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THE

POLAROGRAPHIC DETERMINATION OF
TRACE ELEMENTS IN
BLISTER AND REFINED
COPPER.

-By-

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CONTENTS.

Chapter 1.

INTRODUCTION.

In the complete analysis of copper the following impurities are generally determined: silver, gold, lead, arsenic, antimony, selenium, tellurium, iron, zinc, cobalt, nickel, oxygen, sulphur, and, less commonly, tin and phosphorus. The actual copper content varies around 99.0% in blister copper; in the refined metal the content is somewhat higher, usually over 99.9%. The concentrations of the individual impurities vary from tenths to thousandths of one per cent.

The principal properties responsible for the widespread use of copper are its high electrical and heat conductivities, its ductility, and its resistance to corrosion. These properties are affected by impurities in the copper itself. By far the most serious is the effect on the electrical properties. All elements, when present as impurities, cause a lowering of the electrical conductivity. In some cases this is very pronounced, while in others the effect is hardly noticeable. Oxygen, at low concentrations, is the only element which apparently increases the conductivity. In actual fact this is due to the formation of oxides of other trace elements present. As the oxides, their effect on the electrical conductivity of the copper is not as marked. Impurities also affect other properties of copper, bismuth causing brittleness, arsenic reducing the crystallisation temperature, lead causing difficulties when the copper is to be hot-rolled, and so on.

The purity is therefore of major importance, and consumers require detailed specifications with each consignment. The refineries are also interested in these specifications for the purpose of checking daily on the efficiency of the refining processes.

Although each refinery, or mine, has its own procedures of analysis, the majority of these are based on the standard chemical methods. For purposes of illustration, a typical procedure is given below.

Owing to the small concentrations of the trace elements, large samples, up to 500 grams in the case of refined copper, are used. When the sample is greater than 50 grams it is handled in smaller lots which are recombined after the preliminary separations. Not all the impurities are determined on the same sample, as the separations required would be extremely complex. Gold and silver are determined by assay; bismuth and iron in one portion; lead, nickel, cobalt and zinc in a second; arsenic, antimony, selenium and tellurium in a third. Separate portions are required for sulphur, oxygen, phosphorus and tin, if these are to be determined.

For bismuth and iron the sample is dissolved in nitric acid. Excess ammonia is added to precipitate iron and bismuth hydroxides, which are filtered off. The copper remained in solution as the ammonia complex. The bismuth is separated from the iron by precipitation as the sulphide, and is then determined by a colorimetric method using cinchonine iodide. Iron is converted to ferric chloride and titrated with standard stannous chloride solution. Small traces are determined colorimetrically using ammonium thiocyanate.

A second sample is dissolved in nitric acid and electrolysed for 36 hours to remove most of the copper. Lead is precipitated and weighed as lead sulphate. The insoluble sulphides and hydroxides of groups II and III are removed leaving zinc, nickel and cobalt in solution. Zinc is separated as the sulphide and converted to the carbonate, which is ignited to and weighed as the oxide. Cobalt and nickel are determined together by electrodeposition, the deposit dissolved and the nickel determined by dimethylglyoxime, cobalt being obtained by difference.

The third sample is dissolved in nitric acid as before. Ferric chloride solution is added and the basic acetate separation is effected, the precipitate carrying down the arsenic, antimony, selenium and tellurium. This procedure is repeated on the filtrate. After the precipitates have been dissolved in nitric acid, arsenic is reduced to the trivalent state by ferrous chloride. It is distilled off as arsenious chloride below 110°C in a stream of HCl gas, and determined volumetrically. Above 110°C antimony chloride volatilises with HCl and after collection, is determined by titration with potassium bromate. Selenium and tellurium are precipitated from the residual solution by sulphur dioxide and weighed in the elementary state. They are then again brought into solution and the selenium determined colorimetrically, the percentage of tellurium being found by difference.

In these procedures the majority of the precipitations have to be done twice, or even three times, to overcome adsorption errors. Each additional operation in such an analysis increases the possibility of error and causes the methods to become long and tedious. Using these methods a complete analysis may take a week or more. For control purposes in a refinery laboratory this is a serious disadvantage. Any delay in the availability of the results of analysis may cause considerable losses. Faults in the refinery procedure affecting the quality of the product and the efficiency of the refinery processes, should be detected at the earliest possible stage so that corrective measures may be taken with the minimum of delay.

Instrumental methods of analysis have important advantages under such conditions, provided that they have been properly and satisfactorily standardised. Of these spectrography and polarography seemed particularly suitable. However, Miholic (1) has reported that spectrographic methods are not very sensitive when applied to the analysis of the heavy metals. In addition the apparatus is expensive and requires highly skilled operators for its installation and control. For these reasons it is not suitable in routine control analysis. These disadvantages are not so acute for polarographic methods and it was thought worth while to investigate these more closely in the hope of developing procedures which would be useful for practical control purposes in copper mines and refineries.

In the limited time available it would have been quite impossible to develop a method of analysis for all the impurities. Only the most important ones, (iron, bismuth, lead, antimony, nickel, cobalt, manganese, selenium and tellurium), were considered. The determination of selenium and tellurium has been investigated previously in this laboratory (2) and, therefore, the present research was confined to the determination of iron, bismuth, lead, antimony, nickel, cobalt and manganese. These seven elements will be referred to in future discussion as the impure elements, the minor elements, or simply as the impurities.

Detailed accounts of the polarographic method may be found in many text books on the subject. A brief description is given here, however, to introduce the terms which will be used, without further explanation, in the remainder of the thesis.

Polarography is based on the interpretation of the current voltage (c.-v.) curves that are obtained when solutions of electroreducible substances are electrolysed in a cell in which the one electrode has a small area. In the present research the dropping mercury electrode (d.e.) was used as the cathode.

The polarograph is the instrument which applies a gradually increasing voltage to the cell, and automatically plots the graph of the current flowing as a function of the applied voltage. At voltages below the decomposition potential of the electroreducible ion, only a small current flows (the residual current). When the decomposition potential is exceeded the electrolysis begins and the current rises rapidly and then gradually levels off to a limiting value (the limiting or diffusion current). Thus on a current voltage curve a step-wise increase in current is obtained - called the polarographic wave. The height of this wave (i.e. the distance between the residual and limiting currents) is proportional to the concentration of the electroreducible substance, provided that an excess of some indifferent salt (i.e. one whose ions do not participate in the electrode reaction) is present. The solution of this indifferent salt is called the supporting electrolyte.

An important feature of a polarographic wave is the half-wave potential. This may be defined as the potential of the cathode at the point on a c.v. curve where the current is equal to half its limiting value.

Each reducible ion in a solution has a characteristic half-wave potential which is independent of the concentration of the ion. However, due to the formation of complex ions, its value is affected by the type of supporting electrolyte used. Half-wave potentials are quoted with reference to some other electrode. In this thesis, unless otherwise stated, these potentials will be given with reference to the mercury pool anode.

Thus polarography may be used for both qualitative and quantitative analysis. In the interpretation of current voltage curves the half-wave potential gives an indication of the ion causing a wave, while the wave-height gives a measure of the concentration of the ion.

Since oxygen is readily reduced at the d.e. and usually interferes with the waves of other substances, it is generally necessary to remove dissolved air from the solution to be electrolysed. In all experiments reported in this thesis dissolved oxygen was removed by bubbling pure dry nitrogen through the cell before recording a polarogram.

Two terms in connection with the galvanometer (the current measuring instrument) will be used frequently in the thesis. With the dropping mercury electrode, the current at each value of the applied e.m.f. is not constant but oscillates between a minimum and maximum value to the periodic change in area as each mercury drop grows and falls. These oscillations are referred to as "galvanometer oscillations". The second term is the galvanometer sensitivity. This is expressed as a fraction and refers to the fraction of the current flowing through the cell, that is being recorded by the galvanometer.

From a theoretical point of view it might seem that the solution to the problem under investigation was a simple one, it only being required to dissolve the copper in a supporting electrolyte, record a polarogram, measure the heights of the waves obtained and so determine the concentration of all the impurities. In practical polarography, however, a number of difficulties arise: (1) The current voltage curves are often distorted by polarographic maxima. The discharge curve rises sharply but, instead of leveling off to the limiting current, it continues to rise practically linearly with the applied e.m.f. until at a certain critical potential it falls again to the limiting value. These maxima cause difficulties when the waves are to be used for quantitative analysis, and so have to be removed. This is done by the addition of maximum suppressors to the solution, the most common ones being gelatin, methyl red, methylene blue, etc.

(2) When using the normal polarographic method it is impossible to determine small quantities of one substance in the presence of a large concentration of a more easily reducible substance. A large wave is obtained for the interfering substance which obscures the wave of the minor constituent. In the determination of trace elements in copper this difficulty arises. Copper ions are very readily reduced at the dropping electrode and are present at a very high concentration. In this extreme case it is necessary to remove most of the copper. It was proposed to effect this removal by the method of controlled electrodeposition. This will be discussed in detail in chapter 4. At the time of commencing the research for this thesis, a new polarographic technique was being developed to overcome the above difficulty in cases

where the difference in concentration of the two elements concerned was not excessively high. As the method promised to be of use in the present research it was investigated further. The results of this investigation are discussed in chapter 2.

(3) The most common difficulty encountered in the polarographic analysis of a number of elements, is the overlapping of two waves, which makes it impossible to measure the individual wave-heights. This difficulty may sometimes be overcome by the use of a different supporting electrolyte. However, this is not always effective, especially when a large number of electroreducible substances are present. At the same time as the differential technique was being developed work was started on the technique of derivative polarography which was designed to overcome the third diffulty. This method also promised to be of great value in the main part of the present research, and as little information on the application of the technique was available at the time, it was investigated further in this laboratory. The results of the investigation are discussed in chapter 3.

By far the main task in this research was the search for suitable electrolytes to enable the simultaneous determination of as many of the trace elements as possible. This is discussed in chapter 5.

Very early on in the research it was realised that it would not be possible to develop and thoroughly test a method for the analysis of the seven impurities being investigated. All the problems which occurred in the research proved more complex in practice than was originally anticipated. It was therefore hoped that it would be possible to propose a method of analysis, soundly based on the results obtained in the qualitative investigation of the problem, and possibly to test the method quantitatively in the case of one or two ions. This ambition was realised. In chapter 6 a method of analysis for the 7 ions is proposed, based on the results obtained in chapter 4 and 5, while in chapter 7 the results of the preliminary experiments on the quantitative determination of iron and bismuth are given.

The apparatus used in this research is described in the appendix.

Chapter 2.

DIFFERENTIAL POLAROGRAPHY.

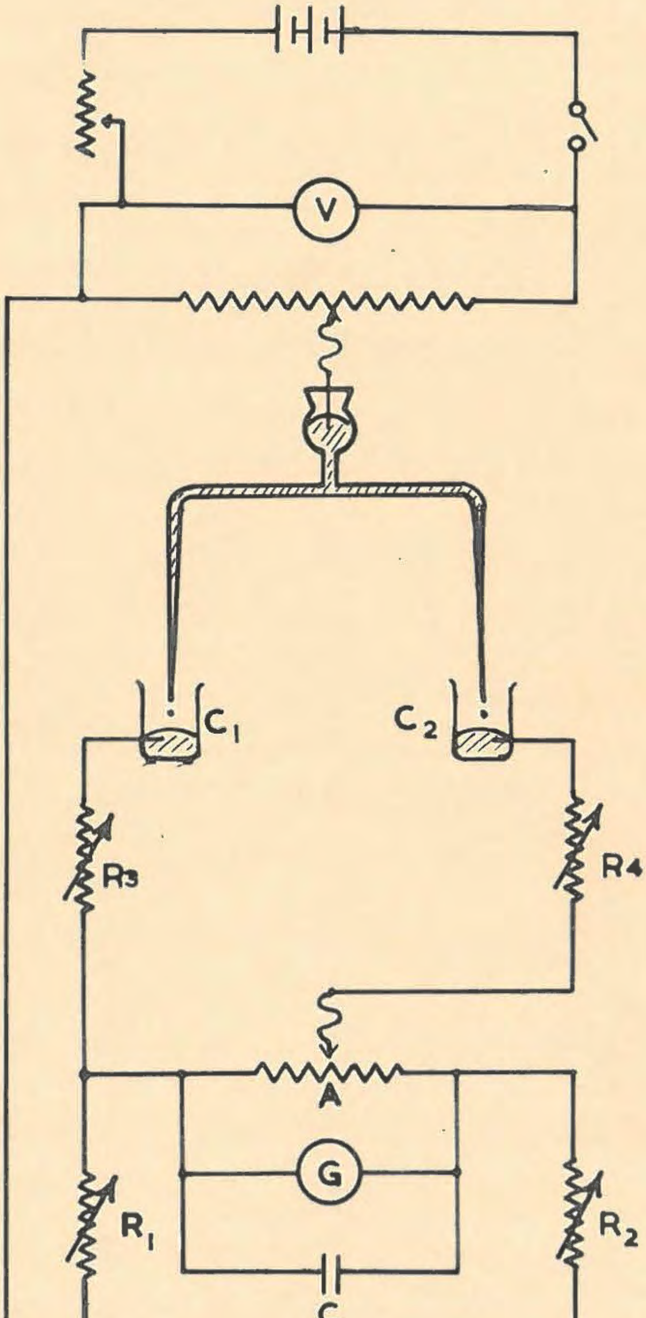
The first record known to us on the use of this method was in the work published by Matherson and Nichols (3). Later Semerano and Riccoboni (4), and then Kanevskii (5) published results on further experimental work on this technique. However, the first readily available publication on the subject was that by Lingane (6) who mentioned the technique in his review on polarographic instrumentation and methodology. He described the circuit used by Semerano and Riccoboni.

Differential polarography may be defined as the technique in which the currents flowing in two solutions, which are electrolysed simultaneously, are opposed to each other, the resulting difference in current being plotted as a function of the applied voltage. The term has been used incorrectly by many workers to describe the derivative technique. This incorrect usage of the terminology will be discussed further in chapter 3.

The circuit used in the research on which this thesis is based, was a modified form of that used by Semerano and Riccoboni and is shown in figure 1. Three of the resistances in the original circuit were replaced by the Ayrton-Mather shunt A, while a condenser C was included in parallel with the galvanometer G to smooth the galvanometer oscillations.

The circuit was designed primarily for the determination of small amounts of a substance in the presence of a much larger quantity of a more easily reducible substance. In this case the large wave of the major

FIG. 1 DIFFERENTIAL CIRCUIT.



interfering constituent makes it impossible to increase the sensitivity of the apparatus sufficiently for the smaller wave to be detected by normal means.

When applying the method the unknown sample is made up in the supporting electrolyte which is being used and the solution placed in cell C_1 . The second cell contains only the supporting electrolyte. A differential polarogram recorded for these two solutions would show no current changes for the supporting electrolyte or dissolved oxygen (which are present in both cells), but only waves due to the reducible ions in the cell C_1. The applied e.m.f. is now set to such a value that the large diffusion current due to the interfering substance is obtained. A solution of the substance is then added to the cell C_2 until the galvanometer is restored to zero. (If an excess of the substance were to be added a negative diffusion current would be obtained). When complete compensation is attained the sensitivity is increased and a polarogram recorded for the minor constituent.

Preliminary experiments carried out in this laboratory showed that although the differential method was very elegant in theory, a number of difficulties arise in practice.

The two dropping electrodes had to have almost identical characteristics. Slight deviations could be corrected by adjusting R_1 and R_2 to obtain perfect compensation when two identical solutions were placed in the cells.

Slight fluctuations in the cell resistances caused irregularities in the curves. These were reduced by the use of large values for R_3 and R_4 (10,000 ohms) which acted as stabilisers.

The dropping rates of the two capillaries had to be synchronised. If this was not done the compensated current underwent positive and negative shifts, due to the periodic change in phase of the mercury drops.

The method could not be applied where the wave of the minor constituent coincided with that of the major one, since the point of complete compensation could not be determined.

However it was found that in cases where only a partial compensation was required and provided the sensitivity of the galvanometer was not very much greater than would be used for the same solutions in ordinary polarography, perfectly reproducible curves could be obtained. The curves under these conditions are much less subject to irregularities, and the oscillations are smaller than when complete compensation is achieved.

At this stage in the research no immediate application of the technique could be seen because of its limitations. The investigation of the method was therefore discontinued, until an opportunity of using the method presented itself. Such an opportunity did in fact arise and further discussion on this method will be given in chapter 5. ("The separation of copper")

The preliminary experiments, although disappointing from the point of view of the usefulness of the differential method in the present research, did give the idea for a new type of polarographic titration. It is proposed to name the new technique, "Differential Polarographic Titration".

In this method the substance to be determined is made up in a suitable supporting electrolyte and the solution placed in the first cell of the normal differential apparatus. The second cell contains an accurately known volume of the supporting electrolyte. A polarogram is recorded and a wave obtained for the substance. A standard solution of the substance is then added, a few ml. at a time, from a burette, to the cell containing only the supporting electrolyte, and a polarogram recorded after each addition. A graph is plotted of the wave height as a function of the volume of solution added. From the graph the volume of standard solution required for complete compensation may be read off, and the concentration of the unknown substance may be determined.

The titration is quite unique as it does not involve a chemical reaction. The 'reaction', if it may be so called, is purely electrical and equilibrium is attained instantaneously. The method is rapid, simple and accurate and may be applied to the determination of any substance which gives a polarographic wave.

Preliminary investigations on the use of the method have already been carried out in this laboratory and the method was found to be most satisfactory. An account of the method, containing these results, has already been submitted for publication.

Chapter 3.

DERIVATIVE POLAROGRAPHY.

This, as the name implies, refers to the technique in which the first derivative of the normal curve $\frac{\Delta i}{\Delta E}$ (i.e. the slope) is plotted as a function of the applied potential. Since in mathematics the process of obtaining the first derivative is called differentiation, it is clear how the incorrect usage of the term differential polarography came about. In the derivative technique the current recorded, for the reduction of any one ion, rises to a maximum and then falls again almost to zero. Thus when determining a number of ions instead of a successi of waves a number of peaks are obtained in the current voltage curve.

The first publication available was one by Heyrovsky (7) in 1946. The following year he reviewed the application of the method to A. C. polarography (8), while Delahay (9) in the same year discussed the use of a condenser to differentiate various types of electrometric curves

All the early workers obtained derivative curves using circuits involving two dropping electrodes in the same solution. The potential of the one electrode system is kept slightly greater than that of the other. The difference in current flowing though the two electrodes is plotted as a function of the applied potential. However in 1949 Leveque and Roth (10) developed a simple circuit for obtaining derivative polarograms. This circuit was used the following year by Vogel and Riha (11) .

These early publications contained two points of special interest to this research.

1. The height of peak, obtained in the derivative curve, is proportional to the concentration of the reducible ion causing it.

2. It was predicted that the derivative method would be widely used in polarography becuase: (a) it could be used for the determination of traces of a substance in the presence of large quantities of a more easily reducible substance; and (b) it could be used for the determination of two substances whose normal waves merge into one.

Because of these reasons the technique promised to be of great use in the research for this thesis, and therefore it was decided to investigate the method more fully than had been done in the past.

The circuit used in the research for this thesis is shown in figure 2a. It is generally similar to that described by Vogel and Riha, but it contained an additional resistance R_2, and a condenser C_2 for damping the galvanometer oscillations.

The variation, with voltage, in the current flowing through the cell, i_c, is shown in figure 2b, and represents a normal polarographic wave. The corresponding variation in current through the galvanometer, i_g, is shown in figure 2c. This is the type of curve obtained in practice by the derivative technique.

None of the early workers offered any explanation of how their circuits worked, so a simple explanation of the circuit mentioned above is suggested here.

Let us consider the potentials at the nodes 1, 2 and 3. (see fig. 2a.) Using the potential at node 3 as a reference, the potentials

FIG. 2a DERIVATIVE CIRCUIT.

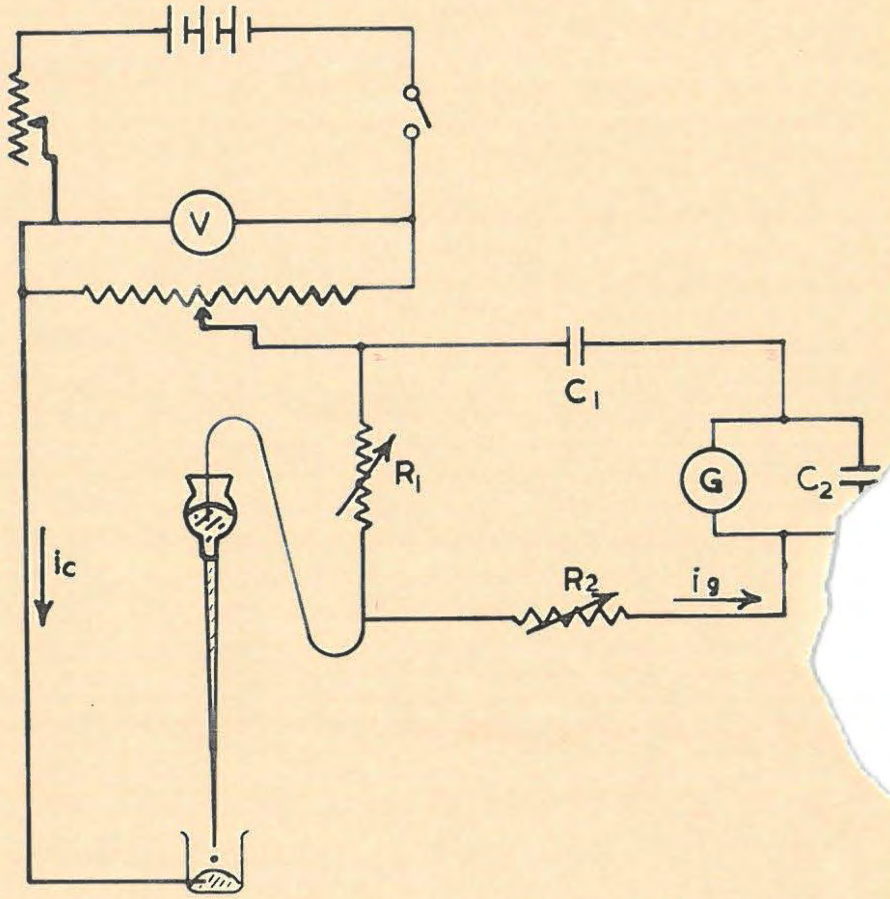


FIG. 2b.

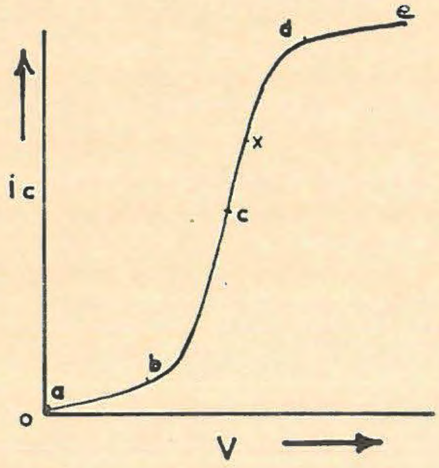
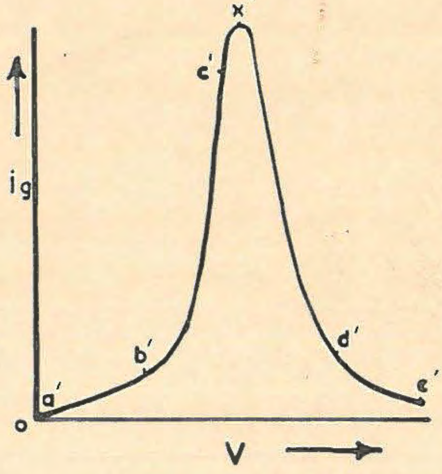


FIG. 2c.



at the other nodes are given by:

at node 1. $V_1 = (i_c - i_g)\ R_1$

at node 2. $V_2 = i_g\ R_g$ where $R_g = R_2$ + galvanometer resistance.

The potential across the condenser C_1

$$= V_1 - V_2$$

$$\text{it also} = \frac{1}{C_1} \int_0^t i_g\ dt.$$

$$\therefore\ i_c R_1 - i_g (R_1 + R_g) = \frac{1}{C_1} \int_0^t i_g\ dt.$$

differentiating we get:

$$C_1 R_1 \frac{di_c}{dt} - C_1 (R_1 + R_g) \frac{di_g}{dt} = i_g$$

$$\text{or} \quad C_1(R_1 + R_g) \frac{di_g}{dt} = C_1R_1 \frac{di_c}{dt} - i_g \quad \text{———— } 1.$$

A complete expression for i_g, during the course of the reduction of an ion at the dropping electrode, could be obtained by inserting the value of i_c obtained from the Ilcovic equation and solving for i_g. This would be extremely complicated and a more simple explanation may be obtained as follows. Assume that over any small interval of time $\frac{di_c}{dt}$ is constant; equation 1 may then be simplified.

$$\text{Rearranging } \frac{di_g}{C_1R_1 \frac{di_c}{dt} - i_g} = \frac{dt}{C_1(R_1+R_g)}$$

Intergrating this over an interval of time from t_1 to t_2 during which i_g changes from i_{g1} to i_{g2} we have

$$\int_1^2 \frac{di_g}{C_1R_1 \frac{di_c}{dt} - i_g} = \int_1^2 \frac{dt}{C_1(R_1 + R_g)}$$

$$- \ln\left(C_1R_1 \frac{di_c}{dt} - i_{g1}\right) + \ln\left(C_1R_1 \frac{di_c}{dt} - i_{g2}\right) = \frac{t_2 - t_1}{C_1(R_1+R_g)}$$

i.e. $$\frac{C_1R_1 \frac{di_c}{dt} - i_{g2}}{C_1R_1 \frac{di_c}{dt} - i_{g1}} = e^{\frac{t_2-t_1}{L}}$$ where L = the time constant $= C_1(R_1+R_g)$.

Subtracting each side of the equation from 1 we get

$$\frac{i_{g2} - i_{g1}}{C_1R_1 \frac{di_c}{dt} - i_{g1}} = 1 - e^{\frac{t_2 - t_1}{L}}$$

$$i_{g2} = i_{g1} + \left(C_1R_1 \frac{di_c}{dt} - i_{g1}\right)\left(1 - e^{\frac{t_2 - t_1}{L}}\right) \text{\_\_\_\_\_} \quad 2.$$

If we consider constant intervals of time, the second bracketed term in equation 2 is constant. Let it equal K. This term is also $<$ 1. The current (i_{g2}) at the end of any interval, is equal to the current at the beginning plus the term $C_1R_1 (\frac{di_c}{dt} - i_{g1})$ K.

In the first interval;

$$i_{g1} = 0.$$

$$i_{g2} = \left(C_1R_1 \frac{di_c}{dt}\right) K.$$

This is less than $C_1R_1 \frac{di_c}{dt}$ since $K < 1$.

The i_{g2} above becomes i_{g1} in the second interval, i.e, while $\frac{di_c}{dt}$ increases.

i_{g1} is less than $C_1R_1 \frac{di_c}{dt}$ and $\therefore$ $i_{g2} > i_{g1}$.

From a to b (fig. 2b) while $\frac{di_c}{dt}$ is small i_{g2} is only slightly larger than i_{g1} and we get the curve a' to b' for i_g (fig. 2c). As $\frac{di_c}{dt}$ increases more and more rapidly, so the difference between i_{g2} and i_{g1} ($\triangle i_g$) increases and i_g rises more and more rapidly.

At the inflection point in the normal curve (c), $\frac{di_c}{dt}$ is at its maximum and $\triangle i_g$ is a maximum. After C $\frac{di_c}{dt}$ decreases, but $C_1R_1 \frac{di_c}{dt}$ is still larger than i_{g1} which is increasing all the time. Therefore, i_g continues to rise until at a point X $C_1R_1 \frac{di_c}{dt} = i_{g1}$ and i_g reaches a maximum at X'. This maximum is past the half-wave potential of the normal wave.

From X to d $\frac{di_c}{dt}$ is decreasing rapidly and $\triangle i_g$ is large but negative, and i_g falls from X' to d'. From d to e a similar result is obtained but $\triangle i_g$ is not quite as large.

The practical experiments were designed to test the two points mentioned earlier in this chapter and so to ascertain whether the technique would in fact be of use in the main part of this research.

In the early experiments the peaks obtained were narrow and sharp. These were found to be unsatisfactory for quantitative use. On some occasions the actual severing of a drop from the cathode occurred at the same instant as the peak maximum was reached. Since, at the instant that a drop leaves the cathode the current tends to fall to zero, instead of a pointed peak a hollow one is obtained. This results in a considerable loss in peak height. It was realised if curves could be obtained with rounded peaks, more than one galvanometer oscillation would occur at the peak maximum, and the above mentioned difficulty would not arise.

It was found from experiments, in which the values of the resistances and condensers were varied, that the most ideally shaped peaks obtained when:

(a) C_1 was kept as low as possible, thus obtaining symmetrical rounded peaks;

(b) R_1 was adjusted to obtain the required peak height;

(c) R_2 was made large thus reducing the galvanometer oscillations;

(d) C_2 was made large to reduce the oscillations still further.

It was found that the peak-height varied proportionally with R_1 when the sum $R_1 + R_2$ was kept constant (see fig. 3). This is in agreement with the theory advanced, since at the maximum

$$i_g = C_1R_1 \frac{di_c}{dt.}$$

$$\text{i.e. } i_g \propto R_1.$$

It was now possible to compare the derivative and the normal method from a quantitative point of view.

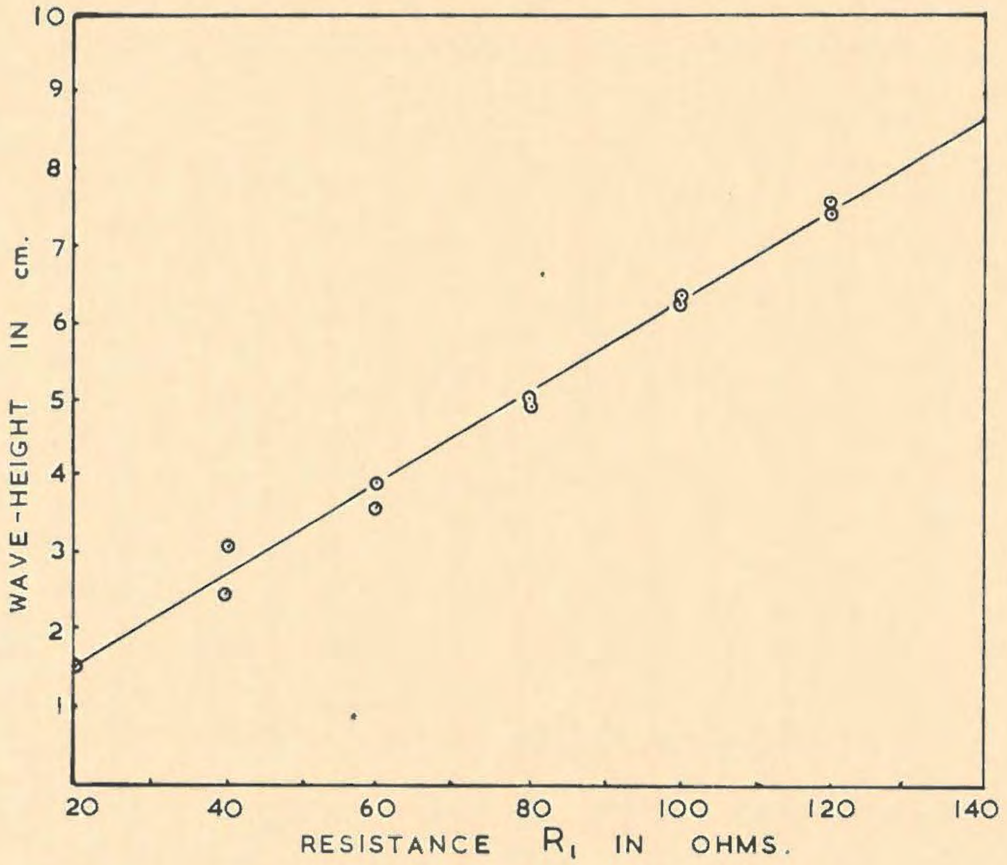
A number of samples were prepared by diluting different volumes of an antimony stock solution to 100 ml. After the dissolved oxygen had been removed by bubbling nitrogen through the solution, both derivative and normal curves were recorded. Three recordings were made, in quick succession, on each solution. The means of the wave and peak heights were calculated and plotted as a function of the number of ml. of stock solution used.

The results, shown in figure 4, indicated that the derivative method was not quite as accurate as the normal one. The small differences were ignored at this stage, as it was felt that, with improved technique, perfect results could be obtained.

It has been suggested previously that the method could be applied to the determination of small quantities of a substance in the presence of large concentrations of a more easily reducible substance. Experiments showed that this is possible in practice provided that (a) the two peaks are not too close together, in which case the first peak has not fallen to zero by the time the decomposition potential of the minor element is reached; and (b) the difference in concentration is not too great. If it is, at the sensitivity required for the detection of the minor constituent, the galvanometer oscillations are too great (due to the high current) to permit the accurate measurement of the wave height.

The great advantage of the derivative method over the normal one was demonstrated by using a solution of antimony and bismuth. In 1N hydrochloric acid the normal waves of the two ions merge almost completely into one. This makes the accurate measurement of the individual wave heights impossible. However the derivative curve showed two distinct peaks, which could be measured without difficulty.

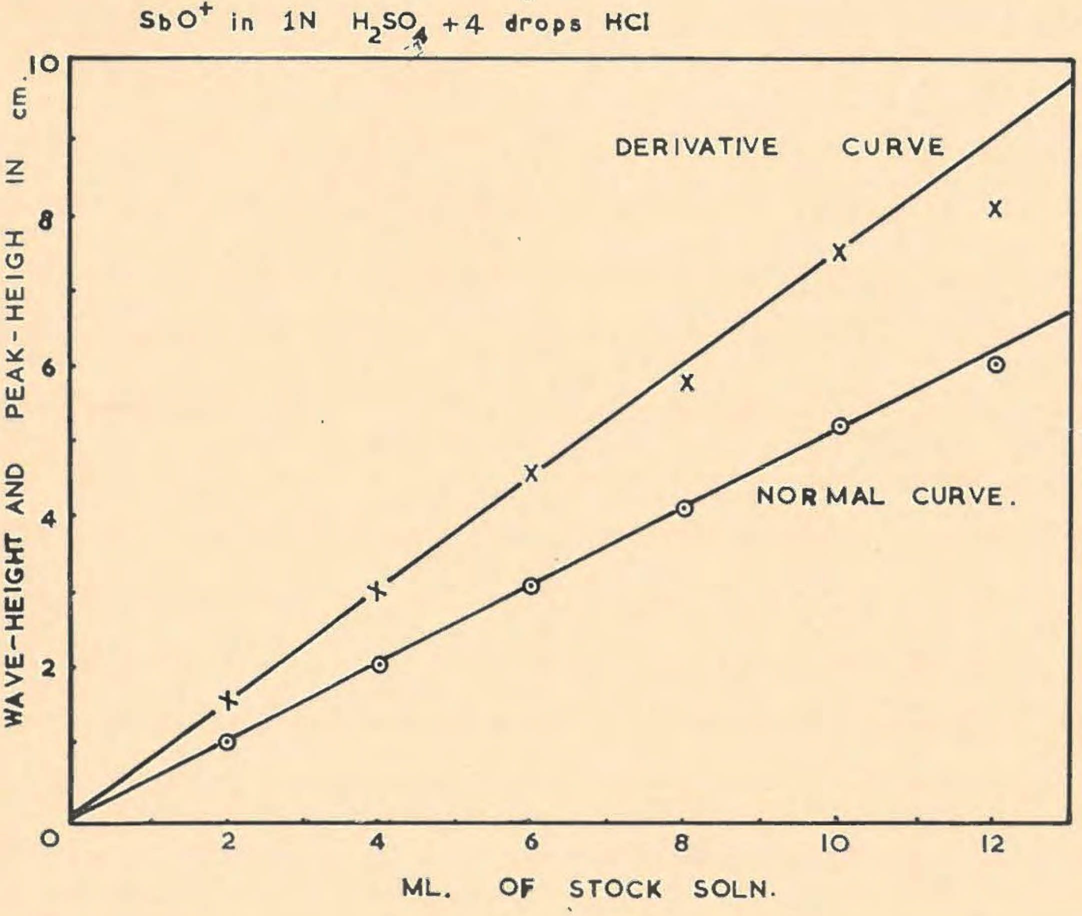
FIG. 3 GRAPH OF WAVE-HEIGHT VS. RESISTANCE.



SOLN. M/1000 SbO^+ IN 1N HCl + METHYLENE -

B

FIG. 4 COMPARISON OF NORMAL AND DERIVATIVE METHOD.



CONCENTRATIONS. SbO^+ $M/_{1000}$ (10 ml.)
to $M/_{5000}$ (2 ml.)

Thus the two points made by the early workers, on the use of the technique, had been proved (with some limitations in the case of the first application.) Because of this the method promised to be of great use in the main investigation.

Chapter 4.

THE SEPARATION OF COPPER.

INTRODUCTION

Before any attempts could be made at the analysis of the trace elements in refined and blister copper it was found necessary to separate the minor elements from the copper itself. In the refined metal the copper concentration is approximately 10^4 times greater than that of any of the trace elements. In addition, in most supporting electrolytes copper is reduced at the dropping mercury electrode before any other ion. With these conditions prevailing it would be impossible to detect, polarographically, any of the minor elements.

A method was therefore required by which the copper could be removed completely from a solution of the refined metal, without removing any of the trace elements. If this ideal could not be accomplished, it was possible that the reduction of its concentration to the same order as those of the impurities would be sufficient. The most desirable property of the method was that all the minor elements were to be unaffected by the separation. This would have meant a great saving in time as it might then have been possible to determine all the impurities on one sample.

For the reason given above the ammoniacal separation was unsuitable as only bismuth and iron remained quantitatively after the removal of the copper.

BY CONTROLLED ELECTRODEPOSITION.

The development in recent years of this method has opened up vast possibilities in the field of analytical chemistry. It was hoped that this method could be applied in the present research. For, by carefully controlling the cathode potential, it had been found possible to separate elements whose reduction potentials were very close together.

In the electrolysis of solutions of blister copper, if the cathode potential was raised, after the deposition of copper, bismuth is the first metal that would be reduced, in most electrolytes. This meant that if in the method of copper separation bismuth was not deposited, none of the other metals would be deposited. The problem therefore resolved itself into the separation of large quantities of copper from traces of bismuth.

First method.

(a) Theory. Lingane (12 and 13) found that the most suitable supporting electrolyte for the separation of copper from bismuth was an acid tartrate solution. Lingane and Jones (14) made use of the polarograph for carrying out preliminary investigations on their proposed methods for electrodeposition. When a platinum electrode was to be used in the electrodeposition experiments, a platinum micro-electrode was used in the polarographic work. Similarly they used the dropping mercury electrode to investigate the possibility of using a mercury pool as cathode in the electrodeposition analysis. Their publication contained results of their investigation of the deposition potentials of copper and bismuth under different conditions. The results showed that from a pH of 1 to 3.5 copper is reduced at a more negative potential than bismuth, while at higher pHs the order is reversed. The maximum difference between the deposition potentials of copper and bismuth is in the pH range from 5.5 to 6.

Using the results obtained above these workers have developed a successful method for the quantitative separation of bismuth and copper. The method was as follows:-

"The sample was dissolved in 10 ml. of 1:2 nitric acid in the electrolysis beaker. To this solution were then added 1 gram of urea (to reduce the oxides of nitrogen), 50 ml. of 1 M sodium tartrate, 2 grams of hydrazine dihydrochloride, and one gram of succinic acid for each 100 mg. of copper present. The solution was diluted to 190 ml. and its pH adjusted to 5.9 ± 0.1 (glass electrode) by the addition of sodium hydroxide solution. The solution was cooled to 25°C or below and immediately electrolysed. The copper was deposited at a potential of - 0.30 volt. vs S.C.E. After it was weighed, the copper-plated cathode was replaced in the solution and the bismuth deposited at - 0.40 volt. The pH after the copper deposition was in the optimum range of 5.2 to 5.4 and no further adjustment was necessary before the bismuth was deposited. The deposition of each metal required about 45 minutes. In each case the electrolysis was stopped after the current had decreased to a constant minimal value for 10 minutes."

The samples used above contained about 400 mg. of each element, but no reason could be seen why the method could not be extended to larger quantities. Investigations were therefore started in this direction.

(b) Apparatus. The conventional type of electrodeposition apparatus was used. One improvement which may be mentioned is the electrical contact to the rotating anode. A small hole was drilled into the top of the axle and filled with mercury. The copper lead wire dips into this, making perfect contact. This simple type of contact has been found to be much more satisfactory than the conventional brush type.

The polarising voltage was taken from the 250 volt A.C. mains supply, through a variac, a transformer and a full-wave rectifier. A system of resistors in the circuit provided the means of adjusting the applied voltage.

The potential of the cathode was measured against a $Hg/Hg_2\ SO_4$ (Satd), 1N $H_2\ SO_4$ electrode which, according to Kolthoff and Lingane (15), has a potential of +0.682 volt when measured on the hydrogen scale. The measuring instrument was a Cambridge unipivot potentiometer which was frequently standardised against a Weston standard cell.

A number of investigators (16,17, 18, 19, 20, 21) have constructed potentiostats for controlling the cathode potential automatically. In the present research, however, the potential was controlled manually, there being no automatic apparatus available.

All pH measurements were made on a Marconi pH meter Type No. T.F. 717 A.

(c) Practical. Five grams of blister copper were dissolved in the minimum amount of 1:2 nitric acid and the excess acid boiled off. The residue was dissolved in water and to the solution was added 1 gram of urea, 20 grams of succinic acid and 150 ml. of a solution 1M with respect to sodium tartrate. The resulting solution was diluted to 190 ml. and the pH adjusted to 5.9.

Before this pH could be reached copper began to precipitate, presumably as the hydroxide. It was assumed that the solution was not sufficiently concentrated with respect to the tartrate ion to prevent the copper from precipitating. This assumption was found to be correct, for, when sodium tartrate was added to a sample of the above solution the copper precipitate redissolved. However the amount of tartrate that would have to have been added is so great that the method would be uneconomical for industrial purposes. It was therefore abandoned with the hope of finding a more suitable method for the electrolytic removal of copper.

Second method.

(a) Theory. In acid solutions bismuth is reduced according to the equation:-

$$BiO^+ + 2H^+ + 3e^- \longrightarrow Bi + H_2O \qquad E^o_{Bi} = +0.32 \text{ volt.}$$

The potential of the bismuth electrode, E_{Bi}, at 25°C is given by;

$$E_{Bi} = E^o_{Bi} + \frac{0.0591}{3} \log \left[BiO^+\right]\left[H^+\right]^2$$

Using a five gram sample of blister copper and an electrolysing volume of 200 ml. the BiO^+ concentration would be of the order of 10^{-6} gram ions/litre. Allowing a margin for error, the concentration was taken as 10^{-5} gm. ions/litre. In a solution of 1N acid the bismuth would start to deposit at a potential given by

$$E_{Bi} = 0.32 + \frac{0.0591}{3} \log 10^{-5}$$

$$= 0.221 \text{ volt. on the hydrogen scale.}$$

Referred to the saturated mercurous sulphate electrode ($E = +0.682$ volt) this would be at a potential of -0.461 volt. In other words, as long as the cathode potential is not raised above this value, bismuth should not deposit from acid solutions, in the absence of complex forming ions.

Under similar conditions copper is reduced according to the equation

$$Cu^{++} + 2e^{-} \longrightarrow Cu \qquad E^{o}_{Cu} = 0.3448 \text{ volt.}$$

The potential of this electrode is given by

$$E_{Cu} = E^{o}_{Cu} + \frac{0.0591}{2} \log \left[Cu^{++}\right]$$

If the electrodeposition was carried out at a cathode potential of +0.282 volt, on the hydrogen scale, (i.e. -0.4 volt against the saturated mercurous sulphate electrode) the concentration of the copper remaining in solution may be calculated as follows

$$\begin{aligned} \log \left[Cu^{++}\right] &= (E_{Cu} - E^{o}_{Cu}) \frac{2}{0.0591} \\ &= (0.282 - 0.3448) \frac{2}{0.0591} \\ &\doteqdot -2. \end{aligned}$$

$$\text{i.e.} \quad \left[Cu^{++}\right] \doteqdot 10^{-2} \text{ gm. ions/litre.}$$

The theory showed that the copper concentration could be reduced, quite safely, to 10^{-2} gm. ions per litre without the deposition of bismuth. The acids used in the practical experiments were nitric and sulphuric. The introduction of chloride ions was most undesirable, as these formed complexes with both copper and bismuth.

(b) Practical. Five grams of the blister copper were weighed out and dissolved in 1:2 nitric acid. The excess acid was removed by evaporation. One ml. of concentrated sulphuric acid was added and the solution evaporated almost to dryness. After dissolving the residue in

190 ml. of water, 2.5 ml. of sulphuric acid and one gram of hydrazine sulphate were added. The solution was cooled to 25°C and electrolysed at a cathode potential of -0.40 volt measured against the saturated mercurous sulphate electrode. One gram of hydrazine sulphate was added every hour.

The initial current was only 1 amp, and the hydrazine sulphate seemed to form an insoluble complex with the copper. Assuming a current efficiency of 60% and an average current of 0.5 amp., (since the initial current was 1 amp) it could be calculated that 16 hours would have been required to deposit all the copper. In an attempt to reduce this time the volume of the solution was changed to 100 ml. and the hydrazine sulphate was not added.

The samples were treated as before, up to and including the second evaporation. The paste was dissolved in 100 ml. of water with the addition of 2.5 ml of concentrated sulphuric acid, and the solution electrolysed.

The initial current was 2.4 amps. and by allowing the current to fall to 0.003 amp., 97% of the copper was deposited in five hours.

The deposition of 97% of the copper was not sufficient. The experiment was repeated a number of times with improved results. Finally, the electrolysis was continued for one hour after the current had fallen to a steady value of 0.0015 amp. The remaining solution was analysed polarographically in an acid tartrate solution and found to contain copper at a concentration of approximately 10^{-2} gram ions/litre. Thus the theoretical calculations had been borne out by practical experiment.

(c) Discussion. By the method of electrodeposition in acid solution the concentration of copper could be reduced to 10^{-2} gm. ions/litre without the deposition of any of the other impurities. The latter half of this statement was only backed by theory and had yet to be proved by practical experiment.

At this stage there were three possible ways of continuing the separation:

(i) The resulting solution could be evaporated, made up in an acid tartrate solution and electrolysed by the method of Lingane and Jones (14).

(ii) The potential in the electrodeposition could be raised and more copper deposited. By raising the cathode potential to -0.514 volt against the mercurous sulphate electrode the copper concentration could be reduced to 10^{-6}M. Naturally this would mean a loss of bismuth which would also deposit. This could in turn be solved by the use of two samples. From the first copper could be separated by the ammoniacal separation, leaving bismuth and iron; the second sample could be electrolysed at a potential high enough to remove the copper without depositing the impurities other than bismuth.

(iii) Attempts could be made to apply the derivative and differential techniques to the determination of the minor elements in the presence of copper at a concentration of 10^{-2}M.

The first method would be very long, as it involved two electrodeposition experiments and a tedious evaporation between them.

The second would also suffer from this objection but not to the same degree since analysis could be carried out on the two samples at the same time.

Since the main idea of the present research was to reduce the time taken for analysis as much as possible, these two methods were ruled out, that is, initially for the reasons given above. This was done in spite of the fact that it seemed that the development of these methods would present but few difficulties.

The third method, however, seemed to be ideally suited and research was carried out on its application.

The derivative method.

Since the concentration of the copper left in the solution after the electrodeposition was of the order of 10^{-2}M, and the bismuth concentration 10^{-4}M, the derivative technique was applied to solutions containing copper and bismuth at these concentrations. The supporting electrolyte was a solution 0.3M with respect to sodium potassium tartrate whose pH had been adjusted to 6.

Initial experiments were unsuccessful, and in order to test at what concentration the method failed, four fresh solutions were prepared. Each of these solutions contained bismuth at a concentration of 10^{-4}M, with copper at concentrations of 0, 10^{-4}, 10^{-3} and 10^{-2}M respectively. Both derivative and normal curves were recorded on these solutions.

The first solution gave a well defined normal wave and a satisfactory peak for bismuth in the derivative curve. Similar results were obtained for the two solutions containing copper at concentrations of 10^{-4} and 10^{-3}M. But in the presence of 10^{-2}M copper no wave or peak could be obtained for bismuth. In the recording of the normal polarogram, at the sensitivity required for the detection of a bismuth wave, the current, due to the reduction of copper, was greater than the maximum possible on a polarogram. When using the derivative technique no curve could be traced after the copper peak. From this point until after the deposition potential of bismuth large fluctuations in the current occurred which made the recording of any curve impossible. These fluctuations were attributed to the galvanometer oscillations which, at the sensitivity used, were large. The derivative method tends to magnify these oscillations.

In spite of the fact that many attempts were made to overcome these difficulties, successful results were not obtained. It was concluded that although very useful in overcoming other difficulties, the derivative method was not suitable for the determination of trace elements in the presence of large concentrations of other elements. This conclusion applies to the derivative method in its present form. Should a method be found to eliminate galvanometer oscillations completely, then the method might succeed. But since this problem is a subject for research on its own, the derivative method had to be abandoned.

The differential method.

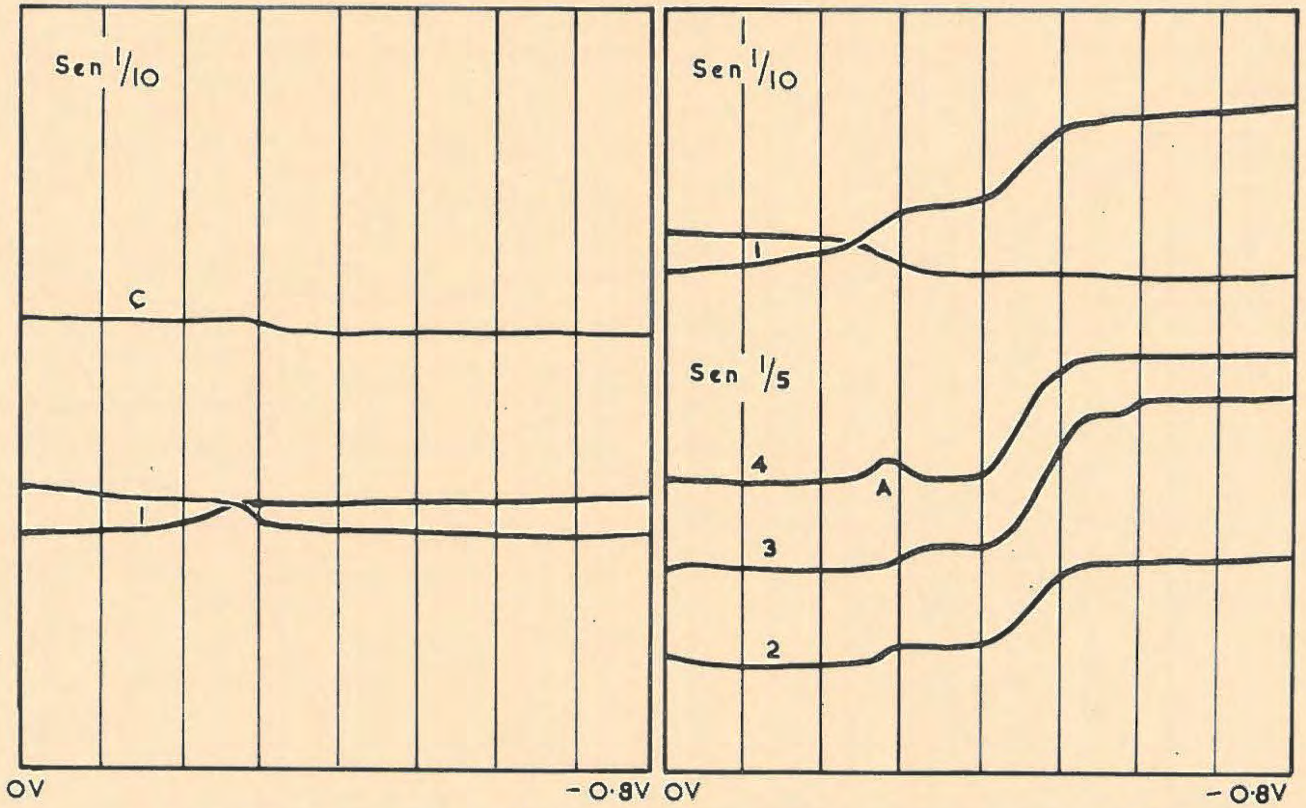
(a) General. It was hoped that where the derivative method had failed this one would succeed, since it had originally been developed for the purpose of overcoming difficulties of the type which occurred here. The method was applied in the same manner as had been done in the previous experiments. Polarograms were recorded on four pairs of solutions which contained copper at concentrations of 0, 10^{-4}, 10^{-3} and 10^{-2}M respectively. In addition one solution of each pair contained bismuth at a concentration of 10^{-4}M. The supporting electrolyte in each case was an acid tartrate solution. In every case normal curves were obtained for each solution before recording the differential curve. This was done by disconnecting first the one cell from the circuit and then the other. The curves so obtained are numbered 1. in the polarograms shown.

The differential curve run on the first pair of solutions (no copper present) should have given a perfect wave due to bismuth, with all effects due to the electrolyte absent. In practice the bismuth wave had a negative slope for the residual and diffusion current portions of the curve. This indicated that the one cell was contributing more current, due to the electrolyte, than the other. The trouble was traced to unequal dropping rates in the two cells. The difference was compensated for by adjusting the resistances R_1 and R_2. The technique of effecting this adjustment was described in chapter 3.

When the solutions contained copper at a concentration of 10^{-4}M (see figure 5a) very good compensation was obtained. The first half of the diagram shows the polarograms recorded with both cells containing copper solutions without any bismuth. Curve c shows the compensation of the currents from the two cells. The compensation was not complete due to a difference in dropping rates. The polarograms shown in the second half of the diagram were recorded with one cell containing bismuth in addition to copper. The effect of altering the resistances to balance a difference in dropping rates is shown in curves 2, 3 and 4. The slight peak in the final curve is due to copper being reduced at a more positive potential in the presence of bismuth. The change in the half-wave potential is attributed to a change in anode potential caused by the bismuth. The phenomenon is discussed under the heading of "The anomalous effects in the bismuth wave" in appendix II

The compensation of the currents when the solutions contained copper at a concentration of 10^{-3}M (figure 5b) was not very successful.

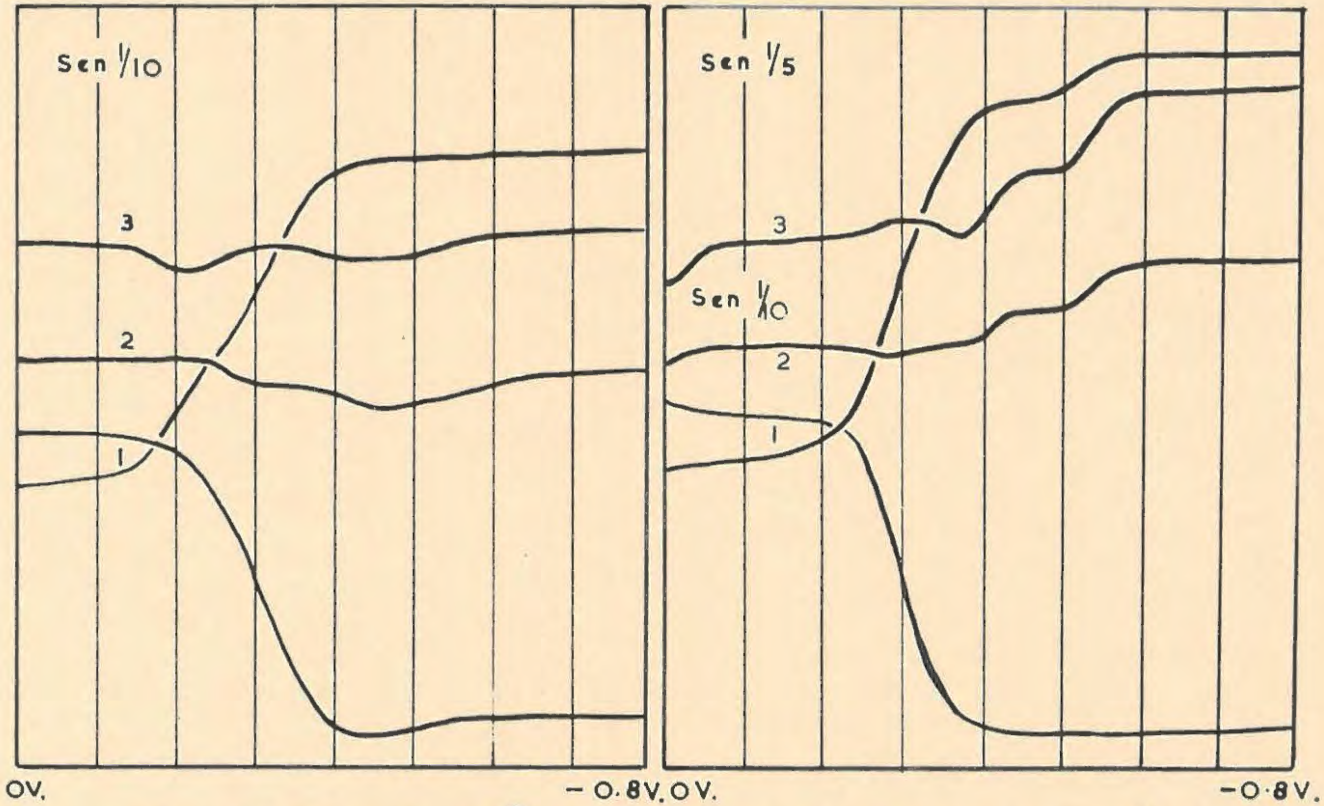
FIG. 5a DIFFERENTIAL CURVES OF 10^{-4}M Cu in 0·3M TARTRATE SOLUTION.



COMPENSATION OF 10^{-4}M Cu.
$R_1 = R_2 =$ 10,000 ohms.

COMPENSATION OF 10^{-4}M Cu
+ 10^{-4} NBi WITH 10^{-4}M Cu.
R_2 = 10,000
R_1 = : 1. 4,000 2. 4,000
3. 5,000 4. 6,000
ORIGINAL RECORDED
MANUALLY.

FIG. 5b DIFFERENTIAL CURVES OF 10^{-3}M Cu in 0.3M TARTRATE SOLUTION.



COMPENSATION OF 10^{-3}M Cu.

R_2 = 10,000 R_1 = :
1. 6,000
2. 7,400 } ohms.
3. 6,800

COMPENSATION OF 10^{-3}M Cu + 10^{-4}N Bi WITH 10^{-3}M Cu.

R_1 = 6,800 R_2 = 10,000 ohms.

ORIGINAL RECORDED MANUALLY.

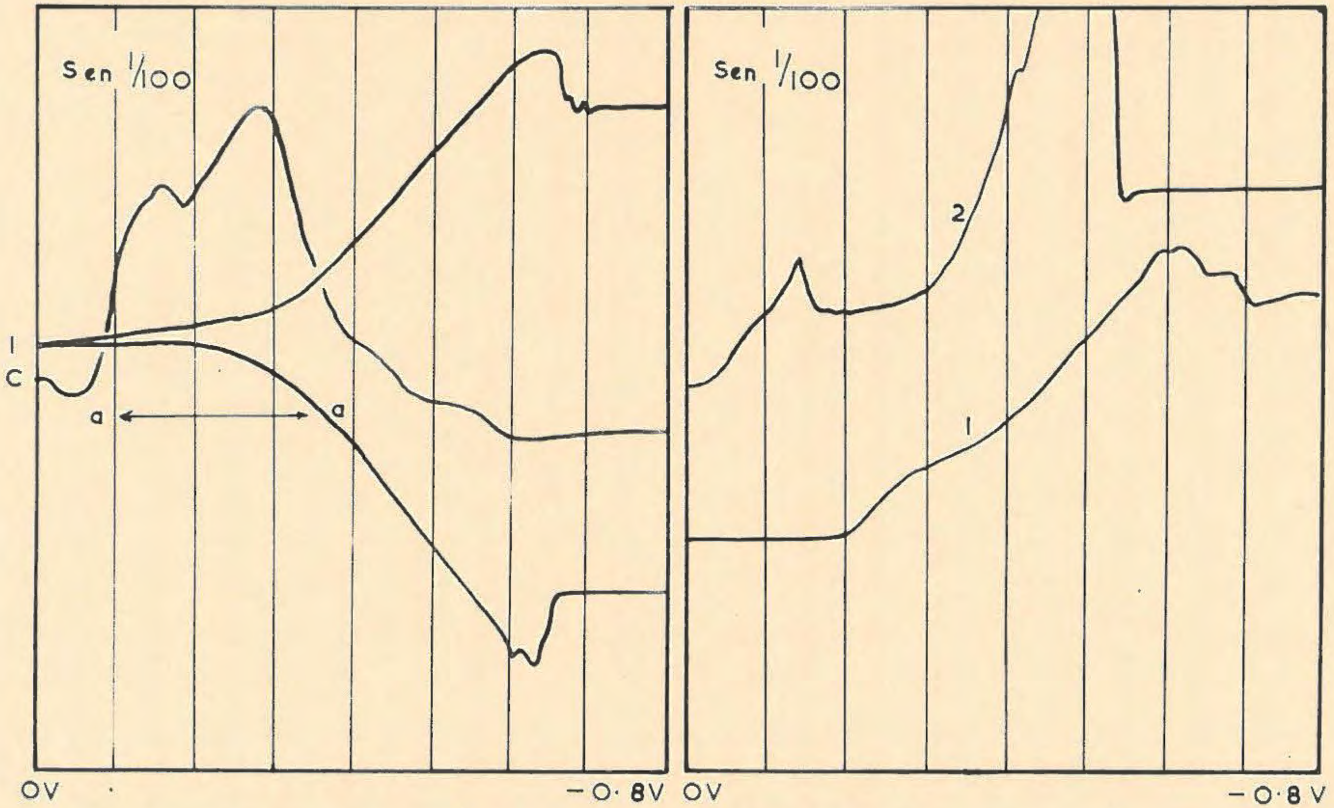
It proved as simple to determine the bismuth from the normal curve as the differential curve. However, on applying the technique to the concentrated copper solutions (10^{-2}M) satisfactory results were not obtained, even on adjusting the resistances. Numerous attempts were made to obtain suitable curves but without success. In most instances, the differential wave was quite unexpected. Large distortions appeared at potentials where the two normal curves were quite regular. (e.g. a —— a in figure 5c).

As a result of these experiments, it seemed that there were two problems which required solution before it could be expected to obtain successful differential polarograms. The copper maximum which occurred in the more concentrated solutions (see figure 5c) would have to be suppressed and the dropping rates of the two capillaries would have to be synchronised.

(b) The copper maximum. The use of gelatin , the most common maximum suppressor, was investigated. Results showed that this was only effective, in suppressing the copper maximum, at relatively high concentrations. The results of further experiments showed that the presence of large concentrations of gelatin was undesirable from the point of view of the reduction of bismuth. Under these conditions the wave of bismuth is flattened and at very high relative gelatin concentrations (one or two per cent) the bismuth wave is suppressed altogether. Methyl red, on the other hand, was found to be most suitable, the presence of 0.002% was sufficient to remove the copper maximum completely.

(c) Synchronisation of the dropping rates. This, it was felt, was the only problem requiring solution before the method of

FIG 5c DIFFERENTIAL CURVES OF 10^{-2}M Cu IN 0·3M TARTRATE SOLUTION.



COMPENSATION OF 10^{-2}M Cu

$R_1 = R_2$ = 10 000 ohms.

COMPENSATION OF 10^{-2}M Cu + 10^{-4}N Bi WITH 10^{-2}M Cu

1.) $R_1 = R_2$ = 10000 ohms.

2.) " 1000 "

ORIGINAL RECORDED MANUALLY.

differential polarography could be successfully applied even to concentrated solutions and at high sensitivities.

Arey and Smales (22) claimed that their method of drop control was applicable in cases where the interfering substance was present at a concentration 100 times greater than the substance being determined. An idea of the principle of their method will be obtained from the description of the apparatus used in the present research.

The apparatus used in this department, based on the principles used by Arey and Smales (22), is shown in figure 6. The parts were taken from a Struthers Dunn magnetic relay system. The two larger coils, which could be activated by A.C. or D.C., were modified so that they could be screwed down firmly onto the thermostat cover. Wooden capillary carriers were made and attached to the armatures. A screw for adjusting the amplitude of the armature movement was fitted above the coil. The coils for the two capillaries were wired in series and connected to the pulse-generating circuit as shown in figure 7. In this circuit a condenser is charged, through two variable resistances R_1 and R_2 , by a 110 volt DC supply. When the potential on the condenser reaches the striking potential of the neon lamp. the first relay coil is activated. This closes the circuit containing the 250 volt AC supply and the capillary coils. The armatures snap closed, thus moving the tips of the capillaries slightly, but sharply, thereby dislodging the mercury drops. The two coils are activated at the same instant of time thus synchronising the dropping rates. This rate may be changed by making an adjustment to the resistances R_1 and R_2 , which alters the time constant of the charging circuit.

FIG. 6 VIBRATING ELECTRODE.

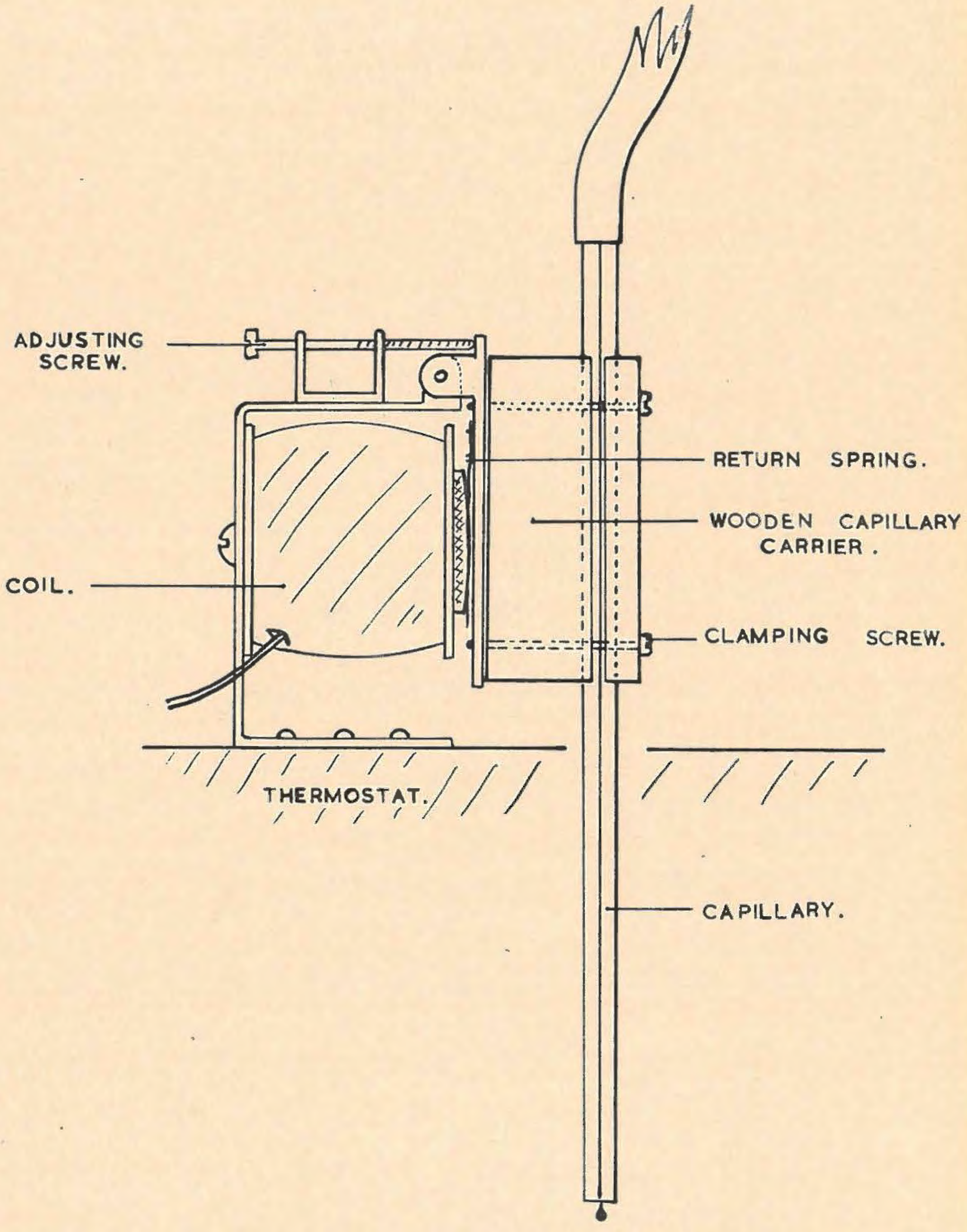
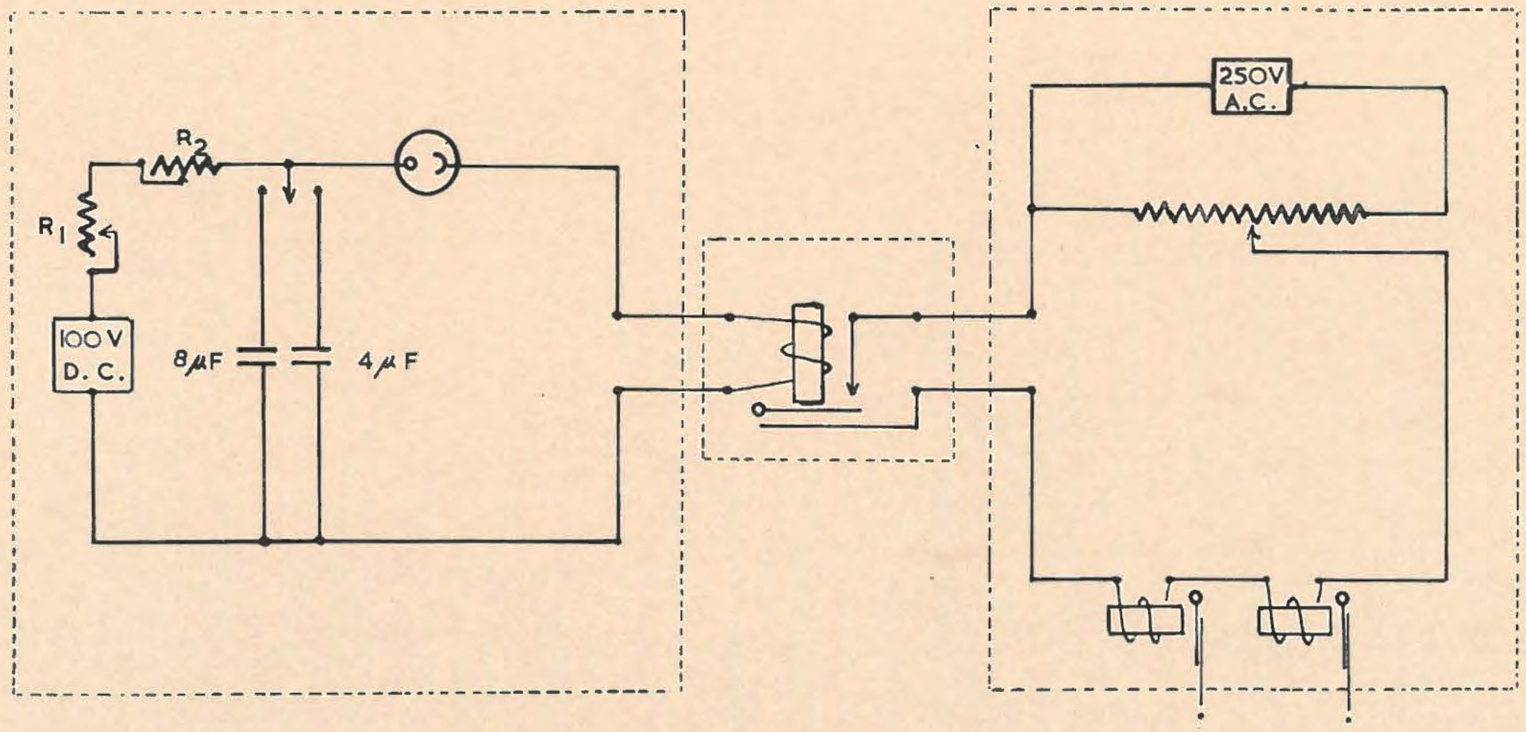


FIG. 7 SYNCHRONISATION CIRCUIT.



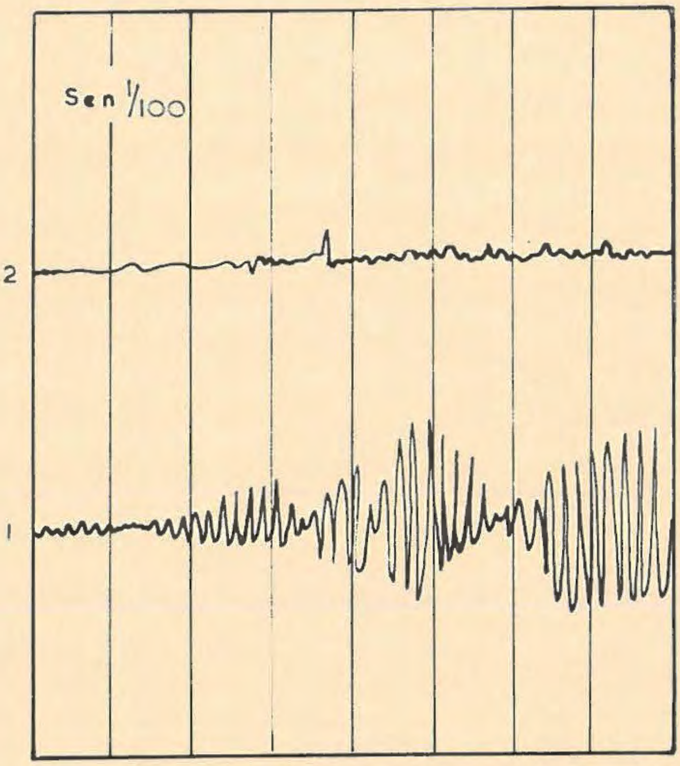
PULSE GENERATING CIRCUIT. 1st RELAY. CAPILLARY RELAY CIRCUIT.

It was found, by experiment, that the most satisfactory voltage to use in the capillary coil circuit was 70 volts. A smaller voltage would not activate the coils, while a higher one caused relay-bouncing which is a most undesirable condition, as it has the effect of stirring the solutions.

The apparatus was first used in the differential polarography of tartrate solutions containing copper at a concentration of 10^{-2}M., in the presence of methyl red as maximum suppressor. Standard calomel electrodes were used as anodes to avoid any difference between the anode potentials of the two cells. Differential curves were recorded, firstly, by using the normal electrodes without a galvanometer damping condenser and secondly, by using the vibrating electrode. The vibrating electrodes eliminated the effects of the galvanometer oscillations, but a large number of irregularities were present (see figure 8). The polarograms shown were recorded at a sensitivity of 1/100, and it can be appreciated that at 1/5 the magnitude of the irregularities was greatly increased. Under these conditions the detection of a wave due to bismuth would be impossible. Many attempts were made in an effort to eliminate the irregularities and, at the same time, to gain some idea as to their cause. Experiments were conducted with different activation voltages, pulse times and armature pole gap settings. Numerous types of materials were used as resilient buffers which were placed in the pole gaps. None of these experiments were successful and the method had to be abandoned.

Thus it had been found that of the three methods for completing the separation of copper proposed (page 29), the third and most ideal was not successful. Attention was therefore turned to the second.

FIG. 8 SYNCHRONISATION OF DROPPING RATES.



TWO SOLUTIONS OF 10^{-2}M Cu IN 0·3M TARTRATE.

1. NO DROP CONTROL OR DAMPING CONDENSER.
2. SYNCHRONISATION OF DROPPING RATES AT 10 DROPS IN 0·31 MINUTES.

ORIGINAL RECORDED PHOTOGRAPHICALLY.

This method involved the use of two samples, one for the determination of bismuth and iron after the ammoniacal separation of copper, the other for the determination of the remaining five trace elements after the electrolytic separation of copper. The treatment of the latter sample will be discussed first.

Of the elements to be determined on this sample antimony is the one which is reduced first in acid solutions. It may be calculated that when present at a concentration of 10^{-5}M, it would start to deposit at a potential of -0.568 volt (against the mercurous sulphate electrode). By using a cathode potential of -0.514 volt, thus allowing a safe margin, it is theoretically possible to reduce the copper concentration to a value of 10^{-6}M. Up to this stage in the research the lowest value obtained in practice was 10^{-2}M using a potential of -0.40 volt.

Experiments were carried out using a potential of -0.514 volt for the electrolysing voltage. The solutions of the copper samples were prepared as in previous experiments. The electrolysis was continued for 30 minutes after the current had fallen to a steady value. Polarograms recorded on a small sample of the resulting solution indicated that the copper concentration was of the order of 10^{-3}M. The remainder of the solution was electrolysed for a further 30 minutes, using a clean platinum cathode. It was shown polarographically that the copper concentration had been reduced to 10^{-4}M. From these data it seemed that in a sulphate-supporting electrolyte an equilibrium was being set up between the copper ions in the solution and the copper metal on the electrode. This was tested by electrolysing a bismuth solution at a potential of -0.514 volt for two hours using a copper plated cathode. At the end of this period a polarogram recorded on the solution showed a wave for copper corresponding to a concentration of 10^{-3}M. It should be pointed out that the usual technique of lowering the electrolysis vessel before breaking the circuit was adopted.

Returning to the electrolysis of the copper solution, it was found that by continuing the electrolysis, the copper concentration was eventually reduced to 10^{-6}M. It was realised that if the minor elements could be determined in the presence of copper at a concentration of 10^{-4}M it would mean a great saving of time. But the answer to this could not be given until the method of analysis had been worked out.

After the completion of the electrolysis the remaining solution was evaporated down to 20 ml. and transferred quantitatively to a 50 ml. beaker and evaporated to dryness. The residue was then ignited at 400°C for ten minutes to destroy any organic material. The residue could now be used for the determination of the trace elements.

It must be noted that lead is insoluble in the 1N sulphuric acid used for the electrodeposition. It is filtered off before the electrolysis but it is returned to the group after the separation of the copper. This will be described in detail in chapter 6.

BY A CHEMICAL METHOD.

The method used for separating the bismuth and the iron from the copper was based on the one described by Scott (23).

The sample was weighed out and dissolved in nitric acid. After the evaporation of the excess acid, the residue was dissolved in 100 ml of distilled water. Sufficient concentrated ammonia solution was added to redissolve the copper hydroxide. Ammonium carbonate was added and the mixture was left on the water-bath for twelve hours. It was filtered and the precipitate immediately washed with very dilute hot ammonium hydroxide. The filter-paper and precipitate were transferred to a 50 ml. beaker and after the paper had been burnt off at as low a temperature as possible in a furnace the residue was ignited at 400°C for 10 minutes to destroy any organic material. The residue could be used for the determination of iron and bismuth.

A detailed description of this method will be found in chapter 6.

Chapter 5.

THE QUALITATIVE DETERMINATION OF THE TRACE ELEMENTS.

Introduction.

Having discussed the separation of the copper from the impurities, attention may now be focussed on the main problem investigated in the research for this thesis, namely, the qualitative analysis of the trace elements. Usually in polarographic research, of the type undertaken here, once a method or scheme of analysis has been established on a qualitative basis, it is a relatively simple task to convert it to a quantitative one.

The methods of copper separation made it necessary to use at least two copper samples for the determination of the trace impurities. Ideally what was required, therefore, were two supporting electrolytes. The first of these would be used for the determination of iron and bismuth on a single sample, and the second for the simultaneous determination of lead, antimony, cobalt, nickel and manganese.

The following approach to the problem was adopted. Seven standard stock solutions were prepared from the purest salts available of the elements being considered. Samples of these solutions were then used for investigating the characteristics of the different elements in a number of supporting electrolytes. In early experiments attempts were made to obtain a curve for a group of elements, without preliminary investigation. This approach was found to be impracticable as it was difficult to trace any irregularity which occurred in the polarogram, to the particular element causing it.

To overcome this difficulty the following procedure was adopted. When a new electrolyte was being investigated, the reduction of one element, in the solution, was followed. Not before a suitable polarogram had been obtained for the first element would a second be added to the system, and so on. The results obtained after each addition will be discussed below. However the only supporting electrolytes which will be mentioned, are those which gave satisfactory results.

The remainder of the discussion may be divided under two headings corresponding to the analysis of the two copper samples.

The determination of iron and bismuth.

These were the only two elements that would be present quantitatively, in the precipitate after the ammoniacal separation of copper. But the scheme of analysis would have to be designed in such a way, that the possible inclusion of the other minor elements due to adsorption, would not interfere with the determinations of iron and bismuth.

The first electrolytes used were the three strong acids; hydrochloric, nitric and sulphuric, as these were presumed to be the best solvents for the residue from the copper separation.

Antimony was the other minor element to be considered, as, according to Lingane's 'Polarographic Spectrum' (24), it is the first one reduced after bismuth.

A set of curves was recorded to compare the separation of antimony and bismuth in each of the three acids. Where necessary the curves were recorded both normally and by the derivative technique.

The experiment using hydrochloric acid has been mentioned before, in chapter 3, in connection with the Levèque-Roth circuit. In the normal polarograms the waves of antimony and bismuth were poorly separated. However when using the derivative technique, the results indicated that this method could be used for the quantitative determination of antimony and bismuth in hydrochloric acid. These results are of considerable importance, as it has not been found possible in the past to use hydrochloric acid in this determination.

The results obtained when using nitric acid as the supporting electrolyte were most unsatisfactory. Poorly defined waves were obtained for both antimony and bismuth.

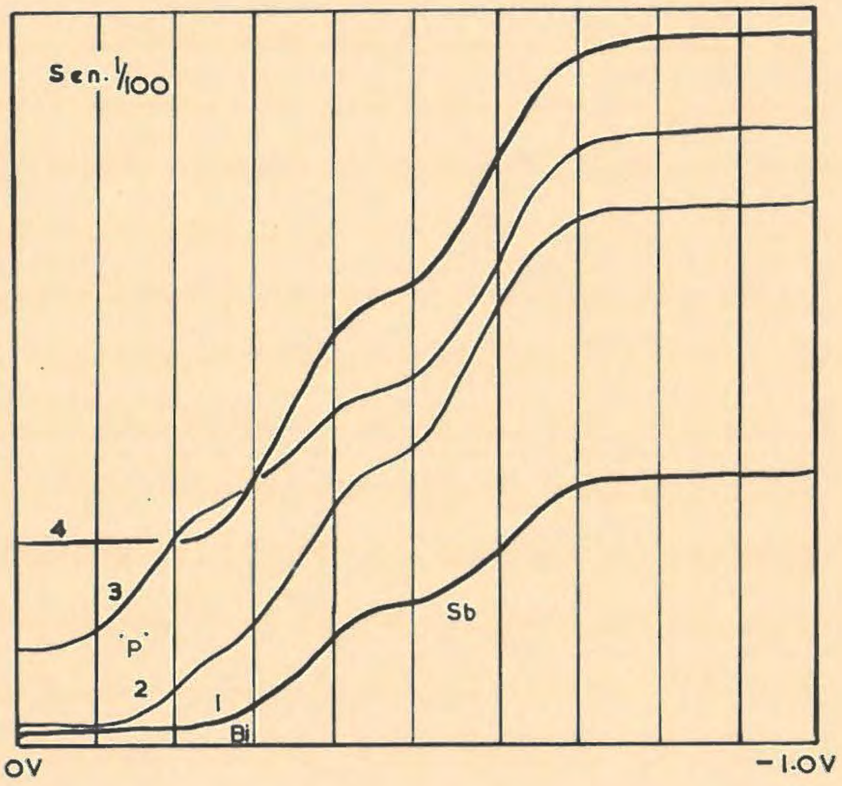
A most interesting set of results was obtained when using sulphuric acid. The first polarogram recorded on a solution containing the two elements, showed well-defined waves for each of them. The separation, using the normal technique, of the two waves was sufficient to allow quantitative determination. However, on repeating the experiment on the same solution at a higher sensitivity, two waves were found at a potential range where previously there had been only a single wave for bismuth. When the curve was repeated for the third time two distinctly separate waves for bismuth were present. It was found that the shape of the bismuth wave could be restored to normal, by bubbling N_2 through the cell. After this had been done perfect waves resulted. The results of this experiment are shown in figure 9. Note: Curve 1 was recorded at a sensitivity of 1/200. The wave which formed and was removed by nitrogen, (it will be referred to in future as the 'pre-wave'), is marked 'P' in the figure.

Although a 'side-track' to the main course of investigation, the interesting phenomenon of the pre-wave was investigated further.

FIG. 9 THE BISMUTH 'PRE-WAVE.'

10^{-3}M Bi 10^{-3}M Sb in 1N H_2SO_4

+ 0.05% GELATIN.



REMOVED O_2 BEFORE CURVE 1.
CURVES 1, 2, and 3 RUN IN SUCCESSION.
BUBBLED N_2 FOR 10 MINUTES BEFORE CURVE 4.

ORIGINAL RECORDED MANUALLY.

The results obtained will be found in appendix II.

It was realised that, on occasions, the copper separation might not be complete, which would result in the presence of copper ions in the solution. This possibility was not overlooked. Experiments were conducted to determine the effect of the presence of this ion on the determination of antimony and bismuth. Using 1N. sulphuric acid as the supporting electrolyte curves were recorded on solutions containing bismuth and copper. The results indicated that the presence of traces of copper would cause high results in a bismuth determination, since the waves of the two ions merged into one. In addition to the above difficulty, which occurred in all three acid solutions, these supporting electrolytes were found to be unsuitable for the determination of iron. The iron wave started at zero potential which made the measurement of its wave-height very difficult and in addition the wave overlapped with the copper wave. With all these objections raised, it was obvious that the acids would have to be abandoned and a more suitable electrolyte found, for the determination of iron and bismuth.

It has already been mentioned, page 23, that an acidic tartrate solution is a suitable supporting electrolyte for the separation of bismuth from copper. In addition, the results reported in the literature indicated that the other minor elements would not interfere. Kolthoff and Lingane (15) reported a wave for ferric iron in alkaline tartrate but made no mention of one in acid solutions. Both lead and antimony are reduced in this supporting electrolyte but at a more negative potential than the half-wave potential of bismuth.

Polarograms were recorded on two solutions, one 10^{-2}M with respect to ferric iron and the other 10^{-4}M with respect to bismuth. (These concentrations were chosen as they are the approximate concentrations of the elements in a 10 ml. solution of 5 grams of the copper sample). The results indicated that, in fact, iron is reduced in acid tartrate solution at a half-wave potential of -0.15 volt. The wave was well-defined, but contained a large irregular maximum at a potential of -0.5 volt, i.e. at a potential well after that at which the limiting current was reached. This maximum was successfully suppressed by the addition of methyl red. The resulting wave seemed most satisfactory for use in the analytical determination of iron.

Bismuth was reduced at a half-wave potential of -0.5 volt, giving a well-defined wave when the curve was recorded at a sensitivity of 1/5. At 1/100, (the sensitivity at which the iron wave was recorded) the bismuth wave was so small that it would have been unsatisfactory for quantitative analysis.

In the above scheme, therefore, iron caused the same difficulties as copper had done in the experiments discussed in chapter 4. Once again the derivative and differential techniques were applied, in an attempt to obtain waves for bismuth in the presence of large concentrations of iron, but without success. In both cases irregularities occurred in the potential range of the iron maximum, in spite of the fact that it had been suppressed by methyl red. These irregularities made the detection of any wave or peak of bismuth quite impossible.

Attempts at overcoming these difficulties by recording the curves at higher pH's were unsuccessful. Kolthoff and Lingane (15) found that ferric iron is reduced in alkaline tartrate at a potential of -0.9 volt measured against a S.C.E. Kny-Jones (25) has used tartrate to prevent bismuth hydroxide from precipitating in alkaline solutions. In practice it was found that bismuth and iron waves were separated in alkaline solutions. The iron wave was displaced from a potential of -0.4 volt at a pH of 5 to -1.4 volt at a pH of 8. But the polarograms of bismuth at higher pHs than 7 gave very poorly defined waves. This method of separation was therefore not satisfactory.

In the results of their investigation on the use of sodium fluoride as supporting electrolyte, West, Dean and Breda (26) made no mention of a wave for iron. West and Dean (27) have used sodium fluoride to prevent the interference of iron in the determination of nickel in steel. From these results it was assumed that sodium fluoride could be used to eliminate the interference of iron in the determination of bismuth.

A solution was prepared containing iron and bismuth in a solution of sodium potassium tartrate as supporting electrolyte. A polarogram recorded on this solution revealed, as was expected, a wave for iron only. With the applied potential set at a value just high enough to obtain the limiting current for iron, very small quantities of solid sodium fluoride were added to the solution with shaking. These additions were continued until the current due to the reduction of iron was decreased to zero. A polarogram recorded on the resulting solution contained a wave at a potential of -0.5 volt which was identified as being due to bismuth.

The above experiment represented a successful conclusion to the first part of the main task, as bismuth and iron could be determined on the same sample. This meant a great saving in time as the recording of the two polarograms only took ten minutes. It is estimated that the determination of the two elements, after the copper separation, by the classical method, would take a few hours.

The determination of lead, antimony, cobalt, nickel and manganese.

Although these were the only elements to be determined on the second sample, iron and bismuth were included in the scheme. This was necessary as small quantities of these elements might remain after the electrolytic separation of copper.

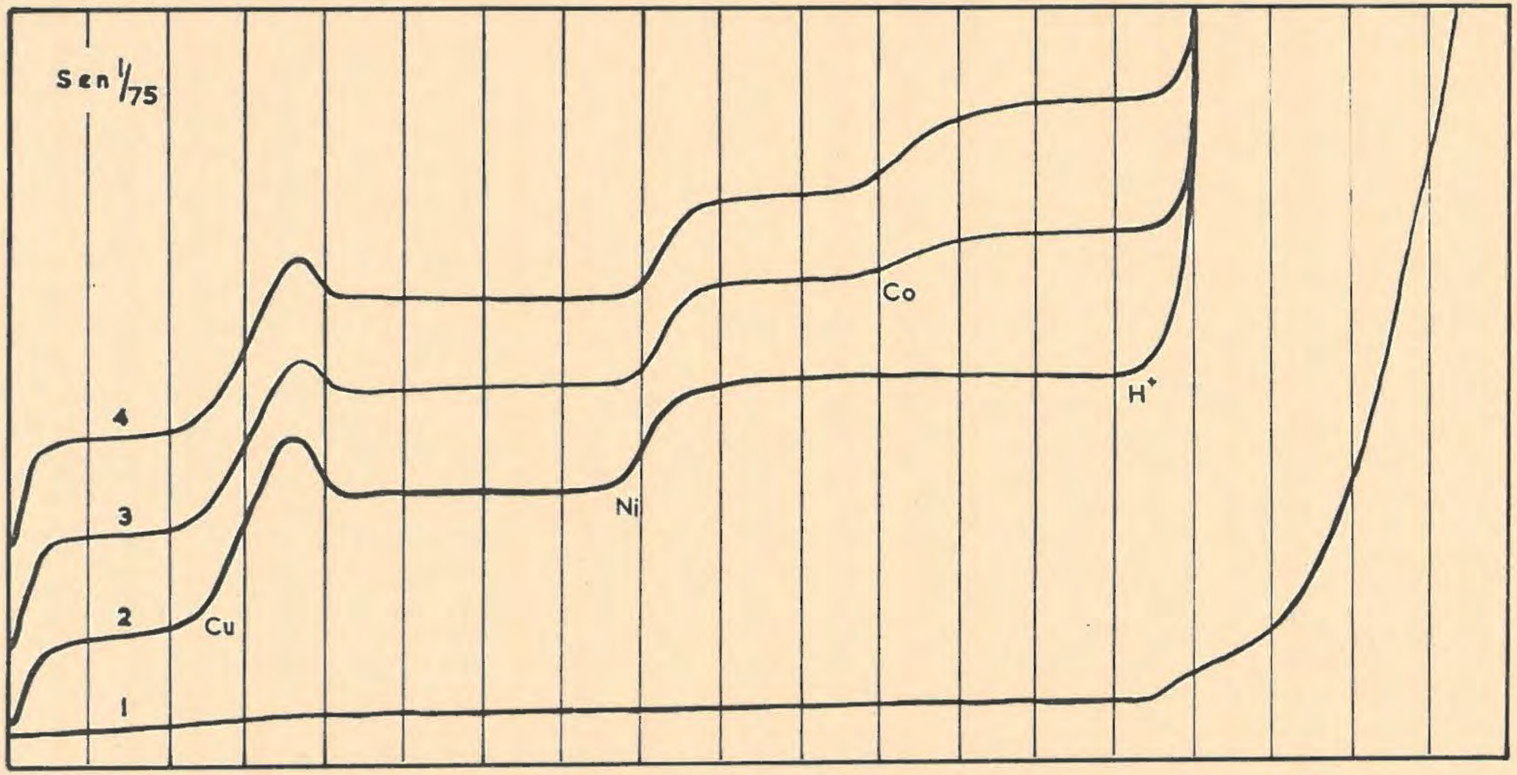
Results were available in the literature on the determination of nickel and cobalt and these were therefore used as a starting point. Lingane and Kerlinger (28) found that an electrolyte 1N with respect to KCl and 0.008M with respect to pyridine, was most suitable for the simultaneous determination of cobalt and nickel.

Curves were recorded on the pure supporting electrolyte, and after the addition of each of the ions, copper, nickel and cobalt. The results are shown in figure 10. (Copper was included to ascertain whether its complete separation was necessary.) The waves obtained for the elements were most satisfactory, since they were well-defined and well-separated.

The attempt to include manganese in the scheme was not successful. Dilute solutions of this element produced excellent polarographic waves, but in the presence of nickel and cobalt the hydrogen wave obscured that of manganese. In addition to this difficulty, the electrolyte was unpleasant to use. It was therefore shelved, temporarily, in the hope that a more suitable supporting electrolyte would be found.

In 1948 West, Dean and Breda (26) published the results of their work on the use of sodium fluoride as a supporting electrolyte. They investigated the reduction of 69 different ions, individually, in a 0.5M

FIG. 10 Cu, Ni, Co, in 1N KCl + 0·008M + Pyridine 0·05% Gelatin.



1. Pure electrolyte.
2. 0·002M Cu, 0·001M Ni.
3. 0·002M Cu, 0·001M Ni, 0·0005M Co.
4. 0·002M Cu, 0·001M Ni, 0·001M Co.

ORIGINAL RECORDED PHOTOGRAPHICALLY.

solution of sodium fluoride (Na_2F_2). (The correctness of this formula is questioned, NaF being suggested as the correct one. NaF is the formula which will be used in the ensuing discussion). These workers investigated all the ions which were reduced at the dropping electrode in the above electrolyte. However no results were discussed for the simultaneous determination of two or more ions. Table 1 gives a list of half-wave potentials, and the pHs at which they were obtained. Only the ions being considered in this investigation are listed. Although simple ionic formulae of the ions are used in the table, it must be borne in mind that they probably exist, in the sodium fluoride solution, as complex fluorides.

Considering the results given in the table and bearing in mind the possible use of derivative polarography, it would seem that copper, bismuth, lead, antimony, nickel, cobalt and manganese could be determined simultaneously.

Initially the electrolyte used was a 1M solution of sodium fluoride containing 0.01% of gelatin without any pH control. Polarograms were recorded for each of the three elements, cobalt, nickel, and manganese, in turn. The curve for manganese was most satisfactory, showing a well defined wave at a half-wave potential of -1.7 volts. The waves of nickel and cobalt were, however, very poor, both occurring at potentials between -1.25 and -1.30 volts.

West and Dean (27) found that the waves of nickel were affected if fresh gelatin was not used. Fresh solutions of gelatin were prepared from both the commercial samples available. These were used in similar experiments to those reported in the preceding paragraph, but no improvement

TABLE I.

HALF-WAVE POTENTIALS OF IMPURITIES IN SODIUM FLUORIDE.

ION.	POTENTIAL VS. S.C.E.	pH.
Cu^{++}	− 0·003	5·1
Bi^{+++}	− 0·074	0·7 − 2·1
Pb^{++}	− 0·414	1·1 − 2·75
Sb^{+++}	− 0·683	3·0 − 4·4
Ni^{++}	− 1·12	4·3 − 6·4
Co^{++}	− 1·38	2·9 − 6·0
Mn^{++}	− 1·55	2·4 − 6·8
Fe^{++}	IS NOT REDUCED.	

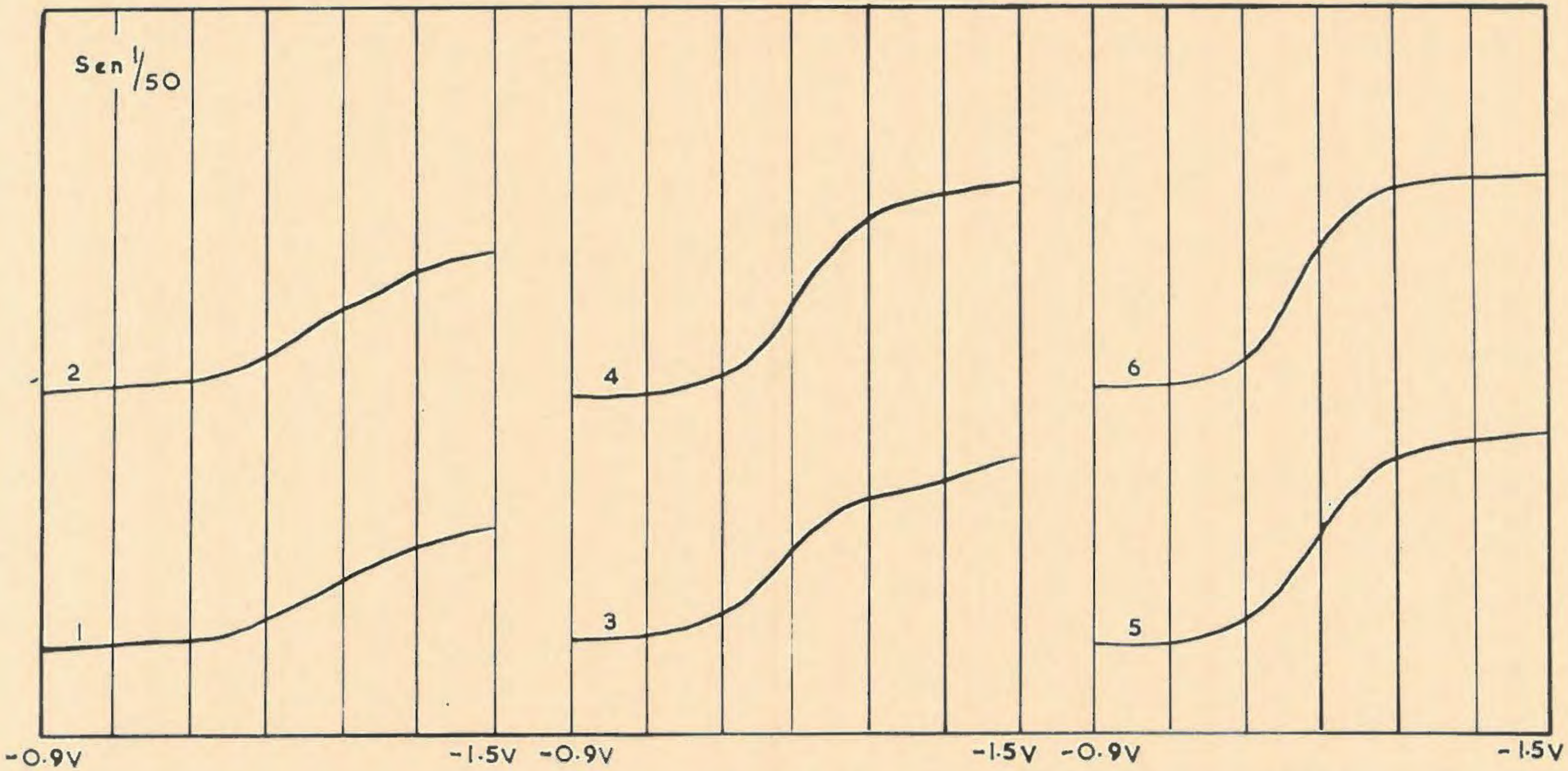
in the nickel waves was noticed.

The supporting electrolyte was also considered as a cause of the trouble. Six solutions were prepared with the concentration of sodium fluoride varying from 1M to 0.05M. In addition, each solution contained nickel at a concentration of 10^{-3}M and 0.05% gelatin. Polarograms recorded on these solutions (see figure 11) revealed that the shape of the nickel wave was being affected by the concentration of the supporting electrolyte. In the 1M solution the nickel wave was small and poorly defined, but the wave in the 0.05M solution suffered from neither of these defects. These polarograms were repeated a short time later using the same solutions and another improvement was noted. This seemed to indicate that the shapes of the waves could be improved by allowing the solutions to stand for some time before recording the polarograms. This assumption was validated when polarograms were recorded on a fresh set of solutions, immediately, and after three days. In every case the curves after three days were better than the earlier ones. The slope of the waves had been increased as well as the wave-heights.

Similar experiments were made using cobalt solutions and similar results obtained, only in the case of cobalt the wave-heights did not alter to the same degree.

The effect of the concentration of the supporting electrolyte on the separation of cobalt and nickel was also investigated. Polarograms were recorded on six solutions similar to those used before, containing these two elements together. The solutions in which the supporting electrolyte concentration was relatively high, resulted in curves in which

FIG. 11 THE EFFECT OF THE NaF CONCENTRATION ON THE Ni WAVE.



10^{-3}M Ni in 1.) 1M 2) 0.5M 3.) 0.25M 4.) 0.15M 5.) 0.1M 6.) 0.05M NaF.
+ 0.05% GELATIN.

ORIGINAL RECORDED
MANUALLY.

it was quite impossible to measure the individual wave heights. This became practicable however, in the case of the solutions in which the sodium fluoride concentration was below 0.15M.

In routine analysis a delay of three days, between the preparation of solutions and the recording of the polarograms, could not be tolerated. An experiment was carried out to ascertain the minimum time required for this interval. Curves were recorded on a nickel solution at various intervals up to 48 hours. The final curves were ideal, having horizontal portions for the residual and limiting currents, with a very rapid rise in current between them. However, the curve obtained after 45 minutes was reasonably satisfactory.

A possible explanation of this time-effect was thought to be that the reaction leading to the formation of the fluoride complex is not an instantaneous one. However, in this case the more concentrated solution of sodium fluoride should have given the best results. West, Dean and Breda (26) made no mention of the effects of time and supporting electrolyte concentration on the nickel and cobalt waves. This was in spite of the fact that they used a solution of 1.0M sodium fluoride (NaF) at which concentration the effects are clearly evident.

Naturally there is a limit to which the supporting electrolyte may be diluted. It must be sufficiently concentrated to permit of the formation of the complexes and to carry most of the current. In subsequent work, when three or more ions were to be determined, an electrolyte concentration of 0.1M sodium fluoride was used.

Having successfully obtained polarograms for cobalt and nickel the inclusion of manganese in the group may be discussed. Polarograms were recorded on 0.1M solutions of sodium fluoride containing copper, nickel, cobalt and manganese. The final curve obtained showed extremely well defined waves for manganese and copper, while these of cobalt and nickel were quite satisfactory. Thus sodium fluoride had proved a superior electrolyte to potassium chloride containing pyridine.

All the ions already included in the scheme had given waves at potentials approximately 0.1 volt more negative than the half-wave potentials listed in table 1. On this basis, when antimony was introduced, it was expected to give a wave at approximately -0.8 volt. A polarogram recorded on a sodium fluoride solution containing copper, nickel, cobalt, manganese and antimony revealed a well-defined wave for antimony at a potential of -0.57 volt. Since antimony is reduced in acid solution according to the following equation (29):

$$SbO^+ + 2H^+ + 3e^- = Sb + H_2O$$

the anomalous deposition potential was attributed to the high acid concentration of the solution. The hydrogen ions were introduced by the stock bismuth solution, which was strongly acidic. Two other effects after the introduction of antimony were noted. The wave of manganese was almost obscured by the hydrogen wave and the waves of cobalt and nickel were poorly defined. On neutralising the acid in stages and recording the polarograms after each addition, the antimony wave was gradually displaced to a more negative potential and eventually removed altogether. This occurred as antimony ions are not reduced in the absence of hydrogen ions. At pHs approaching 7 the waves of cobalt, nickel and manganese were restored to their previous form.

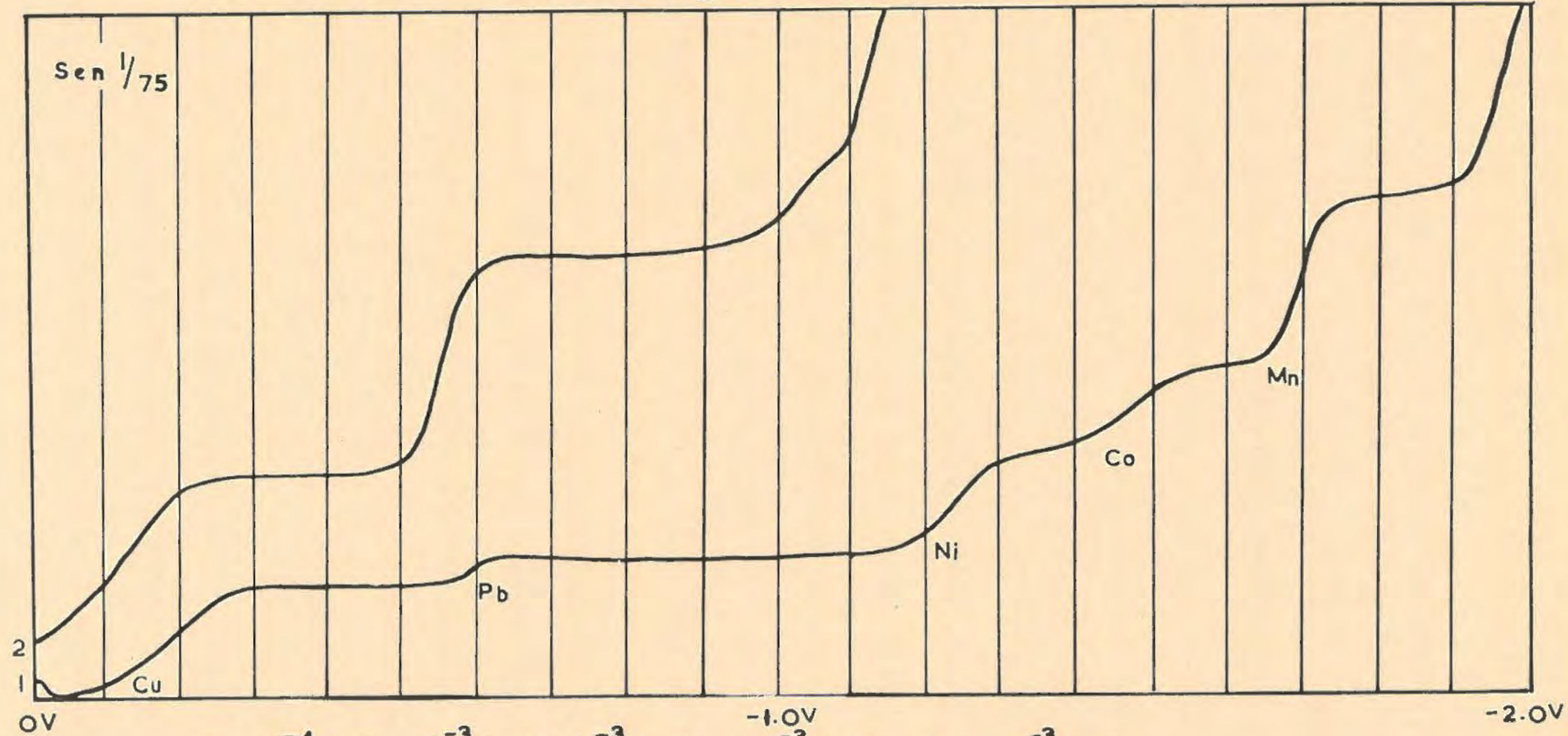
Leaving out the antimony, but adding lead to the previous group, a new difficulty was introduced. Lead fluoride is sparingly soluble and as a result the polarogram recorded on the above solution showed only a small wave for lead. The waves of nickel, cobalt and manganese were however not affected. This step indicated that nickel, cobalt and manganese could be determined in the presence of lead. Sufficient nitric acid was added to dissolve the lead fluoride and the polarogram was recorded again. In this case a perfect wave was obtained for lead; the results are shown in figure 12.

All the results obtained, up to this point, on the use of sodium fluoride as a supporting electrolyte, were now combined to give a method for the qualitative determination of lead, antimony, nickel, cobalt and manganese.

A neutral 0.1M solution of sodium fluoride was prepared containing the five ions mentioned above. A polarogram recorded on this solution gave most satisfactory waves for nickel, cobalt and manganese. Just sufficient nitric acid was added to dissolve the lead fluoride without reducing the pH to a value which would cause the antimony and lead waves to overlap. The polarogram recorded on this solution contained waves for antimony and lead and a poor wave for cobalt and nickel. The manganese wave was obscured by that corresponding to the reduction of hydrogen.

Copper had been included in the above scheme and was found not to interfere. Iron is not reduced at the dropping electrode in sodium fluoride solutions. This left bismuth as the only element which could cause difficulties. Experiments carried out showed that, like antimony, it was not reduced in neutral solution while in acid tartrate solutions

FIG. 12 Cu, Ni, Co, Mn and Pb IN 0.1M NaF. SATD. Na_2SO_4 TO REMOVE DISSOLVED O_2 + 0.05% GELATIN.



5 X 10^{-4}M Cu, 10^{-3}M Ni, 10^{-3}M Co, 10^{-3}M Mn and 10^{-3}M Pb

1.) IN NEUTRAL ELECTROLYTE.

2.) Pb DISSOLVED IN HNO_3 pH ± 1.2.

ORIGINAL RECORDED MANUALLY.

it gave a wave which coincided with that of copper, but did not interfere with the reduction of lead.

Thus it had been shown that, by using sodium fluoride as the supporting electrolyte, lead, antimony, cobalt, nickel and manganese could be determined on one sample. This represented a most satisfactory conclusion to the second half of the main task.

In the following chapter the successful results obtained so far in this research will be reviewed in the form of a proposed method of analysis for iron, bismuth, lead, antimony, nickel, cobalt and manganese in blister and refined copper.

Chapter 6.

THE PROPOSED METHOD OF ANALYSIS.

As a result of the research carried out on the separation of copper and the qualitative determination of the elements, the following method of analysis is proposed for the seven trace impurities.

The complete analysis is carried out on two samples of the copper. In the case of blister copper 10 gram samples are used, while 30 grams of the refined metal are required. The method is divided into two parts.

(a) The determination of iron and bismuth.

The sample is weighed out and dissolved in the minimum volume of 1:2 nitric acid. Any excess acid is evaporated and the solution diluted to 100 ml. with distilled water. Sufficient ammonium hydroxide is added to precipitate the bismuth and ferric hydroxides, and to form the copper ammonia complex. Five grams of ammonium carbonate is added and the solution left on the water-bath for twelve hours. It is then filtered, and the precipitate immediately washed as free as possible of copper with a very dilute solution ammonium hydroxide and ammonium carbonate.

The filter paper and precipitate are transferred to a 50 ml. pyrex beaker which is then placed in a muffle furnace. The paper is burnt off at as low a temperature as possible and the residue ignited at 400°C for ten minutes to destroy organic material. This residue contains all the iron and the bismuth plus traces of the other minor elements.

Exactly 10 ml. of a supporting electrolyte, 0.3M with respect to sodium potassium tartrate, and containing 0.002% of methyl red, is added. The solution is warmed to 60°C, to aid in the dissolving of the residue, cooled, and poured into the polarographic cell. After bubbling nitrogen through the solution a polarogram is recorded using a mercury anode and the dropping mercury cathode. The resulting polarogram contains a wave for iron.

The applied potential is now set to a value just high enough to obtain the limiting current for iron. Very small quantities of solid sodium fluoride are added to the solution with shaking. These additions are continued until no current, due to the reduction of iron, flowed. A second polarogram is recorded which now shows a wave due to the reduction of bismuth.

A number of solutions, containing different volumes of bismuth and iron standard solutions, are made up in 50 ml. beakers. The contents of the beakers are evaporated to dryness and the residues treated in the same manner as before to enable polarograms to be recorded for bismuth and iron. Standardisation graphs for these two elements are prepared by plotting the wave heights obtained as a function of the concentrations of the respective ions. By comparing the heights of the waves of bismuth and iron obtained for the unknown samples with these graphs the concentrations of these two elements in the copper could be calculated.

(b) The determination of lead, antimony, nickel, cobalt and manganese.

The second sample is weighed out and dissolved in the minimum volume of 1:2 nitric acid. Two ml. of sulphuric acid is added and the solution evaporated until fumes of sulphuric acid are evolved.

The residue is dissolved in 50 ml. of water and a further 2 ml. of concentrated sulphuric acid is added. The lead sulphate precipitate is filtered off, washed carefully and then set aside for later use. The filtrate and washings are united in a 150 ml. beaker and the solution diluted or evaporated to 100 ml. This solution is then electrolysed at a cathode potential of -0.514 volt against a $Hg/Hg_2\,SO_4$ (satd.) 1N H_2SO_4. electrode, and the electrolysis continued until the current has fallen to a steady value. The platinum cathode is removed taking care to wash it well collecting all the washings in the electrolysing solution. A clean cathode is fitted to the apparatus and the electrolysis continued for a further 30 minutes.

The solution is evaporated to about 20 ml., transferred quantitatively to a 50 ml. beaker and the solution evaporated to dryness. The filter paper and lead sulphate precipitate are added to the residue and the beaker placed in the muffle furnace. After burning off the paper at as low a temperature as possible the residue is ignited at 400°C for 10 minutes.

The beaker with its contents is cooled, and exactly 10 ml. of the supporting electrolyte, 0.1M with respect to sodium fluoride and containing 0.05% gelatin, is added. The beaker is warmed to effect a solution of its contents, cooled, and the solution poured into a polarographic cell. The dissolved oxygen is removed from the solution by bubbling nitrogen through the cell for ten minutes, and a polarogram is recorded. The resulting curve contains waves for any residual copper, nickel, cobalt and manganese.

Just sufficient nitric acid is added to dissolve the lead fluoride and another polarogram is recorded, which contains waves for lead and antimony.

Once again standard solutions of the ions being determined are prepared in 50 ml. beakers. The solutions are evaporated to dryness and the residues treated as outlined above to enable polarograms to be recorded for the five ions present. The wave-heights are measured and plotted as a function of the concentrations of the individual ions. By comparing the wave-heights obtained on the polarograms recorded on the 'unknown' solutions, the concentrations of lead, antimony, nickel, cobalt and manganese, in the copper could be determined.

The estimated time for the complete analysis of the seven impure elements is in the region of fourteen hours. This estimate includes the twelve hours that the first solution spends on the water-bath. In comparison with the few days that are required for a similar analysis using classical methods, this represents a great saving in valuable time.

Unfortunately the amount of time spent in reaching this stage in the research was much greater than originally anticipated. It was, therefore, impossible to perform extensive practical tests on the proposed method. However, preliminary experiments were carried out on the determination of iron and bismuth.

Chapter 7.

THE DETERMINATION OF IRON AND BISMUTH.

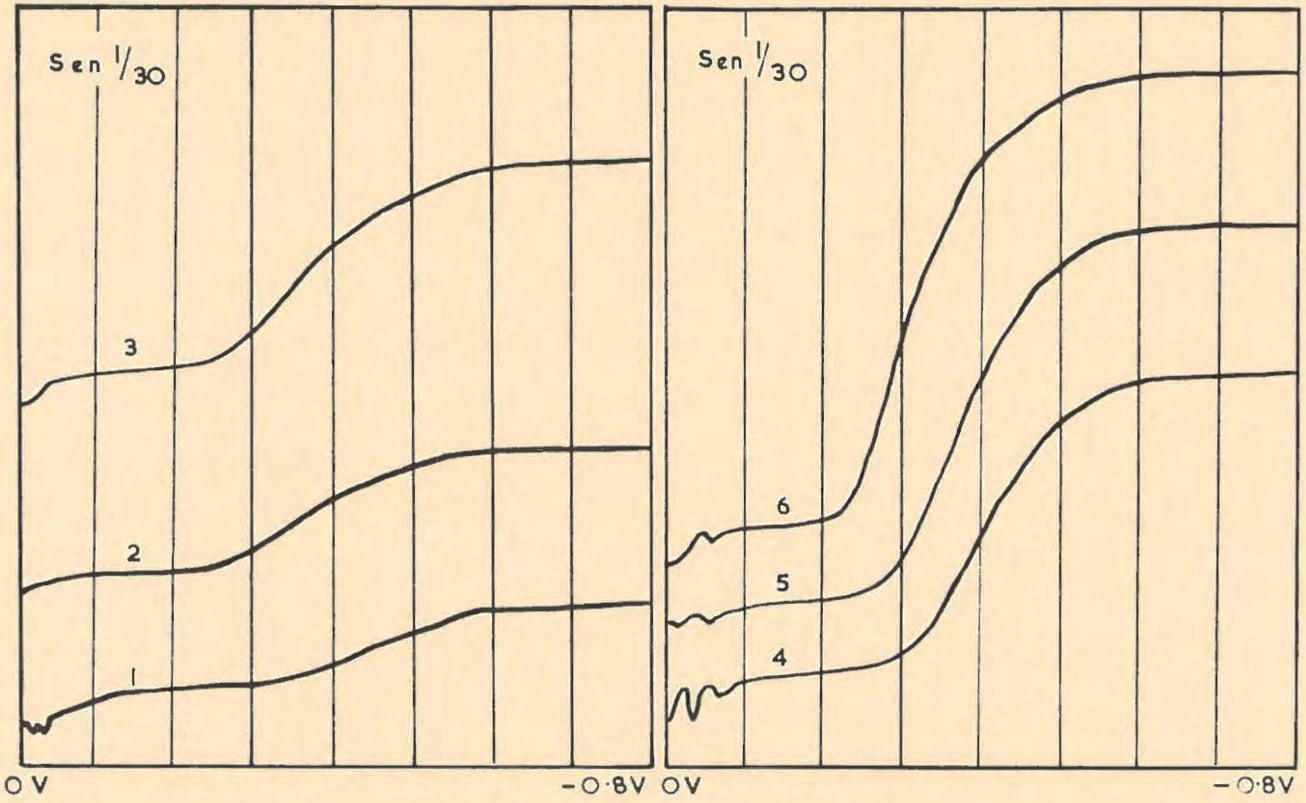
Three samples (A, B and C.) of blister copper, and one (J) of the refined metal were weighed out and treated exactly as recommended in the proposed method. When drawing up the standardisation graphs one alteration was made. The wave-heights were plotted as a function of the volume of the stock solutions used, and not as a function of the concentration. Each polarogram (for the 'known' and the 'unknown' solutions) was recorded three times, and the mean of the three wave heights used in the determination.

Determination of Iron.

The iron stock solution was prepared by dissolving 0.771 grams of a pure sample of Fe_2O_3 in the minimum volume of concentrated hydrochloric acid, and diluting the solution to 1000 ml. This was stock solution A. A second solution (B) was prepared by diluting 100 ml. of A to 1000 ml. with distilled water. This second solution was used for preparing the standard iron samples of low concentration.

Results. The wave heights for the standardisation graph, (figure 13b), which were obtained from the curves shown in figure 13a, are tabulated below.

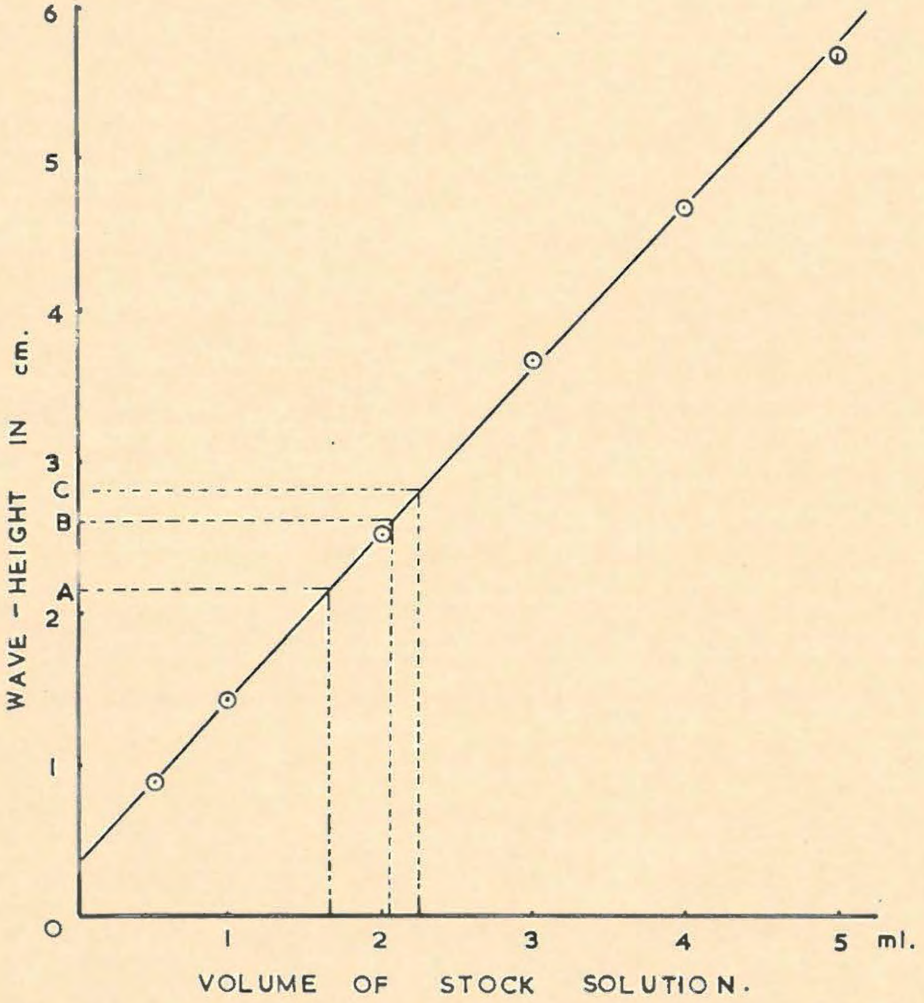
FIG. 13 a STANDARDISATION CURVES OF IRON IN 0·3 M TARTRATE + 2 ml METHYL RED per. 100 ml. pH 6. Temp. 30·50 °C.



1) 0·5, 2) 1, 3) 2, 4) 3, 5) 4, 6) 7 ml OF STOCK SOLUTION MADE TO 10 ml.

PHOTOGRAPHIC ORIGINAL. ONE CURVE FROM EACH SET SHOWN.

FIG. 13 b STANDARDISATION GRAPH FOR IRON.



Volume of iron stock solution in ml.		Wave height in cm.	Mean wave-height in cm.
5	(B)	0.90, 0.90, 0.90	0.90
10	(B)	1.43, 1.45, 1.44	1.43
2	(A)	2.60*, 2.51, 2.53	2.52
3	(A)	3.70, 3.69, 3.65	3.68
4	(A)	4.72, 4.70, 4.69	4.70
5	(A)	5.69, 5.70, 5.40	5.70

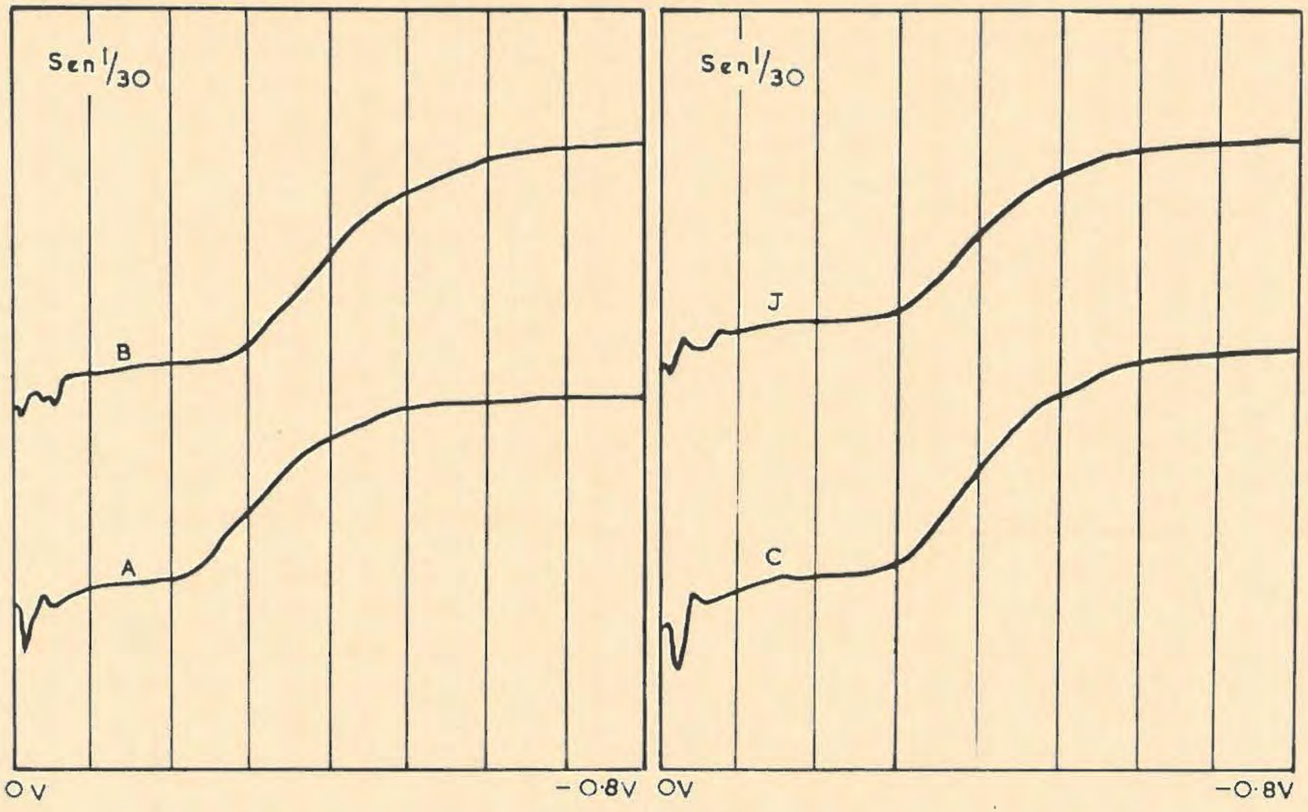
* Value ignored.

The results obtained for the unknown samples are tabulated below. The curves from which the wave-heights were taken are shown in figure 13c.

No. of sample .	Weight in gms.	Wave-height in cm.	Mean.	% Iron.
A	9.99	2.16, 2.15, 2.10	2.15	0.9×10^{-2}
B	10.03	2.54, 2.67, 2.61	2.60	$1.1(2)\mathrm{x}10^{-2}$
C	10.20	2.80, 2.79, 2.80	2.80	$1.1(9)\mathrm{x}10^{-2}$
J	30.07	2.18, 2.14, 2.13	2.15	0.3×10^{-2}

Although the results obtained for the blister copper samples A, B and C differ quite considerably amongst themselves, they compare very favourably with the results obtained by three different analysis using the conventional method. Their results were 0.0195%, 0.0105% and 0.011%.

FIG. 13c DETERMINATION OF IRON IN REFINED COPPER.



MADE TO 10ml WITH ELECTROLYTE OF 0·3M TARTRATE
+ 2ml OF METHYL RED per 100ml.
pH 6 Temp. 30·50 °C.

PHOTOGRAPHIC ORIGINAL. ONE CURVE FROM EACH SET SHOWN.

The determination of Bismuth.

The stock bismuth solution was prepared by dissolving 1.778 grams of pure $Bi_2(SO_4)_3$ in 10N sulphuric acid and making up the solution to 500 ml. in a volumetric flask, using the 10N acid. Ten ml. of the resulting solution were diluted to 1000 ml. with distilled water. This diluted solution was used in the determination.

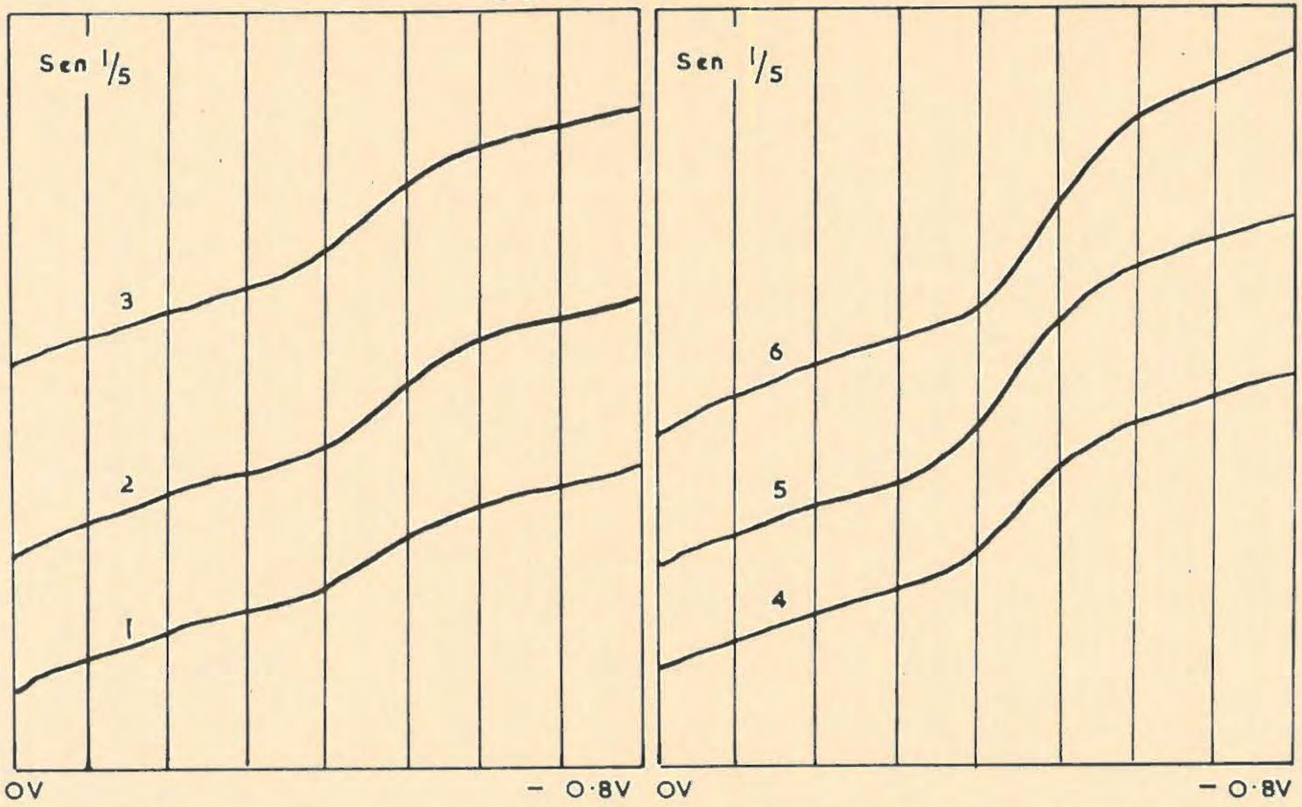
Results. The table immediately below gives the wave heights obtained from the curves shown in figure 14a. The standardisation graph for bismuth is shown in figure 14b.

Volume of stock bismuth solution in ml.	Wave height in cm.	Mean wave height in cm.
10	2.86, 2.92, 2.95	2.91
8	2.43, 2.45, 2.43	2.44
6	1.83, 1.83, 1.83	1.83
5	1.57, 1.61, 1.63	1.60
4	1.40, 1.40, 1.39	1.40
2	1.04, 1.06, 1.03	1.04

The curves obtained for the unknown samples are shown in figure 14c. The wave-heights and percentages are tabulated below.

Sample.	Weight in gms.	Wave height in cm.	Mean wave-height in cm.	% Bismuth.
A	9.99	1.54, 1.46, 1.50	1.50	9.5×10^{-4}
B	10.03	1.49, 1.50, 1.55	1.51	9.6×10^{-4}
D	10.20	1.52, 1.53, 1.53	1.53	9.6×10^{-4}
J	30.07	0.80, 0.78, 0.82	0.80	0.4×10^{-4}

FIG. 14a STANDARDISATION CURVES OF BISMUTH IN 10% TARTRATE + 0·25 M Na_2F_2 pH 7. Temp. 30·05 °C



1.) 2, 2.) 4, 3.) 5, 4.) 6, 5.) 8, 6.) 10 ml OF STOCK SOLUTION MADE TO 10 ml.

PHOTOGRAPHIC ORIGINAL. ONE CURVE FROM EACH SET SHOWN.

FIG. 14b STANDARDISATION GRAPH FOR BISMUTH.

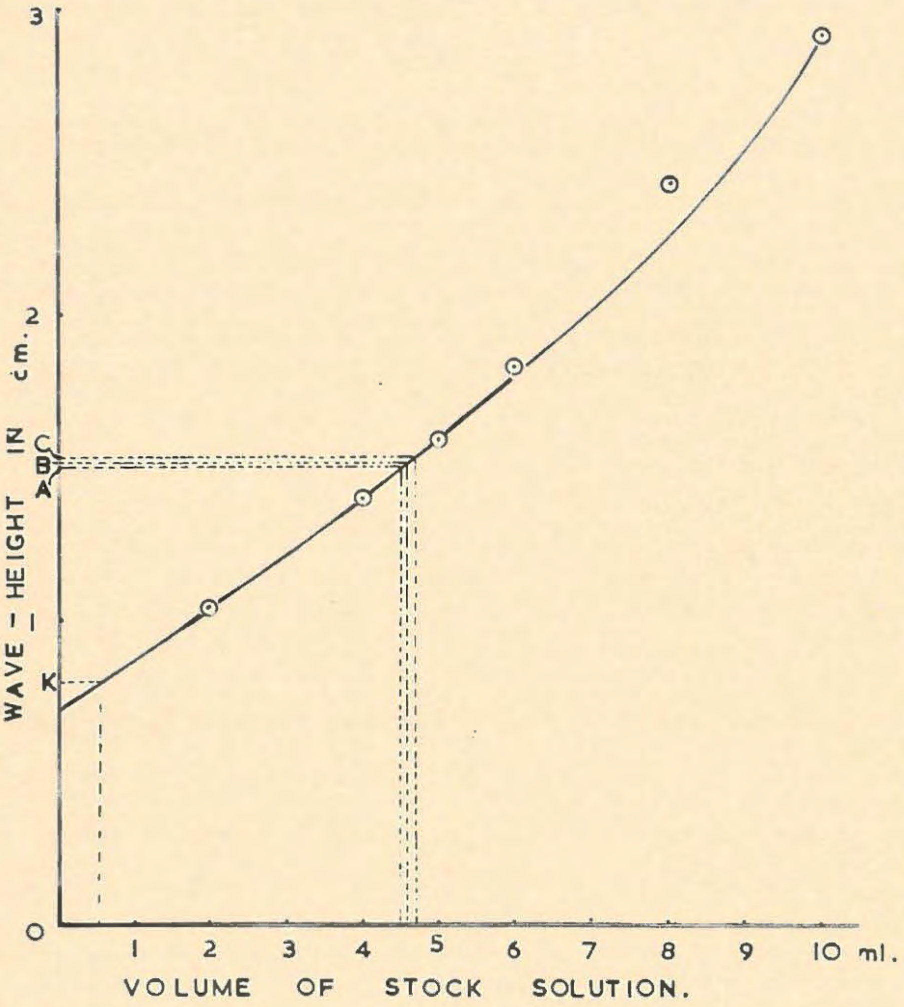
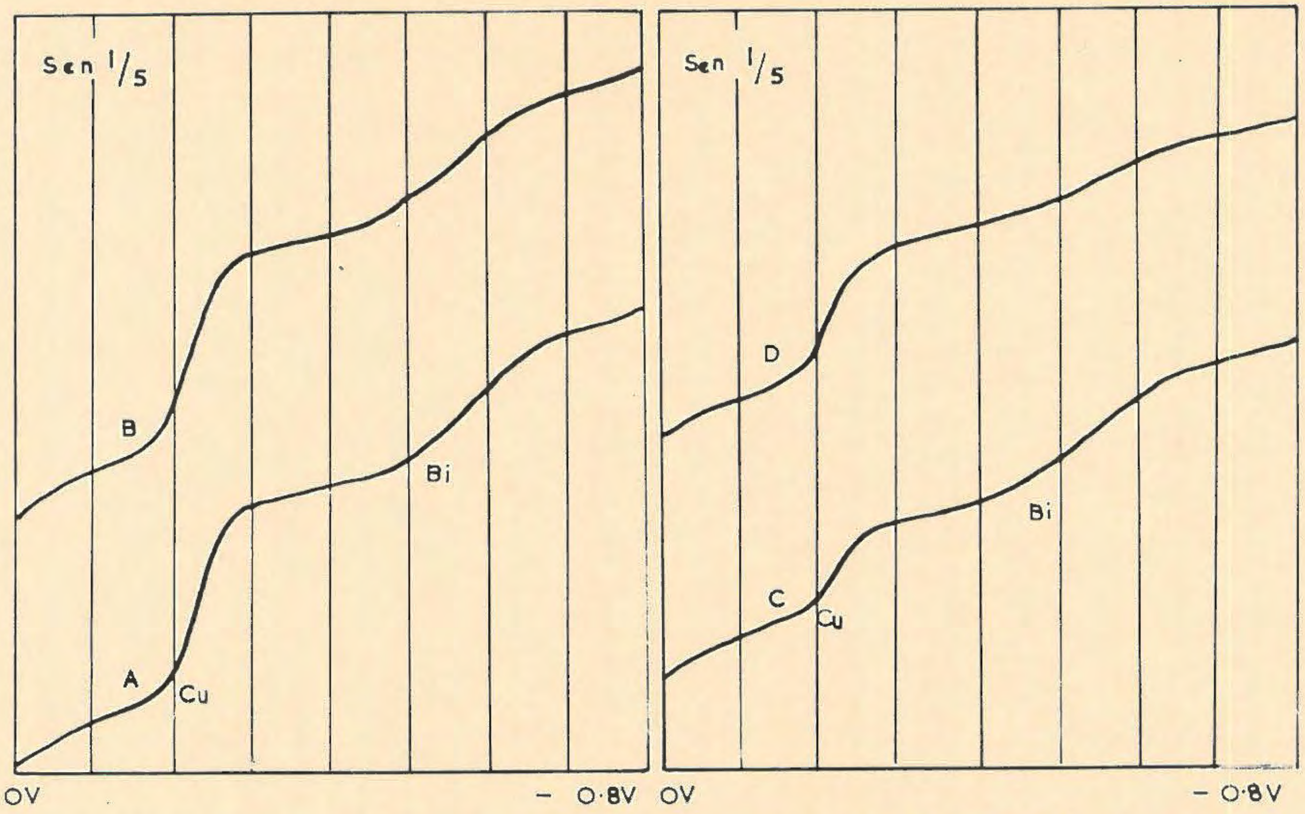


FIG. 14c DETERMINATION BISMUTH IN REFINED COPPER.



MADE TO 10 ml WITH ELECTROLYTE (see fig 14a).
Temp. 30·05 °C

PHOTOGRAPHIC ORIGINAL. ONE CURVE FROM EACH SET SHOWN.

Note: Sample C was lost and a fourth sample was prepared to get the third value for bismuth in the blister copper.

The values obtained in the determination of bismuth in the blister copper although 33% lower than the value supplied by the mine (0.018)% (0.01%) differ amongst themselves by only 1%. This is an excellent result for a determination at so low a concentration. It is felt that the low results may be due to a fault in the standardisation. It is possible that the sample of bismuth sulphate used was not as pure as claimed by the manufacturers. However this was the purest one available at the time.

Although only these preliminary results on the determination of bismuth and iron are available, it is suggested that they indicate that the proposed method of analysis might prove to be a most satisfactory one.

On completing this thesis it is intended to continue the quantitative experiments so that the proposed method may be thoroughly tested before it is published.

APPENDIX.

I. APPARATUS.

A. The Polarograph.

The instrument used was a Leybold-Nachfolger polarograph which had been modified from time to time. The moving contacts on the axle of the potentiometer drum had been altered to give a larger surface of contact. Originally the slightest speck of dust or dirt between the contacts caused irregularities on the polarograms. The larger surface prevents this.

A large capacity 6 volt lead accumulator by itself was found to be unsatisfactory as a source of potential. The potential was not sufficiently constant and the accumulator required frequent charging. This difficulty was overcome by using a Heayberd 6 volt battery charger, with the accumulator floating across the output, as the source of potential.

A great deal of trouble was experienced with the moving contact on the potentiometer drum. This consisted of a platinum wheel running on the potentiometer wire. The wire, the wheel and the platinum contacts to the wheel had to be cleaned frequently. Since the completion of the experimental work for this thesis, the contact has been replaced by a fixed loop of platinum wire which has led to greatly improved results.

Many of the polarograms obtained during the course of this investigation were recorded manually. This was done by using a special attachment consisting of a thin metal beam, to the one end of which was attached a recording pencil in contact with the recording drum; a piece of ground-glass, with a vertical black line on it, was fixed to the other end.

The beam was geared to a small handle by means of which the whole assembly could be moved horizontally in either direction. In this way the galvanometer light beam could be kept trained on the black line, the recording pencil thus tracing out the galvanometer movements. By diligent operation a completely accurate polarogram could be recorded.

An additional circuit was set up alongside the polarograph in a way which made it a simple matter to alter the polarographic circuit from normal to a derivative or differential one. The differentiating and damping condensers C_1 and C_2 shown in figure 2a, consisted of one or more electrolytic condensers (T.C.C. 2,000 and 1,000 μF. 12 volt D.C. working voltage) in parallel. For most work one 2,000 μF condenser was used for C_1, while C_2 was varied from 2,000 to 5,000 μF.

B. The Thermostat.

Because the height of the waves in a polarogram varies with temperature, a thermostat was used. It was constructed in the department and consisted of a glass tank containing approximately 6 litres of water. It was heated by a 40 watt, 250 volt electric light globe. The temperature was controlled by means of a Sunvic thermostat (type T.S. 1) and vacuum switch relay (type F 102/4). Unless otherwise stated all experiments were carried out at 25°C ± 0.05°C.

C. Cells.

Most of the conventional cells were found to be clumsy, difficult to adapt to use in a thermostat and to have large anodes which were wasteful of pure mercury. Two cells were designed to overcome these objections. The first was for use with a mercury anode; the second was for use with an external anode. This was usually a mercury / saturat mercurous sulphate in normal sulphuric acid half-cell. The saturated calomel electrode (S.C.E.) was not used, as the introduction of chloride ions had often to be avoided.

D. The Electrode System.

This consisted of a simple dropping mercury cathode and a mercury pool anode. The latter was used in preference to an external anode, as it is simpler and does not require the same amount of care or maintenance, all desirable qualities in routine analysis.

In early experiments the cathode capillary was connected to the mercury reservoir by rubber pressure tubing. This was found to give rise to contamination of the mercury, which in time blocked the capillaries. Tygon tubing, used instead of rubber, was found to be very satisfactory. In addition, as the tubing was transparent, air locks in the mercury column were easily detected.

E. Purification of the Mercury.

The mercury used for polarographic analysis must be of the highest degree of purity. In the first part of this work it was purified by the method of Newbery and Naude (30). The apparatus used in this department has been described by Carter (31). Although spectrographically pure mercury is produced, the method is cumbersome and slow.

The Sargent Company (32) recommended the method, suggested by Hulett (33), of distillation under reduced pressure. This method (described in detail in the Sargent Company publication (32) is now used in this department. The mercury, after filtration through a glass funnel with a very small orifice, is found to be of satisfactory quality.

II. THE ANOMALOUS EFFECTS IN THE BISMUTH WAVE.

In numerous experiments it was noticed that a number of elements, but bismuth in particular, produced double waves. Since it is the first of the two waves which is the anomalous one, it will be referred to in the discussion which follows as the 'pre-wave'. This wave was difficult to explain as it was not always present, and its shape and size did not remain constant.

The following is a review and analysis of the work which was done from time to time on the pre-wave, and the various hypotheses, as to its cause, which were investigated. The discussion may be grouped under a number of general headings.

1. The effect of oxygen.

During the course of an experiment in which antimony and bismuth were being determined simultaneously in a supporting electrolyte of 1N sulphuric acid, the pre-wave occurred and became larger in successive curves (see fig. 9). Nitrogen was bubbled through the solution and this restored the shape of the bismuth wave. The experiment led to the assumption that oxygen was being reabsorbed into the solution and the pre-wave was actually a wave for oxygen. However, on repeating the experiment on a solution of bismuth in 1N sulphuric acid the pre-wave was not removed by the nitrogen. In addition it was noticed that its presence or absence did not affect the total wave-height. These facts indicated that the wave was due to bismuth and not to oxygen.

2. The effect of time.

The formation of the wave was next investigated. Curves were recorded on a fresh sample of the previous solution and were then re-record at regular intervals. As may be seen from the results, shown in figure 15, the pre-wave formed and became larger in successive polarograms, reaching an equilibrium shape and size after 20 minutes. It was removed by bubbling nitrogen through the cell, but this was achieved only after bubbling for 95 minutes. This led to the assumption that the pre-wave was due to bismuth which was present in some 'form' other than BiO^+, probably as a complex ion which caused it, the bismuth, to be reduced at a more positive potential. In the experiment above the bismuth is gradually changed into the second 'form' until a state of equilibrium is attained. This equilibrium must be affected by small changes in the conditions under which an experiment is carried out, to account for the presence of the wave on some occasions and not on others. It was assumed further that the removal of the pre-wave by bubbling nitrogen through the cell was due to stirring effects and not to the nitrogen itself.

3. <u>The effect of stirring</u>.

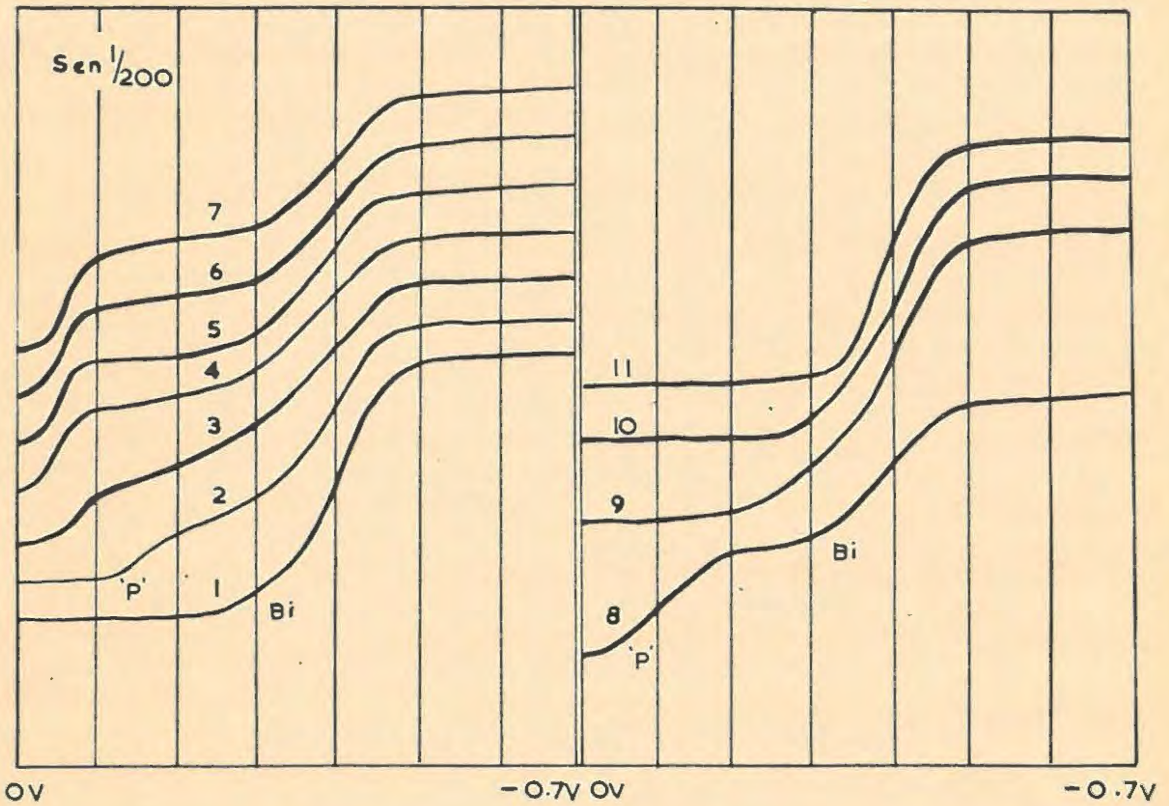
Successive curves were recorded on a fresh solution of bismuth in sulphuric acid, until the pre-wave had attained its equilibrium shape. The cell was removed from the thermostat and shaken gently for 30 seconds; the wave in the subsequent curve was much smaller. The shaking was repeated for 2½ minutes. This removed the pre-wave altogether, but on recording a polarogram after the cell had been standing for 10 minutes, it was present once again. Thus shaking provided the first effective method of removing the pre-wave.

4. <u>The purity of the mercury used</u>.

On some occasions prior to these experiments irregularities in the curves had been traced to impurities in the anode and cathode mercury

FIG. 15 THE NATURE OF THE BISMUTH PRE-WAVE.

10^{-3}MBi in 1N H_2SO_4 + 0.05 % GELATIN.



BUBBLED N_2 FOR 15 MINUTES BEFORE CURVE 1.
CURVES 1, 2 and 3 RUN IN SUCCESSION.
WAITED FOR 5 MINUTES BETWEEN CURVES 3&4, 4&5, 5&6, 6&7.
BUBBLED N FOR 15 MINUTES BEFORE CURVE 8.
– .. .. 20 .. .. .. 9.
.. .. – 30 .. .. .. 10.
.. .. .. 30 .. .. .. 11.

ORIGINAL RECORDED
MANUALLY.

used. However, when experiments on the pre-wave were carried out, using freshly purified mercury and a sample which had been purified six months previously, no difference was noticed.

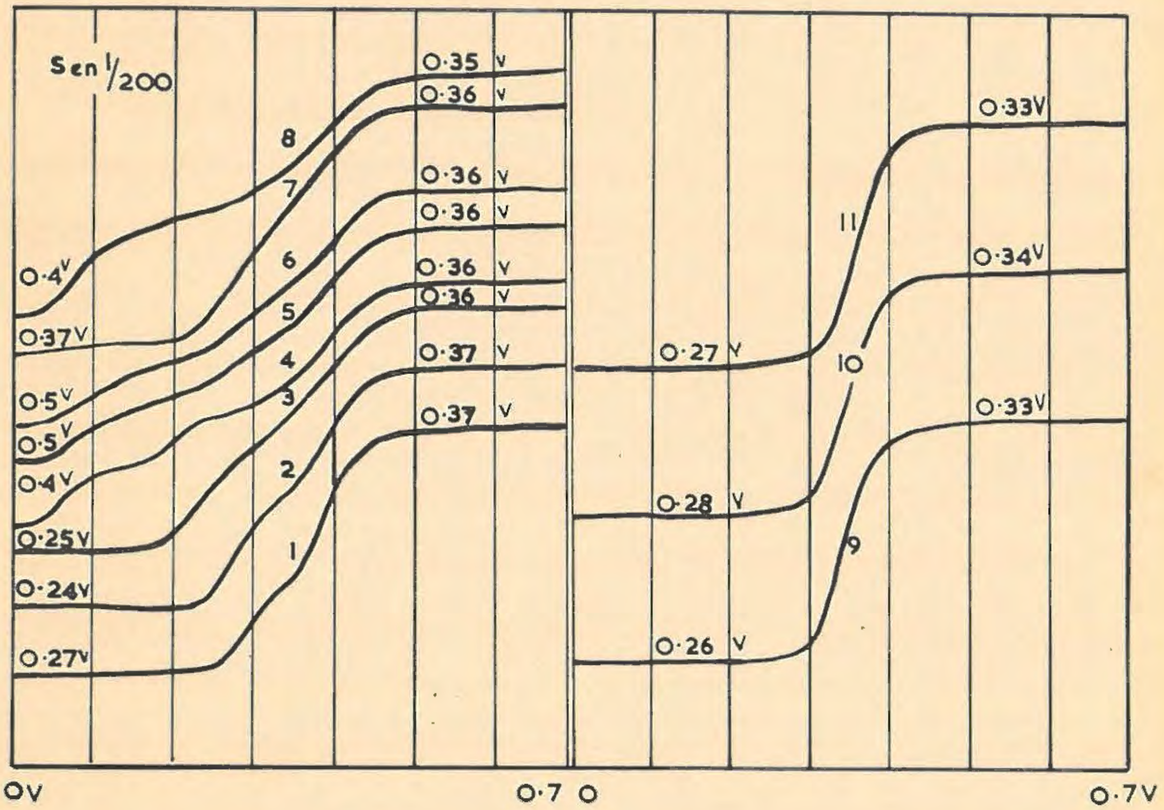
5. The effect of an applied potential.

During the last experiment, which was conducted in a similar manner to that described in paragraph 2 , an interesting effect was noted. At the end of the fifth curve the potential across the cell was left at -0.7 volt, instead of at 0, for five minutes. In the subsequent curve the pre-wave was considerably smaller. Two curves later the 'mistake' was repeated intentionally, with the same result. This indicated that the size of the pre-wave could be reduced by an applied potential, and that the cause of the pre-wave must also be reduced during the actual recording of a polarogram.

6. The anode potential.

These experiments led to the assumption that the pre-wave was actually due to a change in the anode potential. This change caused the bismuth to be deposited at a more positive applied potential. Shaking the cell or applying a potential, caused the anode potential to return to normal. A set of curves was recorded similar to those described in paragraph 5. In this case, however, the anode potential was measured, against a S.C.E., at the beginning and at the end of each curve. The potentials obtained are given in figure 16. The results indicated that the presence and shape of the pre-wave does depend on the initial anode potential. Note; in each case the potentials at the end of the curve were the same. This, together with the result obtained in the experiments described in paragraph 5, indicated that it did not require,

FIG. 16 CHANGE OF ANODE VOLTAGE MEASURED vs. S.C.E.
10^{-3} MBI in 1N H_2SO_4 + 0.05% GELATIN.



BUBBLED N_2 FOR 15 MINUTES BEFORE CURVE 1.

CURVES 1, 2 and 3 RUN IN SUCCESSION.

WAITED FOR 5 MINUTES BETWEEN CURVES 3 & 4, 4 & 5, 5 & 6 WITH POTENTIAL OFF.

" - 5 MINUTES BETWEEN CURVES 6 & 7 WITH POTENTIAL ON -0.7V.

SHOOK CELL BEFORE CURVES 9, 10 and 11.

ORIGINAL RECORDED
MANUALLY.

as previously stated, twenty minutes for the pre-wave to attain its equilibrium shape, five minutes being sufficient.

7. Stabilisation of the anode.

A possible explanation of the change in anode potential was as follows. It was assumed that in 1N sulphuric acid, under normal conditions, the anode behaved as a mercury/saturated mercurous sulphate electrode. Due to some reaction the mercurous sulphate was being removed which caused the anode to change to some other form with a resulting change in potential. If this was the case then the addition of sufficient mercurous sulphate, to keep the solution saturated in spite of the 'reaction', should cause the anode potential to remain constant. In practice it was found that a very small amount of mercurous sulphate effected the stabilisation of the anode, and subsequent polarograms showed no signs of any pre-wave.

8. The cathode drops.

A suspicion arose that the change in the anode potential was connected with the drops from the cathode. To test this a cell was used in which the cathode drops are prevented from reaching the anode (The cell was designed by Kalousek and later described by Struble (34). None of the curves recorded using this cell showed a pre-wave. Since all that is present in a cathode drop is mercury and bismuth atoms from the reduction of the bismuth ions, the change in anode potential was associated with a reaction involving bismuth atoms.

9. Summary.

Summarising the evidence collected on the pre-wave we find:

(a) The wave forms gradually, reaching an equilibrium after five minutes.

(b) The total wave height remains constant.

(c) The process is accompanied by a change in the anode potential. It is suggested that this change is brought about by a reaction involving mercurous sulphate, and bismuth atoms.

(d) The wave may be prevented or removed by shaking the cell; isolating the cathode drops from the anode; applying a potential greater than the half-wave potential of bismuth; and by stabilising the anode by the addition of mercurous sulphate.

10. The theory of the pre-wave.

It is realised that a great deal more evidence would be required before a complete theory of the formation of the pre-wave could be formulated. However, the following theory is proposed based on the evidence already obtained.

The residual current is supposed to be caused by the discharge of bismuth ions at the cathode. Thus as soon as the current starts to flow (even before the decomposition potential of bismuth is reached) bismuth atoms are present in the cathode mercury drops which introduce the bismuth atoms to the anode.

The bismuth, probably present as a bismuth amalgam on the surface of the anode, gradually decreases the anode potential. This decrease is caused by a change which takes place in the surface layers of contact between the anode and the electrolyte. Although obscure, a possible form of the change may be deduced from a consideration of the possible anode reactions. These are:

$$BiO^+ + H^+ + 3e^- \longrightarrow Bi + H_2O \qquad E^o = 0.32 \text{ volt}$$

$$Hg_2SO_{4(s)} + 2e^- \longrightarrow 2Hg + SO_4^= \qquad E^o = 0.615 \text{ volt.}$$

The potential of a bismuth electrode at 25°C is given by

$$E = E^{o} + \frac{0.0591}{3} \log \frac{a^{BiO^+} \, (a^{H^+})^2}{a^{Bi} \quad a^{H_2O}} \quad \text{where a is the activity.}$$

On the convention used for obtaining the above E^{o} values the activity of pure solids and liquids is taken as 1. Since the solution is dilute (10^{-3}M with respect to BiO^+) $_aH_2O$ may be taken as equal to 1. Assuming the solution to be ideal the activities of BiO^+ and H^+ may be replaced by their concentrations in gram ions per litre. The activity of the bismuth, a^{Bi}, may be replaced by the concentration of bismuth in the amalgam expressed as a mole fraction (This is the only method which will make the activity of a pure bismuth solution equal to 1.) For the purposes of the calculation we will assume that the mole fraction of bismuth in the surface layer of the anode is as low as 10^{-12}

$$\therefore \; a^{Bi} = 10^{-12}; \quad a^{H^+} = 1 \; (1N \; H_2SO_4); \quad a^{BiO^+} = 10^{-3}$$

$$\therefore \; E = 0.32 + \frac{0.0591}{3} \log \frac{(10^{-3})(1)^2}{10^{-12}}$$

$$= 0.32 + 0.1773 \text{ volt}$$

$$\fallingdotseq 0.5 \text{ volt.}$$

Before the addition of the bismuth, since the amount of mercurous sulphate required to saturate the surface layer of the solution in contact with the anode, is very small, the anode behaves as a mercury/saturated mercurous sulphate electrode.

The potential of the mercurous sulphate electrode is given by

$$E = E^{o} + \frac{0.0591}{2} \log \frac{1}{[SO_4^{=}]} \qquad [SO_4^{=}] = \text{sulphate ion concentration}$$

$$= 0.615 + \frac{0.0591}{2} \log \frac{1}{0.5} \qquad \text{since } [SO_4^{=}] = 0.5 \text{ gram ions/litre.}$$

$$\fallingdotseq 0.62 \text{ volt.}$$

The potentials obtained for the two electrodes give a positive value for the affinity of the reaction:

$$3Bi + 3H_2O + 2Hg_2\,SO_{4(s)} \longrightarrow BiO^{+} + 2H^{+} + SO_4 = +2Hg_{(l)}$$

Thus when bismuth atoms are present in the surface layer of the anode, even at a mole fraction as low as 10^{-12}, they will reduce the mercurous sulphate. As this reduction takes place, the anode potential decreases until it eventually behaves as a dilute bismuth amalgam electrode.

The decrease in the anode potential results in the cathode reaching the decomposition potential of bismuth at a more positive applied potential than is normally the case. The bismuth wave therefore starts to form earlier on in the curve than is normally the case, however, as soon as a large current starts to flow, the bismuth atoms are electrolysed out of the surface layer, and the anode potential is gradually restored to its normal value.

The theory outlined above is supported by most of the practical evidence collected so far.

(a) The wave forms gradually while the bismuth amalgam concentration in the anode is built up, and the mercurous sulphate is being reduced.

(b) The total wave-height remains unchanged since the pre-wave is part of the normal one.

(c) The reduction of the mercurous sulphate decreases the anode potential by approximately the same amount (0.13 volt) as was found in practice. However the potentials measured in practice do not correspond to those obtained theoretically. e.g. Before the formation of the pre-wave, the anode potential against the mercurous sulphate electrode was -0.25 volt (see figure 16). This does not correspond to the mercurous sulphate electrode which has a potential of 0 on the same scale.

(d) Shaking the cell removes the bismuth from the surface layer of the anode, and aids in the formation of mercurous sulphate by the action of the sulphuric acid on the mercury. Isolating the cathode prevents the bismuth atoms from reaching the anode. The applied potential electrolyses the bismuth out of the surface layer. The addition of mercurous sulphate provides a sufficient amount to react with the bismuth and still keep the solution saturated.

The theory given above is by no means a complete one. However it is the only one of the many put forward which could account for the majority of the practical results. It is intended only as a guide for future study.

Unfortunately in the limited time available it was not possible to continue with the above research. However it is intended to do so on completion of this thesis, with the idea of being able to advance a complete and conclusive theory of the pre-wave.

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