calculated from these plots, however, were not in agreement for the two concentrations studied. For the solution 3.88 millimolar in dye and aluminum ion triplicate determinations yielded second order rate constants with the values 50.6, 50.0, and 53.2 liters $mole^{-1}$ min^{-1}; for the solution 0.776 millimolar in dye and aluminum ion duplicate determinations yielded rate constants with the values 112 and 113 liters $mole^{-1}$ min^{-1}.

Analysis of Standard Samples

Six samples were analyzed as follows. The preparation of the sample solutions up to the mercury cathode electrolytic separation step was carried out as described in Part I. The entire solutions were electrolysed at the mercury cathode with a current density of 0.13 to 0.19 amp. cm^{-2} until a test for iron with potassium thiocyanate was negative, and then electrolysed for an additional 15 minutes. Twenty ml aliquots of the electrolysed solutions were transferred to 100 ml beakers and evaporated on a sand bath until sulphur trioxide fumes ceased to be evolved. About 5 ml of distilled water and 5 drops of concentrated sulphuric acid were added, and the contents were again fumed to dryness. The sides of the beakers were washed down and the fuming procedure repeated once again, to ensure the expulsion of all traces of fluoride ion.

The residues were taken up in 3 ml of 5 N perchloric acid, with heating, and transferred quantitatively to 50 ml volumetric flasks. A saturated sodium hydroxide solution was added until the solutions were just basic to methyl red and then 5 N perchloric acid was added until the solutions were just acidic again. Twenty-five ml of the 8 millimolar dye solution buffered at pH 4.7 was added and the solutions made up to volume at 25°C with water. After immersion in a 54°C constant temperature bath for 20 minutes the flasks were cooled in tap water and aliquots were transferred to polarographic cells, deoxygenated, and polarographed.

To convert the diffusion current data into per cent Al_2O_3, the aluminum ion concentration in millimoles per liter, read from the calibration curve (Figure 12) was multiplied by 2.55, as described in Part I. The results of triplicate determinations are listed in Table V.

Table V

Analysis of Standard Samples

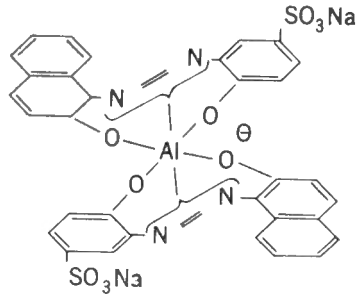
Sample	Per cent Al_2O_3			
	Certified Value	Values Found		
G 1	14.30	14.30	14.56	14.34
W 1	15.08	15.48	15.55	15.20
Glass sand, NBS 81	0.265	—	0.38	0.31
Soda feldspar, NBS 99	19.06	19.41	19.00	19.09
Opal glass, NBS 91	6.01	5.95	5.97	6.10
Limestone, NBS la	4.16	4.28	4.18	4.13

Discussion

Several theories regarding the structure of the aluminum-Pontachrome Violet SW complex have been proposed to explain its observed polarographic behaviour (Dean and Bryan, 1957; Perkins and Reynolds, 1958c). Stabilization by aluminum of the *cis* isomer of the dye has been eliminated on the grounds that the half-wave potential of the aluminum-dye complex is shifted to a more negative value from that of the free dye, whereas the *cis* isomer of azobenzene is observed to have a more positive half-wave potential than the stable *trans* form of this compound (Winkel and Siebert, 1941). Secondly, steric hindrance and the resulting strained structure would make the *cis* form unlikely. Stabilization of the anionic form of the dye might seem to be a reasonable explanation, because the inductive effect of the extra negative charges might make the azo group more difficult to reduce. This, however, has been ruled out as an explanation by the absence of the second wave at higher pH values where the dye should be mainly in the anionic form (Dean and Bryan, 1957). Perkins and Reynolds (1958c) favour the explanation that the azo group is involved in complex formation with aluminum. They conclude that aluminum forms a true Werner complex by replacement of the hydrogen ions of the *ortho*-hydroxyl groups and the acceptance of an electron pair from the nitrogen atoms (Callis, Nielsen, and Bailar, 1952). Therefore the dye acts as a tridentate ligand, and forms with aluminum two fused chelate rings. These authors suggest that the fused ring structure gives sufficient stability to the complex to cause the observed shift in half-wave potential, as in complexes with other metals involving an azo dye with only one *ortho*-hydroxyl substituent, there was no shift in half-wave potential. Dean and Bryan (1957) have also considered this possibility, but eliminated it on the grounds that some metals have been found to form a 3:1 dye: metal complex, which means that the metal would have to have an impossible coordination number of 9 if the ligand was truly tridentate. As it has been found that both *ortho*-hydroxyl groups are necessary for complex formation with aluminum (Beech and Drew, 1940), they concluded that the azo group does not enter into complex formation. Bailar and Callis (1952), on the

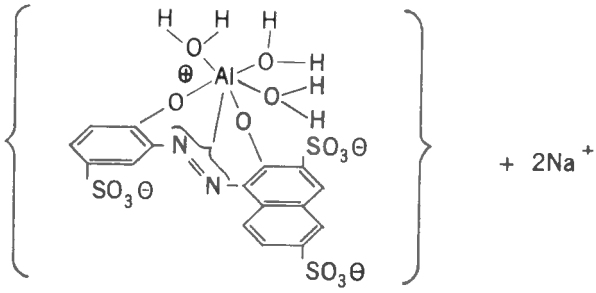
other hand, in dealing with a 3:1 dye:cobalt (III) complex, assumed that it was one of the hydroxyl groups of each dye ligand rather than the azo group, which was not attached to the cobalt. Dean and Bryan have explained the observed shift in half-wave potential on the basis that the rigidity of the complex, as compared with the flexibility of the free dye anion, interferes with normal azo reduction. The fused ring explanation offered by Perkins and Reynolds would contribute a certain amount of rigidity to the complex, so these two explanations do not differ as much as might appear at first sight. The main difference is that Perkins and Reynolds believed that the azo group is involved in covalent bond formation with aluminum, whereas Dean and Bryan believed that this type of bond is absent.

Perkins and Reynolds (1958b) reported that the dye to aluminum ratio in their complex with Pontachrome Violet SW at pH 4.65 was 2:1; Dean and Bryan (1957) reported the ratio under the same conditions to be 1:1. Evidence gathered here in Part I of this report supports the findings of Perkins and Reynolds. The structure proposed by the last-named authors for the complex species formed from the aluminum ion and the dye anion at pH 4.65 is shown below.



Dean and Bryan proposed no particular structure from their findings.

The dye:aluminum ratio for the sulphonated analog of Pontachrome Violet SW was found here to be 1:1. The preference for a 1:1 complex is probably due to the repulsion of the additional negative charges due to the extra sulphonic acid groups. The species resulting from the combination of one aluminum ion with one dye anion would have two negative charges. The probability of the addition of another dye ligand, thus adding five more negative charges to the complex, would certainly be unfavourable. From the above considerations it is thought that the structure of the complex species existing at pH 4.7 would be as follows:



The possibility that one of the coordination positions of the aluminum is filled by another anion such as the acetate ion has not been eliminated. It is unlikely, however, that a perchlorate anion would be in the coordination sphere about the aluminum, because of the difficulty in coordinating perchlorate ion with any metal.

Although results indicate that there is a definite decrease in the diffusion current of the dye-aluminum complex both below pH 4 and above pH 5.5, it is unlikely that this effect is due to a breakdown of the complex species at these pH ranges. Rather it is likely that a purely chemical or polarographic phenomenon of the dye itself is involved, because diffusion currents of the free dye were found to behave similarly over the same pH range. As the pH range studied was very limited, no more definite conclusions about the cause of this lowering of diffusion current can be drawn. Studies involving determinations of the number of electrons transferred during reduction, through a larger pH range, and an analysis of the reduction product(s) formed during prolonged electrolysis at a mercury cathode under conditions similar to those used for the polarographic analysis would be valuable in formulating the electron reactions at different pH values.

Although the results of the kinetic determinations are certainly not complete, certain conclusions can be drawn regarding the type of reaction involved between the aluminum ion and the dye cation. If the reaction path merely involved a simple bimolecular reaction between the aluminum and dye ions, then the rate constant should be independent of the initial concentrations of the reactants. The fact that different rate constants were found, corresponding to different initial concentrations of the reactants, indicates that a more complicated reaction path is involved. Although acid or base catalysis may be involved in the reaction this does not account for the variations in rate constants found, because the hydrogen ion concentration was kept constant throughout the determinations. Neither would a primary or secondary salt effect account for the variation in the results, because the ionic strengths of the solutions were kept constant for the various determinations. It is evident, therefore, that the rate determining step of the complexing reaction is not a simple bimolecular reaction between the aluminum ion and the dye anion. Certainly very much more data at varying pH values, varying initial concentrations of reactants, varying ionic strength and varying temperature is needed before the exact nature of the reaction path can be proposed.

It is obvious from the results that the type of interference caused by titanium ion is complex. The magnitude of the interference is always much less than would be expected from the amount of titanium added, and moreover it depends upon the order in which the reactants are added to one another. The studies made to date, however, have not elucidated the nature of the reactions involved.

Conclusions

Results indicate that the method described here can satisfactorily be used for the determination of aluminum in most rocks, with a maximum error of 3 per cent. The final aluminum concentration in the polarographic solution should lie between

0.010 and 0.170 millimoles of aluminum per 50 ml, which corresponds to 1.28 per cent and 21.6 per cent Al_2O_3 in the original rock. The pH of the polarographic solution should lie between 4.5 and 5.3.

Those elements present in the rock that adversely affect the results can conveniently be removed by mercury cathode electrolysis. The levels of tolerance for other ions tested are well above those concentrations normally encountered in rocks; however, the amount and nature of ions added during the preliminary preparation of the sample solution are important. It is recommended that only sodium, perchlorate, and acetate ions be added to the aliquot used to prepare the final polarographic solution. It is inadvisable to add any potassium ion because of the low solubility of its perchlorate. Any fluoride ion added in the initial decomposition procedure must be removed completely because of the strong complex it will form with aluminum, and any sulphate ion added in large excess during preliminary procedures must be reduced in concentration. These latter aims can conveniently be accomplished by fuming to dryness the acidic solution containing these ions.

To save time, the dye-aluminum solutions should be allowed to attain equilibrium at an elevated temperature, the optimum range being 55-70°C for 15 to 20 minutes.

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