The manganese standard of the permanganate is calculated from the reaction which may be represented thus:

$$Mn^{++++} + 2Fe^{++} \longrightarrow Mn^{++} + 2Fe^{+++}.$$

Or the value of the permanganate in terms of iron multiplied by 0.4918 gives the value in terms of manganese.

The following table of results will give an idea of the accuracy of the method:

No.	Mn. taken.	Mn. found.	Error.
1	0.0981	0.0979	—0.0002
2	0.0981	0.0975	—0.0006
3	0.0981	0.0973	—0.0008
4	0.0981	0.0974	—0.0007
5	0.0981	0.0980	—0.0001
6	0.0981	0.0981	±0.0000

The method is quite rapid and the end point is sharp and distinct, being the usual pink color in a solution containing a white precipitate. The application of the method to the analysis of spiegel and manganese ores is now under way, and we hope to work out a method which will be rapid and accurate and not possess the disadvantages inherent in the Volhard method.

QUANTITATIVE LABORATORY.

THE USE OF ORGANIC ELECTROLYTES IN CADMIUM SEPARATION.

BY MARY E. HOLMES AND MARY V. DOVER.

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In a previous paper[1] it was shown that currents below one ampere possess undoubted advantages for electrolytic separations when the rotating anode is employed, that study was concerned with the separation of cadmium from the metals of Groups III and IV and from magnesium at currents of 0.3–0.4 ampere, using the sulphuric acid and also the acetate electrolyte, and comparing the results obtained with those of other investigators working at high currents. It was clear that the possibilities of work in the line of electrolytic separations were almost limitless and that the work on cadmium alone called for a much more extended investigation, using other metals and a greater variety of electrolytes.

The present work was undertaken in order to test further the usefulness of low currents in cadmium separations. The alkaline earth metals were used and the acetate, formate, and lactate electrolytes. Corresponding separations were made with both low and high currents (*i. e.*, five amperes), but in no case did the high currents prove desirable. Whether cadmium was used alone or in presence of other metals, the deposits were dark in color, spongy, not adherent, difficult to dry, and in

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[1] THIS JOURNAL, 30, 1865.

most cases very evidently not worth weighing. Whenever they were weighed, the results were very high. In the case of low currents, however, interesting and accurate results were obtained, though the deposits varied considerably in character and in accuracy with the different electrolytes employed.

During this work it has been evident that each variety of ion present in the solution exerts a very definite influence on the deposit. The presence of two kinds of ions in a solution may produce a decidedly different deposit from that obtained by the influence of either ion alone. For instance, in the previous work conducted with cadmium sulphate solutions with the sulphuric acid electrolyte, smooth adherent deposits of fine crystalline structure were obtained. The deposits from a cadmium sulphate solution using the acetate electrolyte were more coarsely crystalline, and if another metal were present, *e. g.*, aluminium, the crystals tended to sponginess and therefore to occlusion of the mother liquor, unless carefully washed with hot water. These same conditions were observed when a cadmium acetate solution was used with the acetate electrolyte, so that in general it may be said that the sulphate ion aids in forming a finely crystalline, compact deposit, while the acetate ion causes the deposit to be more coarsely crystalline with a tendency to sponginess. The presence of the sulphate ion always seems to improve the character of a deposit, no matter what other ion may be present.

As in the previous work, a platinum dish of about 200 cc. capacity was employed as the cathode, but as a dish anode was not available, the ordinary spiral anode was used, the time required being not much more than is necessary with the dish anode, *i. e.*, forty-five minutes to one hour. It is possible that the dish anode may produce firmer deposits, but certainly the spiral anode has proved to be very useful in such cases. Solutions of cadmium salts containing not more than 0.2 gram of cadmium metal in 10 cc. were used.

I. The Acetate Electrolyte.[1]

The acetate electrolyte was first suggested since it was impossible to use the sulphuric acid electrolyte with all the alkaline earth metals. To 10 cc. of cadmium acetate solution, 2 grams of ammonium acetate and 1 cc. of acetic acid were added, the solution diluted to about 125 cc., heated to the boiling point, and electrolyzed for one hour, using 0.3 ampere and 2.4–3 volts. As a result, 0.1744 gram of cadmium was repeatedly deposited and the remaining solution showed no test for cadmium when treated with hydrogen sulphide. Then a series of separations was made of cadmium from the alkaline earth metals under the same conditions. About 0.2 gram of metal was represented by the amounts of calcium, strontium, and barium acetate solutions used. Two sepa-

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[1] THIS JOURNAL, 27, 1275.

rations from calcium gave 0.1744 gram of cadmium, two from strontium, 0.1742 gram and 0.1744 gram respectively, and one from barium 0.1746 gram. Another separation was tried from a mixture of all three metals, calcium, strontium, and barium, the cadmium obtained weighing, as before, 0.1746 gram.

Owing to the fact that calcium sulphate is comparatively easily soluble, it was found that the separation of cadmium from calcium is possible, using a cadmium sulphate solution with an acetate electrolyte. Better results were obtained, however, when the free acid was omitted from the electrolyte. To 10 cc. of a cadmium sulphate solution, 2 grams of ammonium acetate were added, the solution diluted as usual, and after heating to the boiling point, electrolyzed, using 0.3 ampere and 2.5–3 volts for one hour. In two successive determinations, 0.1968 gram and 0.1970 gram were deposited, no test for cadmium being obtained in the solution. When 1 gram of calcium acetate was added to 10 cc. of the same cadmium sulphate solution and electrolyzed under the same conditions, 0.1968 gram of cadmium was obtained. These deposits were very satisfactory, clean and smooth, with few crystals of any size, easily washed and dried, showing the valuable influence of the presence of the sulphate ion. The character of the deposit was not changed by the presence of calcium. Determinations corresponding to these were made, using as electrolyte 1 cc. of acetic acid in addition to the 2 grams of ammonium acetate. The character of the deposits was almost as good as in the other cases, but the weights were low. From the cadmium sulphate solution alone, only 0.1958 gram and 0.1956 gram were deposited in two successive trials instead of 0.1968 gram. In presence of 1 gram of calcium acetate, 0.1960 gram and 0.1962 gram were obtained. The solutions all gave slight tests for cadmium with hydrogen sulphide. Hence it was concluded that in these cases the free acid hindered the complete precipitation of the cadmium. Similar trials were made, using the cadmium sulphate solution with strontium and barium acetates, but as was to be expected, precipitates of strontium and barium sulphates interfered with the work.

II. The Formate Electrolyte.[1]

The effect of the formate electrolyte was next investigated Conditions were first determined for the complete deposition of cadmium from a cadmium formate solution; then the separation of cadmium from calcium, strontium, and barium was effected, using the formates of these metals. The electrolyte used was ammonium formate in presence of formic acid. With 10 cc. of the cadmium formate solution were mixed 2 grams of ammonium formate and 1 cc. of formic acid, the solution diluted as usual, heated to the boiling point, and electrolyzed for forty-five min-

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[1] THIS JOURNAL, 27, 1275.

utes, using 0.3 ampere and 1–2 volts. In one trial, 0.1942 gram of cadmium was deposited and again, 0.1944 gram. In presence of 1 gram of calcium formate, under the same conditions, 0.1944 gram of cadmium was obtained. Using 1 gram strontium formate, the deposit weighed 0.1946 gram, and with 1 gram barium formate, 0.1946 gram. In all these cases, no other ion was present except the formate ion, so that the character of the deposits was due entirely to that ion. Whereas the deposits were crystalline and adherent and of good color, and the weights obtained were concordant, very careful washing was necessary, particularly when the alkaline earth metals were present. The results on the whole were better than when the acetate electrolyte was used alone.

When cadmium sulphate solution was used, however, with the formate electrolyte, very excellent deposits were obtained, showing again the influence of the sulphate ion. To 10 cc. of the same cadmium sulphate solution (containing 0.1968 gram of cadmium metal in 10 cc.) were added 2 grams of ammonium formate and 0.5 cc. of formic acid. After diluting and heating to the boiling point, the solution was electrolyzed for one hour, using 0.3 ampere and 0.8–1 volt. A deposit was obtained weighing 0.1968 gram. In another trial 0.1970 gram of cadmium was obtained. Upon the addition of 1 gram of calcium formate, using similar conditions, 0.1968 gram of cadmium again came down. The deposit seemed not to be altered in any way by the presence of calcium. Some free acid was found necessary in all these determinations, as cadmium formate is somewhat difficultly soluble; and if a formate is used alone as electrolyte, a white precipitate of cadmium formate interferes with the work.

A third series was made using cadmium acetate as a starting point with the formate electrolyte. From 10 cc. of a cadmium acetate solution, it was found that the cadmium could be fully deposited in forty-five minutes, using 0.3 ampere and 0.8–1 volt, the electrolyte being as before 2 grams of ammonium formate and 0.5 cc. of formic acid. The deposit weighed 0.1760 gram. Mixed with 1 gram of calcium formate, 0.1760 gram of cadmium was obtained; and with 1 gram of strontium formate and 1 gram of barium formate, respectively, 0.1762 gram and 0.1760 gram of cadmium were thrown down. The character of these deposits was also good, though perhaps not quite so firm as in the case of those obtained from the sulphate with the formate electrolyte. The deposits were finely crystalline and adherent, but slightly porous.

III. The Lactate Electrolyte.[1]

The action of the lactate electrolyte was then investigated. As before, the first trial was made with only lactate ions present. The electrolyte used was 2 cc. of lactic acid with 1 cc. of ammonium hydroxide. This was added to 10 cc. of a solution of cadmium lactate, diluted as usual,

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[1] THIS JOURNAL, 27, 1275.

and electrolyzed at boiling temperature for one hour, using 0.3 ampere and 2.8–3 volts. The weights of cadmium obtained, although fairly concordant, were not considered reliable. The greater part of the deposit was fine and adherent, but had also coarse crystalline plates which scaled off and were not easily handled. Again, however, the use of the same electrolyte with the cadmium sulphate solution resulted in the formation of a very excellent deposit. It was silvery-white, very finely crystalline, clean, and easy to wash. The same excellence was seen in the metal deposited from the cadmium sulphate solution in presence of 1 gram of calcium lactate. To 10 cc. of cadmium sulphate solution were added 2 cc. of lactic acid and 1 cc. of ammonium hydroxide, the solution diluted, heated to boiling, and electrolyzed for one hour with a current of 0.3 ampere and 2.6–3 volts. The weights of cadmium obtained in two trials were 0.1964 gram and 0.1966 gram. When 1 gram of calcium lactate was added, 0.1966 gram and 0.1965 gram were successively obtained.

An attempt was made to use cadmium acetate solution with the lactate electrolyte, but the deposits again showed coarse crystalline plates which scaled off in washing and the weights were always low.

With a solution of cadmium formate, however, the results were better. Although the same tendency to scaling off was observed, it could be controlled more easily. It was found better to make the quantity of lactic acid a little less, a scant 2 cc. giving the best results. From 10 cc. of the cadmium formate solution used, 0.1944 gram of cadmium had been previously obtained. Using the same amount of this solution, with 2 cc. of lactic acid and 1 cc. of ammonium hydroxide, diluting, and heating to the boiling point, 0.3 ampere and 2–3 volts used for one hour gave successively 0.1944 gram and 0.1946 gram of cadmium. A series of separations was then tried from calcium, strontium, and barium. On adding 1 gram of calcium formate to the solution as prepared above, 0.1946 gram of cadmium was obtained; with 1 gram of strontium formate 0.1944 gram, and with 1 gram of barium formate 0.1946 gram of cadmium was precipitated. The character of the deposit was not materially altered by the presence of the alkaline earth metals, although with the barium formate, there seemed to be a tendency towards the formation of coarser crystals.

In conclusion, it seems evident that in work with the rotating anode:

1. Low currents are preferable for the deposition of cadmium, when organic electrolytes are used.

2. Each electrolyte has a decided influence on the character of the deposit, which is not to be foreseen.

3. A mixture of ions improves the character of the deposit. This is most evident when the sulphate ion is present, the best deposits being

obtained from the cadmium sulphate solution, using the acetate, formate, or lactate electrolyte. The formate ion also seems to exert a good influence on the deposit, cadmium acetate solution with the formate electrolyte giving satisfactory results even in presence of the alkaline earth metals, and cadmium formate solution with the lactate electrolyte also giving good deposits. It is of interest to observe that the acetate and lactate electrolytes when used alone are not so successful, and the combination is an extremely poor one.

It is clear that other organic electrolytes should be investigated, and that many interesting and valuable relations may be found in the comparison of the nature of the deposits from different electrolytes and from their combinations. It is hoped that this investigation may be continued in this laboratory.

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DETERMINATION OF AMMONIA NITROGEN IN WATER IN THE PRESENCE OF HYDROGEN SULPHIDE.

By Edward Bartow and B. H. Harrison.

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The tests for free and albuminoid ammonia, since their introduction in 1867, have played an important role in the sanitary examination of drinking-water. They have been criticized because of inaccuracies due to interferences from substances in solution, and it is this phase of the subject that we have been investigating. In the experimental work we have taken the usual precautions to have a uniform rate of distillation, a uniform temperature for Nesslerization, a uniform organic content in comparative tests, all glass apparatus and a room free from ammonia fumes. As an illustration of the necessity for the last precaution we found that 0.036 part per million of ammonia nitrogen was added to a water exposed for 24 hours in the distilling room, which adjoined a room where dogs were kept for experimental work in physiological chemistry, and that 0.566 part per million was added to water in the room where the dogs were kept.

Natural waters sometimes contain substances which may cause interference if these combine with ammonia to prevent its distillation or if they are distilled with the ammonia and interfere with the Nessler test. Of the former class are acids like sulphuric acid, which, as is well known, must be neutralized before distillation. Of the latter class is hydrogen sulphide, which will distil over with the ammonia and will give false results.

We have studied the effect of three substances, calcium acid carbonate.