STUDIES IN THE ANALYSIS OF STEEL: ELECTROANALYTICAL DETERMINATION OF SILICON AND IRON AND COLORIMETRIC DETERMINATION OF BORON

by

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DEDICATION

This thesis is dedicated to my mother,

Odiso

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SUMMARY

A study has been made of the suitability for steelworks chemical analysis of two instruments recently introduced by the Princeton Applied Research Corporation, by developing some new analytical applications of these instruments.

Two procedures have been developed for the determination of silicon by differential pulse polarography using a PAR 174 Polarographic Analyzer. Both procedures are based on the reduction of β-12-molybdosilicate. The heteropoly acid is formed in the presence of methyl ethyl ketone and excess of molybdate is masked with citrate. Methyl ethyl ketone also stabilises the β-12-molybdosilicate and prevents its transformation to α-12-molybdosilicate. The first method was developed for determining silicon at levels above $0.02\mu g.ml^{-1}$. The formation of β-12-molybdosilicate at this level takes about 15 to 20 minutes. The second method was developed for determining nanogram amounts of silicon. In this latter method, a low concentration of molybdate (approximately $5x10^{-5}M$) is used in order to ensure that low blanks are obtained and at these very low levels of molybdate and silicate, formation of β-12-molybdosilicate is complete only after 18 hours. Each procedure is characterised by high precision and for nanogram amounts of silicon, the coefficient of variation is about 3%. A hundred-fold molar excess of arsenate or phosphate does not interfere. Application of the first method to the determination of silicon in steel, after the removal of iron and other interfering elements by mercury cathode electrolysis, yielded accurate results with mean coefficient of variation of 2%. Both procedures together provide a very sensitive and precise pulse polarographic method for the determination of silicon in steel.

Three procedures have been developed for the determination of iron in iron ore by controlled-potential coulometry at a mercury pool electrode. All coulometric measurements are made on a PAR 173/179 digital coulometer. All three procedures are based on the reduction of iron(III) to iron(II) in a supporting electrolyte of IM oxalate buffer solution at pH 4.5. The first procedure involves the direct determination of iron in the sample after its dissolution, at an applied potential of -0.75V vs SCE. The second procedure involves the use of thallium(I) as internal standard with the reduction of Fe(III) to Fe(II) taking place at -0.45V and that of Tl(I) to Tl(Hg) at -0.90V vs SCE. The third method involves the separation of iron from the sample matrix by solvent extraction with tri-n-butyl phosphate, followed by the reduction of iron(III) to iron(II) at -1.00v vs SCE. Solutions containing 1-5mg of iron can be analysed by the first and third procedures with coefficients of variation of 0.3% and 0.2% respectively. Analysis of sample solutions by the second procedure gives an average coefficient of variation of 0.5%. No systematic interference studies have been made but the third procedure was developed in order to separate iron from interfering elements. Details are given of a coulometric cell which uses an ion exchange membrane to separate the main compartment from the auxiliary and reference electrode compartments.

A colorimetric method for the determination of boron in aqueous solution has also been developed. The method is based on the conversion of boron to BF_4^-, which is then extracted as the tetraphenylphosphonium-fluoroborate ion association complex into chloroform. This is followed by the replacement of the BF_4^- ion by orange IV dye anion and the measurements of the absorbance of the tetraphenylphosphonium-orange IV complex which is formed. Application of the method to the determination of boron in steel was unsuccessful.

GENERAL INTRODUCTION

The work described in this thesis is the third in the series of studies on the analysis of steel under a British Iron and Steel Research Association (BISRA) bursary awarded to the Chemistry Department of Loughborough University of Technology.

The first study by D.R.Marriott (Ph.D. thesis 1970) was concerned with the spectrophotometric determination of tungsten and arsenic. The procedure recommended for the determination of tungsten involved the solvent extraction of tetraphenylarsonium thiocyanatotungstate (V) into chloroform followed by measurement of the absorbance of the extract at 402 nm. Methods of eliminating interference by molybdenum and vanadium were also investigated. The procedure recommended for arsenic involved solvent extraction of arsenic (III) iodide into chloroform followed by colorimetric determination of the arsenic using a molybdenum blue procedure.

The second study was by A.Ashton (Ph.D. thesis 1973) and was concerned with the spectrophotometric determination of tin and zirconium. The procedure recommended for tin involved the extraction of tin (IV) iodide into toluene, back extraction of the tin into sodium hydroxide solution followed by colorimetric determination with catechol violet and cetyltrimethylammonium bromide. The procedure recommended for zirconium is based on a pressure digestion technique followed by colorimetric determination with arsenazo III.

The present work concerns the differential pulse polarographic determination of silicon, controlled-potential coulometric determination of iron and colorimetric determination of boron in iron and steel. The growing complexity of steel making has generated the need for analytical techniques capable of quantitatively measuring ultratrace amounts of elements in steel. Such analytical techniques should be very sensitive and accurate, and should be superior to most other physical or physicochemical techniques available. New electroanalytical instrumentation has recently been introduced which allows macro- and microanalytical methods to be used very conveniently and at a considerably lower capital cost than before. The object of the present study was to evaluate the new instrumentation for the purposes of steel analysis and if possible to develop sensitive analytical procedures for the determination of some selected elements in steel.

The Princeton Applied Research (PAR) 174 Polarographic Analyzer is one of these new instruments and was used to develop differential pulse polarographic procedures for the determination of silicon in steel. Silicon is added to steel to produce various beneficial qualities in the steel.[1] It is almost universally present in magnetic sheet in which in combination with low carbon compositions, it aids in the production of desired crystal orientations and raises electrical resistivity. It contributes to the oxidation resistance in several heat-resisting steels. It also enhances the corrosion resistance of steel by formation of a protective surface film under oxidising conditions such as exposure to oxidising acids. It moderately increases hardenability in steels carrying other non-graphitizing elements. It increases ferrite strength in quenched and tempered steels and also pearlitic steels especially when plasticity is not sought. It is a general-purpose deoxidizer. However, silicon is not always a beneficial alloying element. Carbon steels, for example, are badly attacked at elevated temperatures in the presence of hydrogen, resulting in embrittlement. High-silicon irons have poor mechanical properties and particularly low thermal and mechanical shock resistance. They are difficult to cast and are virtually unmachinable. In view of the different effects produced, the amount of silicon in steel needs to be monitored carefully and controlled. The percentage of silicon in iron and steel samples varies and is as high as 75% in ferro-silicon alloys. Parts of the steel industry have in recent times shown considerable interest in the determination of low levels of silicon. The current British Standards Institution methods[2] for determining silicon in steel are gravimetric and photometric methods based on acid dehydration of silica and on the chemical reduction of molybdosilicic acid respectively. At high levels of silicon, both methods are suitable. At very low levels of silicon (0.002%), a highly skilled operator is required to produce reproducible results by the photometric method: the use of the gravimetric method is impracticable at this level. Pulse polarography, on the other hand, is sufficiently sensitive and should be more accurate at this level.

Another instrument recently introduced is the PAR 173/179 digital coulometer and this was used to develop a controlled-potential coulometric procedure for the determination of iron in steel and iron ore. Iron is the base metal of all steels. The present British Standards Institution method (BS 4158: Part 1: 1967) for determining iron involves volumetric titrimetry. Frequently the iron content of steels is obtained by difference when the other metals present have been determined. As an analytical technique, coulometry has several unique characteristics which it was thought could be advantageous in steel works analysis. It is an accurate and very precise analytical technique which, once routines are established, does not require any special skills of the operator. The accuracy and high precision of the technique are retained even in routine analysis. Compared with classical titrimetry and gravimetry, coulometry requires only about 1-10 mg of material per determination to attain its optimal performance.

The two instruments mentioned above are extremely versatile since they allow several techniques to be used with the same instrument.

Boron is used in steel for one purpose only[3] - to increase hardenability. The percentage of boron in iron and steel samples varies and is as high as 15% in ferro-boron alloys. Boron intensifies the hardenability characteristics of other elements present in steel. It is particularly effective when used with low carbon steels. The colorimetric determination of boron in steel remains difficult. One of the current British Standards Institution methods for determining boron in steel[2] involves a tedious photometric procedure which includes a distillation step. The other is a volumetric method and is limited in use to ferro-boron steels. In view of the difficulties associated with the current colorimetric methods for the determination of boron in steel, it was considered advantageous to examine some solvent extraction procedures in which fluoride is coupled with a better chromogenic stage. A colorimetric procedure which avoids distillation and does not suffer from the high blanks of the present British Standards Institution and other direct methods would be advantageous.

The aim of the present work was to develop methods of analysis which will complement or replace the present British Standards Institution methods for the determination of these selected elements in steel.

DETERMINATION OF SILICON IN STEEL BY DIFFERENTIAL PULSE POLAROGRAPHY

I. REVIEW OF METHODS FOR THE DETERMINATION OF SILICON IN STEEL

(a) INTRODUCTION

The properties of silicon-containing heteropoly acids, fluorosilicic acid, soluble silicates and silicic acid have all been utilised in the determination of silicon in various materials, including iron and steel. A survey of the literature shows a vast number of papers on methods for the determination of silicon and a few of these have been proposed for application in iron and steel analysis. The methods recommended for determining silicon in iron and steel include:

1. gravimetric determination after acid dehydration[2,4]
2. titrimetric determination including the use of electrochemical endpoints.[18-24]
3. colorimetric determination as yellow or blue molybdosilicate.[2,4,33-61].
4. atomic absorption spectrophotometry.[62-72]

Other methods include neutron activation, X-ray fluorescence, emission spectroscopy and determinations involving utilisation of thermoelectricity and resistivity. Most of these methods involve preliminary decomposition of the silicon-containing sample; but some methods such as emission spectroscopic methods do not.

(b) GRAVIMETRIC METHODS

Gravimetry is the oldest analytical technique for the determination of silicon and has been adopted by a number of Standards Organisations.[2,4] It is normally used for samples containing more than 0.1% of silicon, at which level the results are both accurate and reproducible. The method involves separation of silicon as polymerized silicic acid from other elements in the sample and its subsequent acid dehydration, drying, ignition and weighing as anhydrous silica, (SiO_2).

In practice, the silicic acid obtained when the precipitate is ignited often contains considerable amounts of accompanying salts either absorbed or chemically bound. Tri- and tetra-valent metal oxides and acidic oxides tend to co-precipitate with the silicic acid even in strongly acidic solutions. The most frequently encountered contaminants are: Fe_2O_3, Al_2O_3, Cr_2O_3, SnO_2, Sb_2O_3, TiO_2, WO_3, P_2O_5, ZrO_2, ZrP_2O_7, $Ti_2P_2O_7$, $Ta(Nb)_2O_5$, $BaSO_4$, $SrSO_4$, $CaSO_4$ and $PbSO_4$.

Thus, in order to determine the silicon content of a sample accurately, the residue obtained after ignition is usually treated with hydrofluoric acid. Silicon dioxide forms gaseous silicon tetrafluoride (SiF_4) with hydrogen fluoride, and therefore the loss in weight of the residue is equivalent to the silicon dioxide content of the sample:

$$SiO_2 + 4HF \rightleftharpoons SiF_4 + 2H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The reaction is only complete in the presence of dehydrating agents. The decrease in weight after treatment with hydrogen fluoride, accurately corresponds to the silicon dioxide content of the sample only if the composition of the accompanying substances is the same before and after the treatment, and if the residue does not contain any other material which is volatilized with hydrogen fluoride.

The basic operations of the variants of the gravimetric technique are the same although the sequences might differ. Initially, the sample is decomposed and in the process silicon is oxidised and converted to silicic acid. Decomposition is usually effected with nitric or hydrochloric acids but for acid-resisting high silicon iron, a mixture of ammonium chloride, bromine and hydrobromic acid has been used.[2] Oxidation of silicon to silica may be incomplete if much carbon or iron is present in the sample. In such cases, it is always necessary to fuse the ignited residue of silica and un-oxidised silicon with sodium carbonate or sodium hydrogen sulphate.

Dehydration, which is in an acid medium renders the silicic acid insoluble so that it could be filtered off, dried, ignited, and treated with hydrofluoric acid. A single fuming of the sample solution with the dehydrating agents is usually sufficient to recover all the silica in the sample solution. However, for samples containing less than 5 mg of silicon, further fuming of the filtrate is necessary if all the silica is to be recovered. Hydrochloric, sulphuric, perchloric and less frequently nitric and acetic acids have been used as dehydrating agents. The effects of these acids are in general, similar, though each has its own merit. Lundell and Hoffman[5] have discussed the factors involved in dehydration by fuming with mineral acids.

Dehydration with hydrochloric acid is safe and requires no special skills. Some complications arise with the use of sulphuric acid for dehydration: lead and barium, if present in the sample solution, are always precipitated as the sulphates. The anhydrous sulphates of nickel, aluminium, cobalt and iron (III) formed when the sample solution is dehydrated with sulphuric acid dissolve very slowly, and hence the sample solution must be heated to accelerate their dissolution. In consequence, some of the silicic acid is also dissolved. Antimony, tin and germanium compounds, if present, may be co-precipitated. Dehydration with perchloric acid is often recommended because dehydration is rapid, bumping during evaporation is reduced, perchlorates are readily soluble in water, the rate of dissolution is rapid and the precipitation of silicon dioxide is almost complete.[6] But frequently, perchloric acid is used with either nitric or hydrochloric acid. The silicic acid is dehydrated first with either nitric or hydrochloric acid and then with perchloric acid. It is always necessary to wash out most of the perchloric acid from the precipitate to prevent possible explosion during the ignition process. Objections to the use of perchloric acid are on safety grounds. It requires strict adherence to safety rules and hence has to be used mainly by skilled workers. Co-precipitation of some metallic compounds have also been reported when perchloric acid is used for dehydration.[7]

Dehydration with nitric acid, acetic acid, mixtures of acids, and acetyl chloride have been suggested but their disadvantages far outweigh any advantages[8] they may have. High-molecular weight organic compounds such as gelatin[9] have also been used for dehydration. Silicic acid liberated with hydrochloric acid is a negatively charged colloid and therefore can easily be precipitated with a colloidal gelatin solution which is positively charged. The advantage of the gelatin method is that the solution need not be evaporated, and when the concentrations of acid and salt are suitable, the precipitation of silicic acid is almost quantitative.

Special problems are encountered in the gravimetric determination of silicon compounds containing fluorine, boron or phosphorus. Large losses of silicon due to its volatilization as silicon tetrafluoride is the main problem. Berzelius was the first to recognise this problem.[10,11] Studies aimed at counteracting this loss have been made and these have led to the modification of the original Berzelius method and introduction of new ones. Publications dealing with these new methods are numerous. Determination of silicon in the presence of boron often leads to high results. The precipitate of silicic acid is invariably contaminated by boron and boron tetrafluoride is volatilized along with silicon tetrafluoride during the final treatment of the silica with hydrofluoric acid. Elimination of boron as the methyl borate[12] has been proposed but sometimes, the determination has been done without first separating boron.[13,14]

Other gravimetric methods which have been used for the determination of silicon in steel involve the precipitation of 12-molybdosilicic acid by organic bases, such as quinoline.[15,16] All gravimetric methods have their disadvantages and systematic errors, and the gravimetric determination of silicon is no exception. These errors will be discussed later. However, the need to minimise these errors makes the use of samples containing large amounts of silicon almost obligatory and hence gravimetric methods are rarely employed for the determination of small amounts of silicon.

(c) TITRIMETRIC AND ELECTROCHEMICAL METHODS

Titrimetric methods have been used in the determination of silicon in cast iron and steel. These methods are based on the properties of molybdosilicic and fluorosilicic acids rather than silicic acid since the latter cannot be titrated with either potassium or sodium hydroxide solution. Molybdosilicic acid is easily reduced to molybdenum blue by reducing agents. The amount of reducing agent consumed in the process being directly proportional to the amount of silicon used initially in the formation of the molybdosilicic acid. The titration of molybdosilicic acid with reducing agents can be followed with the aid of indicators or by electrochemical methods, such as amperometry, potentiometry and conductometry. However, the suitability of the process of neutralization of molybdosilicic acid in aqueous solutions for the determination of silicon is limited, because of the simultaneously proceeding hydrolytic splitting of the heteropoly anion during its neutralization. Titration in non-aqueous solvents prevents the hydrolysis of molybdosilicic acid. Shakhova et al.[17] have studied the potentiometric titration of molybdosilicic acid in non-aqueous solvents.

Procedures based on the titration of potassium fluorosilicate (K_2SiF_6) with sodium hydroxide appear to be more popular and have been reported to be rapid enough for process control.[18-20] The procedures involve the precipitation of K_2SiF_6 from a hot acid solution in the presence of excess of F^- and K^+ ions. The precipitate is then dissolved and hydrolysed with boiling water and titrated with sodium hydroxide in the presence of phenolphthalein. Prumbaum[21] has studied the conditions necessary for accurate determination of silicon by this method.

The use of antipyrine dyes[22] and their derivatives[23,24] as titrants for the titrimetric determination of silicon in steel have also been reported. Silicon was converted to molybdosilicate and then titrated with an acid solution of the dye e.g. antipyrinylbis(4-dimethylaminophenyl)methanol in 1M hydrochloric acid.[22]

(d) COLORIMETRIC METHODS

Colorimetric methods for the determination of silicon have been very important because until recently, they have been the easiest methods for determining small amounts of silicon. The colorimetric method usually used is that based on the reaction of monomeric silicic acid with molybdate in acid solution to form yellow molybdosilicate. Molybdosilicate has an absorption maximum at 352 nm but the absorption has been measured between 345 and 410 nm.[25] The literature on the colorimetric determination of silicon as molybdosilicate is voluminous. King et al.[26] gave a detailed bibliography on the subject. A number of reviews[27-30] on the colorimetric determination of silicon as molybdosilicate, which include its application to silicon determination in steels have also been published. Colorimetric procedures based on the formation of yellow molybdosilicate are not very sensitive. Interferences due to phosphorus, arsenic, vanadium and germanium which also form heteropoly acids with molybdate have been reported, although phosphorus and arsenic, up to at least 0.1 and 0.2% respectively in steel and at least 0.5% of iron, manganese or tin, are all said to be without effect.[4] Various methods have been proposed for the elimination of interferences due to phosphorus, arsenic and germanium and these will be discussed in Chapter IV.

Molybdosilicate is a strong oxidizing agent and is therefore easily reduced, even by weak reducing agents. An intense blue product, due to the reduction of molybdenum, is obtained when reducing agents act on molybdosilicate. This blue product (Molybdenum blue) has an absorption maximum at 820 nm, and although copper and certain other ions absorb at this wavelength, their effect can be compensated for by measuring the absorbance of the sample solution against a second aliquot of the sample solution, in which the formation of molybdenum blue is prevented by citric acid. Other interferences could be removed by preliminary diffusion separation of silicon as silicon tetrafluoride.[31,32] The reduced molybdosilicate (molybdenum-blue) procedure has sometimes been preferred to the yellow molybdosilicate in the determination of silicon in steel because it is about five times more sensitive. It could be applied to the determination of silicon over the range 0.002 to 0.2%. Apart from being more sensitive than the yellow molybdosilicate procedure, the conditions for its formation and use are less critical. At 50°C, the intensity of its colour reaches a maximum within five minutes and it is stable for several hours.

Various reducing agents have been suggested for the reduction of molybdosilicic acid, although most of them are of limited interest. Reducing agents that have been recommended for the determination of silicon in steel include tin (II) chloride, although it suffers from a number of disadvantages,[33,34] tin (II) oxalate,[35-37] iron (II) sulphate,[34,35,37] ascorbic acid,[38-40] and a mixture of ammonium iron (II) sulphate and oxalic acid.[2] 1-Amino-2-naphthol-4-sulphonic acid and a mixture of 1-amino-2-naphthol-4-sulphonic acid, sodium sulphite and sodium metabisulphite are excellent reducing agents but have so far not been used in the determination of silicon in steel. Vietsman[41] reported the use of potassium iodide as a reducing agent. Hydrazine has also been mentioned.[39] Potassium permanganate in slight excess has been used successfully to eliminate the interference caused by certain reducing agents including iron (II). For instance, to determine silicon in slag while it is still in the furnace, it is essential to prevent the premature reduction of molybdosilicate by iron (II) and such reduced ions as sulphide. Braicovich and Landi[42] have outlined precautions necessary for the use of the molybdenum-blue procedure in the determination of silicon in steel.

Since the introduction of the yellow molybdosilicate and molybdenum-blue procedures, for determining silicon, there have been several modifications including automation[43] of both procedures. A few of these modifications have included solvent extraction of molybdosilicate[44-47] with a view of improving the precision of the procedures. Several modifications have also been made in order to adapt the procedures to the determination of silicon in low alloy steels and iron,[45-54] cast iron,[55] iron oxide inclusions, iron ores[56] and slags.[57] Ordinarily, both procedures have found wide application in the determination of acid-soluble silicon in steels.[58-61]

(e) ATOMIC ABSORPTION SPECTROPHOTOMETRY

Silicon is one of the less sensitive elements that can be determined by atomic absorption spectrophotometry but since the introduction of the nitrous oxide-acetylene flame, there has been an increase in the number of reports on the determination of silicon in steel by this method. The method has been successfully used for determining silicon above 0.1%. It is however doubtful whether lower concentrations of silicon can be determined with acceptable accuracy especially since ideal experimental conditions are very difficult to establish. A survey of the literature shows that different pre-treatment techniques have been adopted for the determination of silicon in steel by atomic absorption spectrophotometry. These techniques include precipitation of silica, alkaline fusion and decomposition with hydrofluoric acid.

McAuliffe[62] appears to be the first to apply atomic absorption spectrophotometry successfully to the determination of silicon in steel, but even then difficulties in obtaining optimum operating conditions were reported. It was noted that with the preparation procedure adopted, the sample solutions were only stable for 1 or 2 hours. Furthermore, rapid build-up around the burner slot often changed the operating conditions, thus making it necessary to clean the burner after two or three runs. The results obtained were, however, reported to have a relative error of between 0.5 and 2.0%.

Musil and Halirova[63] studied the application of atomic absorption spectrophotometry in metallurgical analysis and determined silicon by a method which involved the dissolution of the sample with nitric acid and the fusion of the residue obtained with sodium potassium carbonate or a mixture of potassium and sodium carbonates. Gomez Coedo and

Jiminez Seco[64] determined silicon in iron ores by a method which involved the extraction of the sample with hydrochloric acid after fusion with a mixture of sodium carbonate and borax. Interfering elements were masked with a masking mixture containing EDTA, strontium nitrate, lanthanium trioxide, perchloric and hydrochloric acids.

Price and Roos,[65] in probably one of the best atomic absorption methods for the determination of silicon have emphasized the need for proper and complete dissolution of samples. They reported a direct method for determining silicon which avoided the need either for the precipitation of the silica or for an alkaline fusion technique. The method involved the dissolution of steel samples with hydrochloric acid and hydrogen peroxide. Interferences were investigated and the enhancement of the silicon absorption by elements such as aluminium, calcium, sodium, iron and vanadium was explained in terms of the suppression of the ionisation of silicon in the nitrous oxide flame by the interfering element. However, no satisfactory explanation for the suppression of silicon absorption by phosphate was given. At 0.5% level of silicon, precise results were obtained. The precisions of the results were reported to be even better at higher levels of silicon.

The use of hydrofluoric acid for the dissolution of steel samples with high percentages of silicon, was also recommended by Price and Roos.[65] Nakahara et al.[66] in their study of the determination of silicon in some metallurgical materials recommended the treatment of steel samples with hydrofluoric acid before nebulising into a nitrous oxide-acetylene flame. Interferences by other elements were thoroughly investigated as well as the effects of various acids with concentration up to 2 Normal. Addition of water-miscible organic solvents to an aqueous solution containing silicon was reported to enhance the sensitivity of the method. Hydrofluoric acid attack and the subsequent determination of silicon by atomic absorption spectrophotometry was compared with the method which involves the formation of molybdosilicate followed by extraction with methyl isobutyl ketone. Brivot and Cohort[67] have also made a comparative study of the determination of silicon by atomic absorption spectrophotometry and spectrophotometric method in certain steels. For the atomic absorption spectrophotometric study, the samples were dissolved in a mixture containing water, hydrochloric and nitric acids. Rooney and Pratt[68] dissolved the sample in a mixture containing hydrochloric, nitric and hydrofluoric acids and then added sodium chloride (2.5%) to ensure that sufficient alkali metal was present to enhance fully the silicon absorption. They determined silicon in the presence of large amounts of iron, nickel, cobalt and molybdenum. A very fuel-rich nitrous oxide-acetylene flame was used.

An atomic absorption method has been discussed by Feldman et al.[69] for samples containing more than 5% of silicon. Langmyhr and Paus[70] studied the analysis of inorganic siliceous materials including slags, iron ores and ferrosilicon by atomic absorption spectrophotometry and the hydrofluoric acid decomposition technique. They obtained results for silicon which were in good agreement with the British Chemical Standards certificate values of silicon in these materials.

The use of nitrogen-separated nitrous oxide-acetylene flame for the determination of silicon in low-alloy steel by atomic fluorescence spectroscopy has been reported by Kirkbright et al.[71] They noted that the detection limit obtained was better than that obtained by atomic absorption spectrophotometry, although the fluorescence was dependent on the hydrofluoric acid concentration.

A suggestion has been made that with the use of laser sources in atomic absorption spectrophotometry, it would be possible to determine even lower levels of silicon. Krivchikova and Demin[72] demonstrated the possibility of atomic absorption spectrophotometry with laser sources and by using this method analysed 0.1 to 1% of silicon in steel.

(f) OTHER METHODS

Other methods of determining silicon in iron and steel have been widely reported in the literature. Non-destructive neutron activation analysis has been applied in the determination of silicon in steel. Pierce and Haines[73] determined silicon using a low-output neutron generator. Van Grieken et al.,[74] reported a 14-MeV neutron activation analysis for silicon with ^{56}Mn formed from the iron matrix as internal standard. They also reported a method for the simultaneous determination of silicon, phosphorus, oxygen and copper but the method was only suitable for the simultaneous determination of silicon and phosphorus in steels with high phosphorus content.[75] D'arglemont de Tassigny[76] also studied the determination of aluminium phosphorus and silicon in steel by activation with 14-MeV neutrons. In addition, he discussed the chemical separation of these elements. However, all procedures for the determination of silicon by neutron activation analysis are limited by aluminium interferences and a high detection limit.

Pierce et al.[77] have also determined silicon by measuring the 1.77 MeV γ-line emitted by an inelastic proton scattering reaction, using the 0.84 MeV γ-line from the iron matrix as an internal standard.

A method for the determination of silicon and phosphorus in iron ores by infra-red spectroscopy was reported by Lebedeva and Ptushkina.[78] The method involved the formation of molybdosilicic acid followed by its extraction with a 4:1 mixture of acetophenone and chloroform from a 1.8-2.0M hydrochloric acid solution. The extinction of the extract was then measured at 906 cm.$^{-1}$

Baryshanskaya[79] reported a method for the spectral analysis of alloyed steel in the near ultra-violet region using a double spark as a light source. Several other emission spectroscopic methods for the determination of silicon in iron and steel have also been published.[80-82]

A quantitative spectrochemical emission method of analysis of steel by the rotating-disc electrode method has been reported by MaeKawa et al.[83] The samples were dissolved in aqua regia and the analyses of the resulting solutions completed by excitation, in a 150 a.c. spark between a rotating disc of paraffin wax impregnated carbon rod and a tungsten counter electrode.

Gabrovski et al.[84] determined silicon by an indirect flame photometric method. They precipitated silicon as K_2SiF_6 and then determined the potassium component (and hence silicon) photometrically in a propane or butane flame. A method in which silicon is converted to silicon tetrachloride during the direct chlorination of iron and steel, and then determined by gas chromatography was reported by Sie et al.[85] X-ray spectrometry has also been used for the determination of silicon in steel.[86]

Sajo[87] reported a differential thermal analysis procedure in which he made use of the difference in the variation of temperature between a standard and the sample when both were treated with hydrofluoric acid. Ujvary[88] described a rapid thermometric determination of silicon in ferrosilicon based on the measurement of the heat of formation of K_2SiF_6 in solution.

A method which has been reported to be very rapid for control analysis is the thermoelectric procedure. It is based on the variation in the value of the thermoelectric e.m.f. produced when a sample is placed between two standard electrodes and heated together with one of the electrodes.

The thermoelectric e.m.f. is a function of the percentage composition of the constituent species or their compounds, the temperature difference between the cold and hot junctions, and thermal or mechanical treatment of the sample. If all other factors are kept constant, the thermoelectric e.m.f. could be used to determine the percentage composition of a steel sample. Thermoelectric procedures have been used for the determination of silicon in steels,[89-94] cast iron,[95-98] and ferrochromium.[99]

The resistivity of iron depends on its content of additional elements. Studies on the variation of the resistivity of iron as a function of the content of silicon in silicon steels containing different concentrations of carbon, manganese, phosphorus and sulphur showed that the resistivity was mainly affected by the dissolved carbon. The effect of carbon was found to be greater than that of any other element in steel. However, in many steels in which the carbon content was negligible, the resistivity was mainly affected by silicon. The effect of silicon on the resistivity of iron has been used for example, in its determination in transformer steels.[100]

II. CHEMISTRY OF MOLYBDOSILICIC ACID

(a) FORMATION:

Molybdosilicic acid has long been used for the colorimetric and spectrophotometric determination of silicon but the literature on the conditions of its formation and determination is at times confusing and contradictory. The fact that silicate and molybdate species combine to form molybdosilicic acid has long been recognised and since the X-ray work of Keggin,[101] the composition corresponding to the formula $H_4Si(Mo_3O_{10})_4$ has been generally accepted. This composition has been verified and confirmed by other workers.[102-105] Molybdosilicic acid with a 1:12 mole ratio of silicon to molybdenum has generally been regarded as the only compound formed when silicate and molybdate species react (see equation 2), although some workers have reported the formation of a Si: 8Mo compound.

$$SiO_3^{2-} + 12MoO_4^{2-} + 22H^+ = [Si(Mo_3O_{10})_4]^{4-} + 11H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

This contradiction could be explained by the existence of different isomers of molybdosilicic acid. Ferrari[106-107] appears to be the first to report the existence of different forms of molybdosilicic acid. He found that the intensity of yellow molybdosilicic acid decreased to a constant value after several hours and noted that at that point, it appeared an equilibrium was established between a yellow and a colourless form of molybdosilicic acid. Increase in temperature accelerated the transformation of the yellow to the colourless form. Once equilibrium had been established between the two forms, molybdosilicic acid was found to show great resistance to the action of destructive agents such as sulphuric acid. Strickland,[108] in a series of papers, also showed that there were two possible forms of molybdosilicic acid but both forms had the same empirical formula. He called the forms α- and β-silicomolybdic acid. He noted that the critical factor that determined the form produced was the ratio of the concentrations of acid and molybdate used. The α-form was produced in solutions containing 1.45-1.50 equivalents of HCl per gram ion of MoO_4^{2-} and the β-form in solutions containing more than 2 equivalents. He also reported that the β-form was unstable and was slowly transformed spontaneously into the more stable α-form. In the presence of excess molybdate, however, the transformation was inhibited and the half-life of the reaction was about 25 hours. Strickland suggested that in acidified molybdate solution, three species which he called α-, β-, and γ-molybdate also existed. The reaction of α- and β-molybdate with silicic acid produced α- and β-silicomolybdic acid respectively, whereas γ-molybdate was inert. He failed to define the α-species but assumed that β-molybdate was tetramolybdate and the γ-form was molybdenyl ion. Chalmers and Sinclair[109,110] also studied the structure of α- and β-silicomolybdic acids and on the basis of Keggin's work explained the difference between the two isomers. They reported that the α-compound was derived from octamolybdate and the β-compound from deca- or dodecamolybdate. Armand and Bertoux,[111] while confirming Strickland's acid to molybdate mole ratio concept reported that α-silicomolybdic acid was only formed when the acid to molybdate ratio was lower than 1.5 and the β, if the ratio was greater than 3.

Kemula and Rosolowski,[112] on the other hand, suggested that a γ-form of molybdosilicic acid existed and could be obtained at pH 0-4.6, if the α- and β-forms were boiled for 30 minutes. They noted that the transformation of α or β to the γ-form was quantitative. The γ-form was reported to be more stable than both the α- and β-forms and had a formula $H_4[Si(Mo_3O_{10})_4].H_2O$. They also suggested that the silicon to molybdenum ratio of α- and β- was 1:8 whereas γ-silicomolybdic acid has a ratio of 1:12. Sanyal et al.[113] in their spectrophotometric and conductometric study also reported the existence of a complex between silicic and molybdic acids having a 1:8 Si to Mo combination ratio.

The conductometric study was, however, not conclusive. The variations of the conductance of the mixtures for the Job plot were reported to be linear up to 1:3 ratio and then non-linear above this ratio due to the contribution to the conductance from free molybdate.

Since the work of Strickland, which firmly established the existence of two forms of molybdosilicic acid, many analytical procedures for the determination of silicon based on the formation of α- and β-silicomolybdic acid at controlled acid to molybdate mole ratio have been reported. Before then it had been commonly supposed that the essential factor in molybdosilicic acid formation was pH. Various values of optimum pH were reported but this was generally agreed to be between pH 1 and 2. Most workers[114, 115] appeared to have agreed with the acid to molybdate mole ratio concept and in some cases[115] had emphasized its importance. But others, such as Grasshoff and Hahn[142,143] in addition, proposed that hydrolytic equilibrium was also involved in the formation of molybdosilicic acid.

The assumption that the formation of the α- and β-forms were fundamentally dependent on the acid to molybdate mole ratio has gone unchallenged until recently. Truesdale and Smith[116] have rejected the above condition and instead have proposed a mechanism that involves only pH and molybdate concentration as the primary factors that determine which form of molybdosilicic acid is produced when molybdate and silicate species react. Their investigation showed that solutions of constant acid to molybdate ratio could span a wide range of pH values. Thus, either form of molybdosilicic acid or a mixture of both forms could be formed in solutions with the same acid to molybdate ratio. They concluded that the form produced does not depend on the acid to molybdate ratio but on the pH and on the concentration of molybdate.

(b) EFFECT of pH.

While pH control has always been recognised as an important factor in the formation of molybdosilicic acid and has generally been agreed that for β-silicomolybdic acid formation, the pH should be between 1 and 2, various "optimum" values have been reported. Milton[117] indicated that β-silicomolybdic acid could be formed in a pH range of 1 to 5, but Trudell and Boltz[118] reported an optimum pH of about 1·4. Hurford and Boltz[119] used an optimum pH of 1.3, Jakubiec and Boltz[120] confirmed this but specified a waiting period of 10 minutes to allow complete formation of the molybdosilicic acid. Truesdale and Smith[116] reported that α-silicomolybdic acid is formed at pH between 3.8 and 4.8 (possibly slightly higher) and the β-acid at pH between 1.0 and 1.8. At extreme pH values, the rate of formation of both forms of molybdosilic acid was reported to be very slow and complete formation took a long time.

(c) EFFECT OF MOLYBDATE CONCENTRATION

The effects of molybdate concentration have been studied by several workers.[121-123] A relatively high molar excess of molybdate ($>$100%) has always been recommended to ensure complete formation of the acid. DeSesa and Rogers[124] while supporting the acid to molybdate mole ratio concept emphasized the importance of excess molybdate. However, too large an excess of molybdate should be avoided as it increases the blank on the techniques (based on the formation of molybdosilicate) for the determination of silicon.

(d) EFFECT OF TEMPERATURE

Studies have shown that an increase in temperature accelerates the transformation of β- to α-silicomolybdic acid but at the same time, it has been shown that once either form has been produced and if the pH and molybdate concentrations are maintained at constant values, temperature changes have little effect on the measurable parameters (e.g. absorbance) of molydosilicic acid or reduced molybdosilicic acid.[125,126]

(e) MISCELLANEOUS EFFECTS

Water-miscible organic solvents[109] such as ethanol and acetone have been reported to enhance the stability of β-silicomolybdic acid presumably because the organic solvent displaces water from the surface of the heteropoly anion and so inhibits any reorganisation of the structure of the anion. The organic solvents, especially acetone also intensify the colour of β-silicomolybdic acid. Sulpholane[127] has been reported to give better colour enhancement and stabilizing effect than acetone. It also has lower volatility. Tartaric, citric and oxalic acids which decompose arseno- and phosphomolybdic acids do not attack silicomolybdic acid to an appreciable extent. Thus, the use of these complexing agents makes it possible to form and hence determine molybdosilicic acid in the presence of either arsenic or phosphorus. However, the order in which the reagents are mixed may make the determination of molybdosilicic acid without separation from arsenic and phosphorus difficult.[110]

It has been suggested that the order in which reagents are mixed also determines which form of molybdosilicic acid is produced. A careful examination of the literature on this subject shows, however, that this condition is only important in the case of β-acid where a pH less than 2 has to be maintained to ensure its formation. Workers who obtained different forms of the acid depending on the order of mixing silicate with molybdate appear to have forgotten that pH is a primary factor in the formation of molybdosilicic acid. The pH of their mixture is bound to change whichever order the reagents are mixed. Thus the β-acid would only be produced if the final pH of their mixture is between 1 and 2, or remains within this pH range during the mixing. A final pH greater than this range would lead to the formation of the α- or a mixture of α- and β-acids.

III. POLAROGRAPHIC DETERMINATION OF SILICON (REVIEW)

Silicate ions are not reduced at a dropping mercury electrode (DME). The polarographic determination of silicon is therefore based on the reduction of molybdosilicic acid. The reduction of molybdosilicic acid consists of several stages, depending on the supporting electrolyte in the system. There are a number of papers and reviews[128] on the polarographic reduction of molybdosilicic acid but opinions differ as to the number and nature of reduction stages, pH of reduction and the pH of formation of molybdosilicic acid. This is hardly surprising since differing experimental conditions have been employed for the preparation and subsequent reduction of molybdosilicic acid. However, the most widely held opinion is that molybdosilicic acid is reduced in two stages: the first involves the reduction of Mo(VI) to Mo(V) and this corresponds to the first half-wave potential, the second involves the reduction of Mo(V) to Mo(III) and corresponds to the second half-wave potential.

Boltz et al.,[129] in a brief report, appear to have been the first to study the polarographic behaviour of molybdosilicic acid. In a supporting electrolyte containing potassium chloride, hydrochloric acid, sodium acetate and acetic acid in varying proportions, with the pH at 3.5, they detected a wave with a half-wave potential at -0.55V vs SCE. The height of the wave was proportional to the concentration of the molybdosilicic acid.

Jean[128] had noted that when molybdosilicic acid was polarographically reduced in a buffer containing ammonium acetate, acetic acid and potassium chloride at pH 3.5, two waves whose heights were proportional to the concentration of molybdosilicic acid were obtained at -0.35V and -0.85V vs SCE respectively. At pH 4.55, one ill-defined wave was obtained. In addition, a 10^{-4}M solution of crystalline molybdosilicic acid dissolved in a supporting electrolyte consisting of 0.1M potassium sulphate solution at pH 3.5, gave only one wave at -0.25V vs SCE whereas β-silicomolybdic acid had no characteristic wave under the same condition.

Lyalikov and Aronina[130] studied the polarographic behaviour of molybdosilicic acid in a supporting electrolyte consisting of ammonium nitrate and nitric acid at pH 1.1. They obtained one wave with the silicon concentration less than 10 μg $ml,^{-1}$ but as the silicon concentration was increased (> 10 μg ml^{-1}), which was equivalent to the absence of free molybdenum, three waves were obtained. The peak heights of the first and third waves were independent of silicon concentration whereas the peak height of the second was proportional to it over the range 10 to 15 μg. $ml.^{-1}$ These same three waves were obtained when solid molybdosilicic acid was polarographed under the same condition. Lyalikov and Aronina therefore concluded that the difference which they observed in the polarographic behaviour of solid molybdosilicic acid dissolved in the supporting electrolyte and that of the molybdosilicic acid prepared directly in a solution with excess of free molybdate was due to the difference in the nature of the polarographic reduction of α- and β-silicomolybdic acids. Massart[131] reported that it was possible to differentiate α- and β-silicomolybdic acids by using a rotating platinum electrode instead of a dropping mercury electrode.

Most workers seem to agree on the existence of different isomers of molybdosilicic acid but there has been disagreement on which of these isomers is suitable for the polarographic determination of silicon. While some workers prefer to reduce either α- or β-silicomolybdic acid, depending on their choice of optimum experimental conditions, others have proposed that the γ-isomer is most suitable. Kemula and Rosolowski[132-134] reported that α- and β-silicomolybdic acid were inert in the presence of a buffer containing hydrochloric acid, sodium formate and butanol, whereas γ-silicomolybdic acid gave a reproducible kinetic wave under the same condition. The kinetic wave appeared between the two waves of uncombined excess molybdate. It had a half-wave potential which depended linearly on pH and varied from 0.33 to 0.45V vs SCE in the pH range 1.3 to 3.8; best results being obtained at pH 1.9 to 2.6.

Ripan and Calu[135,136] noted that six characteristic waves were produced in the reduction of α-silicomolybdic acid but only the first two waves appeared to be proportional to the silicon concentration. The waves were, however, not reproducible at lower concentration of silicon. This, they attributed to a variation in the internal structure of molybdosilicic acid anion which occurred when the concentration of the solution was decreased.

Sen and Chatterjee[137] noted that chemically reduced molybdosilicic acid could be further reduced polarographically in four reversible steps. The first three waves were reported to be proportional to the concentration of the reduced molybdosilicic acid complex alone, whereas the height of the fourth wave depended on the complex as well as on the concentration of molybdate in the solution. The half-wave potentials of the waves varied linearly with pH. They reduced the molybdosilicic acid with various reducing agents including hydrazine hydrate and polarographed the reduced species in an ammonia-ammonium chloride buffer at pH 9.5. Polotebnova and Furtune[138] investigated the polarographic behaviour of molybdosilicic acid and of the products of its chemical reduction in both aqueous and alcoholic solutions with 0.5M sulphuric acid as supporting electrolyte. The reduction products (molybdenum blue) were produced by reduction with ascorbic acid, tin (II) chloride or sodium sulphite. The polarograms of molybdosilicic acid and molybdenum blue in aqueous solution showed three waves with half-wave potentials at -0.19V, -0.33V and -0.42V vs SCE respectively. The peak heights of the waves varied linearly with the concentration of molybdosilicic acid. In a water-alcohol mixture, the polarogram showed two waves, the first of the three waves observed in aqueous solution having been effectively suppressed in the presence of alcohol. An increase in the proportion of alcohol in solution increased the peak height of the second wave and suppressed that of the third wave. In absolute alcohol solutions, only one wave was observed with half-wave potential at -0.35V vs SCE.

El-Shamy et al.[139, 140] studied the polarographic reduction of molybdosilicic acid in a variety of supporting electrolytes to show the effects of hydrogen ion concentration and of the presence of complexing ions on the wave forms. In 0.1M-KCl solution, two waves at -0.48V and at -1.2V vs SCE respectively, were obtained. The peak heights of the waves were directly proportional to the concentration of molybdosilicic acid in the range 0.2 to 1.0 mM. In oxalic, tartaric or citric acid solution, they obtained two waves at -0.3V and at -0.55V vs SCE respectively but with increasing concentration of molybdosilicic acid, the waves were ill-defined. In sulphuric acid, two waves whose peak sharpness decreased with increase in acid concentration were obtained. They obtained similar results in the presence of phosphoric, nitric and hydrochloric acids. El-Shamy et al. also studied the reduction of molybdosilicic acid in acetate and phosphate-citrate mixtures of varying pH but obtained ill-defined waves which were dependent on pH and on the concentration of the reducible species. At pH 1.1, four ill-defined waves were obtained, but only one wave at pH 4.9.

By using rotating platinum electrodes, Massart and Souchay[141] were able to obtain a three-step reduction of α- and β-silicomolybdic acids. This reduction corresponds to two, four and six electrons respectively. The first two reductions were reported to be reversible.

Grasshoff and Hahn[142, 143] obtained three waves in their study of the polarographic reduction of molybdosilicic acid in a citrate buffer at pH 2.5. The first and third waves were due to the reduction of molybdic acid (sodium molybdate) whereas the second was characteristic of molybdosilicic acid. Determination of the free molybdic and molybdosilicic acids in solution indicated that molybdosilicic acid is 50% decomposed according to the following equation:

$$H_4[Si(Mo_{12}O_{40})] + 6\ H_2O \rightleftharpoons Si(OH)_4 + 2H_3\ (Mo_6O_{21}H_{13}) \ldots\ldots\ldots\ldots (3)$$

This applies only to β-silicomolybdic acid. Thus the three waves were given by β-silicomolybdic acid and by molybdic acid formed by the decomposition of the molybdosilicic acid. In the presence of methyl ethyl ketone, the first wave was effectively suppressed but the second and third waves were not. Methyl ethyl ketone also improved the shape of the second wave (i.e. the β-silicomolybdic acid wave). Increase in temperature led to a decrease in the height and sharpness of the β-silicomolybdic acid wave. The half-wave potential of β-silicomolybdic acid which occurred between -0.35V and -0.40V vs SCE was found to vary with pH. α-Silicomolybdic acid was reported to have a half-wave potential of -0.47V vs SCE, i.e. 90 mV more electronegative than that of β-molybdosilicic acid.

Asaoka[144] described a modification of the methods of Grasshoff and Hahn and of Kemula and Rosolowski. It involved the solvent extraction of molybdosilicic acid into iso-butanol, followed by polarographic reduction in a supporting electrolyte solution containing aqueous alcohol. The total height of the two-step reduction wave (at -0.3V and -0.5V vs the SCE respectively) was reported to be proportional to the amount of silicon present in the extract, although germanium showed the same behaviour under the same condition. The method appears to be the only polarographic method reported in the literature to have been applied for the determination of silicon in steel. The values obtained agreed well with the certificated values of the standard steel samples investigated. It was noted that no interference was obtained from common constituents of iron and steel. Another method involving the measurement of the maximum wave produced in a perchloric acid-hydrogen peroxide-isobutanol mixture was also investigated for possible use for determining minute amounts of silicon and germanium (less than 6 μg of silicon per ml).

A number of papers have appeared on the polarographic reduction of molybdosilicic acid in organic solvents. Kollar et al[145] reported the polarographic reduction of molybdosilicate ions in 1,2-dichloroethane at several working electrodes (platinum, mercury and carbon). Pottkamp and Umland[146] described a method for the polarographic determination of traces of silicon and phosphorus using a mixture of water, butyl acetate and ethanolic lithium chloride solution as supporting electrolyte. A method for the simultaneous determination of both α- and β-silicomolybdates in ethanolic lithium chloride by a.c.-rapid polarography was reported by Umland et al.[147] They also evaluated the rates and energies of transformation of β- to α-silicomolybdic acid. They reported that the polarographic reduction of either α- or β-silicomolybdic acid, which was pH dependent, took place in three steps but β-silicomolybdic acid was reducedat a more negative potential than α-silicomolybdic acid.

Reduction of the dioctylammonium ion associates of α- and β-silicomolybdic acid in a two phase system consisting of chloroform and 1M hydrochloric acid gave different products: the α-molybdenum blue remained in the organic layer while the β-molybdenum blue passed into the aqueous phase thus a quantitative distinction of both isomers can be made. They also reported that β-silicomolybdic acid, hitherto only produced in solution, can be isolated in the solid form as the dioctylammonium salt.

Souchay et al.,[148] in addition to describing the polarographic behaviour of 12-tungstosilicic and molybdosilicic acids at dropping mercury and platinum electrodes have also discussed the influence of the central atom on the electrochemical behaviour and properties of the isomers of molybdosilicic acid.

DeSesa and Rogers[124] compared the polarographic reduction of molybdosilicic acid with a UV spectrophotometric method based on the measurement of the absorbance of yellow molybdosilicic acid, in an attempt to corroborate the accuracy of the results obtained by the latter method. In a supporting electrolyte of ammonium nitrate and nitric acid, a steeply sloped wave with a half-wave potential at +0.15V vs SCE was obtained. At more negative potentials, the wave was essentially that of molybdate alone.

Instead of measuring the limiting diffusion current in the usual manner, DeSesa and Rogers measured the limiting diffusion current of molybdosilicic acid from a point on the polarogram where the limiting diffusion current of the blank was zero.

IV. DEVELOPMENT OF A PROCEDURE FOR DETERMINING LEVELS OF SILICON ABOVE 0.02 μg ml.$^{-1}$ IN AQUEOUS SOLUTION

(a) INTRODUCTION

The literature survey given in chapter II shows that for analytical purposes, it is necessary that one of the two forms (α and β) of 12-molybdosilicic acid as postulated by Strickland[108] should be formed exclusively, if any meaningful results are to be obtained. The formation and subsequent use of β-12-molybdosilicic acid appears to be the more attractive alternative because it is quicker to form and use, provided a means is found to stabilise and prevent its spontaneous transformation into the α-form. Chalmers and Sinclair[109, 110] developed a colorimetric procedure for the determination of silicate based on the formation of β-12-molybdosilicate. The β-12-molybdosilicate was stabilised and prevented from being transformed into the α-form by the addition of acetone. The addition of acetone was also claimed to accelerate the rate of formation, and to intensify the colour of the 12-molybdosilicate. As it was the ultimate aim of the present work to develop a method for determining very low levels of silicon, an analytical technique other than colorimetric determination was utilised. Differential pulse polarography which is obviously more sensitive than colorimetry was considered to be a better alternative.

Grasshoff and Hahn[142,143] had determined silicon by a procedure based on the polarographic reduction of β-molybdosilicic acid. They showed that the addition of methyl ethyl ketone improved the polarographic wave of β-molybdosilicic acid. In a sodium citrate-hydrochloric acid buffer at pH 2.5, in which no methyl ethyl ketone was added, they obtained three waves. The first and third waves were attributed to molybdate whereas the second was attributed to the reduction of β-molybdosilicate.

The addition of methyl ethyl ketone effectively suppressed the first wave but not the second and third waves. It also improved the shape of the second (β-molybdosilicate) wave. The half-wave potential of the β-molybdosilicate wave varied between -0.35 and -0.40V vs SCE depending on the pH of the solution. Grasshoff and Hahn gave a calibration graph for silicon in the range 0.3-1.8 μg of silicon per ml using conventional DC polarography, and also extended the method to the determination of silicon in aluminium and aluminium alloys using cathode ray polarography.

Sen and Chatterjee[137] studied the polarographic reduction of chemically reduced molybdosilicic acid at pH 9.5. At pH values above 7, molybdosilicic acid would normally decompose but reduced molybdosilicic acid is stable at these pH values. In an ammonia-ammonium chloride buffer at pH 9.5, they obtained four waves with half-wave potentials at -0.670, -0.845, -0.910 and -1.070V vs SCE respectively. For the determination of high concentrations of silicon (more than 22 ppm of silica), they recommended that the first wave should be used because the catalytic wave of Mo(V) would not interfere. For trace quantities of silicon, the large diffusion constant of the fourth wave or the sum of the diffusion currents of all the four waves could be used with advantage.

It is of interest to note that the Grasshoff and Hahn, and Sen and Chatterjee methods represent the determination of silicon at two extremes of the pH spectrum. It was decided to make a preliminary study of both methods with a view of finding a suitable method for determining silicon in steel.

(b) OPTIMISATION OF EXPERIMENTAL CONDITIONS

Chalmers and Sinclair[109, 110] prepared β-molybdosilicate by adding aliquots of silicate solution to a 50 ml volumetric flask containing between 5 and 7.5 ml of acetone and a 1:1 mixture of 8% ammonium molybdate solution and 1M sulphuric acid. After diluting the solution to 50 ml with water, it was left to stand for 15 minutes to allow the β-molybdosilicic acid to form. The absorbance of the solution was then measured within 30 minutes. Aqueous sample solutions, prepared according to the procedure of Chalmers and Sinclair, were polarographed but ill-defined waves were obtained (see fig.1). In addition, a blue zone was observed around the dropping mercury electrode even when the blank solution was polarographed. A decrease of the concentration of the molybdate used, neither improved the wave form nor was the blue zone completely eliminated. It was obvious that a reduction other than that of molybdosilicic acid was taking place. One possibility is that excess molybdate was being reduced instead of molybdosilicic acid.

Attempts to polarograph molybdosilicic acid pre-reduced with hydrazinium sulphate according to Sen and Chatterjee's[137] procedure, proved unsuccessful. Ill-defined waves, which could not be of any analytical use, were obtained (see fig. 2). In addition, the molybdenum blue solution which was polarographed, changed colour continually from blue to green and finally brown during the run. This change was more pronounced with the blank solution where even a brown precipitate was obtained. The reducing action of hydrazinium sulphate on molybdate which is the cause of the colour changes, showed that any method based on this procedure would not be reliable. Optimum concentrations of reducing agent and molybdate would have to be found to make the method applicable to the analysis of even the least complex material.

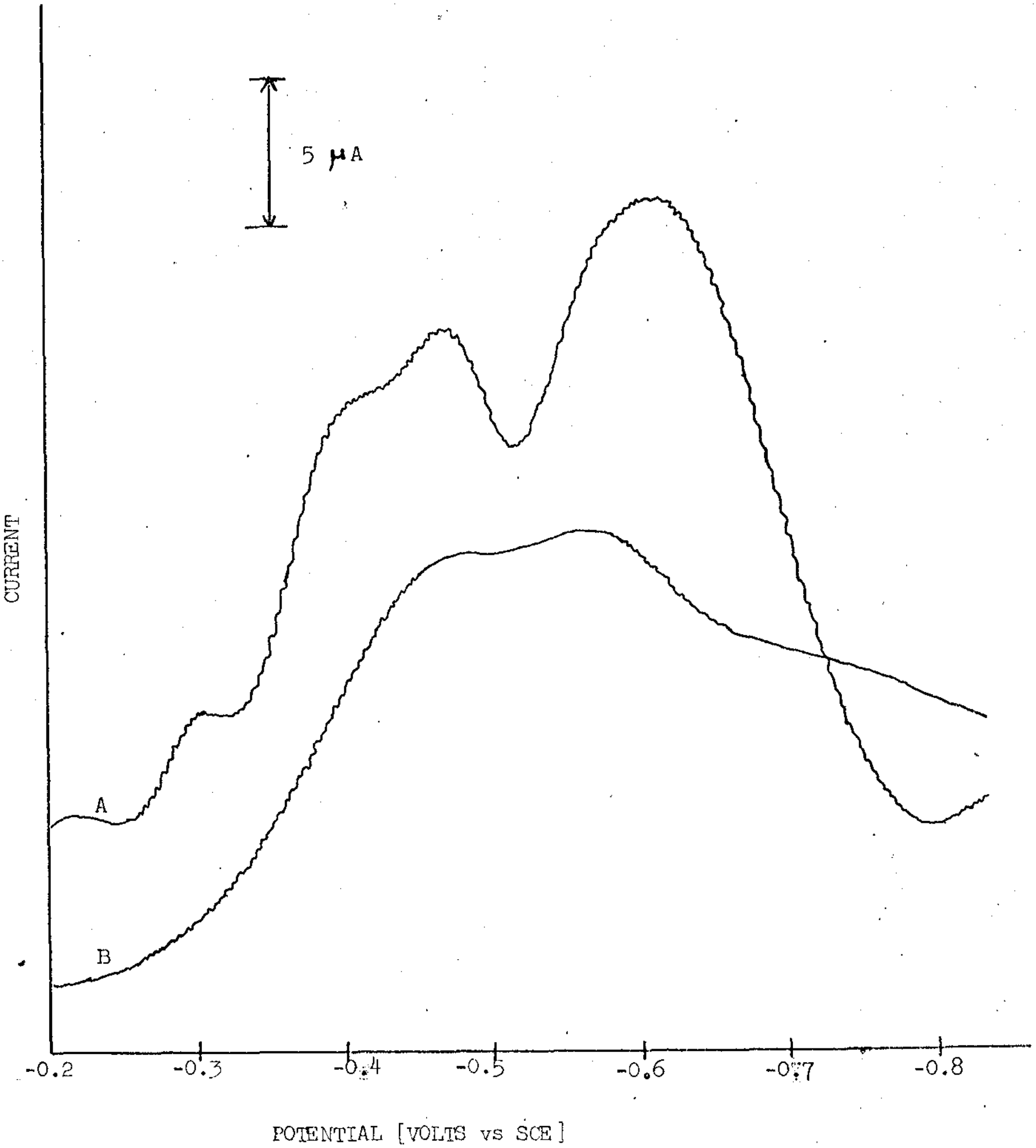


Fig.1 Differential pulse polarogram of molybdosilicate prepared according to Chalmers and Sinclair's[109,110] procedure.

Concentration of silicon (A) 1.4×10^{-3}M (B) zero
Modulation amplitude 25 mV, scan rate 2mV. sec^{-1}
Drop time 2 sec.

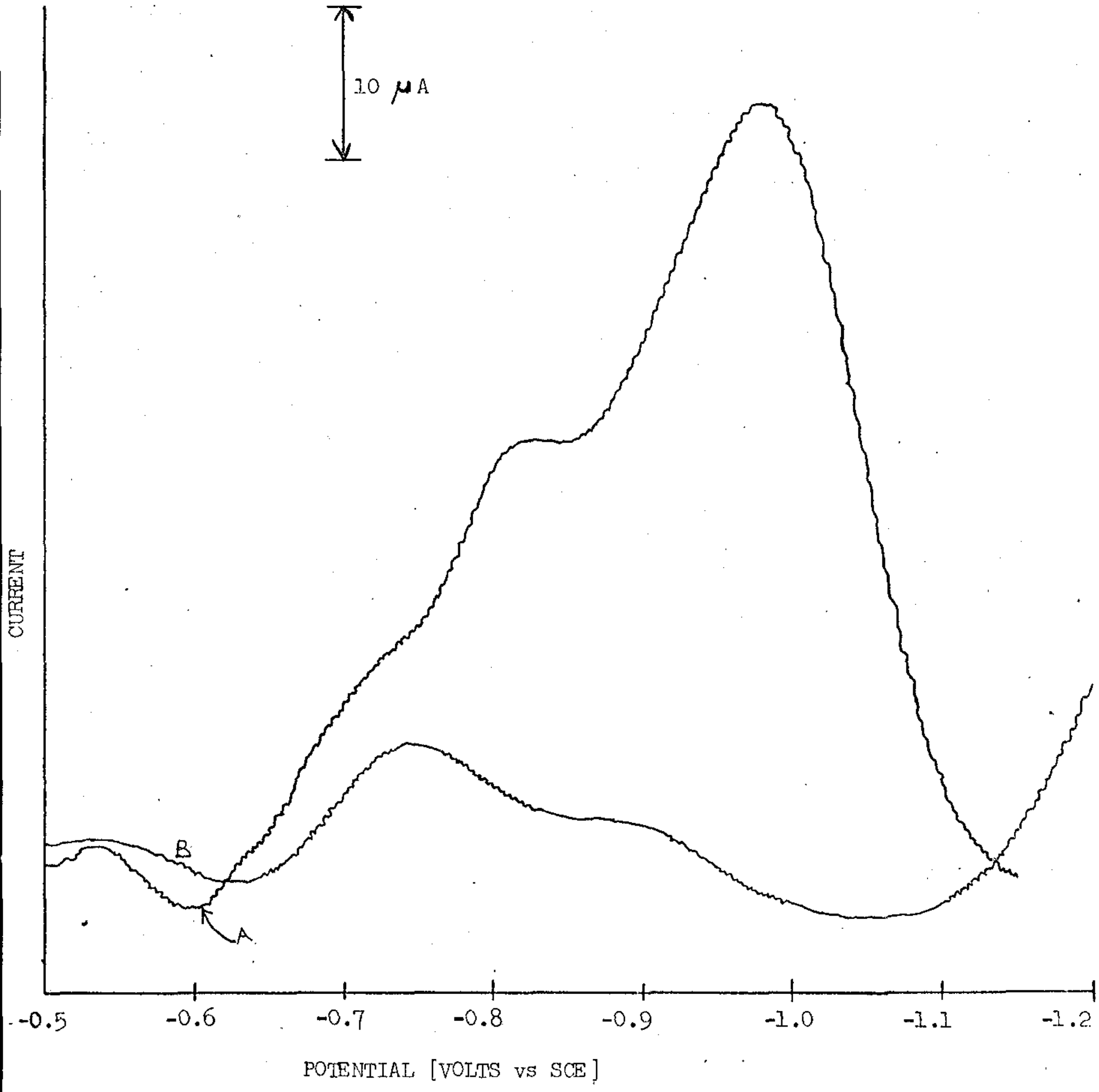


Fig.2 Differential pulse polarogram of molybdosilicate prepared according to Sen and Chatterjee's[137] procedure.
Concentration of silicon (A) 7 x 10^{-5}M (B) zero
Modulation amplitude 25 mV, scan rate 2mV. sec^{-1},
Drop time 2 sec.

In Grasshoff and Hahn's[142] procedure for the polarographic reduction of molybdosilicic acid, an aliquot of silicate solution is adjusted to pH 1.5, molybdate is added and the pH readjusted to 1.6. This solution is then allowed to stand for 24 hours before adjusting the volume to 100 ml. An aliquot of this solution is diluted with a citrate buffer containing methyl ethyl ketone and then polarographed. Good results were obtained with solutions containing at least 0.02 μg of silicon per ml but at levels of silicon lower than this, the blanks became very significant. Typical polarograms at these levels showed no difference between the wave forms of the blanks and those of solutions containing 0.005 μg of silicon per ml.

Various unsuccessful attempts were made to reduce the blank. These included using very low concentrations of molybdate and varying the composition of the working solution (citrate buffer containing methyl ethyl ketone) so that it contained different percentages of methyl ethyl ketone. Omitting methyl ethyl ketone from the working solution and increasing the concentration of the citrate in steps up to about 4M, did improve the blanks but at the same time the β-12-molybdosilicate wave was suppressed. This decrease in wave height might have been due to the increased viscosity of the solution. Substituting tartaric or oxalic acid for citric acid in the working solution did not improve the blanks either. When acetone was substituted for methyl ethyl ketone in the working solution, the polarograms of the blanks were the same as those of sample solutions containing 0.005 μg of silicon per ml. Attempts to improve the blanks under this condition, by reducing the concentration of molybdate used resulted in β-12-molybdosilicate not being formed. Varying the percentage of acetone used between 2.5 and 15% also failed to improve the blank. The loss of acetone during deoxygenation in spite of the inclusion in the deoxygenation train of a bottle containing the same percentage of acetone as in the polarographed solution, posed a serious problem and detracted from the method.

Further investigational work aimed at reducing the time required for the formation of β-12-molybdosilicate from 24 hours (as suggested by Grasshoff and Hahn) to a much shorter time, showed that the solution conditions suggested by Chalmers and Sinclair[109] could be used in modifying Grasshoff and Hahn's procedure. By adopting Chalmers and Sinclair's procedure, it was possible to dispense with the 24 hours waiting period. The procedure finally developed is as described on the next page.

(c) RECOMMENDED PROCEDURE FOR THE DETERMINATION OF SILICON IN AQUEOUS SOLUTION

The procedure is based on the formation, at pH 1.6, of β-12-molybdosilicate which is subsequently stabilised with methyl ethyl ketone. The excess molybdate is masked with citrate at pH 2.5 and the β-12-molybdosilicate polarographed.

APPARATUS

A Radiometer PHM 64 Research pH meter was used. The polarography was carried out using a Princeton Applied Research (PAR) 174 Polarographic Analyzer to which an Advance HR 2000 recorder was connected. Three electrode operation was employed using a dropping mercury electrode and a platinum electrode as working electrodes and a remote saturated calomel electrode as reference electrode. The polarographic cell shown in fig. 3, was made of a 50 ml double walled glass vessel with a perspex plastic top. The top had an O-ring on it to ensure that it fits tightly onto the cell. Four holes on the cell top enabled the three electrodes and the deoxygenation train to be connected to the solution in the cell. Water at any desired temperature could be pumped between the walls of the cell in order to regulate the temperature of the solution in the cell. The nitrogen used for deoxygenation was supplied from a cylinder and scrubbed free of oxygen by passing the stream of nitrogen through a heated silica tube containing copper wires heated to 560°C, and then through a bottle containing 40% methyl ethyl ketone in citrate buffer. The end of the deoxygenation train attached to the polarographic cell consisted of a two-way tap such that a blanket of nitrogen is kept over the solution throughout the duration of the polarographic analysis.

Double distilled water was used throughout the study.

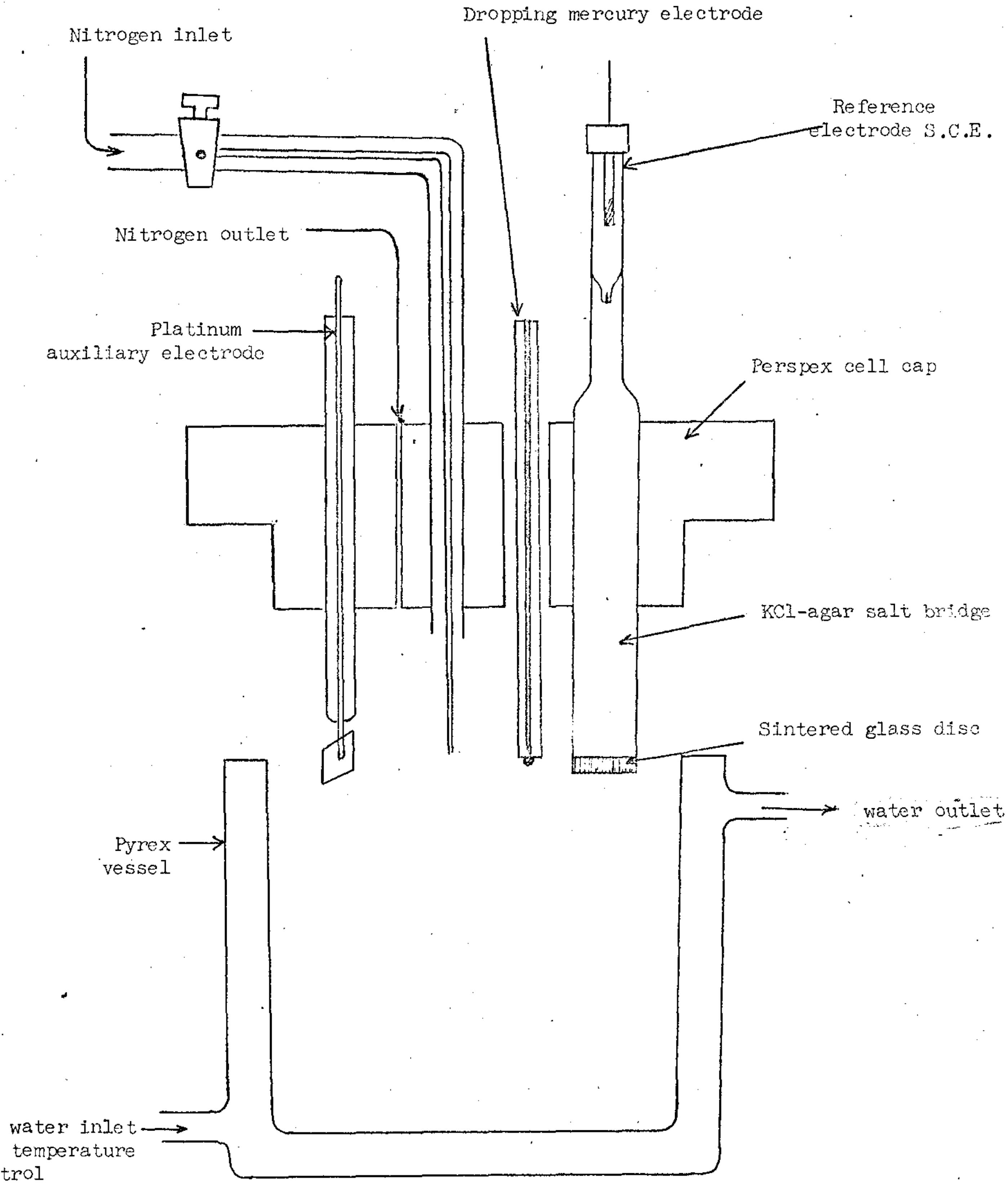


Fig. 3. Polarographic cell

REAGENTS

Concentrated standard silicate solution 100 μg of Si per ml.

Mix 0.1000 g of silicon powder (99.99%, Koch-Light Laboratories Ltd.) with 2 g of analytical reagent grade anhydrous sodium carbonate contained in a platinum crucible. Wet the mixture with a few drops of water and fuse it by heating for about two hours. The crucible lid should be on during the fusion to exclude carbon dioxide. Dissolve the melt in water, dilute the resulting solution to 1 litre with water and store in a polyethylene bottle.

Dilute standard silicate solution, 1 μg of Si per ml.

Dilute 10 ml of the concentrated standard silicate solution to 1 litre with water in a standard volumetric flask, mix and then transfer the solution to a polyethylene bottle. This solution should be prepared fresh whenever it is used.

Ammonium molybdate solution, 10%.

Dissolve 10 g of analytical reagent grade ammonium molybdate $[(NH_4)_6Mo_7O_{24}4H_2O]$ in water, dilute to 100 ml with water and store in a polyethylene bottle.

Ammonium molybdate solution, 1%.

Dissolve 1.0 g of analytical reagent grade ammonium molybdate in water, dilute to 100 ml with water and store in a polyethylene bottle.

Citrate buffer.

Dissolve 21 g of analytical reagent grade citric acid monohydrate in 200 ml of 1M sodium hydroxide solution and dilute to 1 litre with water. Transfer the solution to a polyethylene beaker and adjust the pH to 2.5 with 1M hydrochloric acid solution. Store the buffer solution in a polyethylene bottle.

Triton X-100 solution, 0.2%.

Dilute 0.2 ml of Triton X-100 to 100 ml with water.

Methyl ethyl ketone analytical reagent grade.

Hydrochloric acid, 1M.

Dilute, 86 ml of analytical reagent grade concentrated hydrochloric acid (specific gravity 1.18) to 1 litre with water.

Hydrochloric acid, 0.1M.

Dilute, 8.6 ml of analytical reagent grade concentrated hydrochloric acid (specific gravity 1.18) to 1 litre with water.

Sodium hydroxide, 1M.

Dissolve 40 g of analytical reagent grade sodium hydroxide in water, dilute to 1 litre with water and store the solution in a polyethylene bottle.

PROCEDURE

By pipette, introduce 5 ml of 10% ammonium molybdate solution into a polyethylene beaker (Note 1). Add an aliquot of the standard silicate solution. Dilute the solution to about 30 ml with water. Insert a combined calomel-glass electrode into the solution and adjust the pH carefully to 1.6 by dropwise addition of 1M hydrochloric acid while stirring with a magnetic stirrer. Allow the solution to stand for 20 minutes at room temperature while the stirring is continued. Transfer the solution to a 100 ml volumetric flask, wash the electrode and the beaker with 0.1M hydrochloric acid solution and add the washing solution in the flask. Dilute the solution to 100 ml with 0.1M hydrochloric acid (Note 2). Pipette 10 ml of the solution into a 50 ml volumetric flask. Add 2 ml of 1M hydrochloric acid and 10 ml of analytical reagent grade methyl ethyl ketone. Dilute the solution to 50 ml with water. Shake to mix the content of the flask thoroughly. Pipette 5 ml of this solution into a 25 ml volumetric flask and make up to mark with the citrate buffer. Shake to mix the solution thoroughly (Note 3). Transfer the solution to a polarographic cell and add about 0.3 ml of 0.2% Triton X-100 solution. Deoxygenate the solution by bubbling oxygen-free nitrogen through it for 15 minutes (Note 4) and then record the polarogram between -0.2V and -0.7V.

Run a blank solution following the same procedure but omitting aliquots of silicate solution. The instrument settings on the PAR 174 Polarographic Analyzer and on the recorder should not be altered for the blank run.

NOTES

1. 5 ml of 1% ammonium molybdate solution is used when aliquots of the dilute standard silicate solution are to be polarographed.
2. Addition of 0.1M hydrochloric acid solution is necessary to maintain the pH of the sample solution as near to 1.6 as possible and hence ensure that only β-12-molybdosilicate is formed.
3. Efficient mixing of the solution is necessary at this stage in order to mask any excess molybdate with the citrate.
4. The deoxygenation train should include a bottle containing 40% methyl ethyl ketone in the supporting electrolyte. This solution should be renewed frequently and should be deoxygenated for 10 minutes before attaching the polarographic cell for deoxygenation.

(d) INTERFERENCES

The effect of other elements that form heteropoly acids with molybdate.

A study was made of the effect of phosphorus and arsenic on the polarographic reduction of β-molybdosilicate. The effect of germanium, another element that forms a heteropoly acid with molybdate, was not investigated because it is rarely found in steel samples. Various procedures have been suggested for eliminating interferences due to these elements. The suggestions have included the use of strongly acidic sample solution,[39, 40] solvent extraction,[44-47] the use of organic complexing agents and variation in the sequence of adding reagents when the heteropoly acids are formed.[110]

It is generally known that in the presence of organic complexing agents such as tartaric, oxalic and citric acids, molybdophosphate, and molybdoarsenate are decomposed whereas molybdosilicate is usually unaffected. In the present study, in spite of the use of citric acid as a buffer, it was decided to investigate the effects of phosphate and arsenate on the polarograms of β-12-molybdosilicate because the organic complexing agents themselves have been shown to be not totally selective in their destruction of heteropoly acids.

REAGENTS

Phosphate, 50 mg of P per ml.

Dissolve 10.9758 g of analytical reagent grade potassium dihydrogen phosphate (KH_2PO_4) in water and dilute to 50 ml with water.

Arsenate, 30 mg of As per ml.

Dissolve 6.4478 g of analytical reagent grade di-sodium hydrogen arsenate (Na_2HAsO_4) in water and dilute to 50 ml with water.

PROCEDURE

The procedure as outlined previously for silicate was used except that blanks containing phosphate and arsenate were also run in addition to the normal blank (i.e. molybdate solution containing no silicate).

(e) RESULTS AND DISCUSSION

Figures 4 and 5 show typical polarograms obtained when β-12-molybdosilicate was reduced polarographically. The polarograms show two well-defined peaks at potentials of -0.37 and -0.48V vs SCE respectively. The nature of the waves obtained confirms the observation by Grasshoff and Hahn[142, 143] that two waves are obtained when β-12-molybdosilicate is reduced polarographically in the presence of methyl ethyl ketone and citrate. The polarograms are reproducible but only the peak height of the wave at -0.37V was found to be proportional to the concentration of silicon. This peak height was used in subsequent determinations of silicon in steel. Typical calibration curves are shown in fig.6 and 7.

The relationship between the peak height of the second wave, at -0.47V, with concentration of silicon suggests that this wave could be a catalytic wave. It has been suggested by Grasshoff and Hahn that the second wave is due to reduction of molybdate formed as a result of the decomposition of β-12-molybdosilicate. It is also known that the reduction of 12-molybdosilicate at a dropping mercury electrode goes in accordance with the regular reduction mechanism of simple molybdenum ions. Thus the first wave is usually attributed to the reduction of Mo(VI) to Mo(V) and the second wave is attributed to the reduction of Mo(V) to Mo(III). Taking into consideration the shape of the calibration graph based on the second wave as shown on fig. 8, one is inclined to suggest that the second wave is due to the catalytic reduction of Mo(V) regenerated by the reaction between Mo(III) and some oxidising species in the solution. The scope of the present study was such that it was not possible to conduct further investigations aimed at identifying the catalytic species responsible for this wave or fully elucidating the mechanism of the oxidation-reduction process.

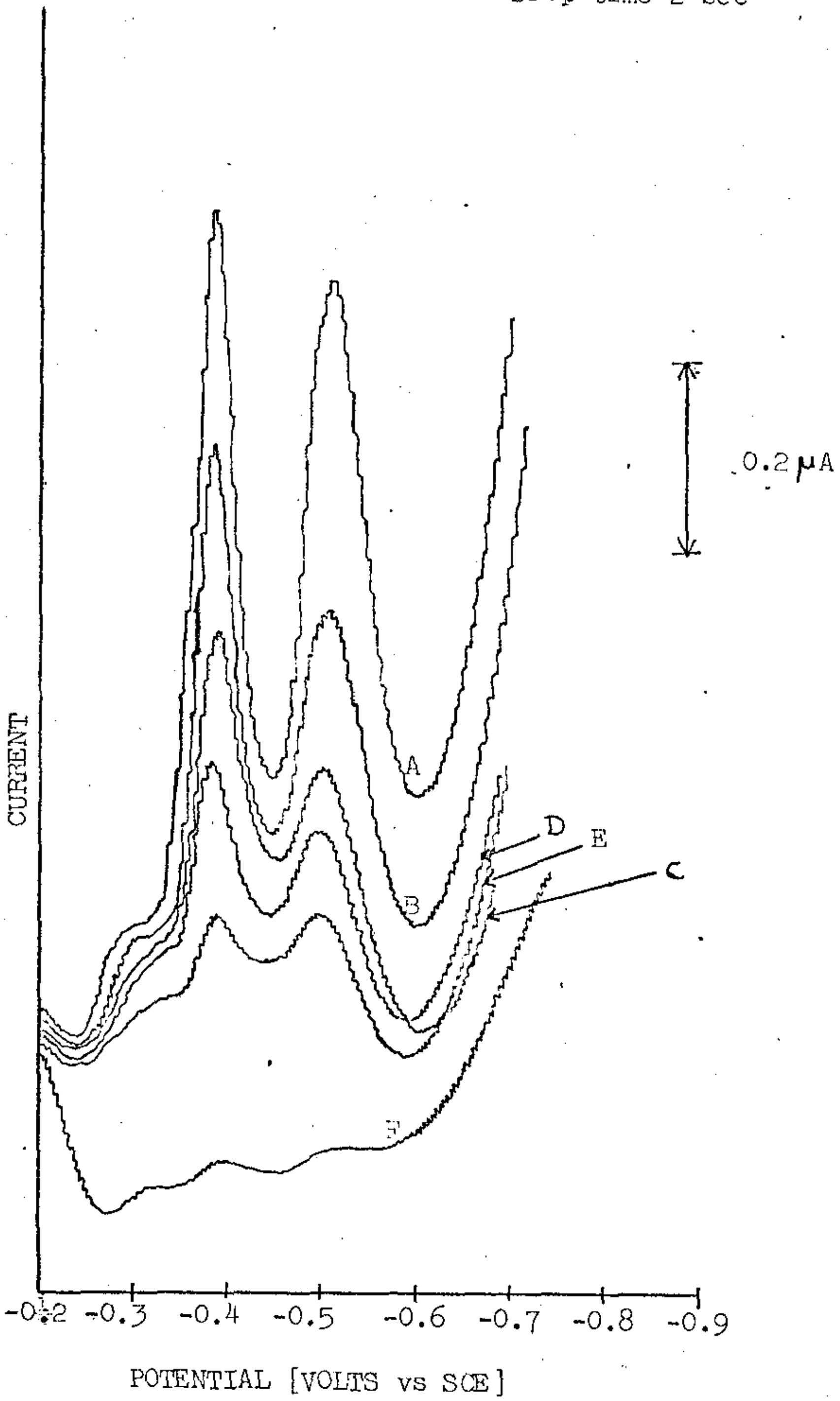
The usual criteria of polarographic irreversibility normally determined by conventional D.C. polarography, namely, the plot of log $(i_d-i)i_d$ against working electrode potential, the numerical value of $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ and determination of the temperature coefficient of the half-wave potential, were not applied in this study but evidence from the numerous publications dealing with the polarographic reduction of β-12-molybdosilicate shows conclusively the irreversible character of the reduction process.

The polarographic reduction of β-12-molybdosilicate was carried out at pH 2.5 because the peak potential was found to vary with pH. There was a shift of peak potential towards more negative potentials with increasing pH as shown in Table 1. This suggests that hydrogen ions are taking part in the whole polarographic process.

TABLE 1

VARIATION OF THE HALF-WAVE POTENTIAL OF β-12-MOLYBDOSILICATE WITH pH.

pH	E_p vs SCE
1.0	-0.10
1.5	-0.27
2.5	-0.37
4.0	-0.48



Modulation amplitude 50 mV
Scan rate 2 mV.sec^{-1}
Drop time 2 sec

Fig. 4. Differential pulse polarograms of β-12-molybdosilicate in citrate buffer at pH 2.5.

Concentration of silicon: (A) 0.12 μg ml^{-1} (B) 0.08 μg.ml^{-1} (C) 0.06 μg.ml.ml^{-1} (D) 0.04 μg.ml^{-1} (E) 0.02 μg.ml^{-1} (F) BLANK

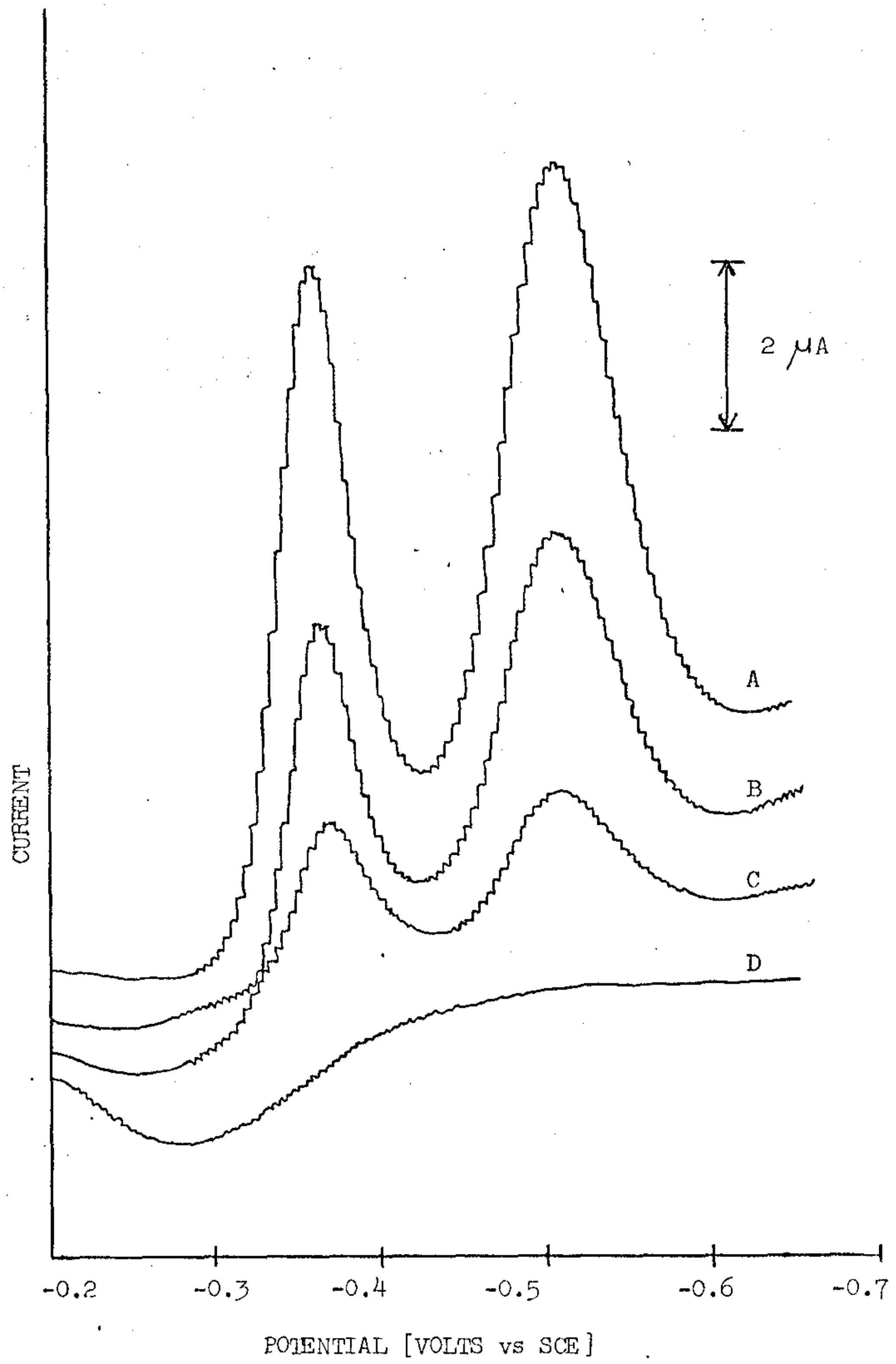


Fig.5 Differential pulse polarograms of β-12-molybdosilicate in citrate buffer at pH 2.5 .

Concentration of silicon (A) 0.8 $\mu g\ ml^{-1}$ (B) 0.4 $\mu g\ ml^{-1}$ (C) 0.2 $\mu g\ ml^{-1}$ (D) zero

Modulation amplitude 50 mV, scan rate 2mV. sec^{-1} drop time 2 sec.

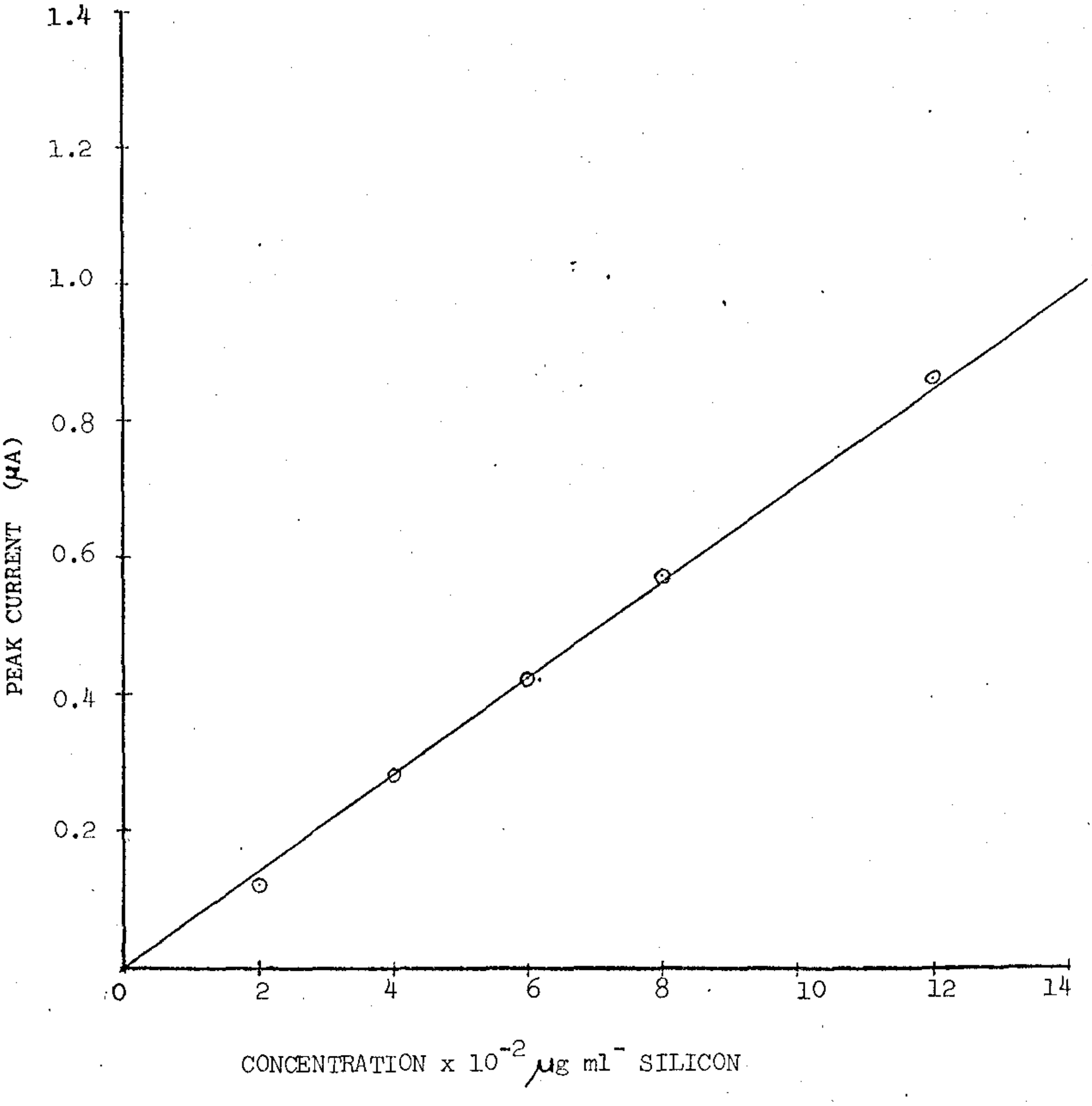


Fig.6. Calibration curve of β-12-molybdosilicate.
Peak current measured at -0.37V vs SCE

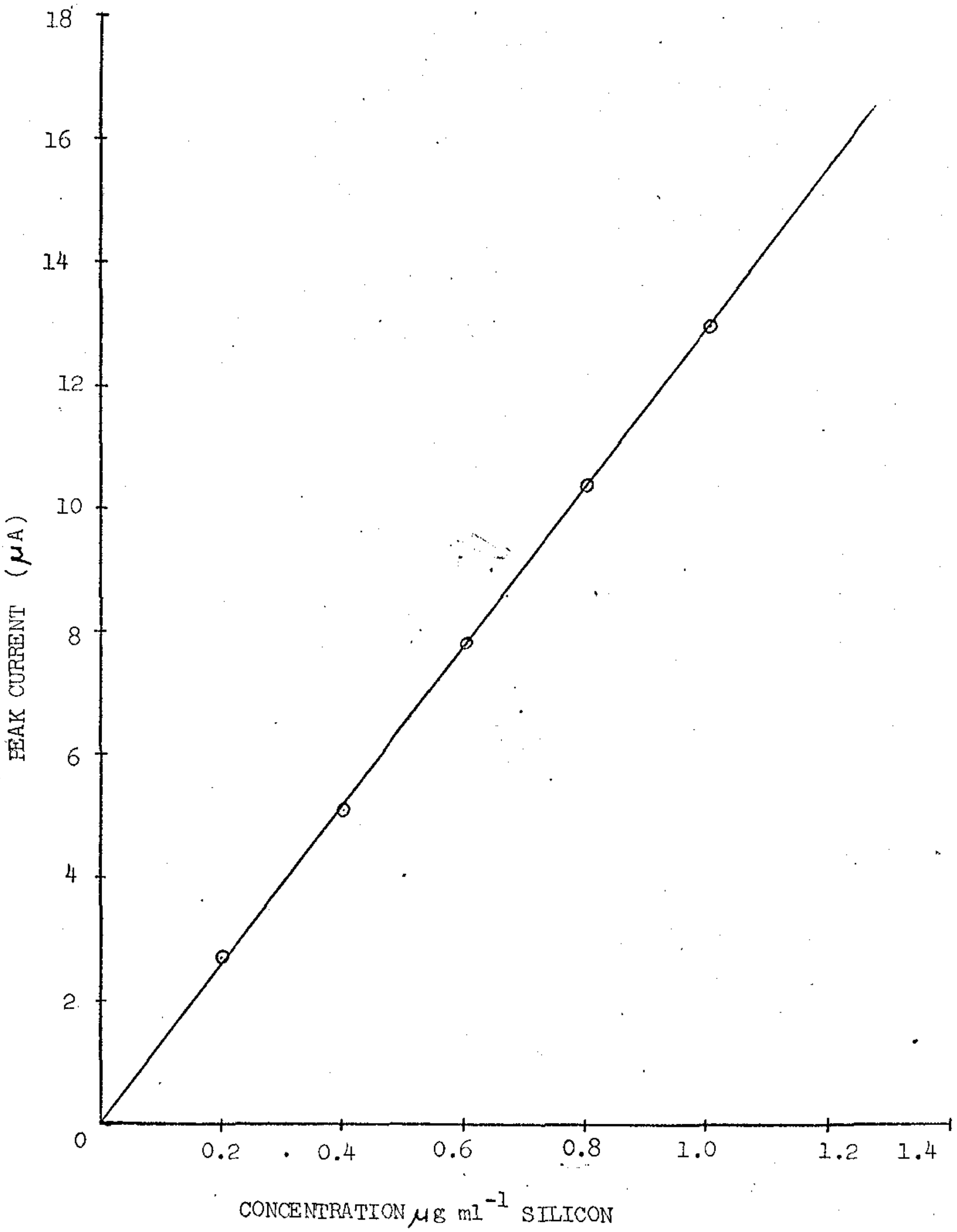


Fig. 7. Calibration curve of β-12-molybdosilicate
Peak current measured at -0.37V vs SCE

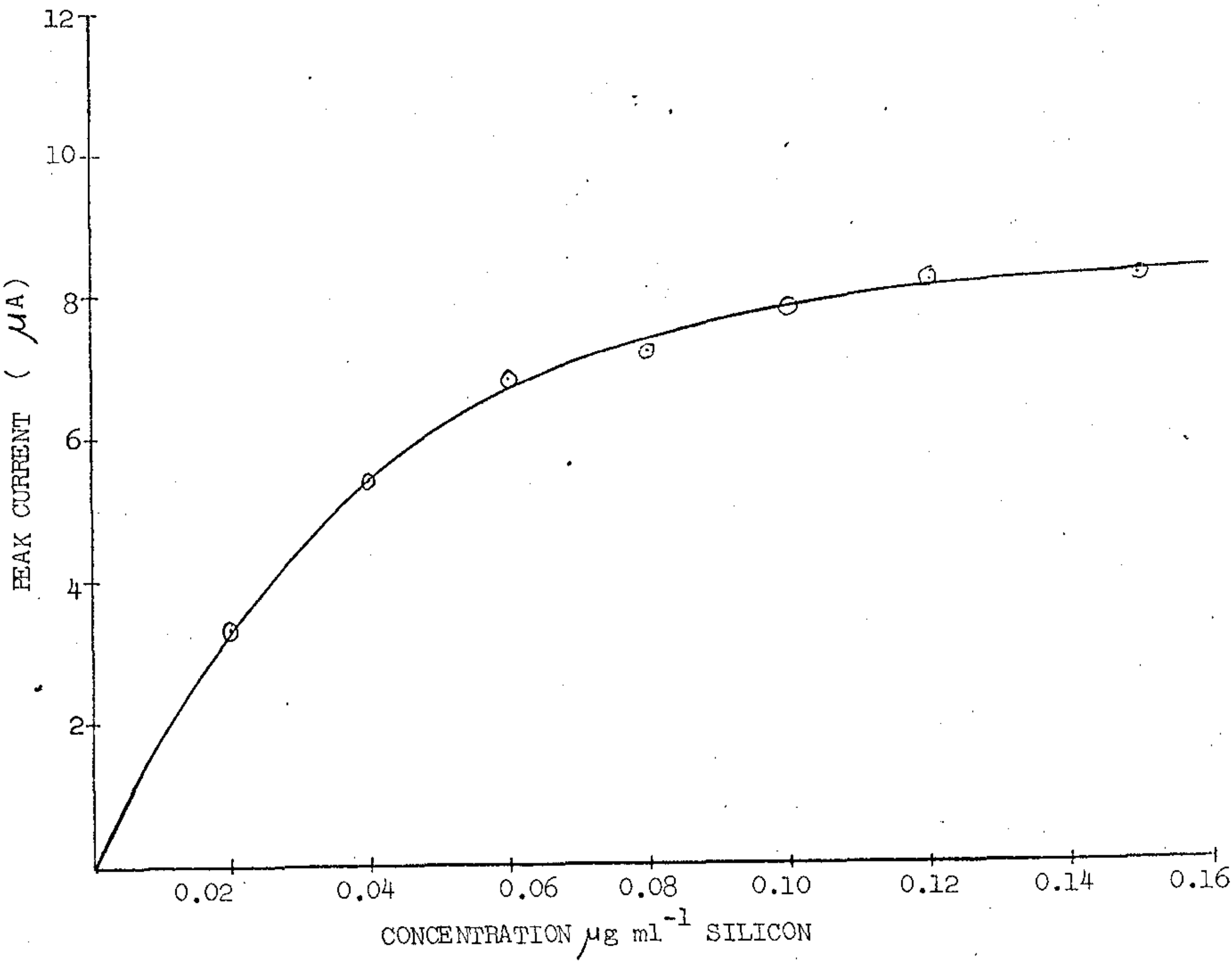


Fig.8. Calibration curve of β-12-molybdosilicate.
Peak current measured at -0.47V vs SCE

Effect of Interfering elements. Figures 9 and 10 show clearly that no interference was observed from phosphate and arsenate. The ratios of phosphate and arsenate to silicate are shown on Table 2. The non-interference of phosphate and arsenate means that citrate can be used successfully in the destruction of their respective heteropolyacids, thus making the selective determination of silicate in the presence of phosphate and arsenate possible. The reactions between citrate and molybdophosphate and molybdoarsenate appear to take place according to the following scheme:

molybdoarsenate + citrate ⟶ citratomolybdate + arsenate

molybdophosphate + citrate ⟶ citratomolybdate + phosphate

TABLE 2

EFFECT OF INTERFERING ELEMENTS

(a) Molar Ratio of Silicate to Phosphate (cf Fig. 9)

  (i) 1:1700

  (ii) 1:700

  (iii) 1:350

(b) Molar Ratio of Silicate to Arsenate (cf Fig. 10)

  (i) 1:500

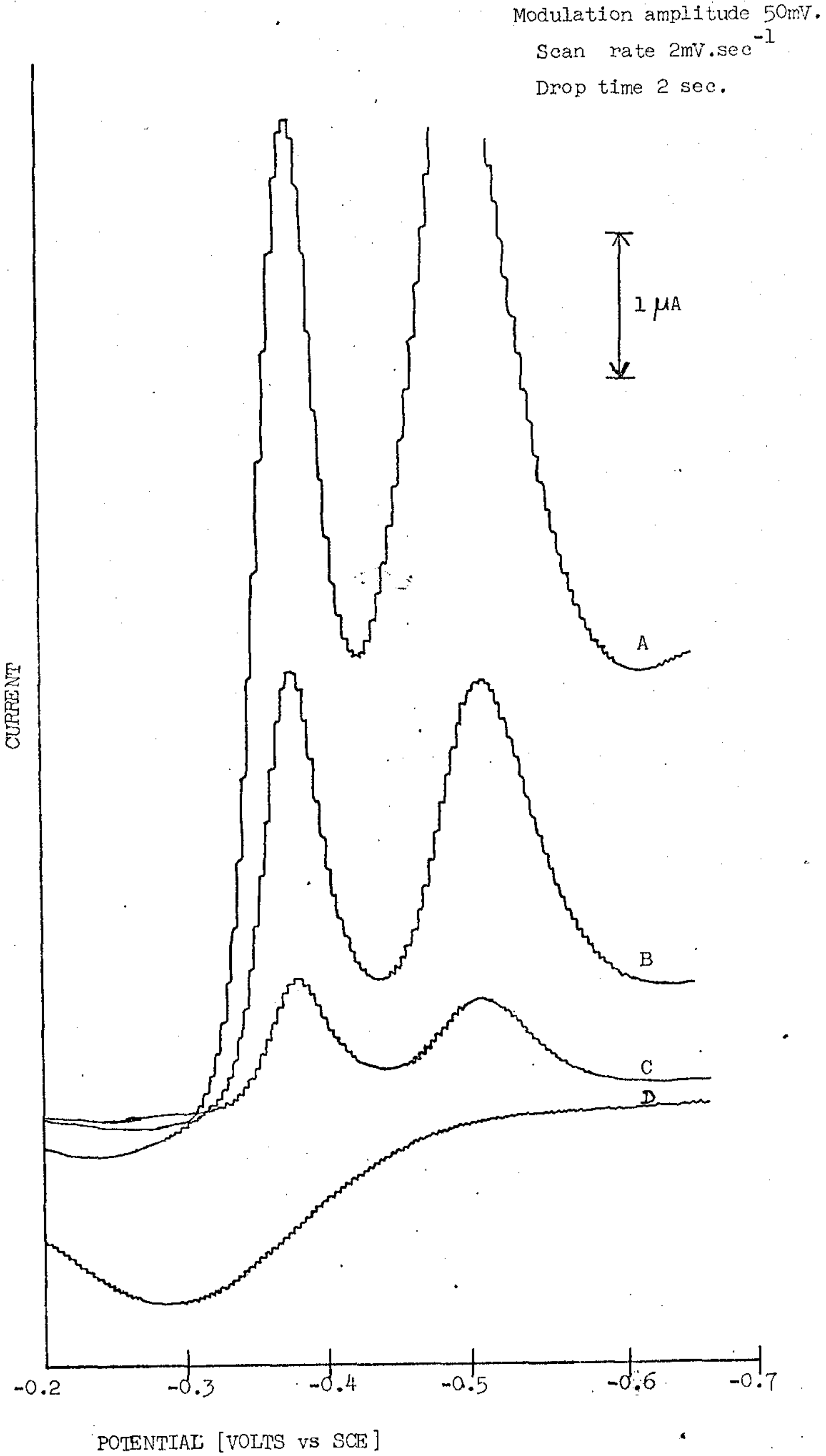


Fig.9 Effect Phosphate
Molar ratio Si:P (A) 1:1700 (B) 1:700 (C) 1:350
(D) Blank.

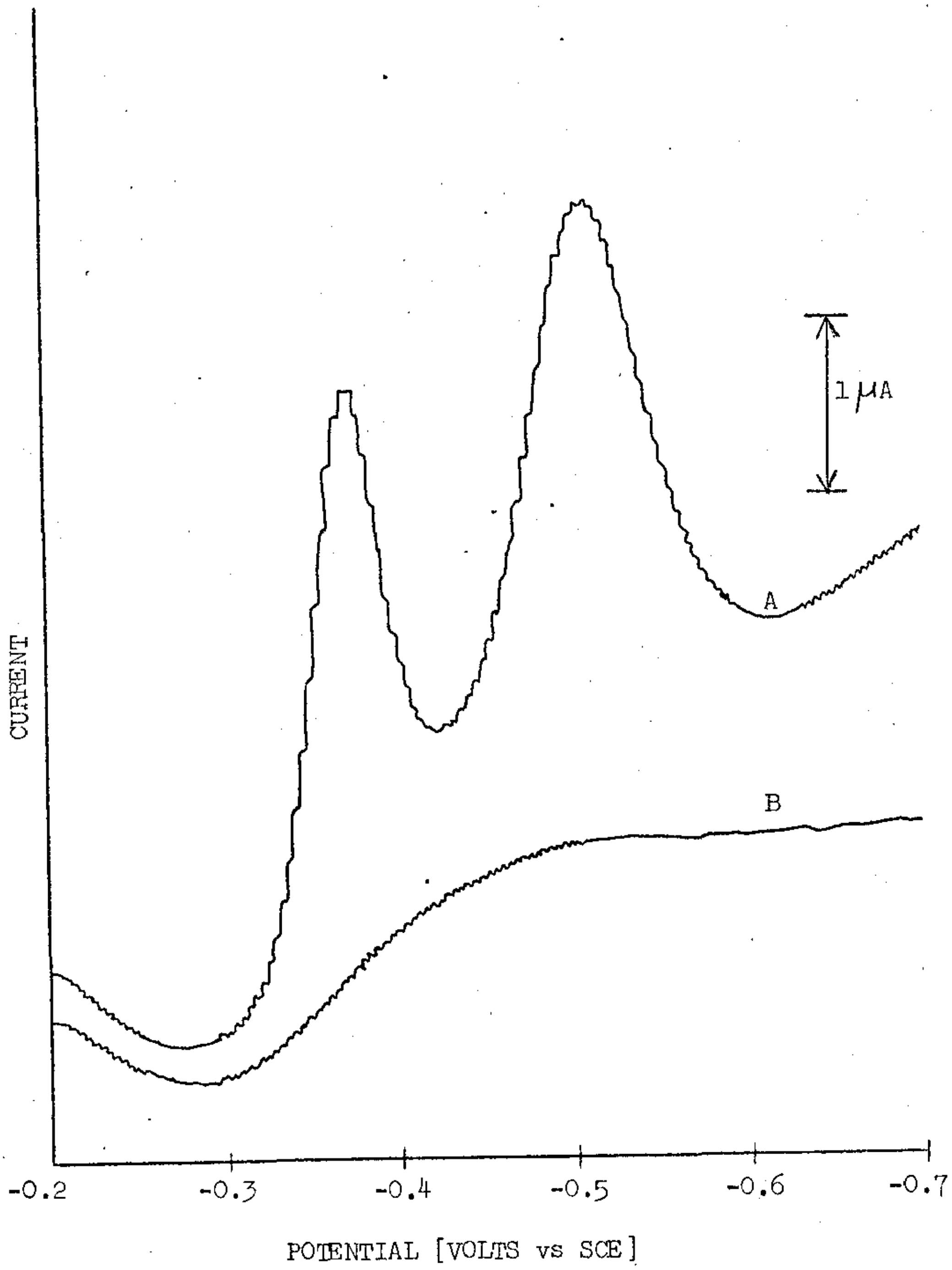


Fig.10 Effect of Arsenate
Molar ratio of Si:As (A) 1:500 (B) Blank.
Modulation amplitude 50 mV, scan rate 2mV. sec^{-1}
Drop time 2 sec.

V. APPLICATION OF THE METHOD DEVELOPED TO THE DETERMINATION OF SILICON IN STEEL

Initial experiments were carried out with samples of steel and the results obtained were unsatisfactory due to interference from other elements present in steel. The β-12-molybdosilicate wave was completely suppressed in sample solutions containing less than 0.1% of silicon (see figs. 11 and 12), and only appeared as a small peak in solutions containing more than 0.1% silicon (see fig. 13). However, all the polarograms showed a well-defined peak at -0.47V vs SCE but the peak heights were not proportional to the percentage concentration of silicon in the samples. A procedure in which iron and other interfering elements were first removed by mercury cathode electrolysis gave satisfactory results.

PRINCIPLE

The method consists of the oxidation of a solution of the steel in dilute sulphuric acid with potassium permanganate, destruction of the excess permanganate, and dilution to a definite volume. The diluted solution is electrolysed on a mercury cathode to remove iron and other interfering metals. The silicon is converted to β-12-molybdosilicate which is reduced polarographically.

APPARATUS FOR MERCURY CATHODE ELECTROLYSIS

The apparatus, the main features of which are shown on fig. 14, was made of a double-walled pyrex vessel capable of holding up to 100 ml of solution. 5-10 ml of tri-distilled mercury was placed in the vessel and a copper wire, enclosed in a glass tube, with a piece of platinum foil at the end, was dipped into the mercury to maintain electrical contact. The anode consisted of a platinum gauze suspended in the solution. Efficient stirring of the solution was provided by a magnetic stirrer. To prevent the temperature of the solution rising

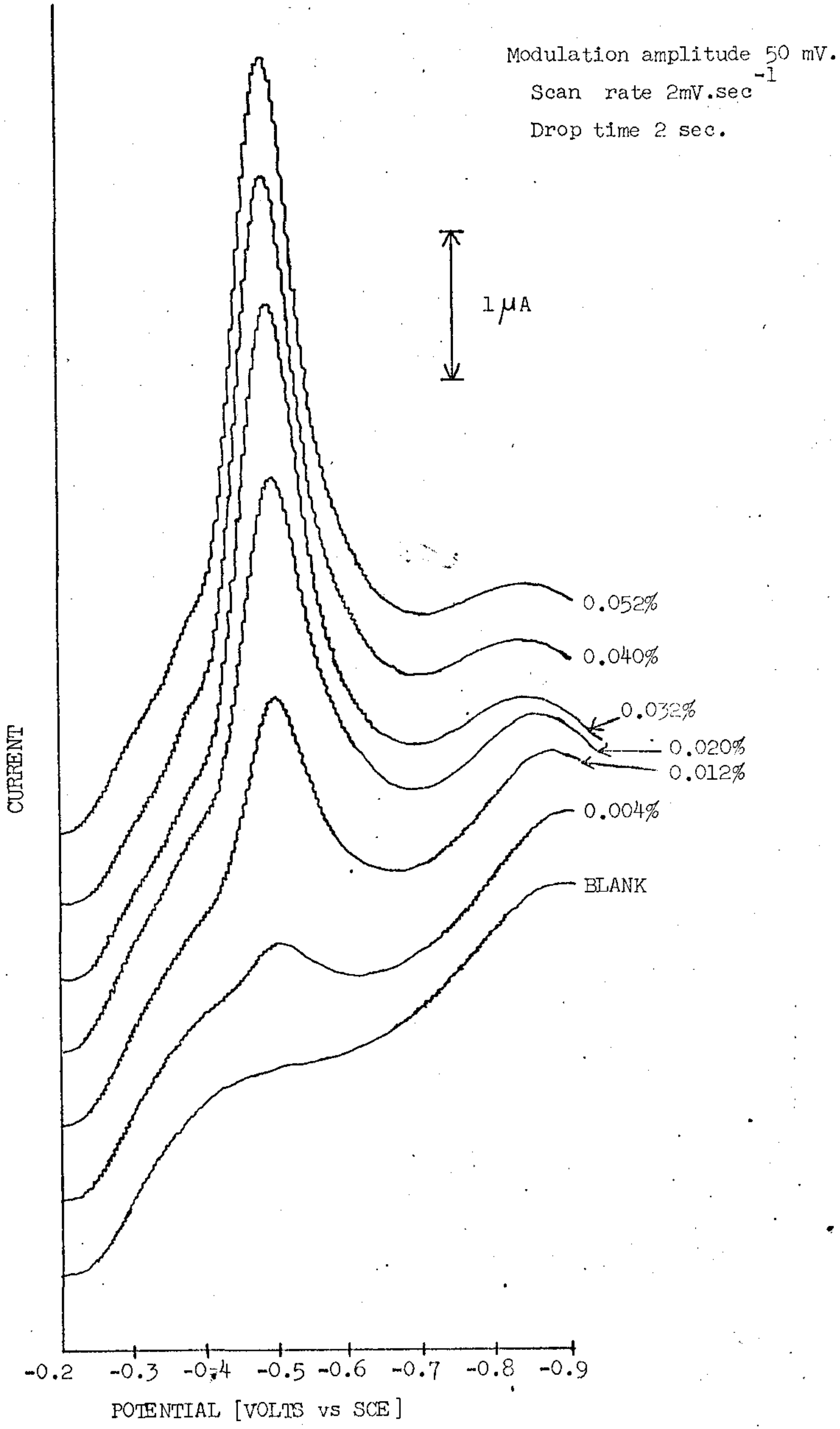


Fig.11 Differential pulse polarograms of β-12-molybdosilicate in the presence of Iron (III). Percentages of silicon are as shown on the polarograms.

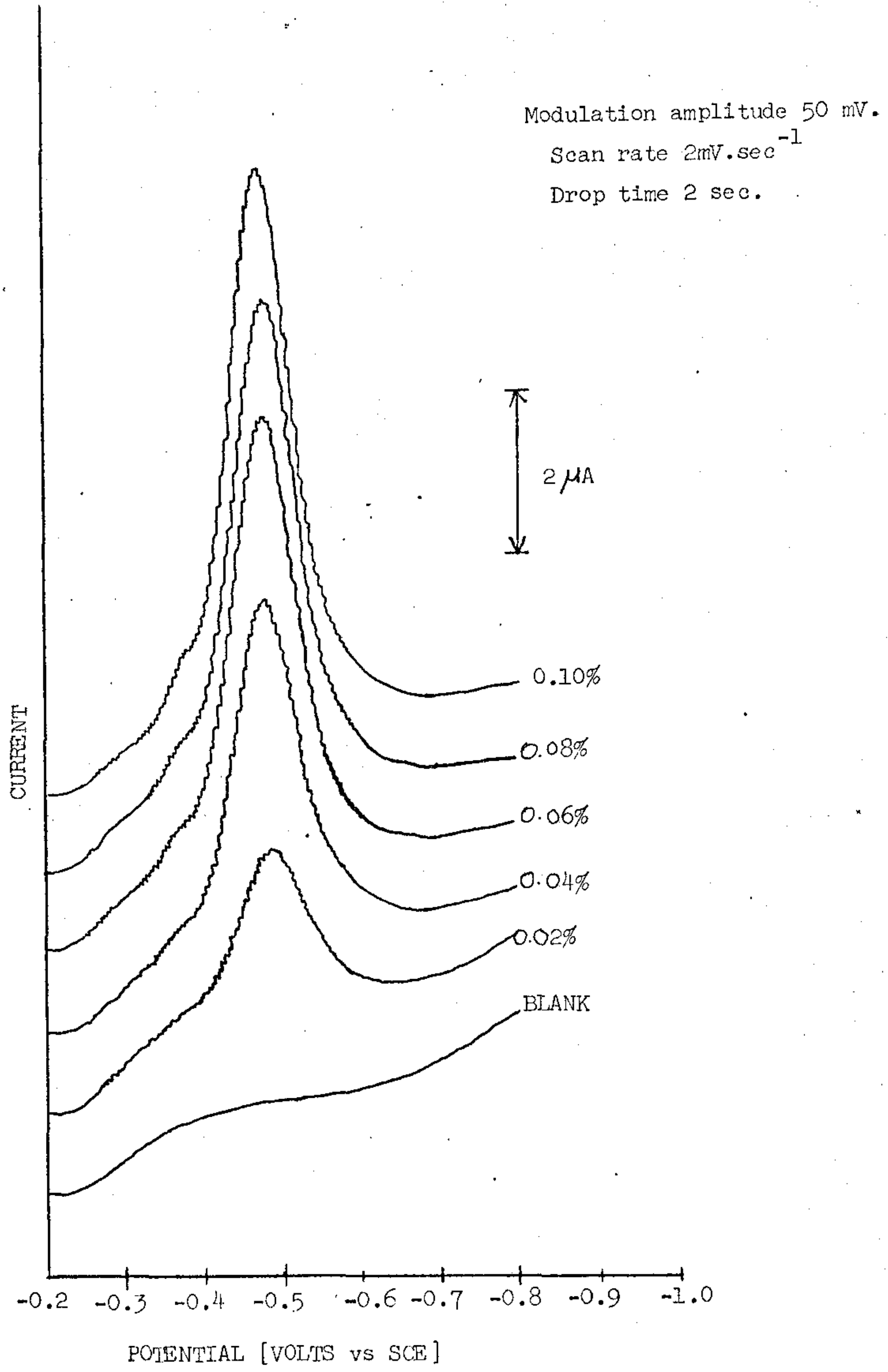


Fig.12 Differential pulse polarograms of β-12-molybdosilicate in the presence of Iron (III). Percentages of silicon are as shown on the polarograms.

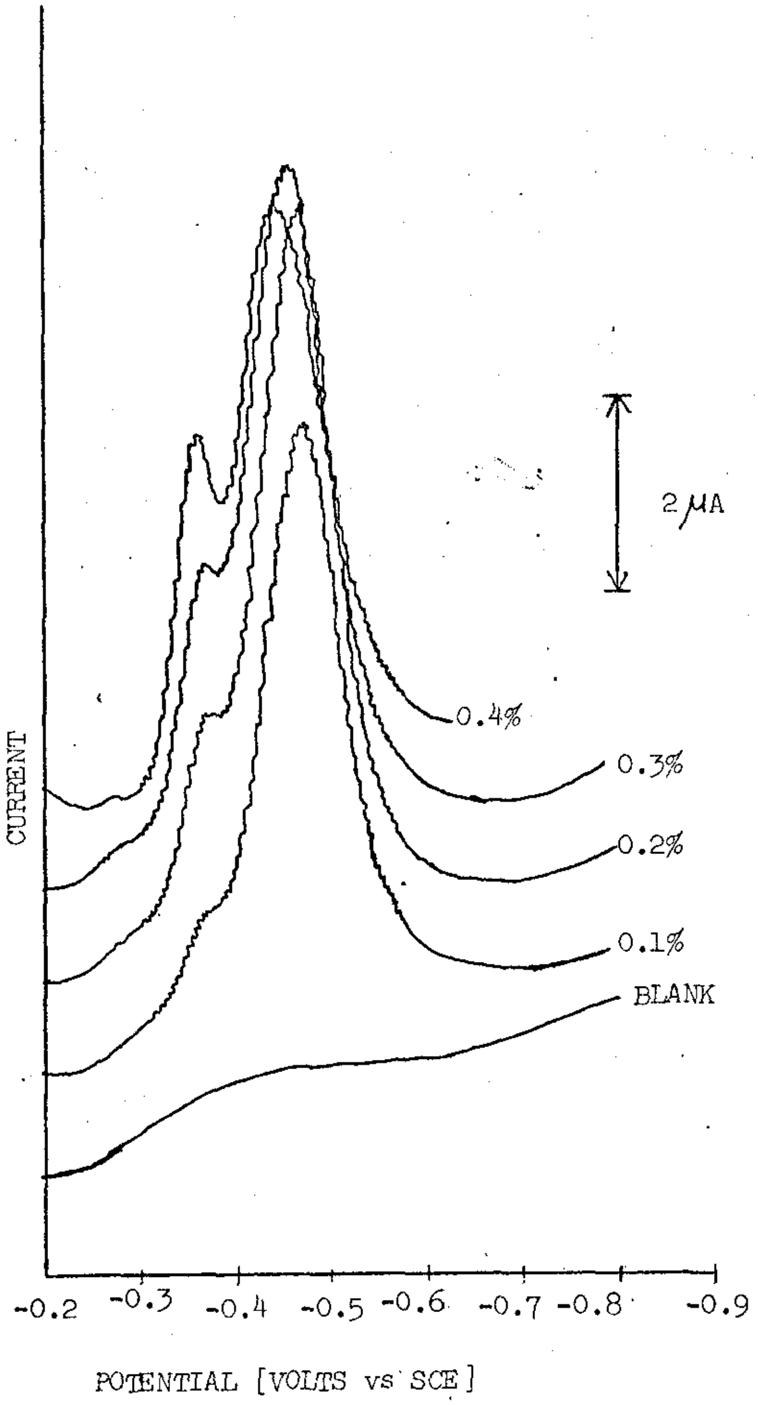


Fig.13 Differential pulse polarograms of β-12-molybdosilicate in the presence of Iron (III). Percentages of silicon are as shown on the polarograms. Modulation amplitude 50 mV, scan rate 2mV.sec.$^{-1}$, Drop time 2·sec.

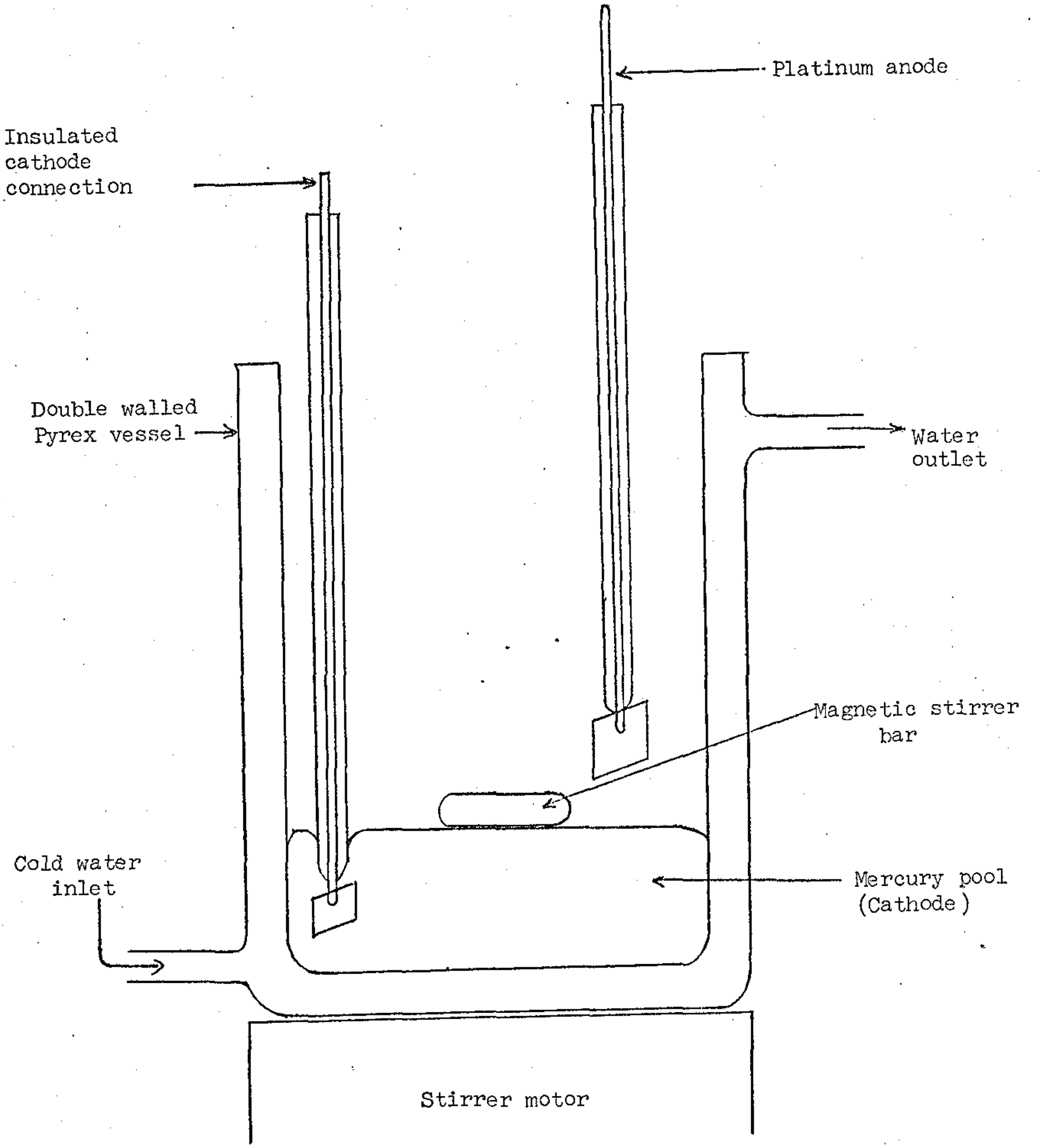


Fig. 14. Cell for mercury cathode electrolysis.

above 40°C during electrolysis, cold water from the tap was passed between the walls of the cell. Current for the electrolysis was provided by a power unit capable of delivering up to 10 amperes of direct current.

REAGENTS

Sulphuric acid solution, 10%.

Carefully add 10 ml of analytical reagent grade concentrated sulphuric acid (specific gravity 1.84) to water in a beaker and mix. Transfer the solution to a 100 ml volumetric flask and dilute to 100 ml with water.

Potassium permanganate solution, 2%.

Dissolve 2 g of analytical reagent grade potassium permanganate [$KMnO_4$] in 100 ml of water in a polyethylene flask and store the solution in a polyethylene bottle.

Hydrogen peroxide "100 volume" analytical reagent grade.

Ammonium molybdate solution, 1%.

Dissolve 1 g of analytical reagent grade ammonium molybdate [$(NH_4)_6Mo_7O_{24}4H_2O$] in 100 ml of water in a polyethylene flask and store the solution in a polyethylene bottle.

Sodium hydroxide solution, 2M.

Dissolve 40 g of analytical reagent grade sodium hydroxide in water in a beaker. Transfer the solution to a 500 ml polyethylene flask and make up to mark with water. Store the solution in a polyethylene bottle.

Hydrochloric acid solution, 1M.

Dilute 86 ml of analytical reagent grade hydrochloric acid (specific gravity 1.18) to 1 litre with water.

Methyl ethyl ketone: analytical reagent grade.

Citrate buffer.

Dissolve 21 g of analytical reagent grade citric acid in 200 ml of 1M sodium hydroxide solution and dilute to 1 litre with water. Transfer the solution to a polyethylene beaker and adjust the pH to 2.5 with 1M hydrochloric acid solution. Store the buffer solution in a polyethylene bottle.

Triton X-100 solution.

Dilute 0.2 ml of Triton X-100 to 100 ml with water.

Concentrated standard silicate solution, 100 μg of Si per ml.

Fuse 0.1000 g of silicon powder (99.99% Koch-Light Laboratories Ltd.) with 2 g of analytical reagent grade anhydrous sodium carbonate contained in a platinum crucible. Dissolve the melt in water, dilute the resulting solution to 1 litre with water and store in a polyethylene bottle.

Dilute standard silicate solution 1 μg of Si per ml.

Dilute 10 ml of the concentrated standard silicate solution to 1 litre with water in a standard volumetric flask, mix and then transfer the solution to a polyethylene bottle. This solution should be prepared fresh whenever it is used.

PREPARATION OF A CALIBRATION GRAPH

By pipette, introduce 5 ml of 1% ammonium molybdate solution into a polyethylene beaker. Add an aliquot of the dilute standard silicate solution. Dilute the solution to about 30 ml with water. Adjust the pH of the solution to 1.6 with 1M hydrochloric acid solution while stirring with a magnetic stirrer. Allow the solution to stand for 20 minutes at room temperature while the stirring is continued. Transfer the solution to a 100 ml volumetric flask, wash the combined calomel-glass electrode used in measuring the pH, and the beaker with 0.1M hydrochloric acid solution and add the washing to the solution in the flask. Dilute the solution to 100 ml with 0.1M hydrochloric acid solution. Pipette 10 ml of the solution into a 50 ml volumetric flask. Add 2 ml of 1M hydrochloric acid solution and 10 ml of methyl ethyl ketone. Dilute the solution to 50 ml with water. Shake to mix the content of the flask thoroughly. Pipette 5 ml of this solution into a 25 ml volumetric flask and make up to mark with the citrate buffer. Shake to mix the solution thoroughly. Transfer the solution to a polarographic cell, add about 0.3 ml of 0.2% Triton X-100 solution, deoxygenate for 15 minutes and then record the polarogram between -0.2 and -0.7V. Draw a calibration graph of peak height of the wave obtained against the concentration of silicate solution used.

PROCEDURE.

Add 40 ml of 10% sulphuric acid solution to 0.5 g of the steel sample (Note 1) in a Teflon beaker and heat gently until the sample is dissolved. Oxidize the hot solution by dropwise addition of 2% potassium permanganate solution until a permanent brown precipitate of manganese dioxide is just obtained. Add drops (2 or 3) of "100 volume" hydrogen peroxide solution until the precipitate of manganese dioxide is just discharged. Boil the solution to expel excess hydrogen peroxide. Cool, (filter if necessary), dilute the solution to 50 ml with double-distilled water and mix thoroughly. Transfer the solution to an electrolysis cell and electrolyse for about 1 hour using a mercury pool cathode and platinum anode. The current density should be 0.2 amp. $cm.^{-2}$ Cold water from the tap is passed through the outer jacket of the electrolysis cell to maintain the temperature of the solution below 40°C. Continue the electrolysis until a spot test (Note 2) shows no iron is present. Continue the electrolysis while removing the solution from the cell with a pipette. Pipette 25 ml of the electrolysed solution into a polyethylene beaker. Adjust the pH of the solution to 1.6 with 2M sodium hydroxide solution. Add 5 ml of 1% ammonium molybdate solution and stir the solution with a magnetic stirrer. Allow the solution to stand at room temperature for 20 minutes while the stirring is continued. Transfer the solution to a 100 ml volumetric flask and make up to mark with water. Pipette 10 ml of the solution into a 50 ml volumetric flask, add 2 ml of 1M hydrochloric acid solution, 10 ml of methyl ethyl ketone and then make up to mark with water. Shake to mix the solution thoroughly. Pipette 5 ml of this solution into a 25 ml volumetric flask and make up to mark with the citrate buffer. Shake to mix thoroughly. Transfer the solution to a polarographic cell, add 0.3 ml of 0.2% Triton X-100 solution, deoxygenate for 15 minutes and then record the polarogram between -0.2V and -0.7V. Compare the peak height of the polarogram at potential -0.37V with those obtained with the standard silicate solution and hence determine the percentage of silicon in the steel sample.

NOTES.

1. For samples containing less than 0.01% of silicon, use 1 g of sample.
2. Spot tests with potassium hexocyanoferrate II are adequate but if a very sensitive spot test is desired, 1,2-dihydro xybenzene-3,5-disulphonic acid can be used.

RESULTS AND DISCUSSION.

The calibration graphs are shown in Figs. 15 and 16. Figs 17-23 show typical polarograms for the differential pulse polarographic determination of silicon in steel. The results obtained are given on Table 3. The coefficients of variation for the different levels of silicon are also shown on Table 3. The results show that differential pulse polarography is sufficiently sensitive and accurate for determining low levels of silicon. Colorimetry, atomic absorption and neutron activation which are of comparable sensitivity and accuracy have been recommended for determining low levels of silicon in steel. Colorimetry (i.e. the molybdenum blue procedure) is recommended by the British Standards Institution[2] for determining silicon over the range 0.002 to 0.05%. The reproducibility of the colorimetric method for steel samples containing 0.01% of silicon has been quoted at ±0.002% and that for samples containing 0.05% of silicon as ±0.005%. The reproducibility of the colorimetric method for steel samples containing less than 0.01% of silicon was not quoted.

Atomic absorption methods have so far been used for determining silicon in steel over the range 0.1 to 1% and the coefficients of variation of results in this range vary from 1.5 to 2.4%.[62-68] The limit of detection by atomic absorption methods has been reported to be about 0.03% silicon with a coefficient of variation of 10%.[65] In fact, it has been suggested that for steels containing less than 0.1% of silicon, alternative analytical methods will give better results.[68]

Neutron activation analysis has reportedly been employed to determine silicon in steel over the range 0.1 to 1%. At the 0.1% level of silicon, the coefficient of variation of the method is reported to

TABLE 3

RESULTS FOR THE ANALYSES OF BRITISH CHEMICAL STANDARDS STEEL SAMPLES

Steel	% Silicon Found	Mean Value	Coefficient of Variation	Standardised Value (%)	Actual value given by individual analyst.
BCS 149/3 High Purity Iron	0.0020 0.0021 0.0017 0.00165	0.0019	3.2	0.002	0.001; 0.002 0.002; 0.002 0.001; 0.002 0.002; 0.002
BCS 204/4 Ferro-chromium (High Carbon)	0.2233 0.2367 0.2100 0.2225	0.2231	4.9	0.22	0.22; 0.22; 0.20 0.24; 0.24; 0.22 0.23; 0.30
BCS 232/1 0.1% Sulphur Carbon steel	0.0735 0.0710 0.0757	0.0734	3.2	(0.07)	0.07
BCS 237/1 0.1% Carbon steel	0.1090 0.1130 0.1130 0.1147	0.1124	2.1	0.11_5	0.10_5; 0.11_5 0.11_0; 0.11_5 0.11_5; 0.10_5 0.12_5; 0.12_0
BCS 240/2 0.4% Carbon Steel	0.2450 0.2460 0.2364 0.2423	0.2424	2.0	(0.25)	0.25; 0.25 0.25
BCS 251 Low alloy steel	0.01135 0.01095 0.01113 0.01128	0.0112	1.8	0.013	0.017;0.012;0.013 0.015;0.016;0.010 0.014;0.010;0.013 0.010;0.016;0.015
BCS 258/1 Low alloy steel	0.9633 0.9500 0.9867 0.9733	0.9683	1.6	0.96	0.96; 0.95 0.97; 0.97 0.96; 0.97 0.97;0.96;0.95
BCS 260/4 High-purity Iron	0.00308 0.00293 0.00303 0.00300 0.00310	0.00303	2.2	0.003	0.003; 0.003 0.002; 0.002 0.003; 0.004 0.002

be 7% and for steel samples containing more than 1% of silicon, the coefficient of variation is said to be 3%.[74,75]

These comparisons show that the current methods for determining low levels of silicon in steel are not as precise as the differential pulse polarographic method. The colorimetric determination of silicon in high purity irons which contain 0.002 and 0.003% of silicon respectively, appears to have been done at the very limit of the sensitivity of this technique. As can be seen in Fig. 17, easily measured and well-defined polarographic waves were obtained with solutions of high purity iron. The precision data are as shown on Table 3. It is possible to obtain still more easily measured analytical signals if the procedure for the determination of low levels of silicon which is described in the next section is applied to the analysis of high purity irons.

Perhaps a disadvantage of the differential pulse polarographic procedure described here is the increase in analysis time caused by the need to electrolyse the sample solution in order to remove interfering elements. The basis of any polarographic technique involving a dropping mercury electrode is the reduction of some species in solution, thus it is only rational to remove other reducible species in the sample solution if these would interfere with the determination of the required element. In dilute sulphuric acid solution, mercury cathode electrolysis is a very effective means of removing large amounts of arsenic, chromium, copper, iron, molybdenum, antimony and many more metals in steel. The alternative methods of removing interferences such as the use of masking agents and solvent extraction would not be suitable. Masking agents are not highly selective and for a matrix such as that of steel, the use of masking agents would only complicate the method. Solvent extraction methods would involve extracting either molybdosilicate from the interfering elements or vice versa. Separation of molybdosilicate from other matrix-elements would not be difficult and a procedure based on this technique has already been published.[144] The alternative, that is the extraction of the other matrix-elements, may be very difficult because it would mean finding suitable solvents and extractable complexes for iron, copper, chromium, arsenic and some other elements found in steel.

The use of potassium permanganate as oxidising agent ensures complete oxidation of the steel samples. Nitric acid was not used for oxidising the samples because nitrate ion was considered a potential source of interference with subsequent polarographic determinations.

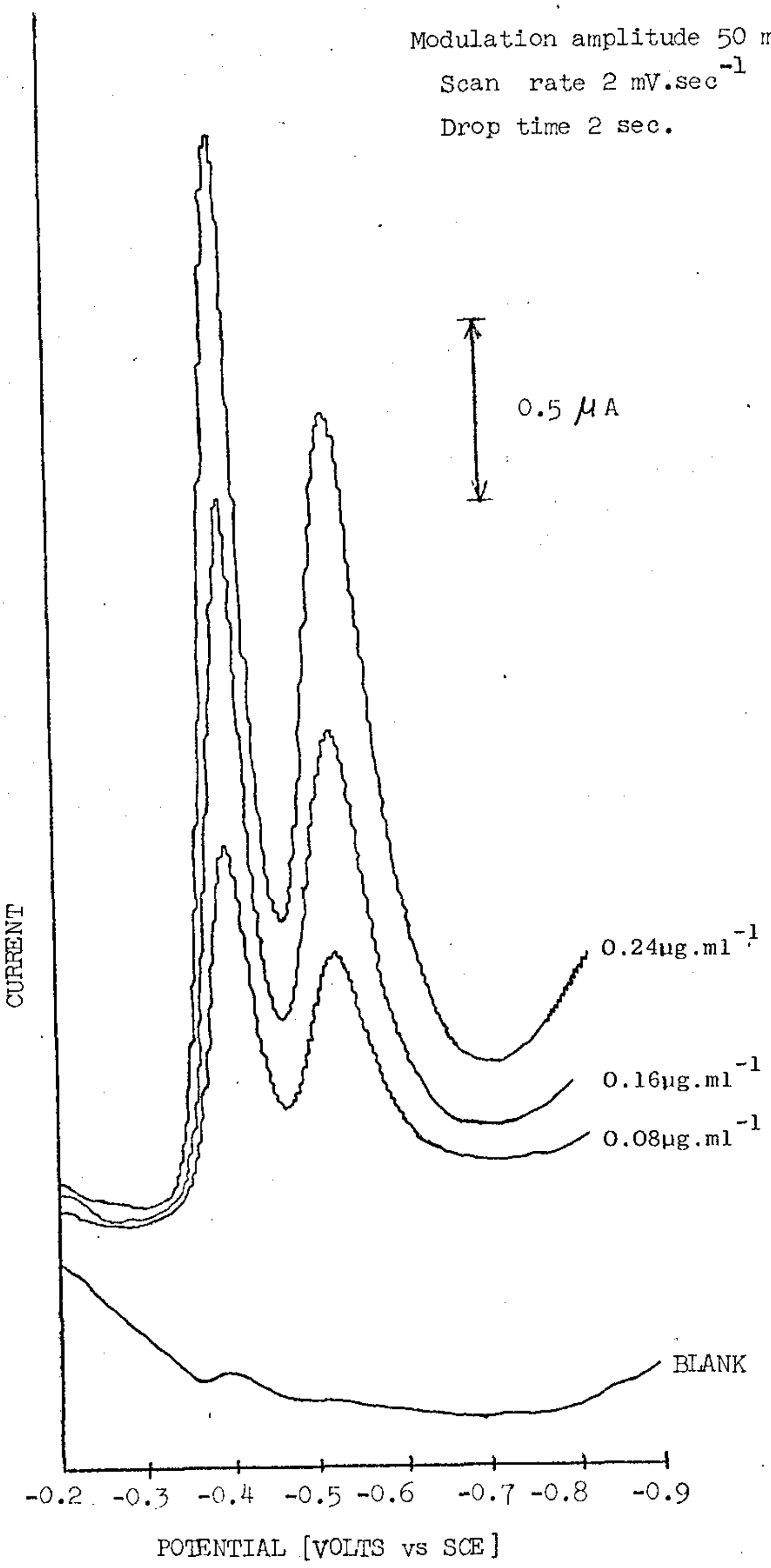


Fig.15 Differential pulse polarograms of β-12-molybdosilicate in citrate buffer at pH 2.5 after the removal of Iron (III) from the solutions by mercury cathode electrolysis. Concentrations of silicon are as shown on the polarograms.

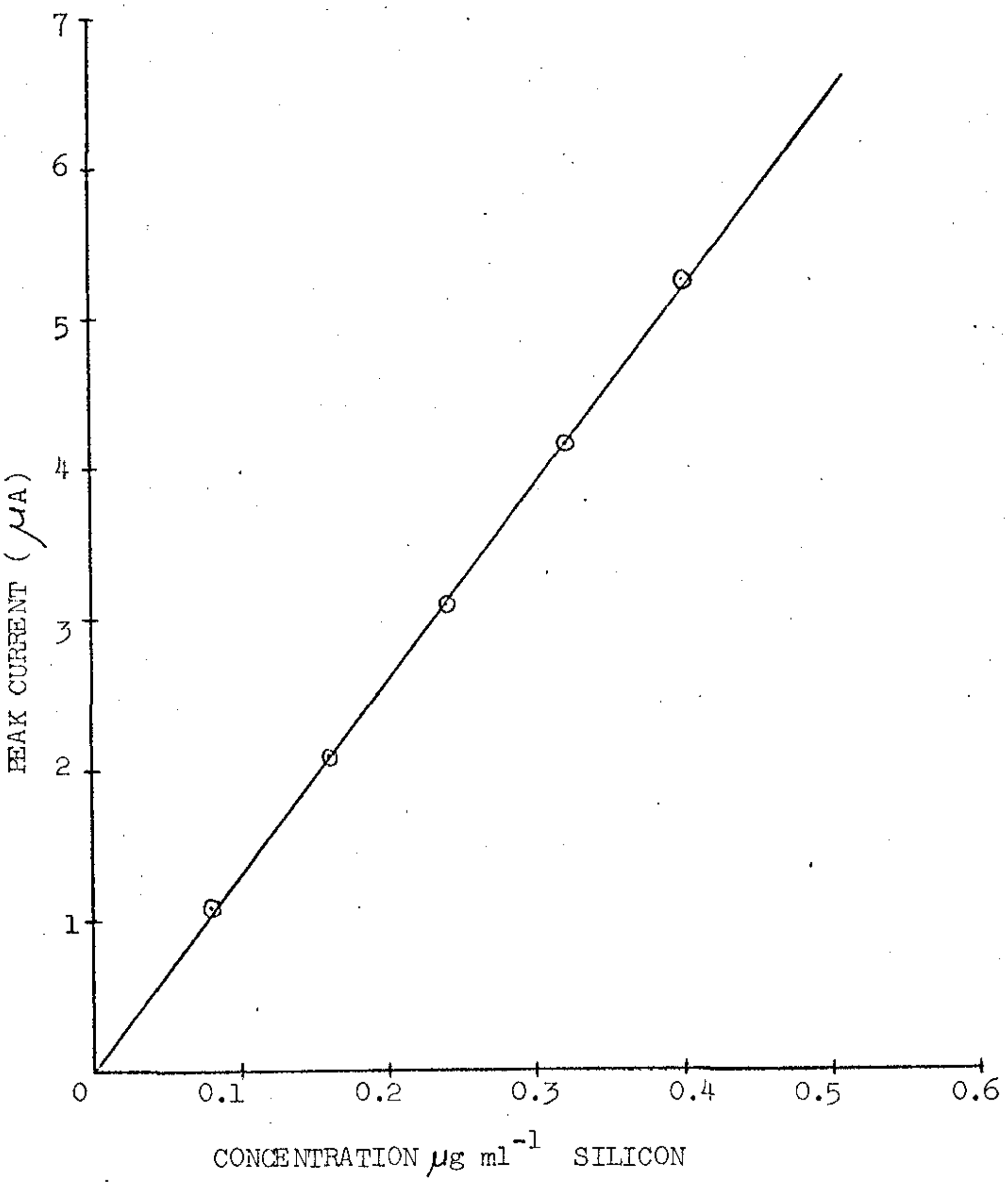


Fig.16. A typical calibration curve obtained after the removal of iron (III) by mercury cathode electrolysis. Peak current measured at -0.39V vs SCE.

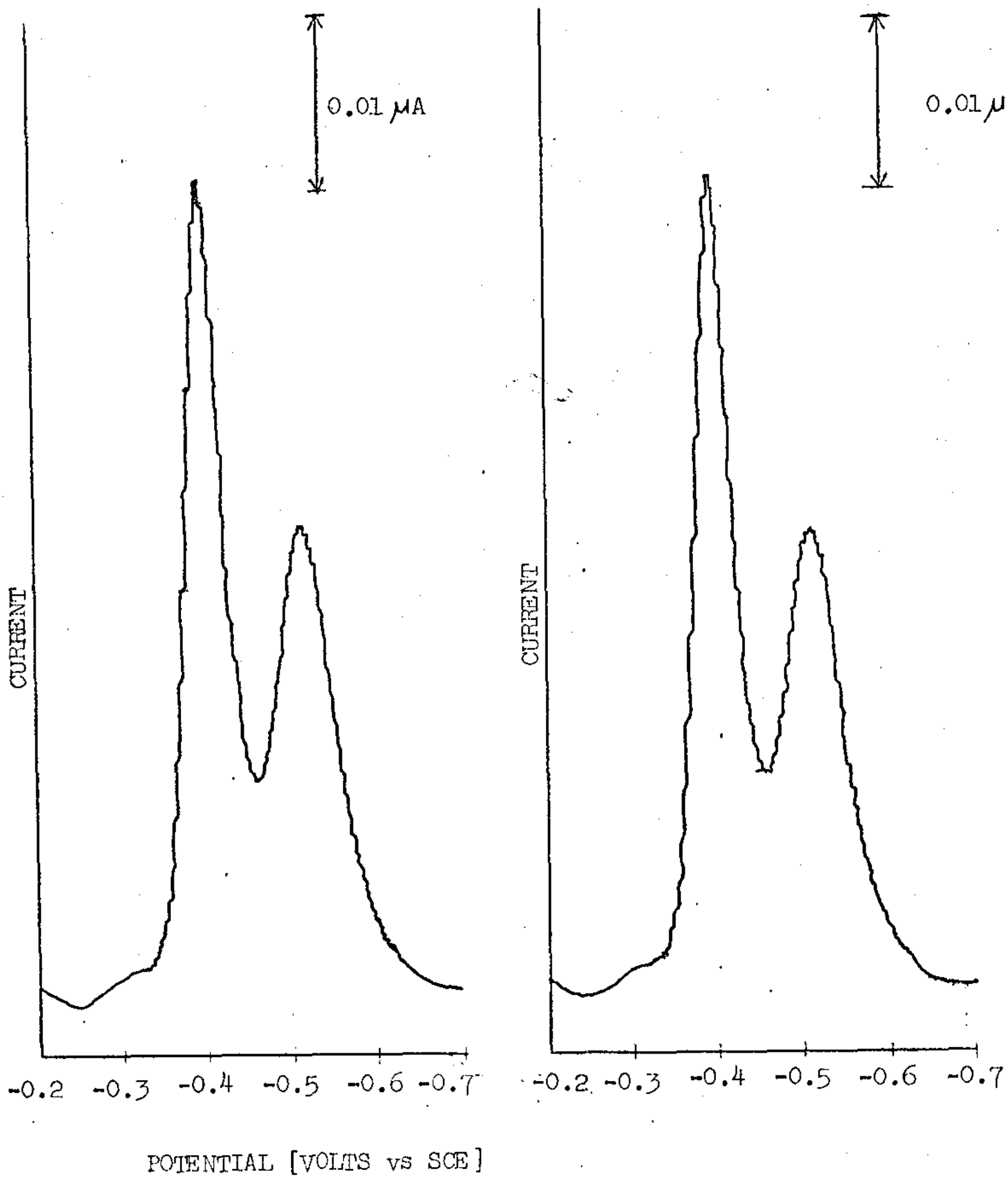


Fig.17 Typical differential pulse polarograms obtained for the determination of silicon in BCS 149/3 (High-purity iron). Modulation amplitude 50 mV, scan rate 2 mV.sec^{-1}. Drop time 2 sec.

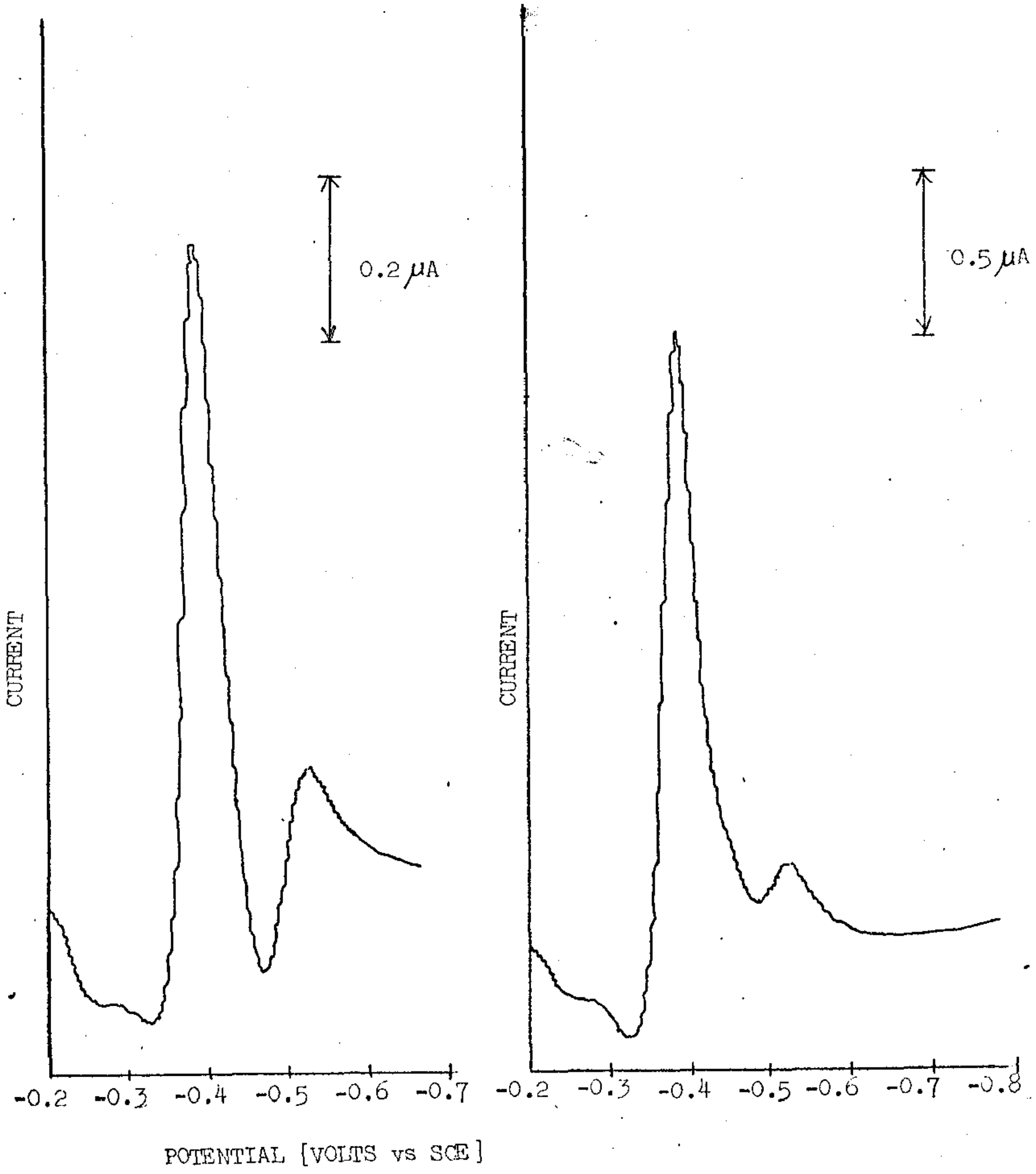


Fig.18 Typical differential pulse polarograms obtained for the determination of silicon in BCS 204/4 (High-carbon ferro-chromium steel). Modulation amplitude 50 mv, scan rate 2 $mV.sec^{-1}$, Drop time 2 sec.

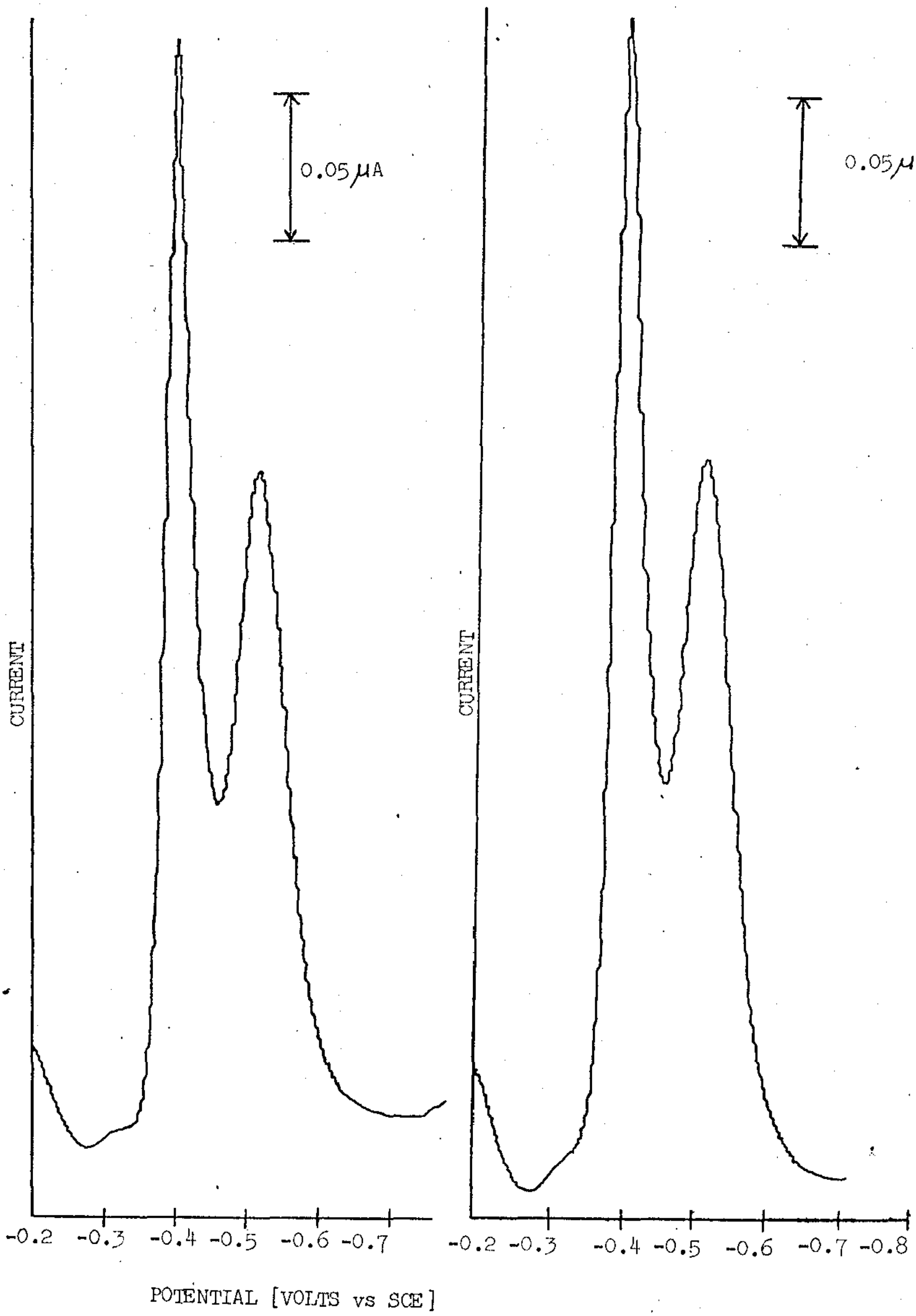


Fig.19 Typical differential pulse polarograms obtained for the determination of silicon in BCS 232/1 (0.1% sulphur carbon steel). Modulation amplitude 50 mV, scan rate 2 mV.sec^{-1} Drop time 2 sec.

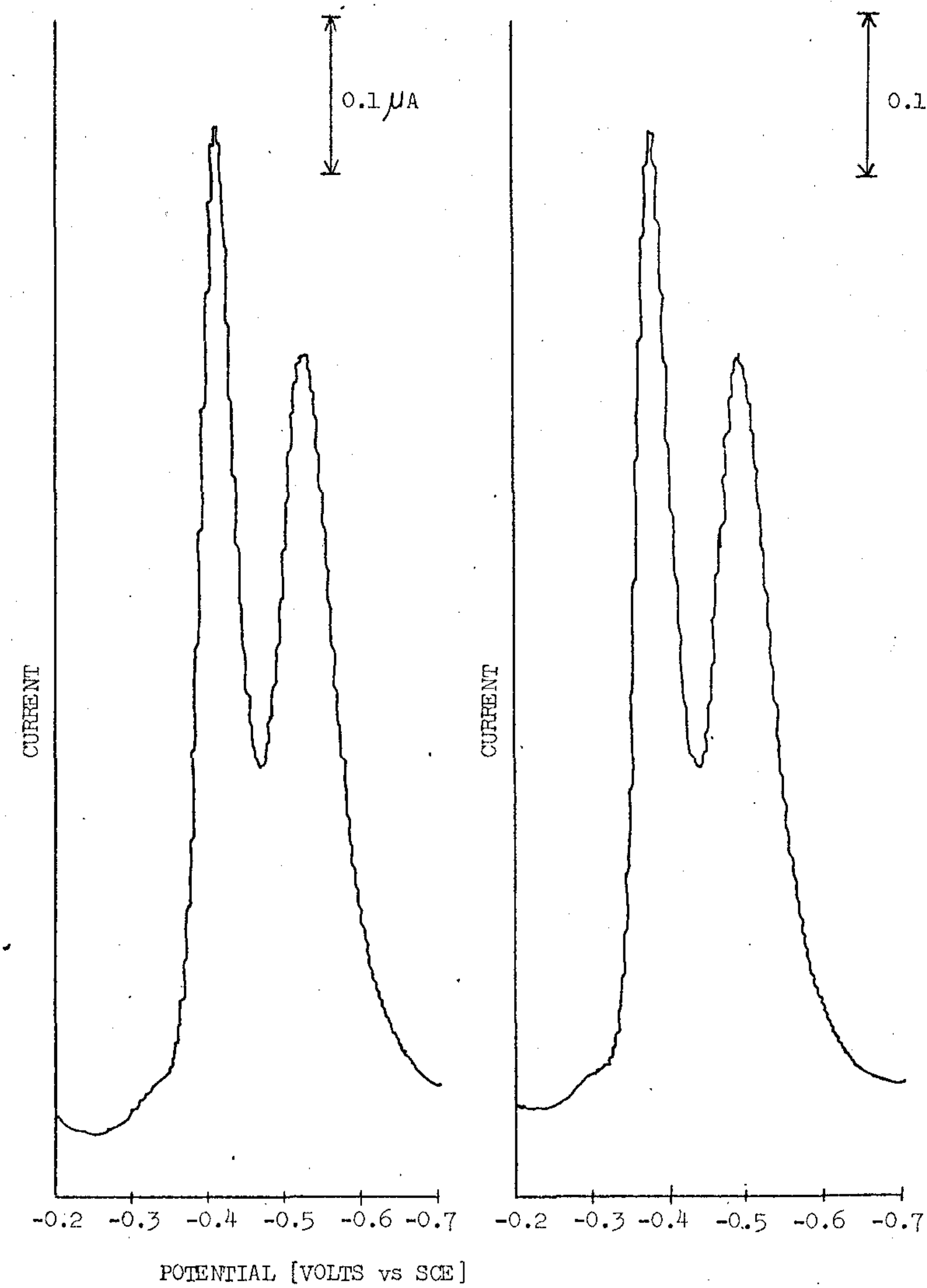


Fig.20 Typical differential pulse polarograms obtained for the determination of silicon in BCS 237/1 (0.1% carbon steel). Modulation amplitude 50 mV, scan rate 2 mV. sec^{-1}. Drop time 2 sec.

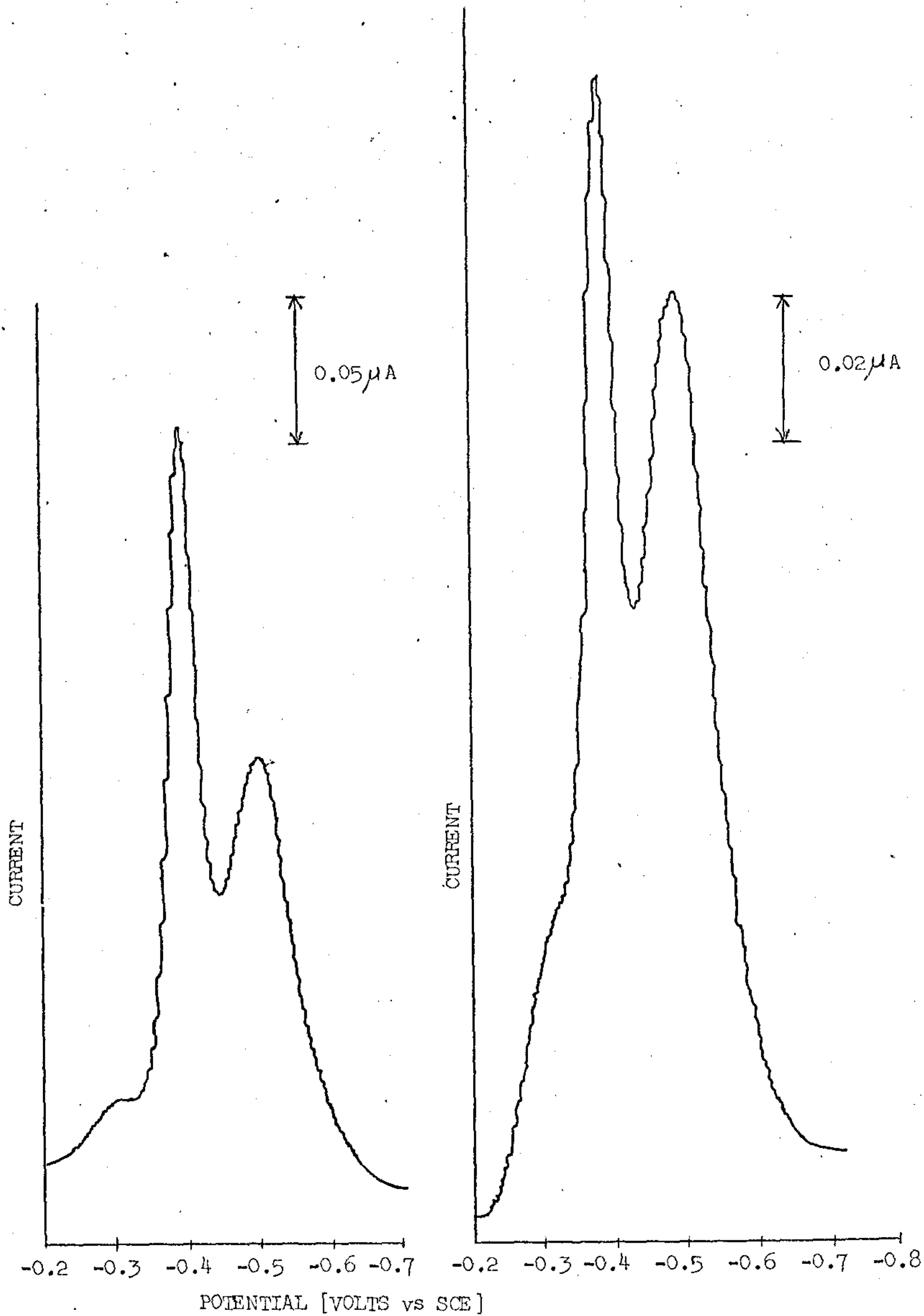


Fig.21 Typical differential pulse polarograms obtained for the determination of silicon in BCS 251 (low alloy steel). Modulation amplitude 50 mV, scan rate 2 mV. sec^{-1}, Drop time 2 sec.

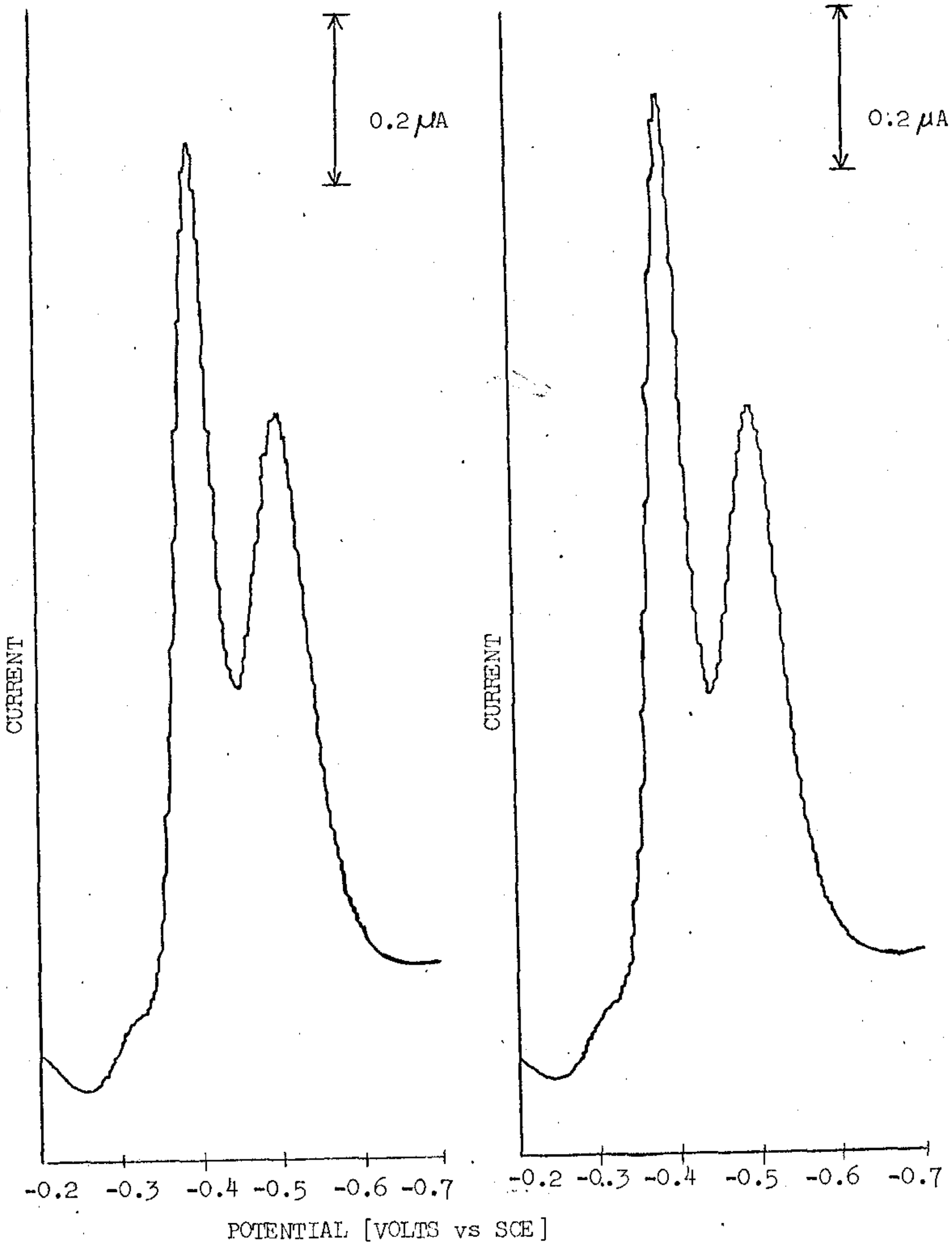


Fig.22 Typical differential pulse polarograms obtained for the determination of silicon in BCS 258/1 (low alloy steel). Modulation amplitude 50 mV, scan rate 2 mV. sec^{-1}, Drop time 2 sec.

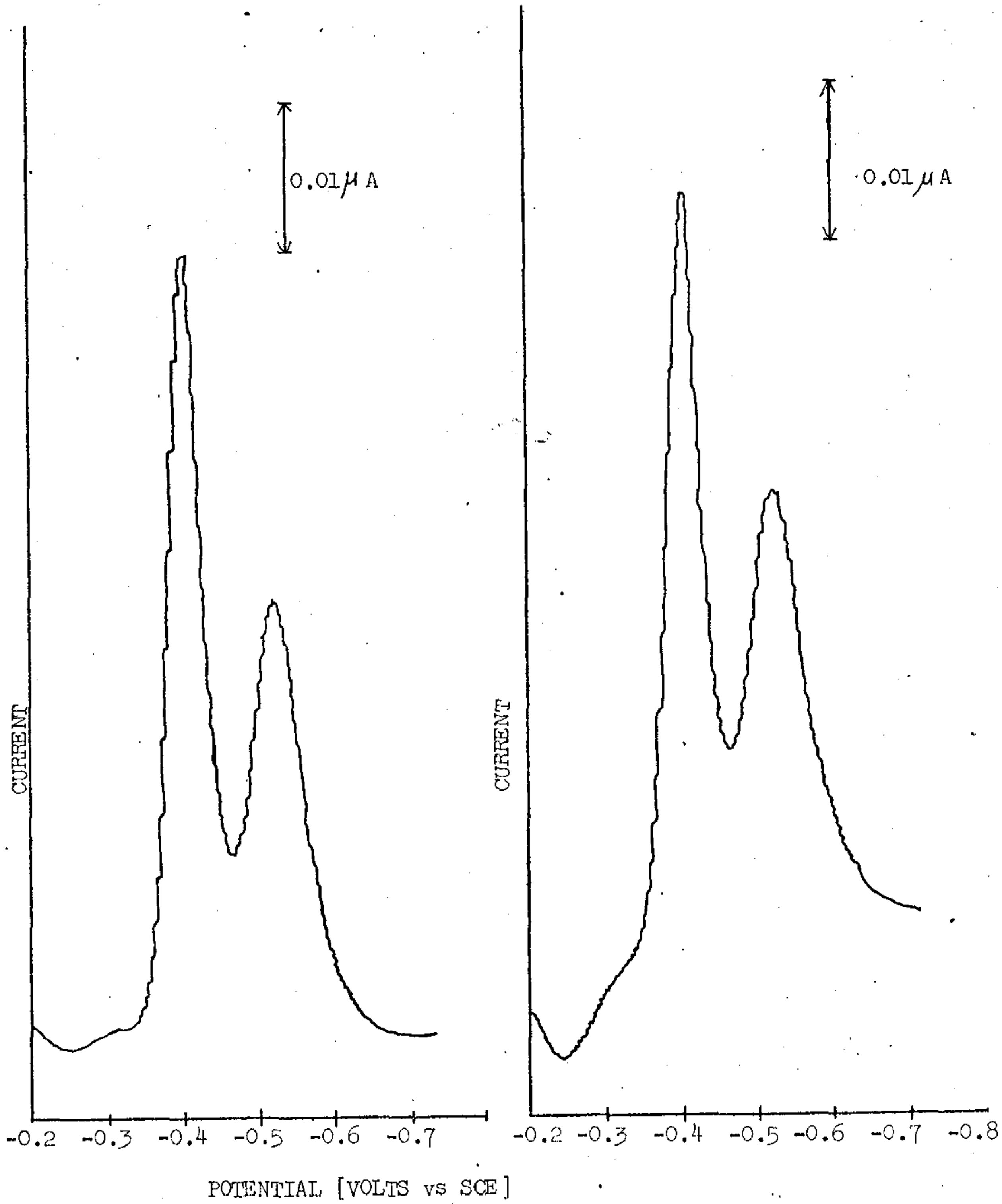


Fig.23 Typical differential pulse polarograms obtained for the determination of silicon in BCS 260/4 (High-purity iron). Modulation amplitude 50 mV, scan rate 2 mV. sec^{-1}
Drop time 2 sec.

VI. DEVELOPMENT OF A PROCEDURE FOR DETERMINING NANOGRAM AMOUNTS OF SILICON IN AQUEOUS SOLUTION.

(a) INTRODUCTION.

Attempts to determine nanogram amounts of silicon by the procedure described in Chapter IV failed because of the high blanks obtained. The procedure was therefore modified in order to determine low levels of silicon. The β-12-molybdosilicate was formed in the presence of methyl ethyl ketone and excess of molybdate was masked with citrate, but a low concentration of molybdate (approximately 5×10^{-5}M) was used in order to ensure that low blanks were obtained. The experimental conditions were optimised with respect to the various factors which affected them; factors, such as the concentrations of molybdate and of the citrate buffer used. At these low levels of silicate and molybdate, it was found that the formation of β-12-molybdosilicate was complete only after 18 hours. The quantity of the maximum suppressor used was also found to affect the shape of the polarograms. After solution conditions had been optimised, it became possible to develop the following procedure in which the solution to be polarographed was prepared directly in one vessel, thus giving maximum sensitivity.

(b) EXPERIMENTAL

APPARATUS

In addition to the apparatus described in Chapter IV, sample tubes of capacity 20 ml fitted with plastic caps were found to be very suitable for the preparation and storage of solutions for the required time period. A combined calomel-glass electrode was used in making pH adjustments. The solution was stirred with a magnetic stirrer.

REAGENTS

Concentrated standard silicate solution, 100 μg of Si per ml.

Fuse 0.1000 g. of silicon powder (99.99%, Koch-light Laboratories Ltd.) with 2 g of analytical reagent grade anhydrous sodium carbonate contained in a platinum crucible. Dissolve the melt in water, dilute the resulting solution to 1 litre with water and store in a polyethylene bottle.

Dilute standard silicate solution, 9 ng of Si per ml.

Dilute 30 ml of the concentrated standard silicate solution to 1 litre with water and mix. Dilute 3 ml of this solution to 1 litre with water and mix thoroughly. This solution was prepared fresh daily from the concentrated standard silicate solution.

Ammonium molybdate solution, 0.1%.

Dissolve 0.1 g of analytical reagent grade ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in 100 ml of 0.1M hydrochloric acid solution and store in a polyethylene bottle.

Citrate buffer.

Dissolve 42 g of analytical reagent grade citric acid monohydrate in 200 ml of 1M sodium hydroxide solution and dilute to 1 litre with water. Transfer the solution to a polyethylene beaker and adjust the pH to 2.5 with 1M hydrochloric acid solution. Store the buffer solution in a polyethylene bottle.

Triton X-100 solution, 0.2%.

Dilute 0.2 ml of Triton X-100 to 100 ml. with water.

PROCEDURE.

Pipette an aliquot of the dilute standard silicate solution or sample solution at pH 1.9, containing less than 40 ng of silicon into a 20 ml sample tube. Add 1 ml of 0.1% ammonium molybdate solution and dilute to 5 ml with water. Insert a combined calomel-glass electrode into the solution, stir the solution with a magnetic stirrer and adjust the pH to 1.6 with 1M hydrochloric acid solution. Add 0.6 ml of methyl ethyl ketone, mix the solution and allow it to stand for 18 hours. Add 10 ml of citrate buffer and 0.3 ml of 0.2% Triton X-100 solution. Mix the solution thoroughly and transfer it to a polarographic cell. Deoxygenate the solution for 15 minutes (Note 1), and then record the polarogram between -0.2 and -0.7 Volts.

Compare the polarogram obtained with that obtained with a blank determination containing no silicate under the same polarographic conditions and without altering the position of zero current on the recorder.

NOTES.

1. It is essential to include in the nitrogen train immediately before the polarographic cell, a solution with the composition of the blank to ensure that the percentage of methyl ethyl ketone in the sample solution remains the same during analysis. This solution should be renewed frequently and should be deoxygenated for 10 minutes before attaching the polarographic cell for deoxygenation. Variation in the percentage of methyl ethyl ketone in the sample solution was found to give irreproducible results.

(c) INTERFERENCES

The effects of a one-hundredfold and a one-thousandfold ratio of phosphate and arsenate on the determination of silicon were studied. The procedure described above was utilised.

REAGENTS

Phosphate 22.5 μg of P per ml.

Dissolve 0.0220 g of analytical reagent grade potassium dihydrogen phosphate [KH_2PO_4] in 100 ml of water. Dilute 45 ml of this solution to 100 ml with water.

Phosphate solution 2.25 μg of P per ml.

Dilute 10 ml of the 22.5 μg P per ml solution to 100 ml with water.

Arsenate solution 22.5 μg of As per ml.

Dissolve 0.0129 g of analytical reagent grade di-sodium hydrogen arsenate [Na_2HAsO_4] in 100 ml of water. Dilute 75 ml of this solution to 100 ml with water.

Arsenate solution 2.25 μg of As per ml.

Dilute 10 ml of the 22.5 μg As per ml solution to 100 ml with water.

(d) RESULTS AND DISCUSSION

Typical polarograms obtained for the preparation of a calibration graph are shown in Fig. 24. Both waves shown in each polarogram are reproducible, the coefficient of variation on ten determinations made at the 5×10^{-8}M silicon level (1.5 ng ml^{-1}) was 3%. Similar to the observations made at high levels of silicon, calibration graphs based on the first wave are rectilinear but not those based on the second wave.

The polarograms shown in Figs. 25 and 26 indicate clearly that no interference is observed from one-hundredfold ratio of phosphate or arsenate. At the one-thousandfold ratio, distinct interference from both ions is observed as shown in Figs. 27 and 28.

The procedure described above for the determination of nanogram amounts of silicon provides a highly sensitive technique for the determination of silicon using low-cost instrumentation. Even at the 1×10^{-8}M level (0.3 ng ml^{-1}) of silicate, an easily measured analytical signal is obtained, as is shown in Fig. 24. This can be compared with the related molybdenum blue procedure for the determination of silicon for which an absorbance of about 0.1 is obtained for a 4×10^{-6}M solution of silicate. The sensitivity for the atomic absorptiomatric determination of silicon using the acetylene-nitrous oxide flame is 0.8 μg $ml.^{-1}$

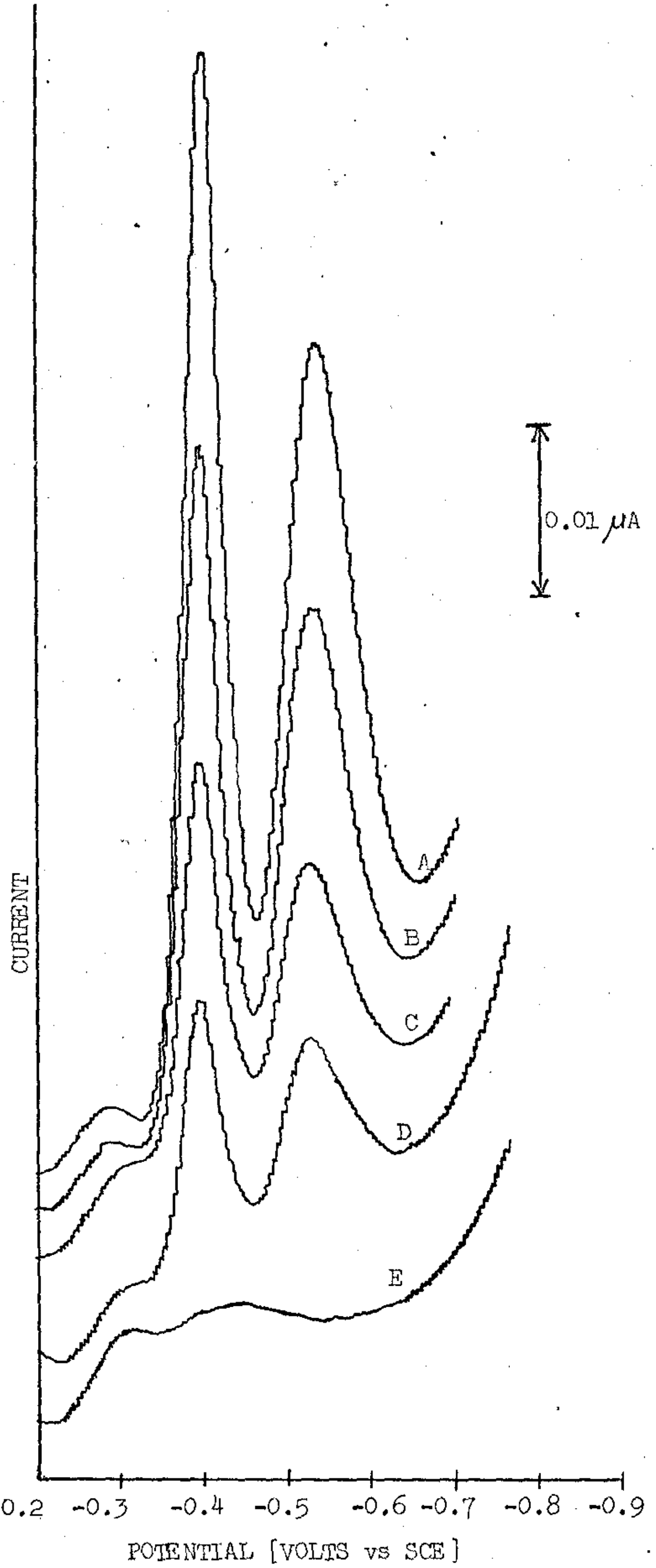


Fig.24a Differential pulse polarograms of β-12-molybdosilicate in citrate buffer at pH 2.5.

Concentration of silicon (A) 5 x 10^{-8} M (B) 3 x 10^{-8}M (C) 2 x 10^{-8}M (D) 1 x 10^{-8}M (E) zero.

Modulation amplitude 50 mV; scan rate 2 mV, sec^{-1}, Drop time 2 sec.

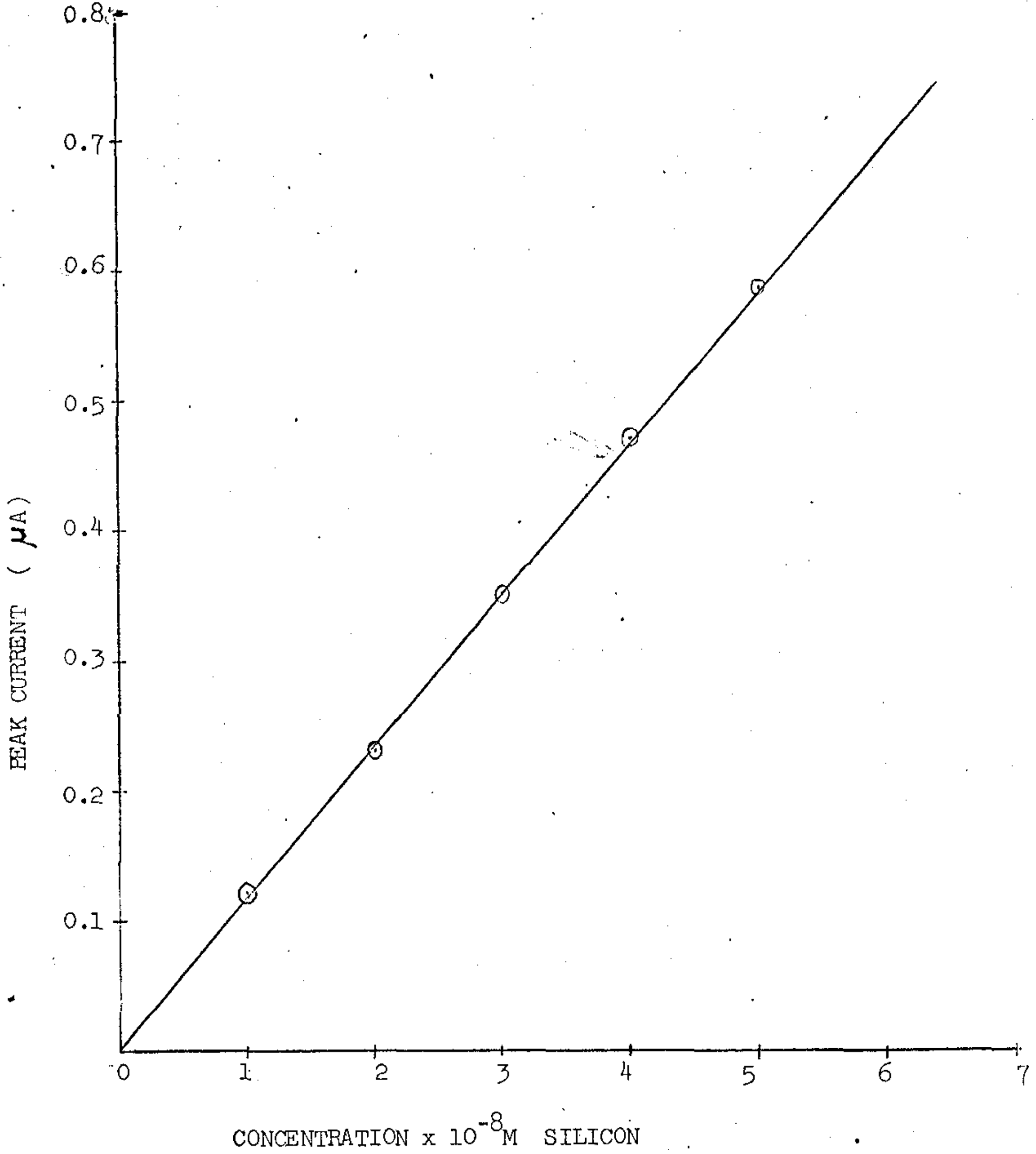


Fig. 24b. Calibration curve of β-12-molybdosilicate at 10^{-8}M level of silicon. Peak current measured at -0.37V vs SCE

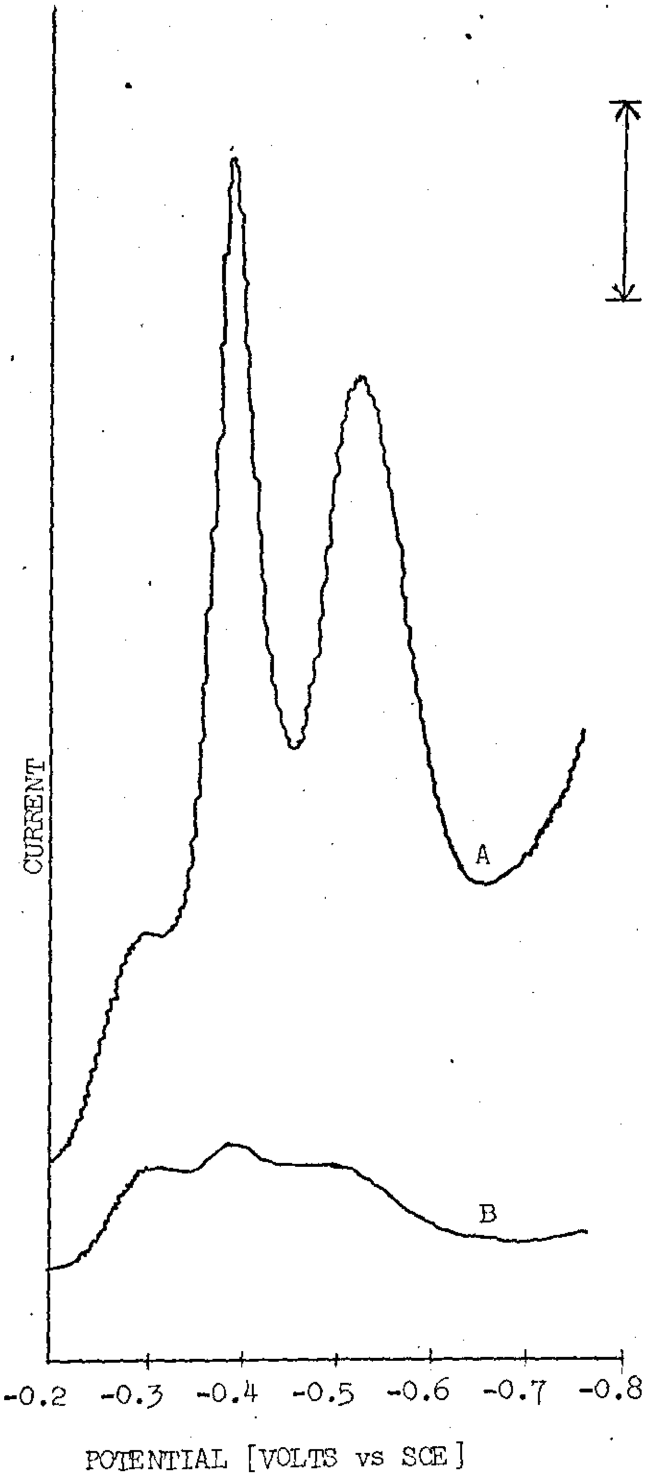


Fig. 25 Effect of phosphate.
Concentration of silicon (A) 5.0×10^{-8}M (B) zero
Concentration of phosphate 4.9×10^{-6}M

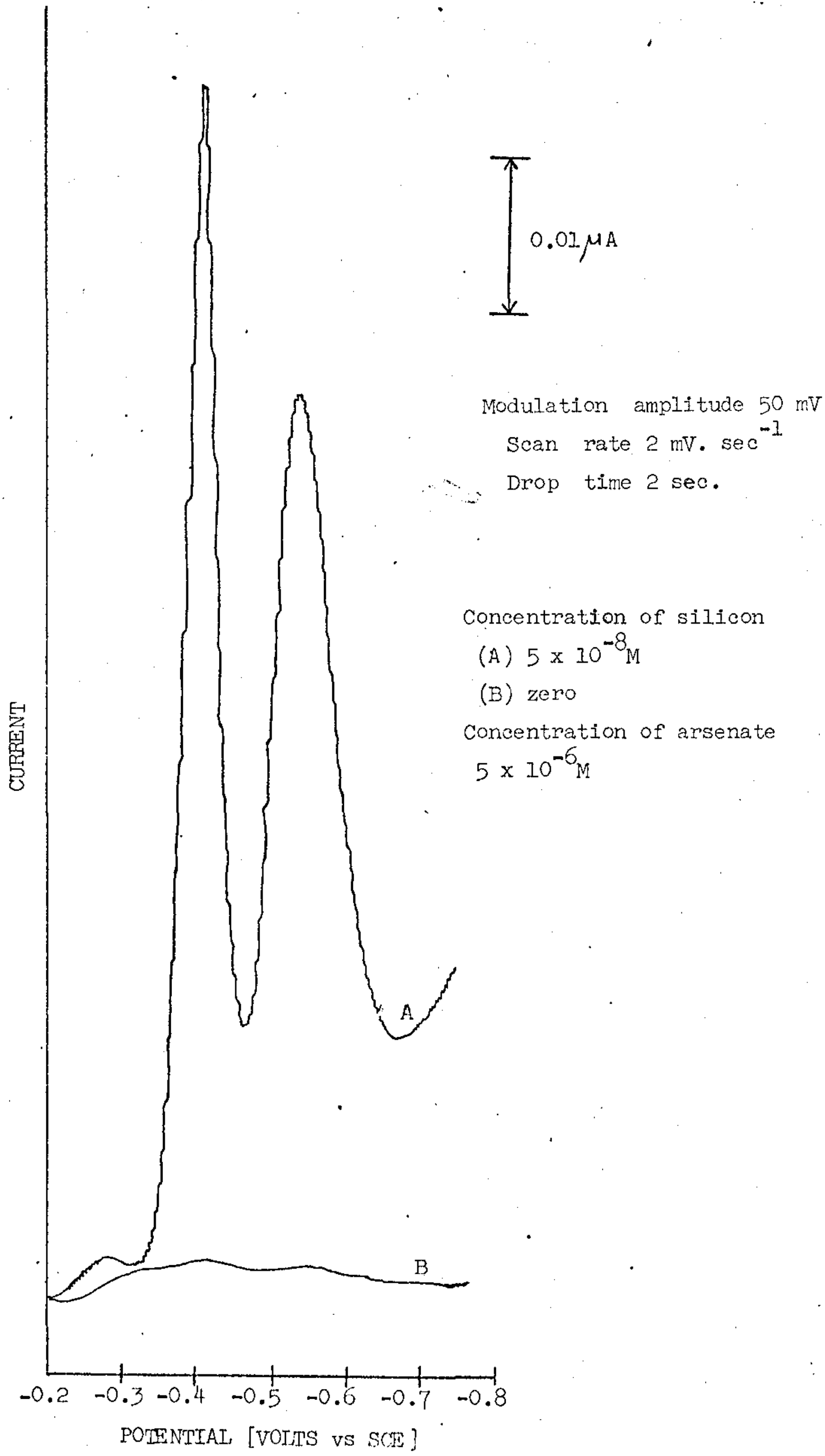


Fig.26 Effect of arsenate

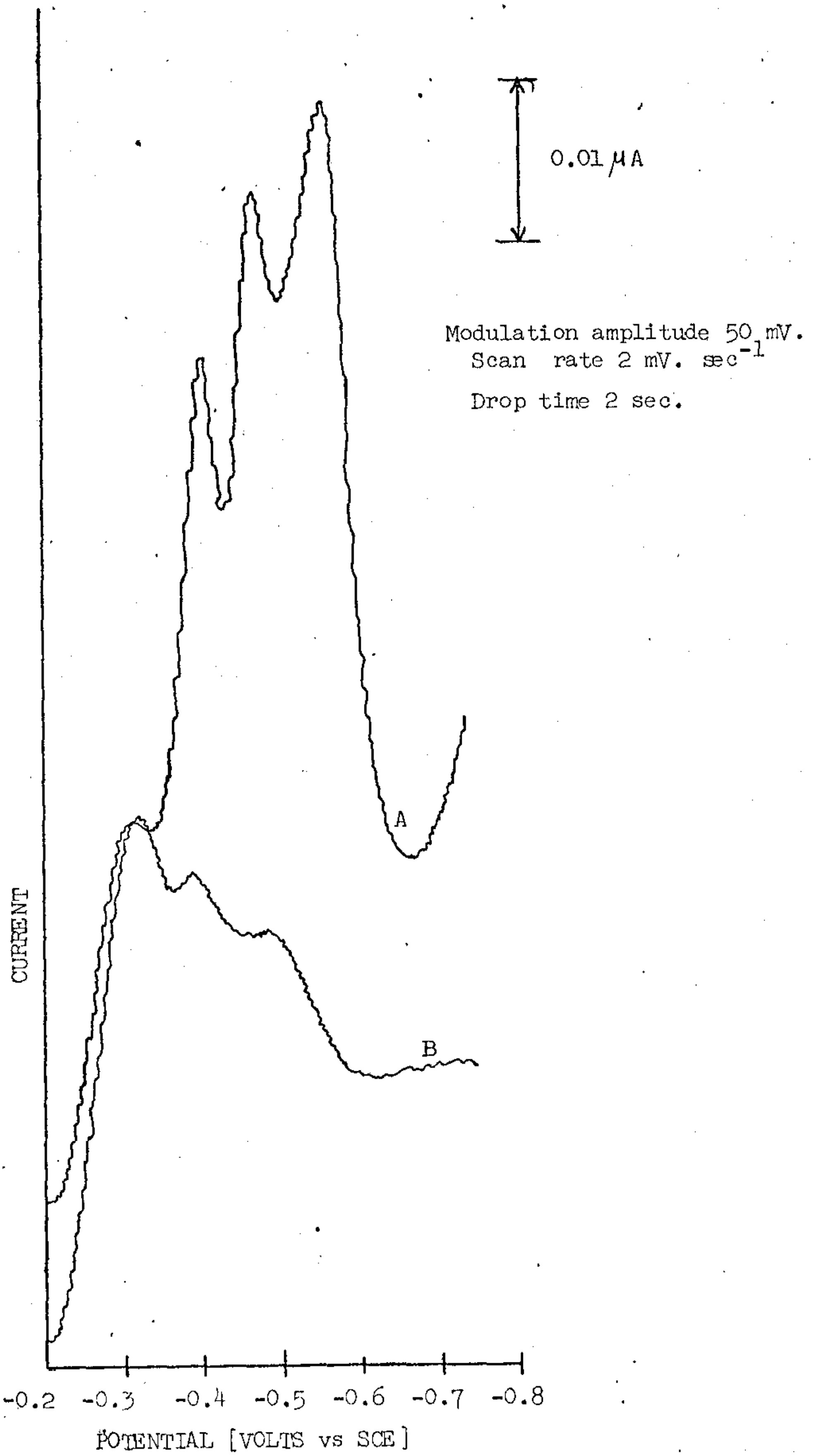
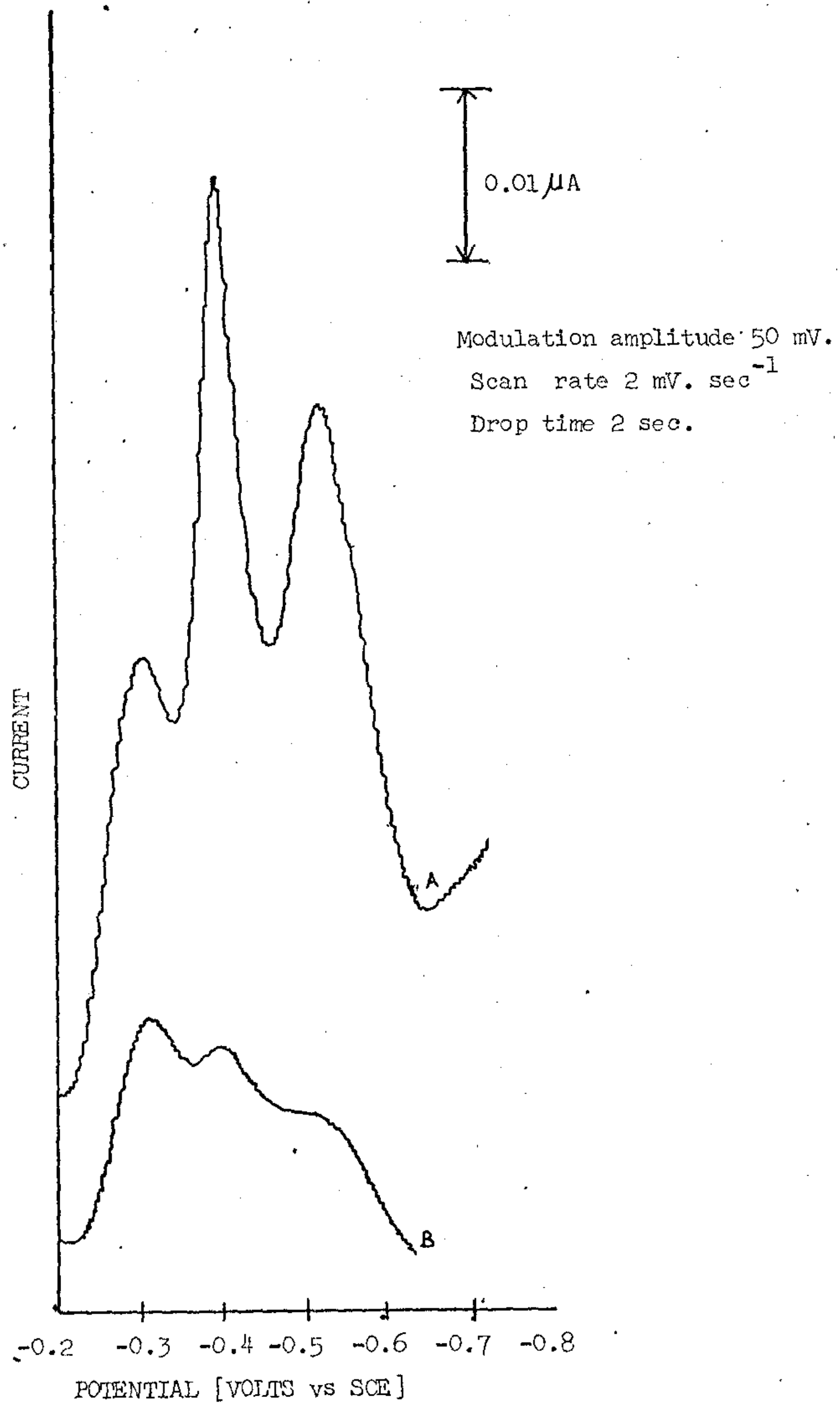


Fig.27 Effect of phosphate on β-12-molybdosilicate and on Blank.

Concentration of silicon (A) 5×10^{-8}M (B) zero

Concentration of phosphate (A) 4.9×10^{-5}M (B) 4.9×10^{-5}M



Modulation amplitude 50 mV.
Scan rate 2 mV. sec^{-1}
Drop time 2 sec.

Fig. 28 Effect of arsenate on β-12-molybdosilicate and on Blank.

Concentration of silicon (A) 5×10^{-8}M (B) zero

Concentration of arsenate (A) 5×10^{-5}M (B) 5×10^{-5}M

VII. CONCLUSION

The two procedures recommended in this study for the differential pulse polarographic determination of silicon can be used to supplement the current methods for determining silicon in steel. If very low levels of silicon are to be determined, the results of the present study show that the differential pulse polarographic method is better than the current methods. The procedures recommended here are simple and can easily be adapted for routine laboratory use. The procedures represent a considerable improvement in the sensitivity, accuracy and precision for the determination of silicon using low-cost instrumentation. The PAR 174 Polarographic Analyzer is relatively cheap, easy to use and extremely versatile. Several polarographic and voltammetric techniques can be used with the instrument. General application of the procedures recommended in this study is feasible, for the determination of silicon in boiler water and ferrous and non-ferrous metals.

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THE DETERMINATION OF IRON IN IRON ORES BY CONTROLLED-POTENTIAL COULOMETRY AT A MERCURY POOL ELECTRODE

I. INTRODUCTION

The term coulometry was first used by Szebelledy and Somogyi[1] who applied the method as an alternative to classical volumetric analysis. Their pioneering work along with subsequent researches by other workers led to the development and establishment of the technique. In coulometric analysis, the species being determined is electrolysed and the quantity calculated from the quantity of electricity consumed by using a form of Faraday's law:

$$\text{Weight of substance electrolyzed} = \frac{M}{nF}\int_{0}^{t} i\,dt \qquad \ldots\ldots\ldots\ldots \quad 1$$

where M is the gram-molecular weight of the species, n is the number of electrons involved in the reaction, F is the Faraday. (The present value of the Faraday[2] is 96,484.6 coulombs per mole based on the assigned, relative atomic mass of ^{12}C as 12), i is the electrolysis current and t is the time of electrolysis. In order to measure the quantity of electricity consumed, the electrolysis current is integrated over the time of electrolysis. Classical chemical coulometers, electromechanical integrators (disk-and-ball or motor type) and electronic integrators, all have been used for measuring the quantity of electricity consumed during electrolysis.

Two types of coulometric analysis may be distinguished dependent on whether the substance being determined is oxidised/reduced directly at the working electrode or indirectly by products of electrode reaction; good precision being achieved if the desired reactions proceed with 100% current efficiency. In coulometry it is theoretically possible to vary both the current and voltage but in practice, the current is kept constant and the applied potential varied or vice versa.

Constant current (galvanostatic) coulometry which was first suggested by Szebelledy and Somogyi[1] and put on a practical basis by Swift et al.,[3] appears to be more versatile and convenient in use. With the exception of a few cases, the reagents used in galvanostatic coulometry are normally generated coulometrically and then used to oxidise/reduce the substance being determined. Many substances can be generated as coulometric intermediates at suitable working electrodes. However, the total reaction does not always proceed through the electrogenerated intermediate. In some cases, the total reaction may proceed partly through the intermediate and partly at the working electrode. Coulometric titration (galvanostatic coulometry) is similar in many ways to classical volumetric analysis and the end point of any coulometric titration can be detected by any of the methods used in classical volumetric analysis. Colorimetry, potentiometry, bipotentiometry, amperometry, biamperometry and conductometry etc. have all been used to detect endpoints in coulometric titrations.

Controlled-potential (potentiostatic) coulometry was originally devised by Hickling.[4] In this technique, the potential of the working electrode is kept constant with respect to a standard reference electrode and the element to be determined is allowed to undergo a stoichiometrically exact reaction so that its quantity can be calculated by Faraday's laws. As the reaction proceeds, the current decreases exponentially from a relatively large value to a finite value, known as the residual current. The potential of the working electrode is kept constant or controlled so that only the species of interest undergoes an electrochemical reaction. Thus one disadvantage of the technique is that optimal conditions have to be selected carefully for each substance that has to be determined.

The main advantage of controlled-potential coulometry over all other electroanalytical methods is its specificity and accuracy combined with great sensitivity.

Since the pioneering work of Szebelledy and Somogyi,[1] there have been many publications on coulometry. Recent treatment of the subject include books by Abresch and Claasen,[5] Milner and Phillips,[6] Rechnitz[7] and chapters in books by Bard,[8,9] Meites[10] and Shults.[11,12]. Several reviews[13-38] have also appeared on the subject. Current advances in coulometry can be followed through entries in the corresponding sections of Electroanalytical Abstracts[39] and through the biennial review issues of Analytical Chemistry.[40-47]

APPLICATIONS

The number of publications dealing with the application of coulometry is so vast that only its application in the steel industry will be discussed herein. Coulometry was developed for use in the steel industry in the 1950's mainly by Milner. He applied coulometry in the analysis of metals in copper-based alloys,[48] binary alloys[49] and minerals[50] and also gave details of the construction of suitable apparatus for controlled-potential coulometry.

Most of the applications of coulometric analysis in the steel industry which have been reported, are for the determination of gases and non-metals. Abresch and Lemm[51] reported the coulometric determination of oxygen in steel by a fusion extraction process in a stream of argon.

Tsugane et al.[52] studied the determination of oxygen in special steels and nickel-based super alloys by argon carrier-coulometry with the addition of a small amount of tin metal as flux. Geigerl[53] determined hydrogen also by a carrier gas method. He degassed the sample at 650°C in argon and oxidised the hydrogen evolved over copper oxide. He then determined the hydrogen after a process of reduction and separation. Sulphur[54-57] was determined as sulphur dioxide by coulometric titration with iodine solution produced by the electrolysis of acidified potassium iodide solution. Boron[58] was determined by pyrohydrolysis and constant current coulometry. Carbon[59-66] has received exhaustive study and has mainly been determined by constant current coulometry.

There have been few reported examples of the application of coulometry for the determination of metals in steel. Kostromin et al.[67] studied the use of generated titanium(III) and tin(II) ions as coulometric titrants for the determination of trace amounts of vanadium in steel, iron in zinc metal, iron and copper in cadmium, and iron(III), copper(II), VO_2^+ and VO^{2+} in model solutions. This study was extended to the determination of metal ions in alloys such as Dural 287 and Magnico.[68] They also reported the differential coulometric titration of a mixture of iron(II), manganese(II), vanadium(IV) and cerium(III) ions with electrogenerated dichromate in phosphoric acid as a means of determining vanadium and manganese in steel.[69] Basov et al.[70] determined vanadium and chromium using electrogenerated tin(II) as titrant. Mitev and Mlädenovich[71] proposed a coulometric titration method for the simultaneous determination of dichromate and iron(III) which they said was applicable to the analysis of iron- and chromium-containing alloys and ores and also steel. They also studied the determination of both dichromate and cerium(IV) in steel and other alloys using electrogenerated iron(II) as titrant and ferroin as indicator.[72] Agasyan[73] titrated molybdenum(VI) in alloy steel with electro-generated tin(II) with the endpoint being measured biamperometrically. Sicha[74] appears to be the only one, so far, to report the use of automated coulometry in metallurgical analytical procedures. He described the principle and various arrangements for coulometric determination of various metals with electrogenerated reagents.

Ibrahim and Nair[75] developed a method for the determination of chromium and molybdenum in steel by controlled-potential coulometry, using a rapidly stirred mercury pool cathode and a silver chloride anode. Lüdering Hans[76] reported the determination of small amounts of iron and chromium in chromium steel using controlled-potential coulometry. Tanaka[77] reported a method for the determination of copper, nickel and zinc in high-purity copper alloys such as brass. Rigdon and Harrar[78] determined milligram amounts of vanadium at a platinum working electrode by controlled-potential coulometry. Altman[79] analysed slag for copper, total iron, iron(II) and iron(III) by titration, controlled-potential coulometry and electrodeposition. Alfonsi[80-86] made a detailed study of the determination of copper, lead, tin, antimony, nickel, zinc and aluminium in different alloys using controlled-potential coulometry.

INSTRUMENTATION

One of the main reasons for the apparent lack of application of coulometric analytical techniques in the steel industry has been the lack of suitable commercial instruments especially for routine analysis. Since the development of electronic instruments by Booman[87,88] and

Kelley et al,[89] there has been a proliferation of commercial instruments for coulometric analysis. However, most of the instruments are either of the galvanostatic or potentiostatic type. Universal coulometric instruments capable of dealing with all types of coulometric measurements have not been available commercially until quite recently. In 1971, Damokos[90] reported the introduction of the Radelkis universal coulometric analysis apparatus type OH-404 which incorporated a potentiostat-galvanostat unit. Other instruments in the same category include the Princeton Applied Research (PAR) 173/179 digital coulometer and Beckman Instruments' coulometer. A detailed summary of instruments currently commercially available has been given by Harrar.[9]

II. METHODS FOR THE DETERMINATION OF IRON IN IRON ORES AND STEEL (REVIEW)

Several methods including gravimetry, spectrophotometry, complexometry, neutron activation, x-ray spectrography and iodimetric determination by solvent extraction of iodine in a sulphuric acid medium[91] have been suggested for the determination of iron in iron ores and steel, but titrimetry which is recommended by both the British Standards Institution[92] and the American Society for Testing Materials,[93] appears to be a more reliable method of determining iron in these materials.

Titrimetric methods for the determination of iron consists of three steps: dissolution of the sample, reduction of the iron to the divalent state and titration of the iron(II) with a standard oxidant.

Many ores are completely decomposed in concentrated hydrochloric acid; the decomposition being enhanced if tin(II) chloride is present. Hydrochloric acid is a much more efficient solvent for the dissolution of iron ore than either nitric or sulphuric acid because of the tendency of iron(III) to form soluble chloride complexes. In order to recover all the iron in the ore, it is necessary to treat with hydrofluoric acid, any residue (mainly silica) left after decomposition of the ore with an acid. Treatment of the residue with hydrofluoric acid effectively separates silica from any iron in the residue by volatilisation as silicon tetrafluoride.

Tin(II) chloride has been used for the reduction of iron to the divalent state but it is always necessary to oxidise excess of the tin(II) chloride used with mercury(II) chloride. Mercury(II) chloride is toxic, hence the reduction of iron with tin(II) chloride is not suitable for routine use. In order to avoid using mercury, Hata et al.[94] have suggested using aluminium as reductant. Saeki et al[95] proposed a method that involved reduction of iron(III) to iron(II) partly by titanium(III) chloride and partly by tin(II) chloride. Endo et al[96] suggested reduction of the iron(III) with a tin(II) chloride solution in excess and then titrating the unconsumed tin(II) chloride with potassium iodate, thus avoiding the use of mercury(II) chloride.

A reductant which has been widely used is hydrogen sulphide. In addition to reducing iron to the divalent state, hydrogen sulphide also removes interfering elements. It has been reported that in determinations of iron in iron ore using tin(II) chloride as reductant, vanadium, molybdenum and copper interfere if they are present in amounts greater than 0.10%, whereas in determinations using hydrogen sulphide, none of the elements normally found in iron ore including vanadium, molybdenum and copper, interferes.[93]

The most widely used oxidant for the titration of iron(II) has been potassium dichromate with sodium diphenylamine sulphonate as indicator. Potassium permanganate has been mentioned but it has not found wide application because, in their lower oxidation state some metals usually associated with iron react with permanganate and this leads to high results.

Biamperometric titrations of iron in iron ore with tin(II) chloride and with ascorbic acid using two carbon-rod electrodes have been suggested by Budilovskii et al.[97,98] They have also proposed a biamperometric titration method for the determination of total iron and iron(III) with sodium thiosulphate and potassium dichromate, using two platinum indicator-electrodes.[99]

An alternative to classical titrimetric determination of iron in iron ore is coulometry. There have been very few reports of the determination of iron in iron ore and steel by constant-current coulometry. However, a method for the simultaneous determination of dichromate and iron(III) in ores and steel using electrogenerated reagents has been suggested by Mitev and Mladenovich.[71]

In 1952, McNevin and Baker[100] pointed out the potentialities of controlled-potential coulometry in the determination of iron. They determined iron(II) by oxidising it in an acid solution at a platinum electrode. The relative accuracy of the determination was reported to be about 2%. The number of coulombs consumed in the oxidation process was measured with a hydrogen-oxygen coulometer. The determination of mixtures of iron and cerium by controlled-potential coulometry with a platinum electrode has also been reported by Davis.[101] In the procedure, iron and cerium were oxidised simultaneously at +1.5v vs SCE. The cerium was then reduced at +0.80v and the iron at +0.20v vs SCE; the error in the determination of milligram amounts of iron was reported to be less than 0.5%. Jones at al[102] built an instrument specifically for the controlled-potential coulometric determination of small amounts of materials at a mercury or platinum electrode and described a method for the determination of milli- and microgram quantities of iron and uranium using this instrument. The method involved the coulometric reduction of iron(III) at +0.295v vs SCE followed by oxidation of the iron(II) produced, at +0.655v vs SCE. The precision and accuracy of the method were reported to be excellent and the relative standard deviation for a single observation was said to be 0.1%. Since the work of McNevin and Baker[100] there have been some papers[103-106] dealing with the determination of iron generally and only a few have been on the determination of iron in ferrous metallurgical materials. However, Milner and Edward[49] have carried out an investigation on the suitability of controlled-potential coulometry for problems in metallurgical analysis.

III. A CONTROLLED-POTENTIAL COULOMETRIC METHOD FOR THE DETERMINATION OF IRON IN IRON ORES

Several factors are essential for the successful development of a procedure for controlled-potential coulometric determination of any element. Firstly, the potential which has to be applied to the working electrode to bring about the desired reaction must be known. In addition, the quantitative effect of interfering reactions on the desired reaction has to be known and ways to minimise or eliminate these interferences have to be found. Finally, there is the problem of the corrections for blanks and other background effects which have to be applied.

WORKING ELECTRODE POTENTIALS

With a stirred mercury electrode, polarographic half-wave potential data can often be used to estimate the applied potentials to give quantitative reactions in coulometry. However, nothing stops one from determining these potentials experimentally with the coulometer, as is always the case when platinum electrodes are used. The potential of a working electrode is represented by the Nernst equation as follows:

$$E = E_o + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{Red}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2$$

which becomes

$$E = E_o^1 + \frac{RT}{nF} \ln \frac{(Ox)}{(Red)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3$$

if activities are replaced by more easily calculable concentrations. E_o^1 is an empirical value which is not strictly constant but depends on the ionic strength of the solution and the junction potentials in the cell. Values of E_o^1 represent the potential of the working electrode measured against some standard reference electrode, when (Ox) = (Red).

Re-writing equation 3 using logarithms to base 10

$$E = E^{1}_{o} + 2.303 \frac{RT}{nF} \log \frac{(Ox)}{(Red)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 4$$

At T = 298°K (25°C) and substituting for values of R and F, the equation becomes:

$$E = E^{1}_{o} + \frac{0.059}{n} \log \frac{(Ox)}{(Red)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 5$$

This equation remains true in terms of the species being determined and is unaltered by the presence of a supporting electrolyte. Thus the potential, E is determined mainly by the ratio (Ox)/(Red). Equation 5 shows also that E decreases with a decrease in the value of the ratio of (Ox)/(Red). Thus, when a mercury working electrode is set at a potential $E = E^{1}_{o} - 1 \times 0.059/n$, equilibrium will be reached when 90% of the electroactive species is reduced and only 10% is oxidised. At $E = E^{1}_{o} - 2 \times 0.059/n$, the concentration of the reduced species is 99% and at $E = E^{1}_{o} - 3 \times 0.059/n$, it is 99.9% and so on.

E^{1}_{o} values can be readily obtained with a coulometer by examining experimentally determined coulograms. In principle, it involves transferring a suitable aliquot of a solution of the element being determined, to a coulometric cell and then electrolysing the element with the working electrode at such a potential that reduction (or oxidation) takes place. To begin with, the coulometer is adjusted to zero and the potential of the working electrode is altered to cause reduction (or oxidation) to take place. When equilibrium is reached at this potential E_1, the coulometer reading Q_1 is noted. The potential is then changed to E_2, E_3 and so on, and the corresponding coulometer readings Q_2, Q_3 etc. are recorded. A graph is then constructed by plotting the values for Q against the potentials of the working electrode. Fig. 29 shows a typical coulogram at a mercury electrode for iron in oxalate buffer at pH 4.5. Each value of Q should be corrected for blank and residual currents, if extreme accuracy is required. These corrections are however usually small and need only by applied if the amount of the element being determined is very low, for example, below 2mg.

The values for Q are proportional to the concentrations of the reduced (or oxidised) form of the electroactive species and Q_t (see fig. 29) to the total concentration of the reduced form, thus values for log (Red)/(Ox) at each potential can be calculated from log $Q_1/(Q_t - Q_1)$. These can be plotted to give a linear graph with a slope of 0.059/n. E^1_o is the potential at which log (Red)/(Ox) is zero.

INTERFERING ELEMENTS

Equation 4 expresses adequately the potential generated for any concentration of oxidised and reduced species in solution but a close examination of the equation shows that coulometric determinations can never be absolutely complete. However, the equation does show that any fraction of the element being determined can be oxidised or reduced by proper selection of working electrode potentials. Theoretically, it is essential for accurate determinations, especially in a complex solution, that there should be a large span between operating potentials but in practice, essentially complete reduction takes place at E^1_o - 0.2V and complete oxidation at E^1_o + 0.2V. For a single electron change, more than 99.9% of the element being determined can be reduced or oxidised under these conditions.

The problem of interference does not, however, end with proper selection of working electrode potentials because in some cases, this approach does not work. For instance, in the coulometric reduction of iron(III), it is impossible to obtain complete reduction of iron(III) to iron(II) without some reduction of copper(II) ions taking place.

The behaviour of interfering elements in the determination of a particular element can be studied by plotting a coulogram. It is possible to calculate the ratio of the concentration of the element being determined and that of the interfering element from a coulogram and hence evaluate the effect of one element on the determination of another. The contribution made by an interfering element to the coulometric determination of another element can also be calculated through the Nernst equation, provided the content of the interfering element in the sample had been previously determined from a separate independent analysis.

An approach which does not appear to have been used previously to eliminate interferences in coulometry is prior solvent extraction. In the present work, iron(III) was extracted in order to separate it from interfering elements.

BACKGROUND CORRECTIONS

It is often the case in determinations by controlled-potential coulometry that the quantity of electricity consumed in the reduction or oxidation of a particular element is different from the theoretical amount. This difference which is referred to as the background has to be corrected for in all controlled-potential coulometric determinations except when it is insignificant. The background current arises mainly from the blank (due to the oxidation or reduction of electroactive impurities) and the residual current. Two other identifiable sources of the background current are due to what may be labelled "kinetic" and "induced" currents but both arise only in the presence of the substance being determined. Kinetic currents which are usually dependent on potential, result from the cyclic oxidation/reduction of the supporting electrolyte or solvent by some product(s) of the main electrolysis process. Induced currents result from some extraneous oxidation/reduction process at the electrodes in the presence of the main electrolysis process.

In theory, the current passing through the electrolysis cell should decay exponentially and approach zero as equilibrium is reached. In practice, however, this never occurs and instead the current approaches a finite limit which is the residual current. The residual current is, with few exceptions, usually small and constant.

The problem posed by the background can be eliminated or minimised by using pure reagents, by carrying out blank determinations and by correcting for residual currents.

In the present study, analytical grade reagents were used, blank determinations were made and on the Princeton Applied Research (PAR) 173/179 digital coulometer, automatic subtraction of any background current can be made by means of a Background Current adjustment.

EXPERIMENTAL

The main objective of the present work was to develop a simple, rapid and accurate coulometric method which would be applicable for the routine determination of iron in iron ore and in steel. In order to keep the method as simple as possible a mercury pool working electrode was used thus avoiding the need for working electrode pretreatment which is often necessary when platinum and other solid working electrodes are used. Careful surface pretreatment of platinum working electrodes is essential in order to obtain reproducible results.[9, 100-102] In coulometry, electrode surface conditions are major factors in determining the background current levels and the rates and mechanism of the principal electrode reaction. A further advantage of mercury as a working electrode is its relatively cheaper price compared to platinum.

With a stirred mercury electrode, polarographic half-wave potential data can be used to obtain the applied potential to give quantitative reactions in coulometry. Since the principal electrode reaction envisaged in the present work was the reduction of iron(III) to iron(II) at a mercury pool electrode, it was considered desirable to select a supporting electrolyte system in which the DC polarographic wave of iron(III) was well-defined even at very low concentrations of iron(III). A survey of the polarographic data on the reduction of iron(III) to iron(II) showed that oxalate buffer at pH 4.5 is probably the best supporting electrolyte for the reduction of iron(III) to iron(II) at a mercury electrode polarographically, and hence coulometrically. The DC polarographic wave of iron(III) in oxalate buffer at pH 4.5 was not only well-defined but the plateau region (limiting current) on which depended the choice of applied potential required to obtain a quantitative reaction in coulometry, was flat and steady over a wide potential range.

One of the factors which are essential for a successful development of a procedure for controlled-potential determination of any element is the corrections which have to be applied for blanks and background effects. In the present work, preliminary experiments were carried out with the aim of optimising experimental conditions especially with respect to the blanks and general manipulative procedures such as pipetting small volumes of sample solution.

BLANK

Initially, difficulties were encountered with the blanks in that the values obtained were very high in spite of prolonged deoxygenation of the oxalate buffer solution. The problem was solved when plastic tubes used in connecting the deoxygenation train to the coulometric cell were replaced by copper tubes. Though the evidence was not conclusive, it appeared that sufficient oxygen permeated through the walls of the plastic tubes into the main stream of nitrogen used for deoxygenation. The reduction of this oxygen might have led subsequently to high blanks being obtained. It must however, be emphasized that an efficient oxygen-excluding system is essential for accurate analysis.

Two procedures were developed to eliminate the effect of the background current (i.e. blanks) and both procedures were satisfactory. In the first procedure, 5 ml of the oxalate buffer solution were electrolysed until the least significant digit on the coulometer did not change during a one-minute period. The accumulated charge as read on the coulometer was then noted and subtracted from the total coulomb obtained in each subsequent electrolysis of the iron sample solution. In the second procedure, 5 ml of the oxalate buffer solution were electrolysed for 10 to 15 minutes and the Background Compensation controls on the PAR 179 were then used to "zero" the integrator and thus eliminate the accumulated charge. The resultant total coulomb reading obtained with aliquots of the iron sample solution required no further correction for background current.

PIPETTING

Since it was the aim of the present work to develop a rapid, accurate and simple coulometric method for the determination of iron in iron ore and steel, it was considered that by using small aliquots of the sample solution, many analyses could be carried out within a short time. Accurate transfer of the sample solution into the coulometric cell was accomplished with a calibrated microsyringe obtained from Scientific Glass Engineering Ltd. To calibrate the microsyringe, water at 24°C (room temperature) was drawn into it and then discharged into a weighing bottle. The needle of the microsyringe was then used to touch the side of the bottle and held there for about 30 seconds to allow all the water in the syringe to drain into the bottle. The cap of the weighing bottle was then replaced and the weight of water discharged into the bottle recorded. A Stanton Instruments Ltd. (Model MC8) six-place balance was used for weighing water discharged from the microsyringe during the calibration. The coefficient of variation on eight determinations for the calibration test was 0.08%.

MAIN EXPERIMENTAL PROCEDURES

Three different experimental procedures were examined for the determination of iron in the iron ore samples which were analysed:

Method A: This method involved pipetting aliquots of an aqueous solution of the iron sample directly into the coulometric cell.

Method B: This method involved the use of an internal standard. This procedure was included with the aim of improving the precision of method A.

Method C: Possible interference in the coulometric determination of iron was anticipated from minor constituents of iron ore, such as titanium, vanadium and chromium, thus it was considered desirable to develop, in addition to the other two procedures, a method which involved the prior separation of iron from the sample matrix by solvent extraction. The principle of the procedure was to extract iron(III) with an organic solvent from an aqueous iron ore sample solution and then to back extract it into an oxalate buffer solution in the coulometric cell, followed by coulometric reduction of the iron(III) oxalate formed in the buffer. Since the iron was to be extracted from an 8M hydrochloric acid solution, its back extraction from the organic solvent into the oxalate buffer would be easy because of the changed solution conditions.

Before any coulometric determinations were carried out, the coulometric cell had to be prepared and details of this preparation are given below. In addition, coulograms had to be obtained for each of the three procedures in order to check the potentials used in each procedure. It is also essential to prepare a coulogram in order to check the potential for each new cell system. The potentials applied to a working electrode system in order to obtain quantitative reactions in coulometry not only depend on the supporting electrolytes but also on the cell system used.[9, 107]

In order to obtain experimental conditions similar to those expected during actual analysis of iron ore samples, coulograms were prepared with aliquots of iron ore sample solutions and then compared with those obtained with standard iron(III) solutions. The method used in preparing the coulograms is described below. The method used in dissolving the iron ore sample was essentially that recommended by the British Standards Institution.[92]

APPARATUS

Coulometer: A Princeton Applied Research (PAR) 173/179 digital coulometric system was used. This consists of a Model 179 digital coulometer which is designed for use with the Model 173 Galvanostat/Potentiostat. Together they form a system for making coulometric measurements at either a controlled potential or current. A four-digit (including polarity and exponent) digital display indicates continuously the accumulated coulombs. Automatic subtraction of any background current is provided by means of a Background Current adjustment.

pH meter: Radiometer pHM64 Research pH meter.

Coulometric Cell: A special cell which is shown in Fig. 30 was constructed for this work. The cell is similar to that designed by Milner and Edwards.[49] The cell can hold 50ml of solution and the important features are as follows:

Main compartment: The main compartment is made of Perspex and it is 3cm in diameter (internal) and 6cm high. The upper section of the cell is threaded so that the top can be screwed on tightly. The cell top has a 7mm diameter hole through which the tube from the deoxygenation train can be inserted into the cell. A very small orifice for letting out excess nitrogen and displaced oxygen is also bored in the cell top. Two flat areas are cut out on opposite sides near the bottom of the cell. A hole (7mm in diameter) is bored in each flat area at a position 1.5cm from the bottom of the cell.

Side compartments: There are two compartments. One compartment (A) has three segments. The first segment is made from a 2cm long perspex tube joined to a 3cm Perspex disc. This segment can be attached to the main compartment by three screws through the 3cm Perspex disc. The second segment is made from a Pyrex glass tube with a right angled bend to give arms each 2cm in length. The third segment consists of a short piece of plastic tube through which saturated calomel electrode is connected to the cell. The second side compartment (B) consists of two segments only. The first segment is similar to that of compartment A, and the second segment consists of a Pyrex tube (1.5cm in diameter) to which the auxiliary electrode can be screwed on. A small hole is bored (near the top of the Pyrex tube) to let out any gases formed in compartment B during electrolysis.

Ion-exchange membranes: These are discs of 7mm in diameter which one can easily cut from sheets of Anion Exchange Membrane Permaplex A20 with a suitable cork borer.

Electrodes: The working electrode is a pool of tri-distilled mercury (5ml). Efficient stirring is provided by a magnetic stirrer. A 2cm, 20 gauge platinum wire is cemented with "Araldite" cement, to the main compartment to permit electrical contact.

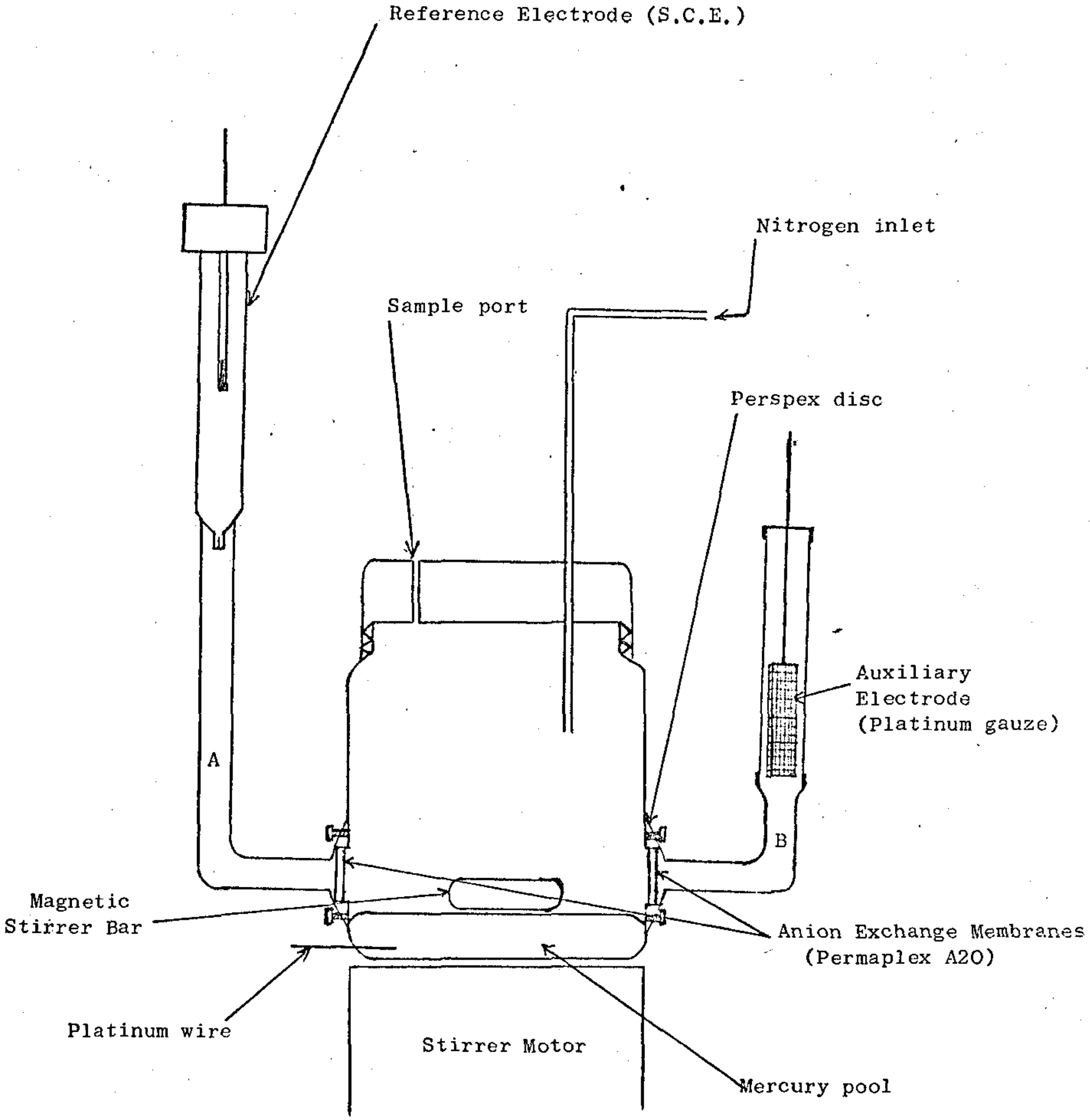


Fig. 30: Mercury-pool electrolysis cell for controlled-potential coulometry

The auxiliary electrode is a platinum gauze which is shaped to fit into side compartment B.

The reference electrode is the fibre type saturated calomel electrode (reference number 09100) supplied by Electronic Industries Ltd. (EIL).

Deoxygenation Train: The nitrogen supplied from a cylinder was scrubbed free of oxygen by passing it through a heated silica tube containing short pieces of copper wires heated to 560°C, and then through a bottle containing distilled water. The short pieces of copper wires are renewed periodically.

REAGENTS

Analytical grade reagents were used throughout. All reagent solutions were made with double distilled water.

Sulphuric acid solution, IM: Cautiously add 54ml of concentrated sulphuric acid (specific gravity 1.84) to 400ml of water in a beaker. Mix and then allow the solution to cool. Transfer the solution to a litre volumetric flask and dilute to the mark with water.

Sulphuric acid solution 50% $^v/v$: Cautiously add 50ml of concentrated sulphuric acid (sp. gr. 1.84) to 40ml of water. Mix and allow to cool and then dilute to 100ml with water.

Oxalate-oxalic acid buffer solution, pH 4.5: Dissolve 18.4g of potassium oxalate $\left\{(COOK)_2 . H_2O\right]$ in water anddilute to 100ml with water. Adjust the pH of the solution to 4.5 with IM sulphuric acid solution.

Thallium(I) solution, 22.5mg.ml^{-1}

Dissolve 0.6947g of analytical reagent grade thallium(I) sulphate $[Tl_2SO_4]$ in hot water and dilute to 25ml with water.

Tri-n-butyl phosphate, (TBP)

Laboratory reagent grade TBP usually contains small amounts of other organic compounds including butyl alcohol, dibutyl phosphoric acid and pyrophosphate esters. A laboratory reagent grade TBP which was obtained from Fisons Scientific Apparatus Ltd., was used as an extractant after purification according to the method of Peppard et al.[108] 250ml of the TBP was stirred with 250 ml of 6M hydrochloric acid solution at 60°C for 12-18 hours to hydrolyse any pyrophosphate components. (This treatment also results in increasing the amounts of dibutyl phosphoric acid and monobutyl phosphoric acid, and presumably results in the formation of some butyl alcohol and phosphoric acid). The separated TBP layer was cooled to room temperature and then shaken with two-250ml portions of water in a separating funnel to remove most of the mineral acid. The TBP layer was further shaken with three-250ml portions of 5% aqueous sodium carbonate solution to remove the mono- and di-esters. The resultant TBP layer was finally treated with three-250ml portions of water and then slowly heated to about 30°C under reduced pressure (water pump) to remove butyl alcohol and water.

PREPARATION OF THE COULOMETRIC CELL:

Fill the three compartments with water and allow the cell to stand for 8-10 hours. This allows the membrane discs to be properly soaked. At the end of the period, empty the compartments, place 5ml of mercury in the main compartment and add 5ml of oxalate buffer solution. Fill the side compartments with oxalate buffer solution and carry out blank determinations at -0.1v and then at -1.0v vs SCE. Complete several blank runs until a constant low figure is obtained at both potentials. These determinations are done in order to remove any electoactive impurities that may be present in the ion exchange membrane.

DISSOLUTION OF THE IRON SAMPLE

Dry a weighing bottle in an oven at 110°C for about one hour. Place the bottle in a dessicator and allow it to cool to room temperature. Put about 1.5g of iron ore sample (previously dried in an oven at 110°C for 2 hours) into the weighing bottle and weigh. Transfer the sample to a 500ml tall-form beaker and reweigh the weighing bottle to obtain the amount of sample in the beaker. Add 35ml of concentrated hydrochloric acid (sp. gr. 1.18) to the sample in the beaker. Cover the beaker and heat it gently until solvent action ceases. Add 5-6ml of concentrated nitric acid (sp. gr. 1.42), digest the solution for about 15 minutes and then add 10ml of sulphuric acid (50%). Heat the solution gently until no more reddish-brown fumes of nitrogen dioxide are given off. Allow the solution to cool and then wash the side of the beaker with hot water. Filter the solution through a Whatman No. 541 filter paper into a 250ml tall-form beaker. Wash the residue with hot water until the yellow colour of iron(III) chloride is no longer observed. Reserve the filtrate and washing. Transfer the residue and the filter paper to a platinum crucible (Note 1). Dry the residue and filter paper over a low temperature Meker burner. Still at this low temperature, char the filter paper without allowing it to burn freely. Ignite the residue at about 900°C until all carbonaceous matter is removed. Allow the platinum crucible to cool and then moisten the residue with water, add a few drops of sulphuric acid solution (50%) and then 5ml of hydrofluoric acid solution, 40% (CARE!). Heat the mixture in the platinum crucible gently in a well-ventilated fume cupboard, to remove silica and sulphuric acid (Note 2). Heat the residue at about 900°C for 30 minutes to ensure the complete removal of any hydrofluoric acid left in the platinum crucible. Allow the residue to cool and then fuse it with sufficient potassium hydrogen sulphate (about 1g) by heating strongly for about an hour (Note 3). Allow the platinum crucible to cool and then place it in a 250ml beaker. Dissolve the melt with water (Note 4). Add the solution of the melt to the reserved filtrate. Evaporate the solution on a steam bath (or with a low heat) to 15-20ml.

Notes

1. If the residue is perfectly white and small in amount, the filtration and treatment of the residue may be omitted without causing significant error.

2. Alternatively, in order to remove silica and sulphuric acid, place the platinum crucible under an infra-red lamp and evaporate the mixture to dryness in a well-ventilated fume cupboard.

3. The residue may be fused with about 3g of sodium pyrosulphate ($Na_2S_2O_7$) instead of potassium hydrogen sulphate.

4. It may be necessary to heat the beaker gently and add 2-3ml of concentrated hydrochloric acid solution (sp. gr. 1.18) to ensure complete and quick dissolution of the melt.

METHOD A: Direct determination of iron in the sample

Transfer the iron sample solution prepared as described above to a 25ml volumetric flask and dilute the solution to 25ml with water. Prepare a coulogram as described below before determining the iron content of the sample.

Preparation of a coulogram:

Pipette 2.0ml of a standard iron(III) solution into a 25ml volumetric flask and dilute the solution to 25ml with the oxalate buffer solution. Shake to mix the solution thoroughly. Transfer 5ml of this solution to the coulometric cell containing 5ml of mercury. Fill the side compartments of the cell with oxalate buffer solution which had been previously deoxygenated for about 10-15 minutes. Deoxygenate the solution in the cell by passing nitrogen over it while stirring vigorously (Note 1). Continue this process of deoxygenation and stirring during the run. Set the working electrode potential at 0.0V vs SCE. Electrolyse the solution until the cell current attains a low constant value (that is, until the least significant digit on the coulometer does not change during a one-minute period). Record the number of coulombs on the coulometer. Set the working electrode potential at -0.1V vs SCE (E_2) and electrolyse the solution again until the cell current attains a constant value. Record the number of coulombs on the coulometer, Q_2. Repeat this procedure several times by changing the potential of the working electrode in steps of 0.1, until making the working electrode potential more negative causes no more or very little increase in the value of Q. Plot the values of Q against E and determine the practical standard potential (E_o^1) for the system.

Determination of the iron content of the sample

Wash the cell thoroughly with water. Then put 5ml of mercury into the cell. Add 5ml of oxalate buffer solution and fill the side compartments with deoxygenated oxalate buffer solution. Deoxygenate the solution for 10 minutes by passing nitrogen over it while stirring vigorously (Note 1). At the same time deoxygenate the iron sample solution in the 25ml volumetric flask by bubbling nitrogen through it. Electrolyse the oxalate buffer solution at -0.75V vs SCE for 10-15 minutes. Adjust the background current compensation of the instrument so that there is no accumulated charge read on the coulometer. Reset the integrator to eliminate any charge accumulated during the background current compensation adjustment step. Open the integrator and pipette 0.1ml aliquot of the iron sample solution into the cell. Electrolyse the solution. Electrolysis is completed when the least significant digit on the coulometer does not change indicating the complete reduction of iron(III) - to iron(II) oxalate. Record the number of coulombs shown on the coulometer. Repeat the experiment by pipetting 0.1ml aliquots of the iron sample solution into the cell and noting the number of coulombs recorded for each aliquot.

Calculate the quantity of iron(III) - reduced to iron(II) oxalate and hence the percentage of total iron in the sample (see Appendix I).

Notes

1. In order to avoid splashing the solution onto the sides of the cell during deoxygenation, nitrogen is passed over the solution in the cell causing an indentation in the surface of the liquid, while it is stirred vigorously but not vigorously enough to splash the solution about. The traditional technique of deoxygenation in which nitrogen is bubbled through the solution is not recommended here because this leads to spray losses.

METHOD B: Determination of iron in the sample using an internal standard

Transfer the iron sample solution prepared as described previously to a 25ml volumetric flask, add an aliquot of the thallium(I) solution and dilute the mixture to 25ml with water. Dilute 2ml of this solution to 25ml with the oxalate buffer solution and use 5ml of the resulting solution to prepare a coulogram as described in Method A.

Determination of the iron content of the sample

Empty the cell including the side compartments and wash the cell with water thoroughly after preparing the coulogram. Put 5ml of mercury into the cell and add 5ml of oxalate buffer solution. Fill the side compartments with deoxygenated oxalate buffer solution. Deoxygenate the buffer solution in the cell for 10 minutes by passing nitrogen over it while stirring vigorously. At the same time deoxygenate the solution containing iron and the internal standard. Electrolyse the deoxygenated oxalate buffer solution at -0.45V vs SCE for 5 minutes and then at -0.90V vs SCE until the accumulated charge on the coulometer remains fairly constant. Adjust the background current compensation of the instrument so that there is no accumulated charge read on the coulometer. Reset the integrator to eliminate any charge accumulated during the eletrolysis of the oxalate buffer solution. Set the applied potential back to -0.45V vs SCE. Open the integrator and pipette 0.1ml of the deoxygenated solution containing iron(III) and thallium(I) into the cell. Electrolyse the solution until the reading on the coulometer remains constant (3-5 minutes) indicating the complete reduction of iron(III) - to iron(II) oxalate. Record the coulometer reading and then set the applied potential to -0.90V vs SCE. Electrolyse the solution until the reading on the coulometer remains constant (5-7 minutes) indicating the complete reduction of the thallium(I) oxalate to thallium. Record the coulometer reading and subtract the previous reading from this to obtain the charge accumulated during the reduction of thallium(I) oxalate. Calculate the amount of iron(III) oxalate reduced to iron(II) oxalate and hence the percentage of total iron in the sample (see Appendix 1).

As thallium metal deposited in the mercury pool is reoxidised at the lower potential, the cell cannot be used for sequential determination. In order to obtain the next experimental readings, it is therefore necessary to empty the cell, wash it thoroughly with water and then use a fresh supply of mercury. The mercury in the cell can be re-used after it had been shaken several times with water in a separating funnel to remove thallium.

METHOD C: Determination of iron after its separation from the sample matrix by solvent extraction

Transfer the iron sample solution prepared as described previously, to a 50ml volumetric flask. Add 34.4ml of concentrated hydrochloric acid (sp. gr. 1.18) and then dilute the solution to 50ml with water. This is a solution of iron(III) in 8M hydrochloric acid solution. Pipette 25ml of this solution into a separating funnel and extract the iron(III) chloride with 7-8ml of tri-n-butyl phosphate by shaking for 3-4 minutes. Transfer the extract to a 10ml volumetric flask and dilute to 10ml with tri-n-butyl phosphate. Pipette 1ml of the extract into a 25ml volumetric flask and dilute the extract to 25ml with oxalate buffer solution. Shake the flask vigorously for about 3 minutes to strip iron(III) from the organic layer. Use 5ml of the aqueous layer to prepare a coulogram following the procedure described in Method A.

Determination of the iron content of the sample

Wash the cell with water thoroughly after preparing the coulogram. Put 5ml of mercury into the cell and add 7ml of oxalate buffer solution. Deoxygenate the buffer solution for 10 minutes by passing nitrogen over it while stirring vigorously. Electrolyse the deoxygenated buffer solution at -1.00V vs SCE for 10-15 minutes. Adjust the background current compensation on the instrument so that there is no accumulated charge read on the coulometer. Reset the integrator to eliminate any charge accumulated during the electrolysis of the oxalate buffer solution. Pipette 0.1ml of the extract, previously deoxygenated for 15-20 minutes, into the cell. Electrolyse the solution until the reading on the coulometer remains constant (10-12 minutes) indicating the complete reduction of iron(III) - to iron(II) oxalate. Record the coulometer reading and calculate the quantity of iron(III) oxalate reduced to iron(II) oxalate and hence the percentage of iron in the sample. Repeat the experiment by pipetting 0.1ml aliquots of the extract into the cell and electrolysing until the coulometer reading remains constant.

RESULTS AND DISCUSSION

Fig. 29 shows the coulogram obtained for the reduction of iron(III) oxalate by method A and Table 4 shows the results obtained for the analyses of some iron ore samples by the same method. In order to check the precision of the results shown in Table 4, a solution of high-purity iron (BCS 149/3) was analysed by the same method and the results obtained are given on Table 5.

Table 4

Results obtained for the direct determination of iron in iron ore samples by Method A

Iron Ore	*Iron Found %	Mean Value %	Coeff. of Variation %	Standardised value %
BCS 175/2 (Nimba Iron Ore)	67.7508, 67.7839 67.9498, 68.1820 67.7176, 68.1157	67.9166	0.29	66.10
BCS 303 (Iron ore sinter)	36.9431, 37.0456 36.8661, 36.7453 36.9201, 36.8837	36.9007	0.28	36.0-
BCS 378 (Iron ore sinter)	62.0196, 62.2791 62.4512, 62.1278 62.3850, 62.2365	62.2499	0.26	61.8-

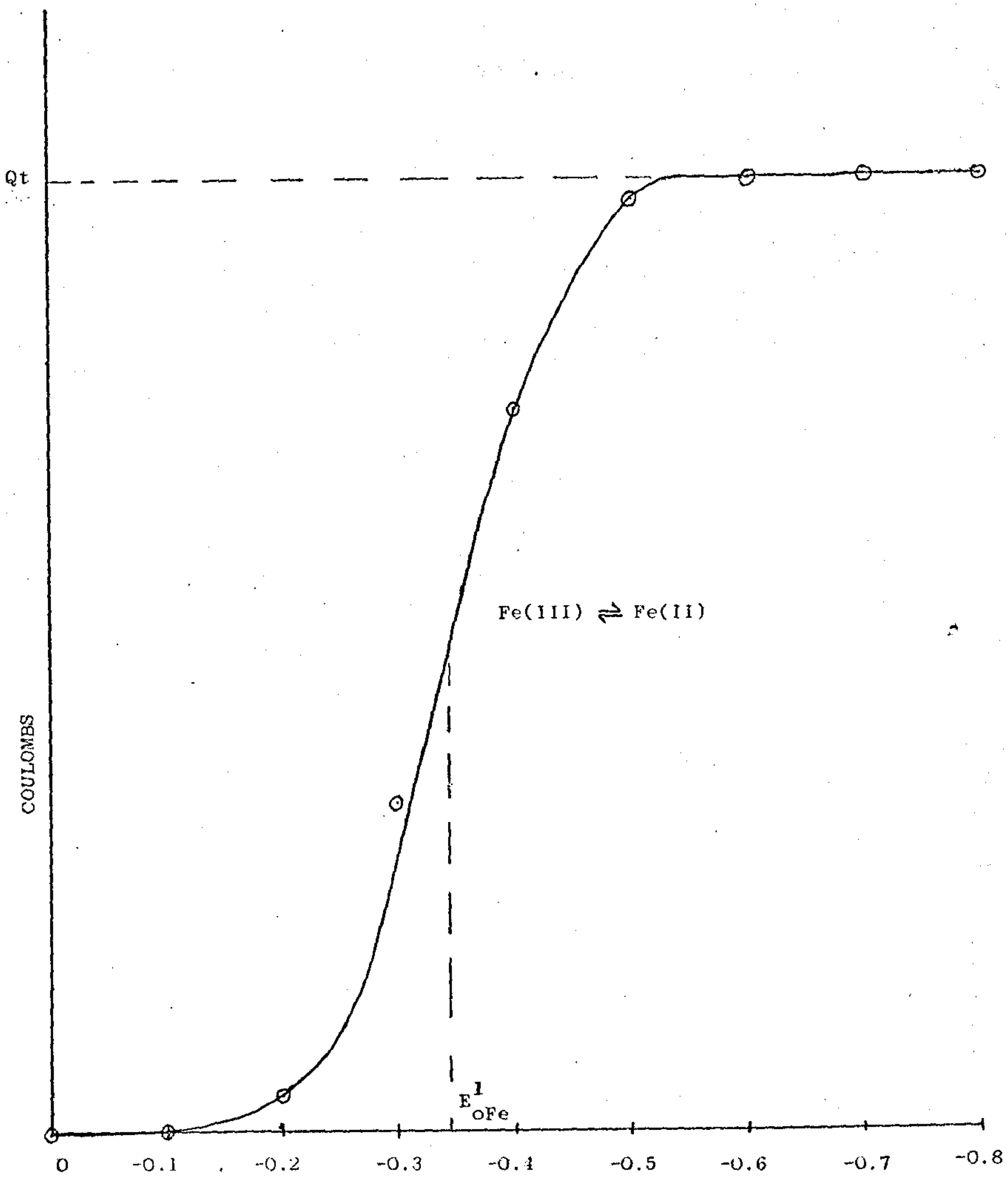
*Each value is the mean of five determinations

Table 5

Results obtained by the direct determination of iron in high-purity iron (BCS 149/3)
Weight of iron taken = 4mg

Coulometer Reading (Coulombs)	Weight of Iron Found (mg)	Percentage of Iron in sample
6.930	4.01132	100.28
6.918	4.00438	100.11
6.902	3.99512	99.88
6.900	3.99396	99.85
6.900	3.99396	99.85
6.910	3.99975	99.99
6.930	4.01132	100.28
6.907	3.99804	99.95
6.906	3.99776	99.94
6.908	3.99840	99.96
Mean 6.911	4.00032	100.00

Mean Percentage of iron found in BCS 149/3 = 100.00%
Coefficient of variation = 0.16%



POTENTIAL OF MERCURY POOL ELECTRODE V vs SCE

Fig. 29: Coulogram for Iron in Oxalate buffer at pH 4.5

Fig. 31 shows the coulogram obtained for the reduction of iron(III) oxalate with thallium(I) oxalate as internal standard (Method B). Table 6 shows the results obtained for the analysis of two iron ore samples by method B.

Table 6

Results obtained for the determination of iron in iron ore samples with thallium(I) as internal standard (Method B)

Iron Ore	*Iron Found %	Mean value %	Coeff. of variation %	Standardised value %
BCS 303 (Iron Ore Sinter)	36.5550, 36.4988 36.5269, 36.5493 36.5774, 36.0324	36.4566	0.57	36.0-
BCS 378 (Iron Ore Sinter)	62.8288, 62.9508 62.8873, 63.2121 62.8405, 62,7999	62.9199	0.24	61.8-

*Each value is the mean of five determinations

Compared with the standardised values of total iron in the iron ore samples analysed, the results obtained by methods A and B were high although the precisions were good. It appeared that other electroactive species in solution were being co-reduced with iron(III). However, the results obtained by method A for the determination of iron in high-purity iron were not only very precise, they also showed that interferences from other constituents of the sample were minimal. It is interesting to note that titanium was not present in the high-purity iron sample analysed and the percentage of each of the other potential interfering elements such as chromium, copper, molybdenum, vanadium and tin was less than 0.001%.

An attempt was made to use indium(III) as internal standard but the total electrolysis time was between 30 and 45 minutes and the results were not reproducible. From the results of the method involving the use of thallium(I) as an internal standard, it does not appear that any advantage was gained by using an internal standard. The coefficients of variation obtained were higher than those obtained by method A. The relatively high values of the coefficient of variation could not be due possibly to the pipetting technique used in this procedure because it has been shown by the calibration test described earlier that the microsyringe is very precise. It might possibly be due to the reaction mechanism involved in the reduction of iron(III) to iron(II) and of thallium(I) to Tl(Hg). Both reactions are reversible both polarographically and in terms of their controlled-potential electrolysis behaviour. In addition the coulogram shown on Fig. 31 reveals that it is difficult to define precisely a suitable applied potential for the complete reduction of iron(III) to iron(II). -0.45V vs SCE was selected because it was considered to be the most suitable potential likely to result in the reduction of iron(III) to iron(II), although an inspection of the coulogram shown in Fig. 29 (obtained by Method A) reveals that complete reduction of iron(III) to iron(II) would not be possible at a potential of -0.45V vs SCE. It is interesting to note that the solution conditions in both methods A and B are similar.

Because the main aim of the present work was to establish optimum conditions for the coulometric determination of iron in a IM oxalate buffer solution at pH 4.5, a complete investigation of the electrochemistry of iron in oxalate solutions was not carried out. However, an examination of the polarographic half-wave potential of some elements in oxalate solution showed that several elements such as Bi(III), Ce(IV), Cu(II), Cr(VI), Pb(II), Mo(VI), Re(VII), Sn(IV), Ti(IV), U(VI), V and W(VI) would interfere with the coulometric determination. The half-wave potentials of these elements including iron(III) in oxalate solutions occur within the range 0 to -0.70V vs SCE. Though the values of the half-wave potential have been reported to vary with pH and concentration of oxalate solution, the variations are in most cases insignificant. Perhaps, titanium constitutes

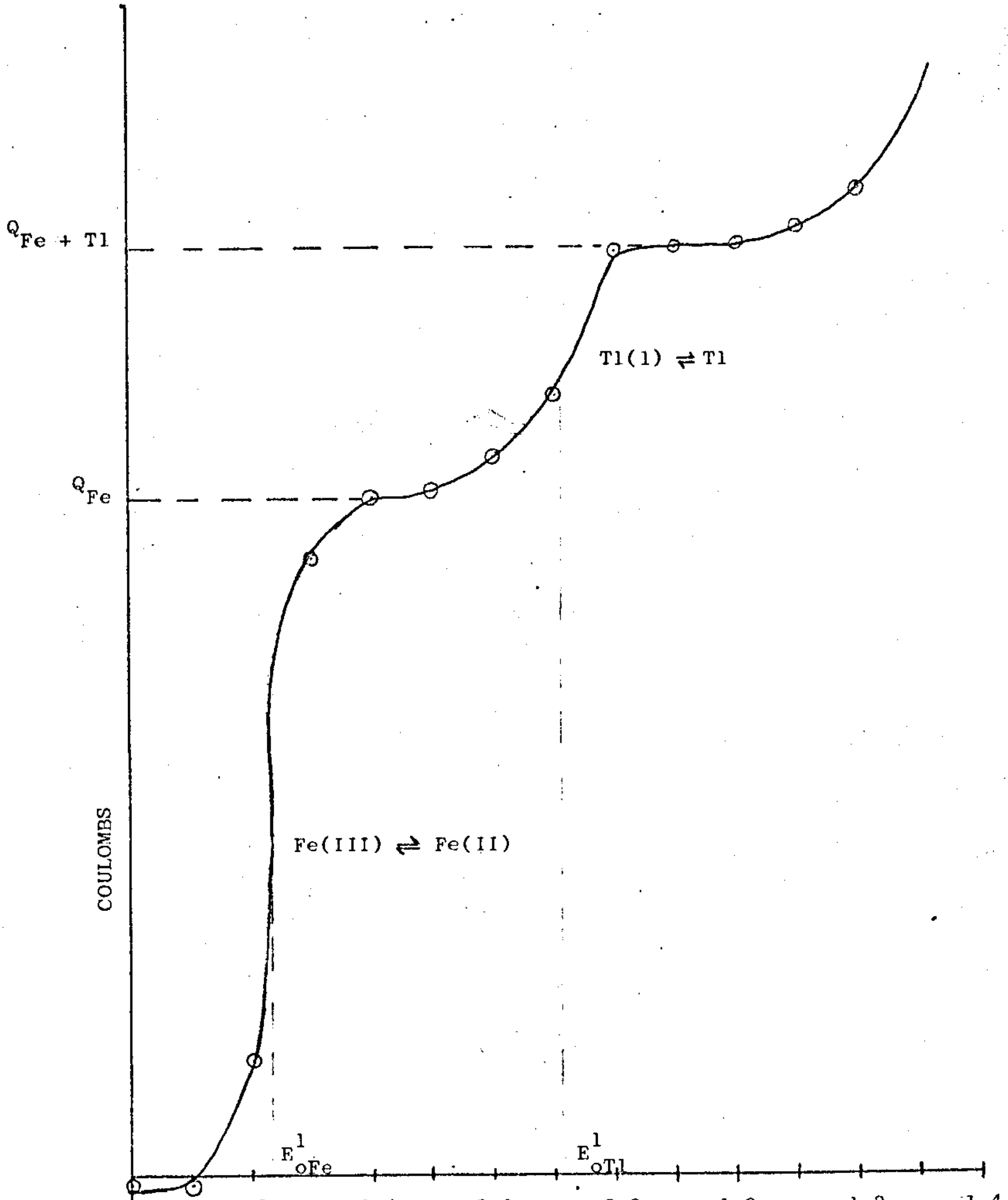


Fig. 31: Coulogram for Iron and Thallium(I) in oxalate buffer at pH 4.5

the greatest source of interference because it is often present in appreciable quantity in iron ore samples. It was considered desirable to include a procedure which involved the prior separation of iron from the sample matrix in order to avoid possible interference from these elements.

It was not possible to correct for these elements (after their co-reduction with iron(III)) by re-oxidation of their reduced forms because most of them except perhaps molybdenum and uranium are easily re-oxidised. Precipitation of some of these elements followed by their separation from iron by filtration, before coulometric determination was not considered because iron may be co-precipitated. Masking of the interfering elements with masking agents was also not considered because most masking agents are not highly selective. Agents that would mask copper, for instance, can also be used to mask iron. Standard-addition method which is often used to compensate for sample matrix effects was not employed here because this might have solved the problem of titanium interference only without compensating for the effects of the other interfering elements.

Since it was not possible to utilise the methods of dealing with interferences mentioned above, it was decided to extract iron from the sample matrix with an organic solvent and then determine the iron in the extract coulometrically. The basis of the procedure was to extract iron(III) from an aqueous iron ore sample solution with an organic solvent and then back extract the iron into an oxalate buffer solution in the coulometric cell. The iron(III) oxalate formed in the buffer was then to be reduced coulometrically to iron(II) oxalate at a suitable applied potential.

A number of organic solvents which have been used previously to extract iron from aqueous solutions were considered. The criteria for choosing an organic solvent were high percentage extraction of iron and non-interference in the coulometric reduction. Methyl isobutyl ketone was found to be unsuitable because it gave a polarographic wave with half-wave potential at -0.08V vs SCE and would therefore interfere. Di-isopropyl ether gave no interfering wave but the extraction of iron(III) in a 6M hydrochloric acid solution with an equal volume of di-isopropyl ether gave consistently low results. Tri-n-butyl phosphate gave no interfering wave and was selected because it gave a higher percentage of extraction. However, it was found that at -0.75V vs SCE, the time required for complete electrolysis of 0.1ml aliquots of the extract was between 45 to 60 minutes. An applied potential of -0.75V vs SCE was selected initially on the basis of the results shown on the coulogram (see Fig. 32). It appeared that in spite of the small amount of organic solvent present in the sample pipetted into the coulometric cell, the rate of transfer of iron(III) from the organic solvent to the oxalate buffer was very slow. Unsuccessful attempts were made to accelerate the rate of transfer by diluting the tributyl phosphate extract, before pipetting it into the coulometric cell, with hydrophilic solvents including alcohol, dimethylformamide, polyethylene glycol 6000 and triethylene glycol. Surface active agents such as Triton X-100 and gelatin were also tried without success.

When the solution was electrolysed at -1.00V vs SCE, the electrolysis time was not only reduced to 10-15 minutes but satisfactory results were also obtained. A possible explanation for the shorter electrolysis time observed at -1.00V as against the 45-60 minutes observed at -0.75V might be that uncompensated iR losses in the solution caused the actual electrode potential to be considerably less than the instrumental control voltage. Thus by increasing the applied potential beyond that dictated by the coulogram, the actual electrode potential required for complete and rapid reduction of the iron(III) oxalate was attained and perhaps these iR losses were compensated for.

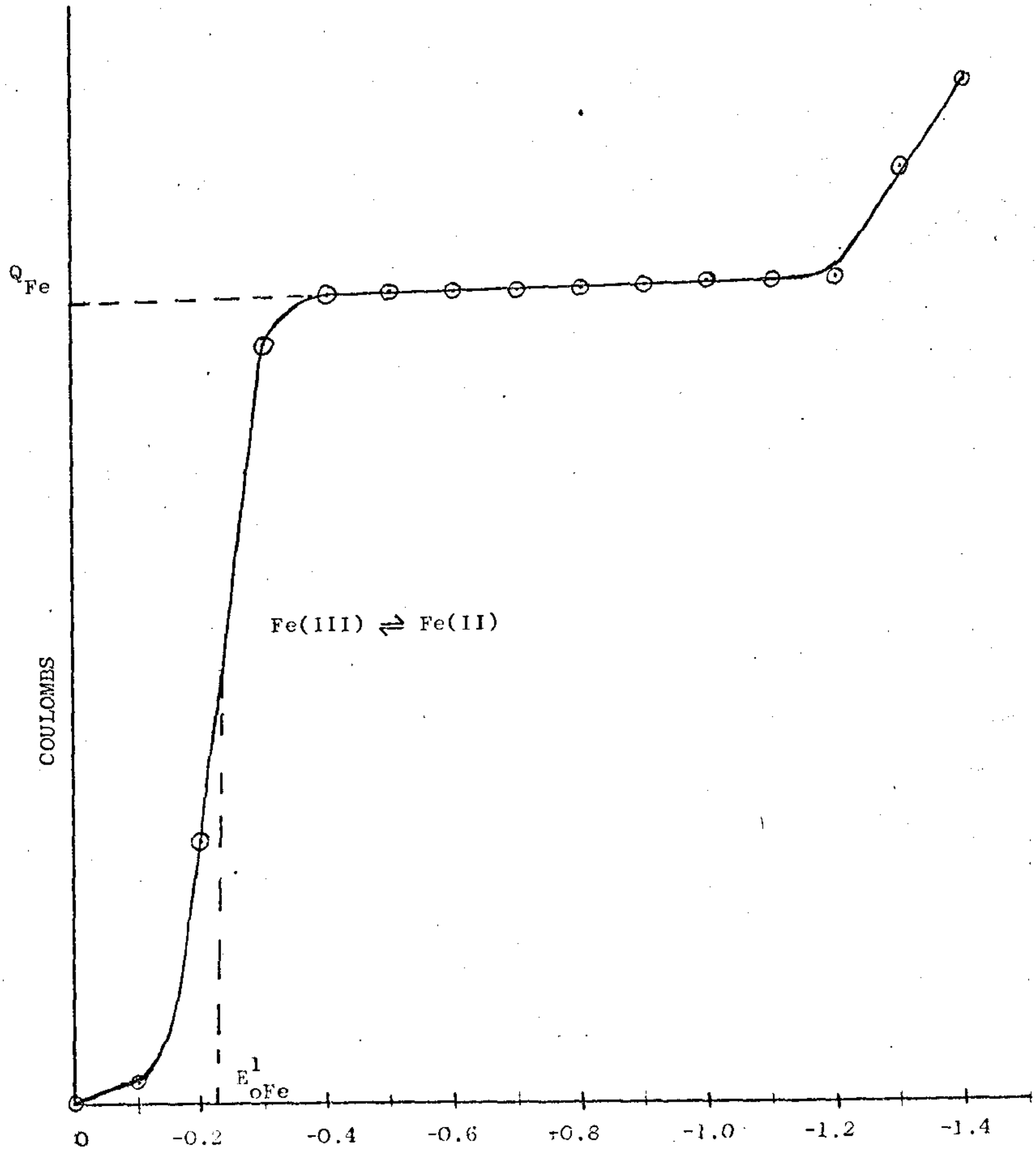
Table 7 shows the results obtained for some iron ore samples by Method C. The results show that the coulometric method involving the extraction of aliquots of iron(III) in 8M hydrochloric acid solution with 7-8ml of tri-n-butyl phosphate is capable of yielding precise and accurate results.

Table 7

Results obtained for the determination of iron in iron ore samples after separation of iron from the sample matrix by extraction with tri-n-butyl phosphate (Method C)

Iron Ore	*Iron Found %	Mean Value %	Coeff. of variation %	Standardised value %
BCS 175/2 (Nimba Iron Ore)	66.0979, 65.9758 66.0556, 66.0151 66.0954, 65.5953	65.9725	0.29	66.1_0
BCS 302/1 (Northamptonshire Iron ore)	33.2617, 33.3456 33.3036, 33.2235 33.1621, 33.2599	33.2594	0.19	33.3_0
BCS 378 (Iron ore sinter)	61.7065, 61.9824 61.7842, 61.5662 61.7162, 61.7243	61.7466	0.22	61.8-
BCS 303 (Iron ore sinter)	35.8787, 35.9163	35.8975	-	36.0-

*Each value is the mean of five determinations



POTENTIAL OF MERCURY POOL ELECTRODE V vs SCE

Fig. 32: Coulogram for iron after its extraction from 8M HCl solution with TBP

Supporting electrolyte: Oxalate buffers, pH 4.5

Table 8 summarises the results for total iron found in the iron ore samples which were analysed by the methods described here compared with the standardised values which were obtained by titrimetry with standard potassium dichromate solution (Standard Method BS 1121:1955 or BS 4158:Part 1: 1967).

Table 8

Comparison between the present coulometric methods with the titrimetric method for determining iron in iron ore samples

IRON ORE	PERCENTAGE OF IRON FOUND						VALUES OBTAINED BY INDIVIDUAL ANALYST AS SHOWN ON THE CERTIFICATE
	METHOD A		METHOD B		METHOD C		
	MEAN	COEFF. OF VAR.	MEAN	COEFF. OF VAR.	MEAN	COEFF. OF VAR.	
BCS 378 (Iron ore sinter)	62.25	0.26	62.92	0.24	61.75	0.22	61.86, 61.99 61.8-, 61.95 61.80, 61.81, 61.70,
BCS 303 (Iron ore sinter)	36.90	0.28	36.46	0.57	35.90	-	35.9-, 35.7_5 35.9_0, 36.0_5 36.1_5, 36.0_5 36.1_0, 35.9- 35.8-, 35.7_5
BCS 175/2 (Nimba Iron Ore)	67.92	0.29	-	-	65.97	0.29	66.1_0, 66.1_0 66.0_5, 66.1_0 66.1_5, 66.1_5 66.2_0, 66.0_5,
BCS 302/1 (Northamptonshire Iron ore)	-		-	-	33.26	0.19	33.28, 33.40 33.39, 33.33 33.25, 33.3- 33.30,

Table 8 shows that the solvent extraction - coulometric method compares favourably with the titrimetric method. In addition, the use of very small volumes of the sample solution for analysis, makes it unnecessary to dismantle the cell in between runs. Many analyses can therefore be carried out using the same supporting electrolyte. Using this technique, it is possible to analyse 20-25 samples within 3 hours. One other advantage of the technique described here over classical titrimetric method of analysis is that it is totally unnecessary to standardise the reagents used. Whereas classical titrimetry has been recommended mainly as a "referee" method for the determination of iron in iron ores, the technique described here can be utilised for routine analysis without any loss in precision and accuracy.

The use of triply-distilled mercury avoids the need for working electrode pretreatment which is often necessary when platinum working electrodes are used. Careful surface pretreatment of platinum working electrodes is essential in order to obtain reproducible results.[9, 100-102] Electrode surface conditions are not only a major factor in determining the background current levels, they also influence the rates and mechanism of the principal electrode reaction.

The solvent extraction-coulometric method described here could be adapted for the determination of iron in various other materials including alloys, cement, slags and ceramic materials.

APPENDIX 1

CALCULATION OF THE PERCENTAGE OF IRON IN IRON ORE

The iron content of the iron ore is calculated from the coulometer reading using the following formula:

$$\% \text{ Fe in iron ore} = \frac{C \times 55.85 \times V \times 100\%}{96{,}484.6 \times v \times W}$$

where:

C = PAR 179 Coulometer reading

55.85 = gram-molecular weight of iron

V = volume of iron ore stock solution in ml

96,484.6 = Faraday's constant

v = volume of aliquot used for analysis (in ml)

W = weight of iron ore sample taken for dissolution (in gram)

Sample calculation

1.5265g of iron ore is weighed out, dissolved and the solution is then diluted to 25ml with water.

A 100 μL aliquot of the iron ore solution yields 7.147 coulombs (corrected for blank)

$$\% \text{ Iron in iron ore} = \frac{7.147 \times 55.85 \times 25 \times 100}{96484.6 \times 0.1 \times 1.5265} = 67.75\%$$

In order to calculate the iron content of the iron ore from results obtained with the Organic Extraction Method, the following formula is used:

$$\%\mathrm{Fe\ in\ iron\ ore} = \frac{C \times 55.85 \times V \times 10 \times 100\%}{96{,}484.6 \times v \times 25 \times W}$$

where C, v, V and W are as explained previously.

1.5786g of iron ore is weighed out, dissolved and the solution made up to 50ml with 8M hydrochloric acid solution. 25ml of this solution is extracted into 10ml of tri-n-butyl phosphate.

A 100 μL aliquot of the extract yeilds 9.013 coulombs (corrected for blank).

$$\%\ \mathrm{Iron\ in\ iron\ ore} = \frac{9.013 \times 55.85 \times 50 \times 10 \times 100\%}{96{,}484.6 \times 0.1 \times 25 \times 1.5786}$$

$$\%\ \mathrm{Iron\ in\ iron\ ore} = 66.098\%.$$

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COLORIMETRIC DETERMINATION OF BORON

I. INTRODUCTION

Colorimetric determination of boron in various materials including steels and alloys has always been difficult. The different procedures recommended for the determination of boron in steel including those adopted by the British Standards Institution[1] and the American Society for Testing Materials[2] appear to suffer from several disadvantages which limit their usefulness considerably. Many of the methods are prone to interferences, have poor sensitivity and are tedious. Their application to routine steel analysis is not therefore completely satisfactory.

Some of the methods for the determination of boron in steel are based on the reaction of boric acid with hydroxy - or aminoanthraquinones and their derivatives. The reactions are usually performed in concentrated sulphuric acid, which makes the analysis more difficult. In recent years new procedures which are based on the reaction of tetrafluoroborate with basic dyestuffs have been developed.[37-57] The ion-pair complexes formed between the dyes and tetrafluoroborate anion are usually extracted with organic solvents and the boron is determined by measurement of the absorbance of the extract. Solvent extraction of the ion-pair complexes separates boron from interferences, but in spite of this, most of the methods still suffer from high blanks. The extraction of dye-tetrafluoroborate complexes by organic solvents is seldom complete. It is usually less than 100%, although this has been said to have no effect on the accuracy of the determinations, provided that calibration curves are plotted and the determinations are carried out under identical conditions. In addition to fluoride ion, phenolcarboxylic acids such as salicylic acid, have been suggested as suitable complexing agents.[58]

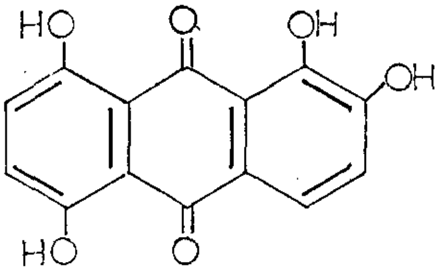
Attempts to improve the accuracy and precision of the solvent extraction method have led to the introduction of new procedures in which boron is converted into tetrafluoroborate ion and an "onium" salt of the tetrafluoroborate is isolated by extraction with chloroform or other suitable organic solvents. The determination of boron is then completed with a dye. Coursier et al.[3] reported a procedure in which tetraphenylarsonium-fluoroborate complex was extracted with chloroform and the determination of boron carried out with curcumin.

In the present study, similar reactions as described above have been utilised. The boron-containing sample was dissolved in dilute sulphuric acid by heating under reflux, and boron converted to tetrafluoroborate by the addition of hydrofluoric acid or its salt. A solution of "onium" compound was added and the onium ion-fluoborate complex which was formed was extracted with chloroform. The analysis was completed by replacing the fluoroborate ion with an anionic dye and the absorbance of the dye-onium ion complex formed was measured. This indirect determination of boron is based on the fact that tetrafluoroborate forms a 1:1 complex with "onium" ions such as tetraphenylphosphonium ion.

II. REVIEW OF COLORIMETRIC METHODS FOR THE DETERMINATION OF BORON IN STEEL

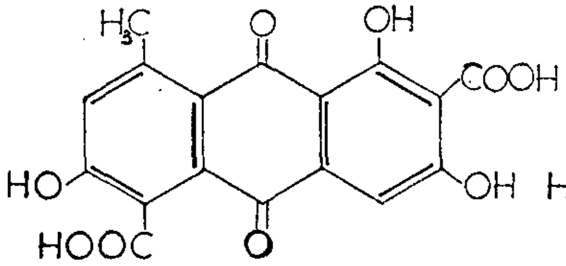
Colorimetric methods for the determination of boron have been widely applied. In the past 25 years, a large number of coloured organic reagents have been discovered. As a result of the large number of colorimetric procedures based on the use of organic reagents, it is, perhaps, convenient to categorize the procedures on the basis of the characteristic nature of the organic reagents. A selection of these reagents are discussed below. Most of the determinations of boron in steel have to be preceded by some form of separation procedure because of the strong interfering influence of other elements. A wide range of separation procedures have been recommended. They include distillation, electrolysis and the use of ion exchangers.

QUINALIZARIN



In 1945 Weinberg et al.[4] published a paper on the determination of boron in steel using quinalizarin. Since then numerous procedures based on the reaction of boric acid with quinalizarin have been developed for the determination of boron in steel.[5-10] The method is suitable for analysing steels containing 0.001 to 0.004% of boron, although it has been used for analysing titanium - and vanadium-free steel samples containing up to 0.2% of boron.[11] The colour of the boron-quinalizarin complex depends strongly on the concentration of sulphuric acid as does the quinalizarin solution itself. A major disadvantage of quinalizarin is the considerable overlapping of the absorption spectra of the solutions of the reagent and that of its complex with boron. Gupta and Boltz,[12] however, showed that this overlapping is eliminated by using quinalizarin in sulphuric acid - acetic acid medium. Acetic acid acetylates quinalizarin forming acetylquinalizarin which has a dark pink colour instead of the blue-violet colour produced by quinalizarin. Divak[13] reported the determination of boron in steel and cast iron down to 0.001% of boron, using a tetra-acetylquinalizarin procedure described by Budanova and Gurevich.[14] In the presence of interfering elements, a preliminary separation of boron by distillation, electrolysis or ion exchange is necessary but a method for the determination of boron in low melting alloys without preliminary separation has been proposed by Jones.[15]

CARMINE AND CARMINIC ACID



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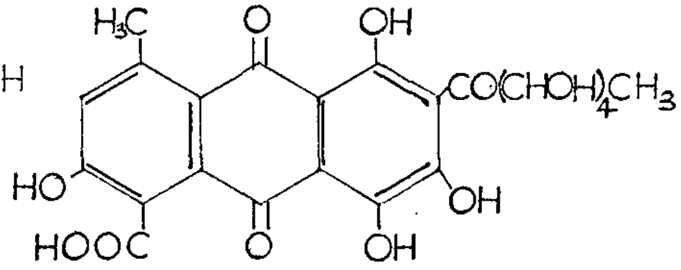
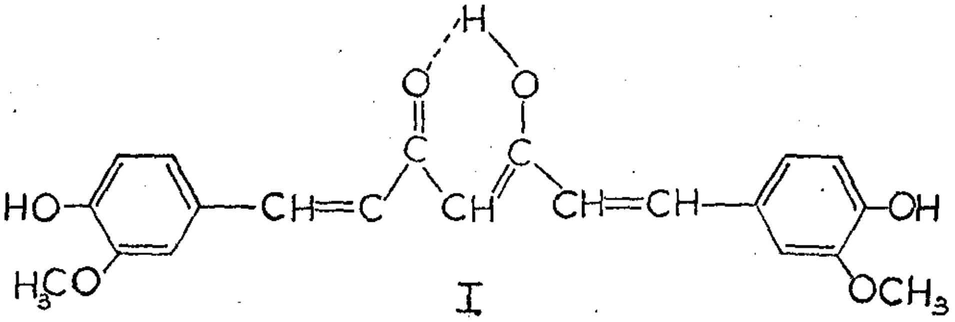


II

Carmine (I), which is also called carmine red is suitable for determining up to 0.02% of boron in steel. Carmine is formed by the saponification of carminic acid (II). In concentrated sulphuric acid, carmine and carminic acid both react with boron and undergo a colour change from red to blue. Studies have shown that the development of the colour, the sensitivity of the reaction, and the optimum concentration of sulphuric acid depend on the quality of the sample of carminic acid.[16] In contrast to quinalizarin, carmine and carminic acid react at a considerably slow rate with boron but Willis[17] has reported that because the method is easily automated, the analysis time can be considerably reduced. In spite of their disadvantages when compared with quinalizarin, carmine and carminic acid suffer less from interferences. However, titanium interferes strongly, and chromium and molybdenun cause high blanks.[17] Different attempts have been made to improve the overall sensitivity of the method. Kazuo Hiiro[18] reported a method in which interferences from metal ions were avoided by using EDTA as masking agent. Svarcs et al.[19] used a solvent extraction procedure to eliminate interferences. Shigeo Wakamatsu[20] used a method involving quantitative distillation of methyl borate from a concentrated sulphuric-phosphoric acid solution in a current of air, the sample having been previously decomposed with an acid. He noted that all mineral acids except hydrofluoric acid could be used to decompose the sample. The distillate was absorbed in sodium hydroxide solution and the boron determined colorimetrically with carmine. The carmine method has been widely utilised for determining boron in steel without preliminary separation because it suffers less from interference than some of the hydroxyanthraquinones such as quinalizarin.[21]

CURCUMIN



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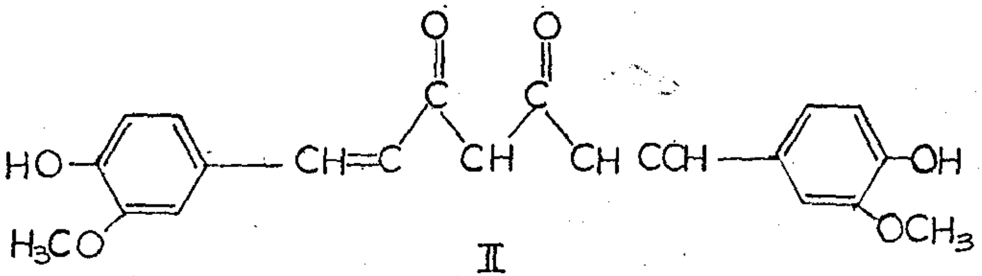
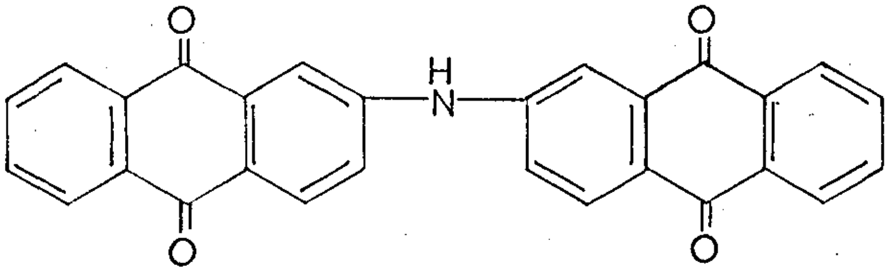


II

Curcumin has been widely used for determining boron in steel[22-25] containing 0.0005 to 0.1% of boron and it is the colorimetric method recommended by the British Standards Institution for the determination of boron in steel.[1] The boron-curcumin reaction is highly sensitive and this sensitivity is improved greatly if the reaction takes place in acetic-sulphuric acid medium.[26] In contrast to hydroxyquinones such as quinalizarin, the boron-curcumin reaction does not require concentrated sulphuric acid. However the sensitivity of the curcumin method and the reproducibility of the results obtained often depends on the quality of the curcumin sample and on rigorous observance of the reaction conditions such as temperature, time, reagent quantities and solvents. In addition, many elements interfere with the determination of boron with curcumin. It is therefore necessary to separate boron as methyl borate by distillation.[1,2,26] All these make the curcumin method tedious and unsuitable for large-scale determination of boron. Hideshiro Goto et al.[27] employed a solvent extraction procedure in which interfering elements were removed with methyl isobutyl ketone. Monnier,[28] and Tolk et al.[29] have reported methods for determining boron without preliminary separation. The procedure reported by Tolk et al.[29] is however limited by the fact that no oxidising agent was used, an omission which leaves uncertain the effect of the carbides etc. inherent in iron and steel. Curcumin with the structural formula (I) has been reported to be the form which reacts directly with boron to form a complex, but some workers[30] have suggested the latter.(II).

1,1' - DIANTHRIMIDE



In 1943, Rudolph and Flickinger[31] made use of 1,1'-dianthrimide to determine boron. Since then 1,1'-dianthrimide has become one of the most widely used colorimetric reagent for the determination of boron in steel. It is a reliable method for determining micro amounts of boron, although the boron-dianthrimide colour reaction is less sensitive than that of curcumin. The BISRA Methods of Analysis Committee[32] made a critical evaluation of the colorimetric determination of boron with quinalizarin, curcumin and dianthrimide, and recommended a method using dianthrimide after preliminary separation of interfering elements by a cation exchange procedure. 1,1'-dianthrimide was recommended because of its good reproducibility and sensitivity. Danielsson,[33,34] in a detailed study of the boron-dianthrimide reaction, reported a procedure of determining boron in iron and low-alloy steels down to 0.001% without a preliminary separation step. A disadvantage of the boron-dianthrimide method is the need to heat in 93-95% sulphuric acid for 1-1.5 hours at 100° or 4-5 hours at 80°C. Prolonged heating of 1,1'-dianthrimide at high temperatures gradually oxidises it to yet unidentified brown coloured products. Most of the procedures based on the boron-dianthrimide reaction still involve preliminary separation of boron from interfering elements because this ensures more reliable and accurate results.

OTHER ANTHRAQUINONE DERIVATIVES

Many other anthraquinone derivatives have been used in the colorimetric determination of boron. Methods have been described for the determination of boron in steels and alloys with 1-hydroxy-4-p-toluidinoanthraquinone (C.I. Solvent violet 13)[35] and tetrabromochrysazin.[36] Most of the reagents in this group have not found wide application because they are difficult to obtain commercially.

COLORIMETRIC DETERMINATION OF BORON AS TETRAFLUOROBORATES USING BASIC DYES

Recently, a new colorimetric method for the determination of boron has been developed based on the reaction of tetrafluoroborate ion with basic dyes. A range of basic dyes have been utilised in the determination of boron in various materials including iron and steel. A number of reviews[37,38] have been published dealing with the determination of boron as tetrafluoroborates using basic dyes. Basic dyes are highly sensitive and are reasonably selective. In steel samples, the dye-fluoroborate reaction has been used to determine boron in the range from 0.0005 to 0.12%. The principle of the method is quite simple and involves the conversion of boron in solution to tetrafluoroborate by the addition of hydrofluoric acid or its salt. A solution of the basic dye is then added and the complex formed by the tetrafluoroborate ion and basic dye is extracted with a suitable inert organic solvent. The boron is determined by measuring the absorbance of the extract. The dye-fluoroborate complex has the formula $(BF_4)R$ where R is the monovalent cation of the basic dye. Tetrafluoroborate is easily hydrolysed and to prevent this, a relatively large excess of hydrofluoric acid is usually employed to suppress hydrolysis. But since at high hydrogen ion concentrations, many of the dyes exist as divalent cations, which form inextractable complexes with fluoroborate ion, the solution after the formation of the fluoroborate ion, is usually adjusted to a pH at which the dye is present as a monovalent cation. Thus preliminary investigations to establish optimum pH values for each of the basic dyes have to be carried out whenever this method is utilised. Excessive dilution of the sample solution, once the dye-fluoroborate complex has been formed is necessary in order to decrease the concentration of excess fluoride ions which otherwise would interfere with the determination. Large amounts of fluoride ions form extractable complexes with basic dyes. The presence of fluoride ions and other extractable anion-dye complexes gives rise to high blanks. This is one of the major disadvantages of the method.

Various basic dyes, most of them belonging to the xanthene, triphenylmethane or oxazine group, have been recommended for the determination of boron in iron and steel. They include methylene blue,[39-50] brilliant green,[51] methyl violet[52] and Nile blue A(C.I. Basic blue 12).[53] Pasztor et al.[54,55] studied the use of thionine derivatives in the extraction and direct colorimetric determination of boron and reported that n-methylthionine (Azure C) was superior to methylene blue. Busev et al.[56] described a method that involved the precipitation and extraction of tetrafluoroborate with antipyrine dyes and noted that the sensitivity of the extraction determination of boron by means of antipyrine dyes was higher than that of the hydroxyanthraquinones. They also studied phenazone dyes and arrived at the same conclusion on their sensitivity with respect to hydroxyanthraquinones.[57]

The choice of a suitable organic solvent for the extraction of the dye-fluoroborate complex is influenced by several factors, some of which are the need to reduce the blanks and to achieve a high percentage of recovery. At present, benzene is used for the extraction of the brilliant green - fluoroborate complex and dichloroethane for the extraction of the methylene blue-fluoroborate complex.

In order to improve the precision of the method, several procedures have been suggested for the removal of interfering elements. Norii Fukushi and Yachiyo Kakita[43] removed iron by extraction with methyl isobutyl ketone and Eremin and Romanov[42] removed tungsten by precipitating it as tungsten oxide.

In an attempt to improve the sensitivity of the determination of boron with basic dyes, Vasilevskaya and Lenskaya[58] exploited the capacity of boric acid to form complexes with salicylic acid and developed a procedure for determining boron in natural materials. The procedure is based on the formation of compounds of the type $(BL_n)A$ where L is salicylic acid and A is a basic dye. They investigated the suitability of basic dyes of the triphenylmethane series as well as thionine derivatives. They found that complexes formed between boron, salicylic acid and dyes of the triphenylmethane series were best extracted by benzene and carbon tetrachloride, while complexes formed with dyes of the thionine derivatives group were best extracted by chloroform. Crystal violet (triphenylmethane dye) was recommended as the most suitable dye because it gave the highest experimental molar absorptivity. Almost all cations were found to interfere and preliminary separation of boron by distillation as methyl borate or by ion exchange was recommended. This detracts from the method's routine application.

More attempts aimed at simplifying and improving the sensitivity of the colorimetric method for the determination of boron have led to the search for better complexing agents for tetrafluoroborate ion. In recent years, the use of "onium" compounds as complexing agents for tetrafluoroborate has been receiving more attention. The method is based on the extraction of the tetrafluoroborate of an onium compound with chloroform followed by the replacement in the extract of the onium cation by a basic dye. The extraction of the tetrafluoroborate of the onium compound effectively separates boron from interfering elements which otherwise would complex with the basic dye used. In aqueous solution at pH 3, tetraphenylarsonium ion, $As(C_6H_5)_4^+$ reacts with BF_4^- anion to form an ion-association compound $As(C_6H_5)_4BF_4$ which is readily soluble in chloroform. Coursier et al.[3] employed this procedure to separate trace of boron and then determined boron colorimetrically with curcumin. Vichlabsky[59] reported a method in which an anionic boron-catechol complex was extracted quantitatively into dichloromethane in the presence of tetraphenylphosphonium bromide. The determination of boron was then carried out with quinalizarin dissolved in a mixture of acetic and sulphuric acids.

III. COMPARATIVE EXPERIMENTAL STUDY OF SELECTED CHROMOGENIC REAGENTS

Perhaps the biggest problems associated with the colorimetric determination of boron have been the high blanks obtained, incomplete extraction, the strong influence of interfering elements and the fact that the popular methods are tedious. The influence of interfering elements could be minimised or eliminated more conveniently by solvent extraction rather than by a time-consuming distillation procedure. As a means of separating boron from interfering elements, the extraction of the tetrafluoroborate of onium compounds appears to be complete and more convenient to use.

A critical examination of the colorimetric procedure for the determination of boron involving solvent extraction of the tetrafluoroborate of onium compounds followed by a colorimetric finish with a dye was carried out with dyes which hitherto have not been reportedly used for this method. A whole range of dyes were tested with the aim of selecting a suitable one for the determination of boron in steel.

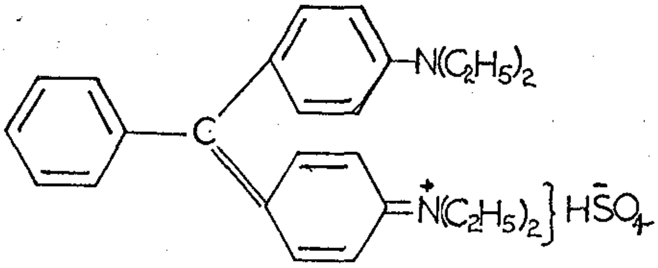
In carrying out the experiments, special attention was paid to the spectral characteristics of the dye-fluoroborate complex in the extracts, apparent molar absorptivities, the values of the blanks, adherence to Beer's law and the reproducibility of results. The spectral characteristics of each dye-fluoroborate complex in the extract were compared with those of the dye itself, with a view of detecting any overlapping of the spectra. This comparison of the spectra in conjunction with the values obtained for the blanks was used in arriving at some conclusions about the suitability of each dye for the determination of boron. Beer's law plots were constructed over a chosen range and the mean apparent molar absorptivity was calculated on the basis of the results of the Beer's law plot.

The procedure involved in each case was simple. To an aliquot of standard sodium tetrafluoroborate solution in a 100ml polyethylene separating funnel was added an aliquot of tetraphenylarsonium chloride solution of comparable concentration. Silver acetate solution was added to precipitate chloride ions because excess tetraphenylarsonium chloride is extracted by chloroform if chloride ions were not removed. The tetraphenylarsonium-fluoroborate complex formed was then extracted with chloroform. The extracted complex was transferred to another polyethylene separating funnel containing 5-10ml of water and the dye or coloured compound. The mixture was shaken in order to replace the tetraphenylarsonium ion component of the complex in the extract, with the dye ion. The dye-fluoroborate complex formed was filtered into a 10 or 25ml. volumetric flask and diluted to the appropriate volume with the organic solvent. Some quantity of the solution was transferred to a 1cm cell and the absorbance measured. It was found that a change in the chromogenic reagent used affected not only the colour of the complexes formed but also their solubilities in organic solvents, thus whenever extraction with chloroform gave unacceptable results, other organic solvents were tried. Extraction of the dye-fluoroborate complexes was also carried out at different pH values. Blanks were determined for each of the selected experimental conditions.

All measurements were carried out on a Unicam SP8000 recording spectrophotometer or a Unicam SP600 spectrophotometer whichever was appropriate for the data required. Double distilled water was used throughout. Polyethylene vessels were employed. No attempt at purification of the dyes was made, the dyes were used as supplied by the makers.

RESULTS

BRILLIANT GREEN (BASIC GREEN 1) C.I. 42040



As shown on Table 9, intolerably high blanks were obtained with all the solvents tested except benzene. Babko and Marchenko[51] had studied the extraction of brilliant green-fluoroborate complex with benzene and noted that the extraction was only 60% complete. With this in mind, it was felt that any procedure involving the extraction of brilliant green-fluoroborate complex with benzene would not only give incomplete extraction (less than 100%) but would also not be entirely new.

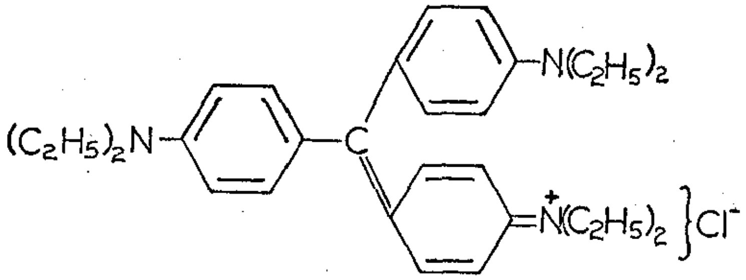
Table 9

0.05% Brilliant green solution in ethanol was used and the sample contained 10µg of boron as BF_4^-

λmax = 640nm

pH of aqueous phase	Organic Solvent	Absorbance		Net Absorbance
		Sample	Blank	
2-4.5	Carbon tetrachloride	0.045	0.045	-
2-4.5	Chlorobenzene	>2	>2	-
2-4.5	Chloroform	>2	>2	-
2-5.0	Isoamylalcohol	>2	>2	-
2-4.5	Cyclopentanone	>2	>2	-
2-4.0	Quinoline	>2	>2	
2-5.0	Toluene	0.57	0.13	0.34
3.5	Benzene	1.70	0.03	1.67
2-4.5	Cyclohexane	0.06	0.06	-
2-4.5	Diethyl ether	0.165	0.160	0.005

ETHYL VIOLET (BASIC VIOLET 4) C.I. 42600



Results obtained are shown on Table 10. High blanks were obtained with the different solvents tried, in spite of the wide variation in pH.

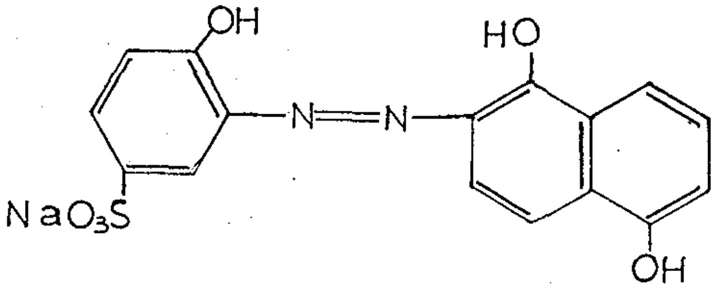
Table 10

0.1% Ethyl violet solution in water was used and the sample solution contained 20µg of boron as BF_4^-

λmax = 600nm

pH of aqueous phase	Organic Solvent	Absorbance		Net Absorbance
		Sample	Blank	
1.66	Benzene	0.145	0.030	0.115
3.64	"	0.23	0.10	0.13
6.41	"	0.48	0.55	-0.07
3.60	Chlorobenzene	0.00	1.5	-1.5
3.60	Chloroform	0.00	>2	
3.60	Toluene	0.08	0.04	0.04

SOLOCHROME BLACK PV200 (Mordant Black 9) C.I. 16500



The absorption spectrum of the tetraphenylarsonium - solochrome black complex showed three well defined peaks at 380nm, 482nm and 518nm respectively, but as the results in Table 11 show, high blanks were obtained at each of these wavelengths of maximum absorbance.

Table 11

The Complex was extracted with chloroform
An aliquot of 10^{-2}M solochrome black solution in
water was used. pH of aqueous phase 4.0

λmax (nm)	Concentration of *TPA$^+$	Absorbance		Net Absorbance
		dye - TPA complex	Blank	
380	2×10^{-5}M	0.340	0.100	0.240
	4×10^{-5}M	0.450		0.350
482	2×10^{-5}M	0.245	0.130	0.115
	4×10^{-5}M	0.290		0.160
518	2×10^{-5}M	0.240	0.145	0.095
	4×10^{-5}M	0.280		0.135

*TPA$^+$ = tetraphenylarsonium ion

SEVRON RED L (Basic Red 17)

The structure of Sevron Red L, which is a monoazo dye has not been released by the manufacturers, (E.I. Du Pont de Nemours & Co., Wilmington, Delaware, U.S.A.).

Very low absorbance values were obtained as shown in Table 12. The results showed that the complex was not very soluble in the organic solvents tested. In other words, the extraction of the complex was far from being complete.

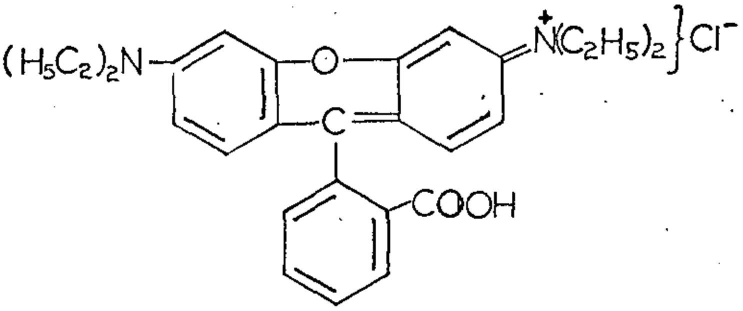
Table 12

0.05% Sevron Red L solution in water was used and the sample contained 20µg of Boron as BF_4^-

$\lambda max = 475nm$

pH of aqueous phase	Organic Solvent	Absorbance		Net Absorbance
		Sample	Blank	
1.5	Chloroform	0.115	0.070	0.045
3.5	"	0.145	0.058	0.087
3.5	Benzene	0.030	0.030	Nil
3.5	Chlorobenzene	0.090	0.040	0.050
4.0	Toluene	0.020	0.020	Nil

RHODAMINE B (Basic Violet 10) C.I. 45170



With Rhodamine B, very low absorbance values were also obtained and these are shown in Table 13. It appeared that the dye-fluoroborate complex was not extracted completely into the organic solvents tested, in spite of the variation in pH.

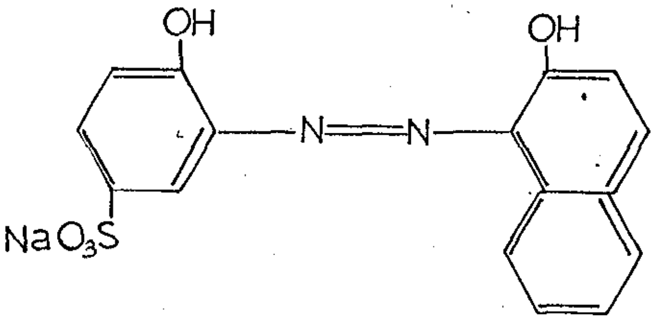
Table 13

0.1% of Rhodamine B solution in water was used and the sample solution contained 10µg of boron as BF_4

λmax = 555nm

pH of aqueous phase	Organic Solvent	Absorbance		Net Absorbance
		Sample	Blank	
1.40-1.47	Benzene	0.195	0.060	0.135
4.0	Toluene	0.070	0.050	0.020
1.4	"	0.030	.020	0.010
3.3	Chloroform	> 2	> 2	
4.5	"	1.70	0.98	0.72

SOLOCHROME VIOLET (Mordant violet 5) C.I. 15670



Preliminary experiments with chloroform, dichlorobenzene, benzene, toluene, ethyl acetate and nitrobenzene showed that only chloroform was suitable for the extraction of the solochrome violet-tetraphenylarsonium ion complex and even then low absorbance values were obtained as shown in Table 14 . In the presence of fluoroborate ion, still lower absorbance values were obtained. In addition, the absorbance of the solochrome violet-tetraphenylarsonium complex was found to increase with time but became steady after 30 minutes (see Table 15). The blank did not exhibit any change in absorbance with time. It appears from the observed phenomenon that the rate of formation of the solochrome violet-tetraphenylarsonium complex was slow. This was a disadvantage which made the procedure based on the use of solochrome violet inferior to some of the existing colorimetric methods for the determination of boron.

Table 14

Aliquots of 10^{-2}M Solochrome violet solution in water was used and the complex was extracted with chloroform.
pH of aqueous phase 3.5

λmax = 480nm

Concentration of TPA$^+$ Dye	Absorbance		Net Absorbance	Apparent Molar Absorptivity, ε ($l.mol^{-1}cm^{-1}$)
	Sample	Blank		
1×10^{-5}M	0.175	0.035	0.140	14,000
2×10^{-5}M	0.350	0.035	0.315	15,700
4×10^{-5}M	0.670	0.035	0.635	15,900

*TPA$^+$ = tetraphenylarsonium ion

Table 15

λmax = 480nm

Time (mins)	Concentration of TPA$^+$ Dye complex	Absorbance		Net Absorbance	Apparent Molar Absorptivity, ε ($l.mol^{-1}$ cm^{-1})
		Sample	Blank		
5	1×10^{-5}M	0.065	0.044	0.021	2,100
	2×10^{-5}M	0.160		0.116	5,800
20	1×10^{-5}M	0.078	0.045	0.033	3,300
	2×10^{-5}M	0.330		0.285	14,250
30	1×10^{-5}M	0.100	0.045	0.055	5,500
	2×10^{-5}M	0.420		0.375	19,000

POTASSIUM THIOCYANATE

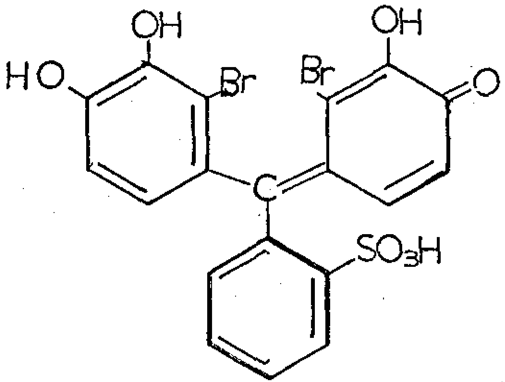
An unsuccessful attempt was made to utilise the anion formed between potassium thiocyanate and iron (III) chloride as a chomogenic reagent. In the attempt, two procedures were adopted: A direct method involving the extraction of iron (III) thiocyanate-tetrafluoroborate complex with dichlorobenzene gave rise to very high blanks. The second method which involved the extraction of tetraphenylarsonium-tetrafluoroborate complex with dichlorobenzene followed by the replacement of the tetraphenylarsonium ion by the divalent iron (III) thiocyanate ion also gave rise to high blanks (see Table 16). In addition, the absorbances of the blanks and sample solutions increased with time and became steady at the same value after about 25 minutes. Moreover, the colour of the iron (III) thiocyanate-tetrafluoroborate extract faded after standing for 1 hour. Obviously, some reaction which interferes greatly with the procedure was taking place.

Table 16

Absorbances of tetraphenylarsonium-fluoroborate complex λmax = 510nm. Each sample solution contained the amount of boron as BF_4^- shown on the table

Time in minutes	Blank	4µg	6µg	8µg
0	0.06	0.13	0.16	0.205
5	0.12	0.27	0.285	0.40
10	0.20	0.34	0.335	0.42
15	0.32	0.345	0.40	0.43
20	0.40	0.360	0.42	0.43
25	0.43	0.43	0.45	0.43

BROMOPYROGALLOL RED (Dibromopyrogallol sulphonphthalein)



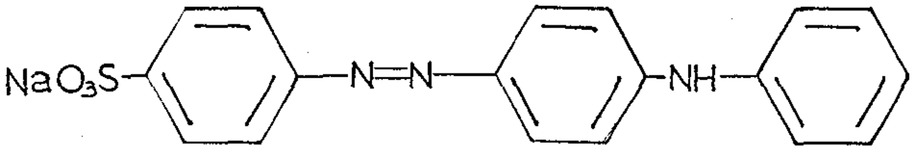
Bromopyrogallol red in the presence of ammonium acetate and EDTA was tested and found to be unsuitable. Ammonium acetate solution (20%) was used as a buffer and EDTA solution was incorporated into the solution as a masking agent for cations which will interfere by reacting with bromopyrogallol red, especially if the method was to be applied to the analysis of steel. While a slight excess of bromopyrogallol red gave reasonable results, a fortyfold excess gave rise to a red precipitate which left the organic solvent completely devoid of any colour. However, in cases where otherwise satisfactory results were obtained, the extraction was found to be between 54 and 62% complete. When the procedure was applied to some steel samples, a violet precipitate was obtained. Measurement of the absorbance of what was left in the extracts showed that the extraction was only about 34% complete. The formation of a precipitate in the presence of excess of bromopyrogallol red tends to suggest that the colour of the extract is dependent on the formation of a precipitate which is not very soluble in the organic solvents used. But it is difficult to say without further investigation whether the precipitation is due to the adsorption of excess bromopyrogallol red ions on the tetraphenylarsonium-bromopyrogallol red complex or vice versa. On the other hand, precipitation may be a straight forward case of insolubility of the bromopyrogallol red itself.

ORANGE IV

Experiments with Orange IV proved successful and details of the investigations carried out are described in the next section.

IV. DEVELOPMENT OF A PROCEDURE FOR THE DETERMINATION OF BORON WITH ORANGE IV.

ORANGE IV (TROPAEOLIN OO) C.I. 13080



Preliminary investigations were conducted with some "onium" compounds with a view of selecting the onium ion - orange IV ion association complex capable of satisfying most of the conditions required for a successful development of the procedure. For instance, the formation constant of the onium ion - orange IV complex should be greater than that of the onium ion - fluoroborate complex. In addition the complex should be stable and it should be highly soluble in chloroform.

3ml each of 10^{-4}M tetraphenylarsonium chloride, tetraphenylphosphonium chloride, tetrabutylphosphonium chloride and (methyl)-triphenylphosphonium bromide solutions were pipetted into different separating funnels containing 5ml of 5×10^{-4}M orange IV solution. Each onium ion - orange IV complex was extracted with 10ml of chloroform. The extracts were filtered into standard volumetric flasks and diluted to definite volumes with chloroform. The absorbance of each extract was measured with chloroform as reference and the apparent molar absorptivities calculated. Blanks (i.e. solutions containing no onium compound) were also determined. The results are shown on Table 17.

Table 17

Absorbances of onium ion - orange IV complexes

Onium Compound	λ_{max} (nm)	Absorbance		Net Absorbance	Apparent molar absorptivity, ε ($l\ mol^{-1}\ cm^{-1}$)
		Sample	*Blank		
Tetraphenylarsonium chloride	405	0.960; 0.955 0.960	0.015	0.945; 0.940 0.945	31,500; 31,300 31,500
Tetraphenylphosphonium chloride	408	0.665; 0.670 0.665	0.001	0.664; 0.669 0.664	55,200; 55,700 55,200
Tetrabutylphosphonium chloride	408	0.585; 0.590 0.590	0.001	0.584; 0.589 0.589	48,750; 49,000 49,000
(methyl)-Triphenyl-phosphonium bromide	408	0.300; 0.305 0.305	0.000	0.300; 0.305 0.305	10,000; 10,000 10,000

*Average of three readings

The usual methods for determining formation constants through the application of the law of mass action were not used here. It is doubtful if the simple mass-action equation will adequately describe the reactions taking place in the water-chloroform interface. With the exception of a few cases, the state of solutes in organic solvents rarely satisfy the requirements of ideal behaviour under which the law of mass action is usually applied. However, on the basis of the values of the molar absorptives, tetrabutylphosphonium chloride and tetraphenylphosphonium chloride were considered to be reagents likely to give good results. In order to confirm this, the experiments were repeated. Separate mixtures of equimolar solutions of tetrafluoroborate and the onium compounds were extracted with chloroform. The extracts were transferred to different separating funnels containing the same amount of orange IV solution as before. These mixtures were shaken in order to replace the tetrafluoroborate ion with the orange IV anion. The absorbances of the onium ion - orange IV complexes were then measured as before. The results obtained are shown on Table 18. Tetraphenylarsonium ion showed a slight decrease in the apparent molar absorptivity but on the basis of sensitivity, tetraphenylphosphonium ion was chosen as the most suitable onium ion.

Table 18

Results of the extraction of onium ion-tetrafluoroborate complex followed by replacement of the tetrafluoroborate ion by orange IV anion

Onium Compound	λmax (nm)	Absorbance		Net Absorbance	Apparent Molar Absorptivity, ε ($l.mol^{-1}$ cm^{-1})
		Sample	*Blank		
Tetraphenylarsonium chloride	405	0.385; 0.385 0.390	0.004	0.381; 0.381 0.386	25,300; 25,300 26,000
Tetraphenylphosphonium chloride	408	0.880; 0.905 0.915	0.002	0.878; 0.903 0.913	29,300; 30,000 30,500
Tetrabutylphosphonium chloride	408	0.750; 0.740 0.750	0.003	0.747; 0.737 0.747	25,000; 24,600 25,000
(Methyl)-Triphenyl phosphonium bromide	408	0.285; 0.290 0.285	0.000	0.285; 0.290 0.285	9,500; 9,700 9,500

*Average of three readings

OPTIMISATION OF EXPERIMENTAL CONDITIONS

After tetraphenylphosphonium chloride had been chosen, attempts were made to improve the overall sensitivity of the method. The results in Table 18 show a dramatic fall in the value of the apparent molar absorptivity of the tetraphenylphosphonium - orange IV complex. There are two possible explanations for this decrease: the first is that the high absorbance and hence high apparent molar absorptivity of the onium ion -

orange IV complexes, in the absence of tetrafluoroborate ion, might be due to the presence of excess onium compound in the chloroform extract. Bock and Beilstein,[60] and Bock and Jainz,[61] in detailed studies of the solubilities of tetraphenylarsonium and tetraphenylphosphonium ions, respectively, in chloroform, showed that up to 15% tetraphenylarsonium - and tetraphenylphosponium chlorides were easily extracted into chloroform. It is therefore possible that 15% of the tetraphenylphosphonium ion that complexed with orange IV in the absence of tetrafluoroborate ion, passed into the organic phase as chloride. Attempts to remove chloride ions by adding silver acetate solution were unsuccessful. Instead of increasing, the absorbances of the solutions decreased further. A possible explanation for this is that silver ions formed soluble complexes with chloride ions, thereby re-introducing chloride ions and possibly other negatively charged complex ions into solution.

The second possible explanation for the decrease in absorbance, observed in the presence of tetrafluoroborate ion, may be hydrolysis of tetrafluoroborate ion. Hydrolysis of tetrafluoroborate would reduce the amount of tetrafluoroborate ions available for complexation with tetraphenylphosphonium ions and result in only a small amount of the tetraphenylphosphonium-fluoroborate complex being formed and extracted. Consequently, the amount of tetraphenylphosphonium ions available for complexation with orange IV anion would be small. Two alternative attempts were made to remedy the situation. The first attempt involved decreasing the pH of the solution containing tetraphenylphosphonium and tetrafluoroborate ions prior to extraction, by the addition of IM sulphuric acid solution. This was done in order to minimise or stop the hydrolysis of tetrafluoroborate and thus ensure that all the tetrafluoroborate ions in solution were available for complexation with tetraphenylphosphonium ions. The alternative attempt was to accelerate the hydrolysis of tetrafluoroborate after it had been extracted as the tetraphenylphosphonium-fluoroborate complex, thus releasing all tetraphenylphosphonium ions for complexation with orange IV anions. This was done by adding 1M sodium hydroxide solution to the extract and neutralising it with 1M sulphuric acid at the end of a period of time (5 minutes to 2 hours). In both attempts, blue precipitates were obtained and the absorbances of the extracts were about half what they should be.

Having failed to establish any link between the low absorbances of the onium ion - orange IV complexes (in the presence of tetrafluoroborate ions), the hydrolysis of tetrafluoroborate and the presence of chloride ions in the mixtures, attention was turned to checking the repeatability of the extraction of the tetraphenylphosphonium-fluoroborate complex with chloroform.

REPEATABILITY OF THE EXTRACTION OF TETRAPHENYLPHOSPHONIUM - FLUOROBORATE COMPLEX WITH CHLOROFORM

A UV spectrophotometric method was utilised to determine the repeatability of the extraction of tetraphenylphosphonium-fluoroborate complex with chloroform. 10ml each of 10^{-3}M tetraphenylphosphonium solution were pipetted into ten different separating funnels containing 5ml of 2 x 10^{-4}M tetrafluoroborate solution and 5ml of water. The tetraphenylphosphonium-fluoroborate complex formed was extracted with 10ml of chloroform and the extracts filtered into different 25ml volumetric flasks. The extracts were diluted to 25ml with chloroform. The UV spectra of one of the solutions was recorded using a Unicam SP8000 recording spectrophotometer and well-defined peaks were obtained at 269 and 276nm. The UV absorbances of the ten solutions were then measured at 269 and 276nm. The coefficients of variation of the results at 269nm was 1.9% and that at 276nm was 2.4%. Compared with published data,[62] the molar absorptivities obtained represent the fact that 100% of the tetraphenylphosphonium-fluoroborate complex was extracted into chloroform.

PROCEDURE FOR THE DETERMINATION OF BORON WITH ORANGE IV

APPARATUS: Unicam SP8000 and SP600 spectrophotometers with 1cm silica cells. Polyethylene measuring cylinders, separating funnels, pipettes and beakers. Radiometer PHM64 Research pH meter.

REAGENTS: Use double distilled water throughout and analytical grade reagents. Prepare all reagent solutions in plastic or polyethylene vessels and transfer immediately to polyethylene bottles or other polyethylene containers with screw closures.

Boron stock solution; $135\mu g.ml^{-1}$: Dissolve 0.7723g of boric acid in water and dilute to 1 litre in a volumetric flask.

Hydrofluoric acid solution 5%. Carefully add 12.5ml of 40% hydrofluoric acid solution to 70ml of water in a polyethylene beaker, transfer the solution to a polyethylene volumetric flask and dilute to 100ml with water.

Concentrated Standard tetrafluoroborate solution $2.5 \times 10^{-4}M$, Pipette 5ml of the boron stock solution into a polyethylene bottle, add 20ml of water and 8ml of 5% hydrofluoric acid solution. Mix and let stand for 24 hours. Transfer the solution to a volumetric flask and dilute to 250ml with water. Store in a polyethylene bottle.

Dilute Standard tetrafluoroborate solution 2.5×10^{-5}M. Pipette 10ml of the concentrated tetrafluoroborate solution into a 100ml polyethylene volumetric flask. Add 1ml of 5% hydrofluoric acid solution and dilute the mixture to 100ml with water. Prepare this solution fresh whenever needed.

Tetraphenylphosphonium solution 5×10^{-4}M. Dissolve 0.1874g of tetraphenylphosphonium chloride in water and dilute to 1 litre with water. Store in a polyethylene bottle.

Orange IV solution 5×10^{-4}M. Dissolve 0.0939g of orange IV powder (Tropaeolin OO) in 100ml of water. Filter through a glass filter and dilute to 500ml with water. Store in a polyethylene bottle.

Chloroform, analytical reagent grade.

Procedure. Pipette an aliquot (1-5ml) of the concentrated standard tetrafluoroborate solution (Note 1) into a polyethylene separating funnel containing 5ml of 5×10^{-4}M tetraphenylphosphonium chloride solution. Dilute the mixture to 10ml with water (if necessary). Extract the tetraphenylphosphonium-fluoroborate complex by shaking the mixture with 10ml of chloroform for 1-2 minutes. Allow the phases to separate and transfer the organic layer to another polyethylene separating funnel containing 10ml of water and 5ml of 5×10^{-4}M Orange IV solution. Repeat the extraction of the tetraphenylphosphonium-fluoroborate complex with a further 10ml of chloroform and transfer the extract to the second separating funnel. Shake this second separating funnel for 2 minutes. Allow the phases to separate. Filter the organic layer through a Whatman 41 filter paper, into a 25ml volumetric flask. Dilute to 25ml with chloroform (Note 2), mix and measure the absorbance of the extract at 408nm using a blue-sensitive photocell with chloroform as reference, in a 1cm cell. Treat the blank (containing no aliquots of the tetrafluoroborate solution) in a similar manner. Obtain the net absorbance by subtracting the blank. To construct a calibration graph, plot absorbance against concentration of boron.

Notes

1. Use the dilute standard tetrafluoroborate solution for lower ranges of boron (less than 0.3 $\mu g.ml^{-1}$).

2. In the lower range of boron (i.e. when dilute standard tetrafluoroborate solution is used), no dilution is needed but the volume of chloroform used for extraction must be measured accurately with a pipette. Filter the coloured extract into a 1cm cell directly.

RESULTS AND DISCUSSION

Fig. 33 shows the spectrum of the tetraphenylphosphonium tetrafluoroborate ion-association complex after the replacement of the BF_4^- component with orange IV anion. For maximum sensitivity of the procedure, the absorbances of the extracts were measured at 408nm. A typical calibration graph is shown in Fig. 34. The slope of the graph shows that the apparent molar absorptivity is 30,000l.mol.$^{-1}$cm^{-1}. Table 19 shows the results obtained at the 10^{-5}M level of boron in aqueous solution. The coefficient of variation for ten determinations at the 1×10^{-5}M BF_4^- level was found to be 1.3%.

Table 19

Results obtained for the determination of boron at the 10^{-5}M level.

Final Concentration of BF_4^-	Absorbance at $\lambda =$ 408nm
0	0.001, 0.003, 0.002
1×10^{-5}M	0.305, 0.300, 0.365
2×10^{-5}M	0.580, 0.600, 0.610
3×10^{-5}M	0.880, 0.905, 0.880
4×10^{-5}M	1.210, 1.220, 1.205
5×10^{-5}M	1.500, 1.510, 1.490

Investigations carried out with 5×10^{-3}M Orange IV solution showed no increase in the blank neither were the results significantly different from those obtained with 5×10^{-4}M Orange IV solution. Higher concentrations of Orange IV solution were not used because such amounts of Orange IV were not completely soluble in water at room temperature (22°C).

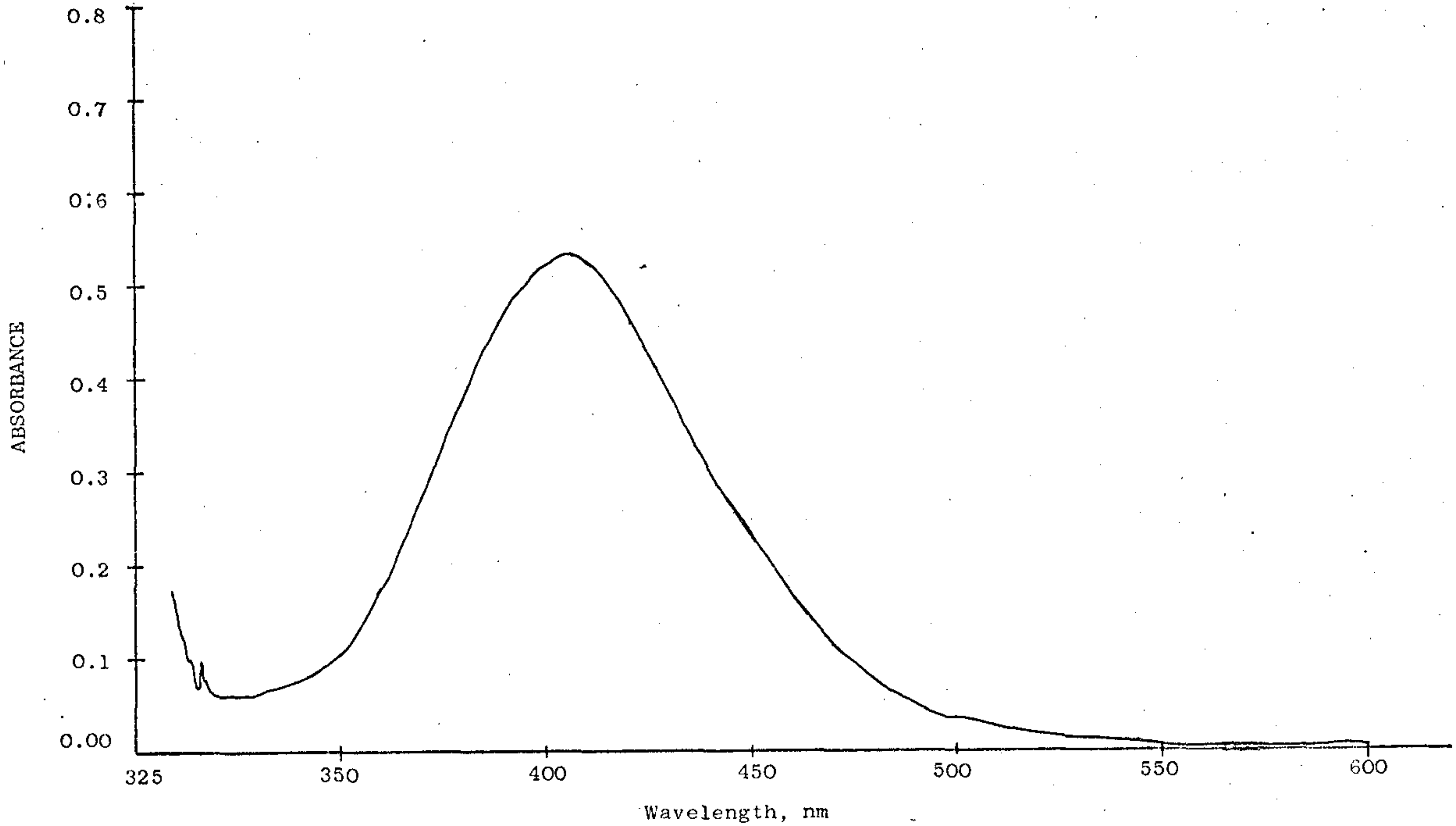


Fig. 33. Spectrum of the final extract of the TPP$^+$-BF$_4^-$-Orange IV system (i.e. spectrum of TPP$^+$-Orange IV extract) obtained with a Unicam SP8000 UV Recording Spectrophotometer. Solvent in the Reference Cell was CHCl$_3$ Path length 10mm, Scan Speed, Fast. Absorbance range 0-1.0A.

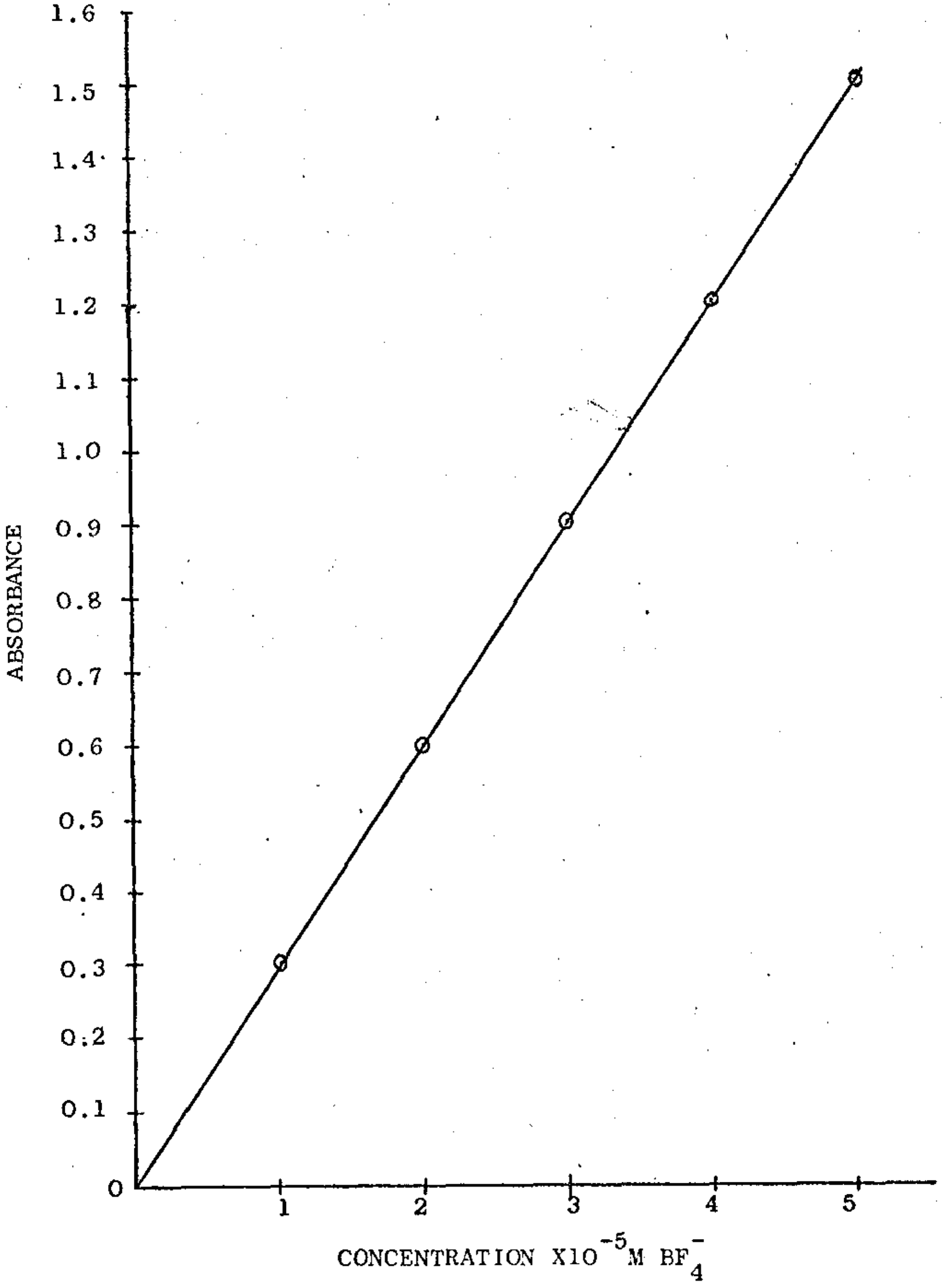


Fig. 34: Calibration graph for the determination of boron with Orange IV. λmax = 408nm.

V. APPLICATION OF THE METHOD DEVELOPED TO THE DETERMINATION OF BORON IN STEEL

Most of the current colorimetric methods for the determination of boron in steel involve preliminary separation of boron from the sample matrix because of the strong influence of interfering elements. In attempts to eliminate the effects of interferences, tedious and time-consuming separation techniques such as distillation and ion-exchange chromotography have been employed, thus making the methods unsuitable for routine application. It was the aim of the present study to develop a colorimetric method for the determination of boron in steel which did not require any preliminary separation step and thus would be suitable for routine application. It was considered that the isolation of the onium salt of tetrafluoroborate by extraction with a suitable organic solvent would not only simplify the method but also eliminate the effects of interfering elements. In addition, it would improve the accuracy and precision of the method. Preliminary investigations described in the last chapter have shown that complete extraction of tetraphenylphosphonium tetrafluoroborate ion-association complex is achieved easily. The colorimetric method for the determination of boron with Orange IV which was described in the last chapter was applied directly to some steel samples. The aim was to determine acid-soluble boron in steel and the dissolution of the steel samples was carried out using essentially the method given in the British Standard.

PRINCIPLE

The steel sample is dissolved in dilute sulphuric acid by heating under reflux. Hydrogen peroxide is added and any insoluble residue is removed by filtration. An aliquot of the filtrate is treated with ammonium hydrogen difluoride solution. The tetrafluoroborate ion (BF_4^-) which is formed is extracted into chloroform as an ion-association complex in which the cation is tetraphenylphosphonium (TPP^+). The BF_4^- in the extract is then replaced by Orange IV anion and the determination is completed colorimetrically.

APPARATUS

1. Boron free glassware should be used for the solution of the sample.
2. Reflux Air Condenser: A 76cm x 3mm internal diameter glass tube with rubber bung to fit a 100ml conical flask.
3. Polyethylene bottles, 100ml capacity, fitted with polyethylene stoppers, and polyethylene beakers, measuring cylinders, standard flasks and pipettes.
4. A Unicam SP600 spectrophotometer was used together with 1cm silica cells.

REAGENTS

Sulphuric acid solution (20% $^v/v$)

To 500ml of water add, cautiously, 200ml of analytical reagent grade sulphuric acid (sp.gr. 1.84). Mix, cool, dilute to 1 litre with water and mix thoroughly.

Hydrogen peroxide "100 volume" analytical reagent grade.

Ammonium hydrogen difluoride, 2M

Dissolve 57.04g of analytical reagent grade ammonium hydrogen difluoride ($NH_4F.HF$) in water and dilute to 500ml with water. Store in a polyethylene bottle.

Transfer the extract to another polyethylene separating funnel containing 5ml of 5 x 10^{-4}M Orange IV solution and 10ml of water. Shake the mixture for about two minutes to replace the BF_4^- component of the tetraphenylphosphonium tetrafluoroborate ion-association complex with Orange IV anion.

Tetraphenylphosphonium solution, 1 x 10^{-3}M

Dissolve 0.3749g of tetraphenylphosphonium chloride $\left\{(C_6H_5)_4PCl\right\}$ in water and dilute to 1 litre with water. Store in a polyethylene bottle.

Chloroform. analytical reagent grade.

Orange IV solution, 5 x 10^{-4}M

Dissolve 0.0939g of Orange IV powder (Tropaeolin OO) in 100ml of water. Filter through a glass filter and dilute to 500ml with water. Store in a polyethylene bottle.

PROCEDURE

Weigh 0.5 - 1.0g of sample and transfer to a 100ml conical flask. Add 25ml of sulphuric acid solution (20% $^v/v$), insert the reflux condenser and digest just below boiling point until solvent action ceases. Add 2ml of hydrogen peroxide (100 vol.) to oxidise carbides etc. Heat gently for about 30 minutes to expel excess hydrogen peroxide. Cool, disconnect and rinse the condenser with 2-3ml of water. Filter the solution through a Whatman No. 540 filter paper into a 50ml standard polyethylene flask and wash the residue with the minimum amount of sulphuric acid (20% $^v/v$). Dilute the filtrate to 50ml with water. Pipette 5ml of the steel solution into a polyethylene beaker and add 2ml of 2M ammonium hydrogen difluoride solution. Allow the solution to stand for 30 minutes to enable the tetrafluoroborate ion to form. Transfer the solution to a polyethylene separating funnel. Rinse the beaker with 3ml of water and add the washing to the solution in the separating funnel. Add 5ml of the tetraphenylphosphonium chloride solution into the separating funnel. Extract the tetraphenylphosphonium tetrafluoroborate ion-association complex with two 10ml portions of chloroform by shaking for two minutes. → Allow the layers to separate and then filter the organic layer into a

25ml standard flask. Dilute the filtrate to 25ml with chloroform and then measure the absorbance of the solution at 408nm using a 1cm cell.

RESULTS AND DISCUSSION

Table 20 shows the results obtained for two steel samples analysed by the method described. The percentages of boron found were obtained with reference to the calibration graph on Fig. 34. Compared with the standardised values, the values obtained are about three to four times greater. Obviously, the influence of interfering elements is quite pronounced and this detracts from the main objective of the study which was to develop a direct method for the determination of boron in steel without preliminary separation.

Table 20

Results obtained for the determination of boron in British chemical standards steel samples.

Steel	Absorbance at λmax = 408nm		Boron Found	Standardised value
	Sample	*Blank	(%)	(%)
BCS 326	0.420 0.530 0.490	0.002	0.0028 0.0040 0.0033	0.001
BCS 329	0.910 0.925 0.900	0.002	0.024 0.025 0.024	0.008

*Average of three readings.

It appears that the extraction of tetraphenylphosphonium tetrafluoroborate with chloroform failed to separate boron completely from other elements in the sample matrix. The high results obtained may be attributed to two reasons. One is that MnO_4^-, $Cr_2O_7^=$, AsO_4^{3-} and PO_4^{3-} which were formed during the dissolution of the steel samples were co-extracted with BF_4^- as ion-association complexes with tetraphenylphosphonium as the cation. These anions were subsequently replaced also by Orange IV anion in the final stage of the procedure. The second reason may be that Cr(III), Mn(III), Ta(V), Fe(III) etc. which form strong anionic fluoro complexes in the presence of excess hydrofluoric acid or fluoride might have been extracted into chloroform as their ion-association complexes with tetraphenylphosphonium ion. Thus in the subsequent replacement of the BF_4^- component of the tetraphenylphosphonium tetrafluoroborate ion-association complex, these anionic fluoro components were also replaced. There was no evidence to support any of these assumptions. It would therefore be desirable to carry out a systematic investigation of the effects of interfering elements.

VI. CONCLUSION

The results of this study show that boron could be determined in aqueous solution using orange IV as a colorimetric reagent. The precision of the determination is good and the reagent is sensitive enough for accurate determination of boron in aqueous solution. Though, in its present form, it is not applicable to the analysis of steel samples, it is considered that other areas of application would be feasible. For instance, it may be applicable for the determination of boron in water, plants and soil.

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GENERAL DISCUSSION

The object of the present study was to evaluate two new electroanalytical instrumentation, the PAR 174 Polarographic Analyzer and PAR 173/179 digital coulometer for the purposes of steel works chemical analysis and if possible to develop sensitive analytical procedures for the determination of some selected elements in steel. These objectives have, in the main, been achieved. Two sensitive electroanalytical methods were developed for the determination of silicon and iron in steel and iron ore samples respectively, and although the colorimetric method which was developed for the determination of boron was unsuccessful when applied to steel analysis.

Two pulse polarographic procedures were developed for the determination of silicon: one for levels of silicon above $0.02\mu g.ml^{-1}$ and the other for nanogram amounts of silicon. The two procedures together provide a sensitive, precise and accurate method for the determination of silicon in steel. The method has a number of advantages particularly for the determination of very low levels of silicon in steel. With the growing complexity of steel making, it might soon be necessary to determine silicon at levels much lower than the detection limits of the current colorimetric methods for the determination of silicon in steel. The pulse polarographic method developed in this study would allow, if required, low levels of silicon in steel to be determined with high precision and accuracy. It would be of particular value for the determination of trace amounts of silicon in high-purity iron, mild steel, cast iron and low alloy steels.

Perhaps, a disadvantage of the method developed in the present study, is the need to remove iron and other interfering elements by mercury cathode electrolysis. The reason(s) why iron interferes is not known but it has been shown that the reduction of iron(III) produces a large polarographic wave which tends to swamp waves due to other elements. In the present study no polarographic wave was observed for the reduction of iron(III) but the presence of iron(III) in the solution to be polarographed resulted in the β-12-molybdosilicate wave being suppressed completely.

However, the removal of interfering elements by mercury cathode electrolysis is not entirely new in steel analysis. It is used for separating major amounts of interfering elements before aluminium in steel is determined by titrimetry or colorimetry.[1] Besides, mercury cathode electrolysis is a very efficient separation technique for removing large amounts of interfering elements.

Despite the need for prior removal of interfering elements from sample solutions before the polarographic determination of silicon, it is hoped that the pulse polarographic method developed in the present study will prove very useful for determining silicon in steel because of its sensitivity, accuracy and precision. In addition, the PAR 174 Polarographic Analyzer may prove useful in steelworks laboratories for the examination of diverse types of materials because of its versatility, relatively low cost and the fact that it can be used for the determination of trace amounts of elements, as the results of the present study show.

A few examples of controlled-potential coulometric determination of iron at a mercury pool electrode have been reported in the literature.[2] It does not appear, however, that any method for the determination of iron in iron ores by controlled-potential coulometry which involves prior separation of iron by solvent extraction has been reported. The results obtained in the present study clearly establish the value of the solvent extraction - coulometric procedure as a precise analytical method. Using a commercially available low cost instrumentation such as the PAR 173/179 digital coulometer, the coefficient of variation for the coulometric determination of iron in iron ores in oxalate buffer was about 0.3%. The present coulometric method can also be utilised for routine analysis without any loss in precision and accuracy. It therefore has a number of advantages which would be of practical value to any large steelworks laboratory. In addition, the procedure can be automated, thus speeding up the entire process of analysis of iron ores in metallurgical laboratories.

Although the procedure which involved pipetting aliquots of iron ore sample solution directly into the coulometric cell was equally precise, the question of the effect of interfering elements still needs to be solved. It may be advisable to carry out a systematic study of the effects of interfering elements with the aim of identifying precisely these interfering elements and if possible, to establish their tolerance levels.

Though the results obtained by the procedure involving the use of thallium(I) as internal standard indicated that the procedure was not as precise as the other two, the fact that some meaningful results were obtained suggest that high precision may be obtained if only a suitable internal standard can be found. An element whose reduction potential, in oxalate solution, at a mercury electrode is much more negative than thallium, for example, and whose reduction is not coulometrically reversible, may be suitable as an internal standard. This is because it would make it easier for the reduction potential of iron(III) to be selected accurately. In the present study, one of the difficulties encountered was in selecting a suitable applied potential for the reduction of iron(III) in the presence of thallium(I).

On the whole, the controlled-potential coulometric method developed in the present study has some advantages over the current classical titrimetric method for the determination of iron in iron ores because it is simple, accurate and precise, and could be used for routine analysis.

A procedure was also developed in the present study for the determination of boron in aqueous solution using orange IV. The results obtained by the method showed that the method was sensitive and may prove advantageous for the determination of boron in aqueous solution. Unfortunately, the method could not be applied directly to the analysis of steel samples because of interference from other constituents of steel. It is therefore be necessary to carry out a thorough investigation of the effects of interfering elements on the method. Bock and Jainz[3] in a detailed study of the extraction of some ions from aqueous solution with tetraphenylphosphonium ion had reported that chloride, dichromate, permanganate, nitrate and to some extent, arsenate and phosphate were readily extracted into chloroform. The high results obtained with steel samples by the colorimetric method developed here, tends to suggest that Cl^-, NO_3^-, $Cr_2O_7^-$, MnO_4^-, AsO_4^{3-} and PO_4^{3-} might have been co-extracted with BF_4^-. Thus the subsequent replacement of BF_4^- by Orange IV anion could have also involved the replacement of the co-extracted anions (with orange IV).

During the course of the development of the colorimetric method for the determination of boron, the repeatability of the extraction of BF_4^- with tetraphenylphosphonium ion was tested by UV measurement of the tetraphenylphosphonium-fluoroborate complex extracted into chloroform. The test showed that BF_4^- was completely extracted by tetraphenylphosphonium ion into chloroform. An idea which appears worthy of further investigation is the UV spectrophotometric determination of boron after its extraction as BF_4^- by tetraphenylphosphonium ion into chloroform.

However, it is considered that the unsuccessful application of the method described here to the determination of boron in steel does not detract from its overall usefulness as a sensitive method for determining boron in aqueous solution.

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