about twice as much of this substance. The Mycenaean pottery is *much* higher in lime than the other varieties, and also contains (*i. e.*, the samples analyzed) considerable carbon dioxide. The amounts of magnesia in the Mycenaean and the Attic varieties are nearly equal, but it is considerably less in the Campanian. The potassium oxide is approximately the same in the samples analyzed at Harvard and in the one sample of Mycenaean pottery in which this constituent was determined. While the former contained over 2 per cent. of sodium oxide, the latter contained but a small amount (0.21 per cent.).[1] Owing to the fact that the Mycenaean clay analyzed is low in silica and comparatively high in lime, it should be more fusible. It was observed that in determining the loss of this variety of clay by ignition in a platinum crucible, it melted quite completely.

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CONDITIONS AFFECTING THE ELECTROLYTIC DETERMINATION OF COPPER.

BY W. C. BLASDALE AND W. CRUESS.

Although the electrolytic method for the determination of copper has been in use since 1864, and the literature of the subject is now voluminous, the application of the method to the analysis of ores and metallurgical products often presents difficulties, which are either ignored or but vaguely suggested in the current descriptions of the process. The frequent failures made by students in this laboratory in attempting to use the process have served to emphasize these difficulties, and have led to the series of experiments, the results of which are recorded below. In carrying out these experiments the needs and resources of the practical analyst have been kept constantly in mind.

Effect of Different Forms of Electrodes upon the Rate of Deposition and the Character of the Deposit.

The results obtained with the use of mechanical stirring devices during the last seven years have emphasized the desirability of maintaining a rapid circulation of the electrolyte during electrolysis. It has not been so generally recognized that the circulation of the electrolyte may be increased by taking advantage of the convection currents produced by the gases liberated at the anode or cathode, and by the substitution of Winkler gauze electrodes for those of the Mansfield type.[2] It seems probable that the relative efficiencies of the different forms of stationary electrodes depend almost entirely upon the extent to which they favor

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[1] Chemical analyses of the different varieties of clay used by the ancient Greeks are still too inadequate to throw much light on the manufactures of different localities.

[2] See, however, the Benner article, p. 1231.—EDITOR.

circulation of the electrolyte, and the equal distribution of the current density over the entire surface of the cathode.

In order to obtain definite data upon this point the rates of precipitation of known amounts of copper under identical conditions, except as regards the electrodes used, were determined. Each of the solutions contained exactly 0.1975 g. of copper as sulphate, 2 cc. of concentrated sulphuric and one of concentrated nitric acids, and water to make 140 cc. They were electrolyzed with a practically constant current of 0.34 ampere and the copper deposited during definite time intervals determined. Except where Classen dishes were employed, the stand to which the electrodes were attached was raised at the end of the desired time interval, and the electrodes plunged in a beaker of water, the current allowed to run for some three minutes longer, after which the cathode was removed, washed in two changes of alcohol and dried and weighed. It was shown, both by determining the rate of action of solutions of this composition on recently precipitated copper, and by testing the washings of the electrodes that this method of removing the cathode involves no recognizable error; it is extremely rapid and convenient.

The cathodes used in the various experiments were as follows:

A. A Classen dish of 200 cc. capacity, with 140 cc. of electrolyte; this gave an available surface of about 120 sq. cm. The anode used with it consisted of a disk of foil with six radially distributed openings near its rim; it was 4.1 cm. in diameter, and was suspended by a stout wire in the center of the dish, slightly below the level of the liquid retained by the latter.

B. A cylinder of foil 2.5 cm. in diameter and 5 cm. in length welded to a supporting wire one mm. in diameter and 12 cm. in length. The total area exposed to the solution was 79 sq. cm. The anode used was a cylindrically coiled spiral of platinum wire suspended in the center of the cylinder. Both electrodes extended nearly to the bottom of the beaker containing the solution; the beaker used was approximately 5.5 cm. in internal diameter.

C. A cylinder of the same dimensions as B, but pierced with 270 holes one mm. in diameter, distributed at approximately equal intervals over its entire surface. The anode and containing vessel were of the same form and size as with B.

D. A cylinder of gauze 3.2 cm. in diameter and 5.5 cm. in length, the gauze composed of platinum wire 0.06 mm. in diameter, with 41 meshes per linear cm. The cylinder was supported by a wire 0.54 mm. in diameter and 13 cm. in length. Assuming that the entire surface of the wire composing the gauze was in contact with the solution, its available area was 93 sq. cm. The anode and containing vessel were the same as those used with B.

E. A cylinder of gauze of the same form and dimensions as D. The anode, however, consisted of a stout wire coiled to form a horizontal spiral, suspended at the bottom of the containing vessel. This was of the same dimensions as with B.

F. A cylinder of gauze 4 cm. in diameter and 4 cm. long; the gauze composed of wire 0.1 mm. in diameter with 25 meshes per linear cm. This was supported by a wire 1 mm. in diameter and 12 cm. long. The calculated surface area was 80 sq. cm. The anode and beaker used were of the same form and dimensions as with B.

The results obtained with these electrodes are shown in part in the series of curves of Plate 1, in which the abscissas represent time in minutes, and the ordinates the copper deposited, in milligrams. The superiority of the gauze electrode D over all others is at once apparent. Its efficiency is due to the fact that it interposes almost no obstacle to the development of convection currents, the direction and intensity of which are easily observed by placing a few mg. of precipitated silica in the solution. It can be shown by this device that the gas liberated at the anode is here distributed over a limited area and produces a current of considerable intensity, which draws the solution through the meshes of the cathode from the periphery. Where foil electrodes are used there is but little interchange of solution between the annular space surrounding the cathode and the cylindrically bounded area within. Further, while the current density is nearly equally distributed over the entire exposed surface of the gauze cathode, it is much greater on the inside than the outside of the foil electrodes, and it is easy to show that only a small percentage of the copper deposited on electrodes of this style separates on the outside of the cylinder.

A comparison of the results obtained with D and F shows that the efficiency increases somewhat with the fineness of the mesh and the wire of which the electrode is composed. This, taken together with its extreme lightness and consequent low cost, places D at the head of the list as regards economy. Although D was somewhat fragile and had to be handled more carefully than F, two such electrodes have been in general use for over three years and are still in good order.

A comparison of the results obtained with B and C show that by providing a number of openings in the foil composing the cathode the efficiency is appreciably increased, but the superiority of the gauze form still remains most striking.

A comparison of the results obtained with E and D shows that the cylindrical form of anode possesses a slight advantage over the disk form. This is due to the distribution of the liberated gas over a greater horizontal area. Still another difficulty arises from the fact that much of the liberated oxygen comes in contact with the precipitated copper and

may produce an appreciable amount of oxidation; dark deposits were frequently obtained wherever the disk form of anode was used. With this exception the deposits obtained in the entire series of experiment were satisfactory. A comparatively small increase in the amperage used gave poor deposits where foil electrodes were used.

The comparative efficiencies of the different forms of electrodes used are summarized in the following table, in which the last column represents the time needed for the precipitation of o. 1975 g. of copper to within ± 0.02 mg.

	Cathode used.	Surface exposed.	Wt. in g.	Time needed. Minutes.
A.	Classen dish................	120	38	400
B.	Mansfield.................	79	11.0	450
C.	Mansfield with holes.........	78	11.0	390
D.	Winkler....................	93	4.2	50
E.	Winkler....................	93	4.2	60
F.	Winkler....................	80	9.4	100

Effect of Varying Amperage upon the Rate of Deposition.

If all the current which passes through the solution were carried by the ionized copper salt the rate of precipitation would be directly proportional to the amperage. In practice other electrolytes are always present and carry more or less of the current. The electrolysis of neutral salts yields free acids, and acid is usually necessary to prevent the separation of other metals present. So long as the decomposition voltage of the copper ions is somewhat smaller than that of the other cations present, and so long as their concentration is sufficiently large as compared with the amperage used, the greater part of the positive current will be carried by them; but as their concentration decreases the proportion of the positive current carried by them must rapidly decrease and finally become zero. Rapid circulation of the solution brings larger numbers of copper ions within the sphere of attraction of the cathode within a given time interval, and increases the proportion of positive current carried by the copper ions during the later stages of the deposition. Increasing the amperage not only increases the rate of deposition directly, while the solution contains a comparatively high concentration of copper ions, but also indirectly by increasing the circulation of the solution through the gases liberated at the anode and cathode.

In order to determine the actual effect of varying current strength the rates of precipitation were determined under identical conditions except as regards amperage. The solution used contained 0.1975 g. of copper as sulphate, 2 g. of ammonium nitrate, 4 cc. of concentrated nitric acid and water to make 140 cc. The gauze electrode D was used throughout. The curves 1, 2, 3, 4, and 5, shown on Plate II, represent the results obtained where currents of 0.19, 0.34, 0.5, 0.78 and 5.5

amperes, respectively, were used. The details of manipulation were the same as in the previous series of experiments. In all but the last series the amount of copper finally obtained differed from the correct amount by less than 0.3 mg.; when 5.5 amperes were used the solution attained a temperature of 60° and the solvent action of the large amount of nitric acid present was so great that the final result was 1.2 mg. low. This loss was due in part to copper in the wash water and in part to copper left in the original solution. The depolarizing action of the large concentration of nitrate ions present was sufficient to prevent the liberation of hydrogen even with the highest currents used. The deposits were all dense and compact; those obtained with the higher amperage showed a slight tinge of brown in place of the normal red color.

It might be noted here that some experiments by Stoddard,[1] which involved the use of a gauze cathode, a volume not exceeding 50 cc., and the presence of only one cc. of nitric acid, gave more rapid precipitation than that here noted. His work has been criticized by Price and Humphreys,[2] who found the time needed under similar conditions somewhat greater than that used by Stoddard.

Effect of Varying Concentrations.

The proportion of positive current carried by copper ions in a series of solutions containing the same amount of copper salt should be greater,
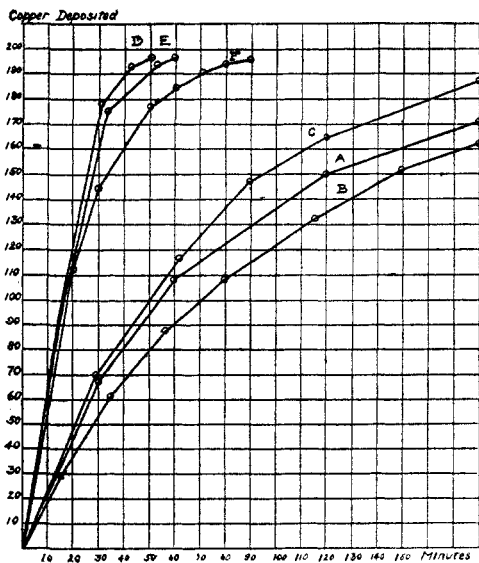

Plate I.—Results with varying types of electrodes.

[1] THIS JOURNAL, 31, 385 (1909).
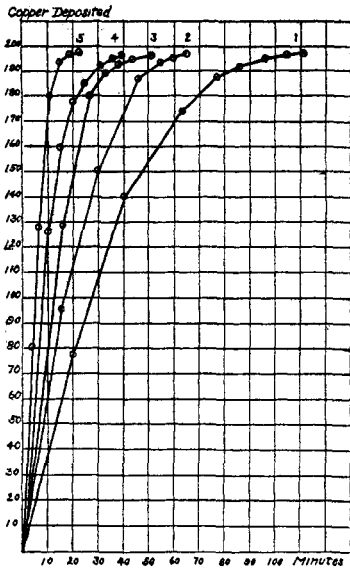[2] J. Soc. Chem. Ind., 29, 307 (1910).

Plate II.—Results with varying cur-
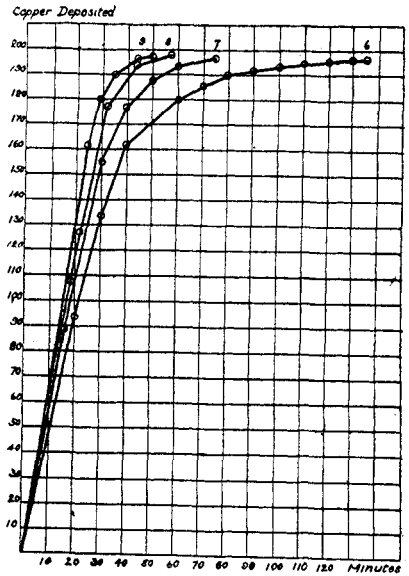rent strengths.

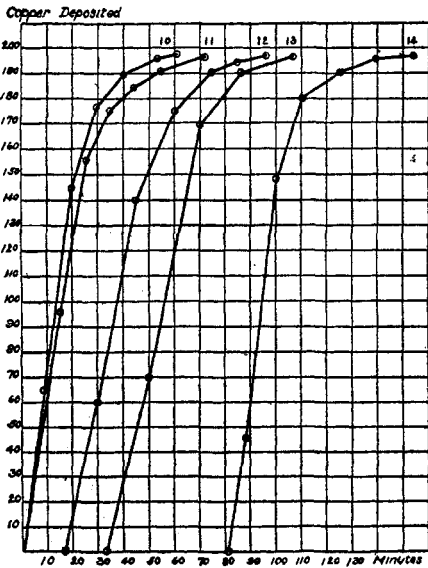Plate III.—Results with varying concen
tration.
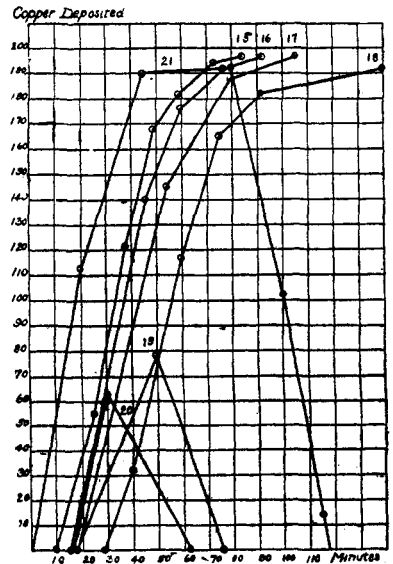

Plate IV.—Results with varying amounts
of iron.

Plate V.—Results with varying con-
centrations of iron and nitric acid.

especially as the deposition approaches completion, with solutions of high than with those of low concentration. The importance of this factor has been shown by Richards,[1] although the method which he recommends for effecting the precipitation is scarcely feasible in routine analytical work.

Some data showing the effect of varying concentration on the speed of precipitation are represented by curves 6, 7, 8 and 9 of Plate III. The solutions used contained 0.1975 gram of copper as sulphate and were diluted to 70, 140, 210 and 280 cc., respectively. They contained nitric and sulphuric acids corresponding to a concentration of one cc. of the former and two of the latter, for each 140 cc. of total solution. The gauze electrode D and a current of 0.34 ampere were used in all cases, but the size and form of the beakers containing the solutions were necessarily changed somewhat from those used in the previous experiments.

The curves show that the time interval during which the rate of precipitation remains practically constant increases greatly with the concentration. Even when the volume is 140 cc. this rate remains practically constant till 90 per cent. of the copper present has been precipitated; beyond this point the rate decreases rapidly. With larger volumes the change in rate occurs earlier and becomes increasingly greater with the larger volumes. This may be taken to mean that up to the point at which the rate shows a decided change the current is carried entirely by the copper ions; beyond this point it is carried to an increasing extent by the hydrogen ions. The final form of the curve is the net effect of the actual change in concentration and the change in stirring efficiency of the anodic gas, owing to the increased volume of liquid to be stirred.

Amount and Nature of Acid Present.

Although copper is readily separated by the electric current from neutral or alkaline solutions, the application of this method to the analysis of ores almost invariably demands the presence of a slight concentration of hydrogen ions. If sulphuric acid is used, and if the cathode consists of a Classen dish or a foil, the current density must be kept low or the deposits are spongy. The difficulty becomes increasingly large as the concentration of the copper ions decreases, and can be remedied, as shown by Richards,[2] by making reductions in the current strengths as the deposition progresses. Rapid circulation largely overcomes the difficulty, since larger numbers of copper ions are thereby rendered available for the transport of the current and virtually increase their effective concentration. A somewhat extended experience has convinced us that this difficulty is reduced to a negligible factor by the use of gauze elec-

[1] THIS JOURNAL, 26, 530 (1904).

[2] Loc. cit.

trodes. We have not yet obtained a spongy deposit where these electrodes were used. This has been noted and used by Förster.[1]

Where a sufficient concentration of nitrate ions is present, the danger of obtaining spongy deposits is small, but another difficulty arises from the formation of brittle, crystalline aggregates, which grow out from the lower edge of the cathode, and sometimes at the point where the sustaining wire emerges from the solution. Apparently this difficulty is also avoided by sufficient circulation of the solution, for it has not been noted where the solution was stirred, or where a gauze cathode was used.

Differences in the comparative solvent action of the two acids on precipitated copper might be expected to affect the rate of precipitation and the difficulty of removing the cathode from the solution without resolution of appreciable amounts of the precipitate. The amount of copper dissolved from a copper-coated gauze cathode by dilute solutions of these acids during a definite time interval was found to vary greatly, but in every instance the action of the nitric acid was much greater than that of the sulphuric acid, and was increased to a much greater extent by increasing the temperature to 60°. In one instance 78 mg. of copper were dissolved by a solution containing 2 cc. of nitric acid per 140 and heated to 60°. The precipitation of the last few milligrams of copper from such solutions is not easily effected and we have not found either the rotating anode or the gauze cathode satisfactory where the solution was heated either externally, or internally by the current. The residual solutions usually showed the presence of copper by the ferrocyanide test, and occasionally faint traces of the same could be detected in the wash water. Where currents of five or more amperes are used, nitric acid should not be present, except in small concentrations.

If the temperature of the solution does not rise above 30° the concentration of the solution with respect to copper is easily reduced below the point recognized by the ferrocyanide test, even where the concentration amounts to as much as 4 cc. of either acid per 140 cc. of solution. The time needed for complete precipitation from such solutions is practically the same, though the rate at which the last ten milligrams are precipitated is slightly less with the larger concentrations of nitric acid.

Effect of Iron Salts upon the Rate of Precipitation.

A. *In the Absence of Nitrate Ions.*—The curves plotted on Plate IV show how the rate of precipitation is affected by the presence of iron salts. The solutions used contained in every instance 0.1975 g. of copper as sulphate, and 2 cc. of concentrated sulphuric acid, and were diluted to 140 cc.; they were electrolyzed with the gauze electrode D, using a current of

[1] *Z. angew. Chem.*, **19**, 1848 (1906).

0.34 ampere. The curve numbered 10 represents the results obtained where no iron was present; No. 11, where the solution contained 0.8 g. of iron as ferrous sulphate. The comparatively large amounts of ferrous ions present reduced perceptibly the normal rate of precipitation during the later stages of the deposition, but did not otherwise affect the precipitation.

The results represented in curves numbered 12, 13 and 14 represent the results obtained with solutions containing respectively 0.2, 0.4 and 0.8 g. of iron as ferric sulphate. They show that no copper is deposited for a definite interval, which is roughly proportional to the amount of ferric salt present. A similar series of solutions were electrolyzed under the same conditions and titrated with a solution of potassium permanganate, at the point at which the copper first began to separate. The results showed that the appearance of the deposit was correlated with the reduction of the concentration of the ferric ions to an approximately fixed value. Evidently we are here dealing with a complex equilibrium in which the important factors are the strength of the current used, the concentration of the ferric ions, and the reaction constant of the equation

$$2Fe''' + Cu \longrightarrow Cu'' + 2Fe''.$$
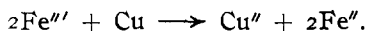
The value of this constant is evidently large, for if a copper-coated electrode is allowed to stand in a solution of a ferric salt till equilibrium is attained, the concentration of the resulting solution with respect to ferric ions is reduced almost to zero. By titrating still another series of solutions it was shown that the reduction of the iron progresses during the deposition of the copper and was completed before the copper was all deposited.

B. In the Presence of Nitrate Ions. General Phenomena.—The curves plotted on Plate V show the effect upon the rate of precipitation of varying combinations of ferric salts and nitric acid. The solutions contained in all cases 2 cc. of concentrated sulphuric acid and water to make 140 cc. and were electrolyzed with the gauze electrode D, using a current measuring 0.34 ampere. In 15 the solution contained 0.2 g. of iron as ferric sulphate and no nitric acid; in 16, 17, 18 and 20 they contained 1, 3, 4, and 5 cc., respectively, of concentrated nitric and 0.2 g. of iron as ferric sulphate; in 21 it contained 0.2 g. of ferrous sulphate and 4 cc. of concentrated nitric acid; in 18 it contained 0.4 g. of iron as ferric sulphate and 3 cc. of concentrated nitric acid. In some cases only a few points on the curves were determined and the exact position of the maxima is only approximately represented. The extreme rapidity with which the resolution sometimes took place, and the difficulty of accurately controlling all the factors concerned, especially the temperature, make accurate determinations difficult; an approximate accuracy is all that the present work requires.

The curves show that so long as the concentrations of both nitrate ions and ferric ions are kept low, the rate of precipitation is merely retarded, but where either of these factors, especially the nitrate concentration, becomes large, deposition may take place normally up to a certain stage, then a rapid resolution of the deposited copper. This phenomenon is well known to analysts, who have had much experience in applying the electrolytic method to the analysis of pyritiferous ores and has been described by Larison[1] and by Farlie and Boone.[2]

Probable Cause of the Phenomenon.

The rapidity with which the process of resolution takes place, and the fact that with a constant amperage it may not take place at all until a large amount of the copper has been precipitated, make it improbable that either nitric or sulphuric acids or ferric salts are the effective agents concerned. Its frequent association with the blackening of the solution (presumably due to the nitroso compound of ferrous sulphate) suggests that the action is due to the presence of one or more of the products resulting from the reduction of nitric acid.

A systematic study of the action of solutions of nitric acid containing the various lower oxides of nitrogen has led to the conviction that nitrous acid is the reagent which is chiefly concerned in this phenomenon, though nitric oxide may play some part in it. Some of the data upon which this statement is based are as follows:

(a) The copper in a solution containing 0.5 g. of copper sulphate, 2 cc. of concentrated nitric acid and water sufficient to make 100 cc. was deposited on a gauze electrode. The latter was then removed and after saturating the solution with nitrous oxide gas was again placed in the solution. The amount of copper dissolved at the expiration of forty minutes was 0.017 g.

(b) A solution and electrode prepared exactly as in (a) were saturated with nitric oxide gas (prepared from copper turnings and nitric acid). The amount of copper dissolved from the cathode by this solution at the expiration of forty minutes was 0.074 g.

(c) A solution and electrode prepared exactly as in (a) were partly saturated with nitrogen peroxide prepared from tin and nitric acid. The copper-coated cathode immersed in this solution for forty minutes lost 0.140 g.

(d) A solution was prepared which contained 2 cc. of concentrated nitric acid and 2 cc. of a solution saturated with respect to both ferrous sulphate and nitric oxide, and water sufficient to make 100 cc. The copper-coated cathode lost 0.007 g. as the result of immersion in this solution for forty minutes.

[1] *Eng. Min. J.*, **84,** 442 (1907).
[2] *Electrochem. Met. Ind.*, **6,** 58.

(e) A solution prepared as in (a) was treated with a mixture of nitric oxide and nitrogen peroxide (prepared from starch and nitric acid). The entire amount of copper on the cathode, that is, 0.1975 g., was dissolved within five minutes.

Recognizing the fact that nitrogen peroxide in contact with water immediately forms a mixture of nitrous and nitric acids, and that the nitric oxide prepared from copper and nitric acid probably contained appreciable amounts of the peroxide, it seems probable that the phenomenon under discussion is mainly due to the presence of nitrous acid. It has been clearly shown by Millon,[1] Veley[2] and others that this acid has a pronounced catalytic action on the dissolution of copper in nitric acid. There is also reason to believe that the acid itself has a remarkable solvent action on the metal. A one-tenth normal solution of potassium nitrite acidified with an equivalent amount of sulphuric acid dissolved 0.1 g. of deposited copper in five minutes, liberating a large amount of nitric oxide gas. A half-normal solution also acidified in like manner dissolved 0.14 g. in three minutes. Its action is much greater than that of corresponding concentrations of either sulphuric or nitric acids. There is nothing surprising in this statement. If it is true that the dissolution of copper by nitric acid depends first upon the comparatively high dissociation constant of nitric acid, and second upon the ability of nitrate ions to reduce the concentration of the liberated hydrogen to an exceedingly small value, it would not be surprising to find a still greater effect with nitrous acid. The latter acid may possess a slightly smaller dissociation constant, but it is probable that the nitrite ions are more efficient in reducing the concentration of the liberated hydrogen than the nitrate ions.

Formation of Nitrous Acid during Electrolysis.—That nitrous acid is actually produced during the electrolysis of solutions containing sufficient concentration of nitric acid and a ferric salt can be shown by titrating such solutions with potassium permanganate. Thus by electrolyzing a series of solutions, all containing 0.196 g. of copper, 0.1753 g. of iron as ferric sulphate, two cc. of concentrated sulphuric and three of concentrated nitric acids, and water to make 140 cc., for definite time intervals, weighing the precipitated copper and titrating the residual solution, the following results were obtained:

Time interval. Minutes.	Weight of copper deposited.	Reducing power of soln. Fe.
60	0.1762	0.1574
90	0.1925	0.1939
120	0.1946	0.2441
180	0.1958	0.2112

[1] *J. prakt. Chem.*, **29**, 338.
[2] *Proc. Roy. Soc., London* **48**, 458.

Although the current strength here used was sufficient to prevent any recognizable re-solution of the precipitated copper, it is interesting to note that the rate of precipitation after ninety minutes had elapsed, even for the low concentration of copper concerned, was far below the normal value.

The exact conditions necessary for the formation of nitrous acid and the mechanism of the reaction have not yet been determined and we have never obtained evidence of the formation of nitrous acid in the electrolysis of copper nitrate solutions containing free acid unless an appreciable concentration of an iron salt was present. Apparently also a low concentration of hydrogen ions favors the formation of it. We offer no theory of the mechanism of the reaction.

The Use of Urea in Destroying Nitrous Acid.—It has been shown repeatedly that the addition of a sufficient amount of urea to solutions in which re-solution of the precipitated copper had taken place, resulted in the liberation of a large amount of gas and prompt precipitation of the entire amount of copper. It was further shown that the addition of urea' to solutions containing several cc. of nitric acid before electrolysis is started will often permit of complete deposition of the copper, whereas in an exactly parallel test, in which the urea was omitted, complete deposition was impossible. The rate of precipitation is, however, still lower than normal, even where 5 g. of urea per 100 cc. of solution are used, which means presumably that this reagent is still unable to reduce the concentration below a value which affects the normal rate of precipitation to an appreciable extent.

Since entirely satisfactory deposits can be obtained with the gauze electrode in the entire absence of nitrate ions, it is undoubtedly preferable to electrolyze solutions of ores containing only copper and iron in he presence of sulphuric acid only. When it becomes necessary to separate copper from solutions containing both iron and nitric acid, urea may be added with advantage, to prevent the accumulation of undesirable concentrations of nitrous acid in the solution.

Effect of the Presence of Arsenic.

Where solutions containing a salt of copper and arsenic acid are electrolyzed mere traces of arsenic are often separated during the deposition of the copper; larger amounts may separate after most of the copper has been precipitated, and is then easily recognized by the smoky color which it imparts to the precipitate, or if large amounts have separated, by its loosely adherent character and black color. Several devices have been used to avoid the resulting error.

Solution of the precipitate in nitric acid and reprecipitation from a solution containing a reasonable amount of nitric acid can be depended on to give good results in practically all cases.

The removal of mere films of arsenic from the surface of the cathode by carefully heating the latter over a gauze often gives good results, but is not entirely reliable, owing to the difficulty of entirely avoiding oxidation.

Attempts to separate the two metals by the constant voltage method we have found unsatisfactory, even where low amperages were used and is incompatible with the rapid methods of precipitation.

The addition of oxidizing agents for the purpose of keeping the arsenic in the pentavalent form has been generally recommended. Hollard claims that the addition of ferric sulphate effects the desired object, but as the iron is itself reduced during the electrolysis, this seems improbable, and we find that the electrolysis of solutions containing arsenic acid and a ferric salt, in addition to copper, give large deposits of arsenic, provided the solution contains no nitrate ions. Since the solution used by Hollard contained nitric acid, we attribute his success to the latter reagent. The exact concentrations of nitrate ions necessary to prevent precipitation of arsenic depend on the concentration of the latter and upon many other factors. We find that where the solution has a volume of 100 cc. and contains 2 cc. of concentrated sulphuric acid and 50 mg. of arsenic, separation of the latter is effectually prevented by the presence of 5 g. of ammonium nitrate, even though the current is allowed to pass through the solution for several hours after the copper, also present, was deposited. Under similar conditions one cc. of concentrated nitric acid prevented the separation of arsenic from a solution containing 10 mg. of the latter. These results were obtained with the gauze cathode using currents of as much as 0.75 ampere. The limits given are only the roughest kind of approximations.

Effect of the Presence of Salts of Zinc and Aluminium.

The addition of either zinc or aluminium to the extent of 0.4 g. has but little effect on the time needed for complete deposition of copper. The solutions used in determining this fact contained only sulphates and sulphuric acid, and were electrolyzed with the gauze electrode, using 0.34 ampere. A very slight decrease in the rate at which the last four mg. were deposited was noted, which increased the time needed by about five minutes.

A second effect has been observed in the electrolysis of solutions containing large amounts of zinc in addition to copper with electrodes of the Mansfield type, namely, a greater tendency for the formation of unsatisfactory deposits. These effects were never observed where gauze electrodes were employed.

[1] *Analyse des Metaux par Electrolyse*, 83.

Effect of the Presence of Lead Salts.

This element may separate in large amounts with the copper from solutions containing sulphuric acid. A large concentration of nitrate ions prevents this, but the amount needed is in excess of that which is desirable, if iron is also present in large amounts. As most of the lead present as ore is usually changed into the sulphate, in preparing the solution, it is preferable to use sufficient care to separate it as completely as possible in this form. We find that, if the insoluble precipitate of the sulphate is left in contact with the solution, very large amounts may be dissolved and precipitated as the deposition progresses.

Practical Application to the Analysis of Ores.

The data presented in the previous sections indicate the difficulties to be avoided in applying the electrolytic method to the analysis of pyritiferous ores. If one-gram samples of such ores are used the resulting solutions may possibly contain 0.2 g. of copper, 0.4 g. of iron and variable amounts of zinc, arsenic and lead.

Assuming first that arsenic is not present and that lead has been carefully removed as sulphate, it should be possible to separate all the copper by the use of the Winkler electrode and a current of 0.75 ampere within ninety minutes, provided the volume does not exceed 100 cc. and the solution does not contain more than five cc. of concentrated sulphuric and no nitric acid. To test the suggestion, a series of solutions containing 0.1956 g. of copper and 0.4 g. of ferric iron were electrolyzed under the conditions named, using the gauze electrode F. The results obtained were:

0.1957	0.1957	0.1958

Assuming that arsenic is also present, either the solution should be electrolyzed under the conditions named above, the deposit dissolved in nitric acid and re-electrolyzed; or, where the amount is small, good results might be expected from a single precipitation by adding to the solution from one to two cc. of nitric acid and 5 g. of urea. To test this suggestion, a series of solutions containing 0.1956 g. of copper and 0.4 g. of ferric iron and 0.01 g. of arsenic (added in the form of H_3AsO_4) were electrolyzed as before, after the addition of one cc. of nitric acid and 5 g. of urea. The results obtained were:

0.1959	0.1948	0.1957	0.1959

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NOTE.

New Normal Solution and Reagent Bottle.—The new normal solution bottle which I have designed is the simplest and most effective of any that has come under my notice. The bottle is of the long narrow type,