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SYNOPSIS—The pH conditions for the complete extraction of certain metals from aqueous solutions by means of a 1 per cent. solution of 8-hydroxyquinoline in chloroform are reported. Metals investigated include aluminium, copper, ferric iron, manganese, molybdenum, nickel and stannic tin. For the photometric estimation of traces of stannic tin, extraction with 8-hydroxyquinoline is put forward as a valuable addition to known methods. As a further example of the application of the results, brief mention is made of the separation of iron, nickel, cobalt, copper and manganese from very pure molybdenum trioxide. It is shown that the extraction of 8-hydroxyquinolinates of the heavy metals is a useful method of purifying solutions of many reagents used in trace analysis.

THE solubility in chloroform of the 8-hydroxyquinolinates of many metals can be of analytical importance in three respects:

- (a) as a means of separation of trace impurities prior to their determination by other methods,
- (b) as providing a medium for photometric or fluorimetric analysis, since the chloroform solutions are strongly coloured and some show a marked fluorescence,
- and (c) for the purification of reagents by extraction of the metallic impurities.

The first systematic publication on the extraction of metals with a chloroform solution of 8-hydroxyquinoline, by Moeller,<sup>1</sup> described the use of a 0.01 M reagent solution with four extractions for each determination. Under these conditions the pH ranges for complete extraction were very narrow for some of the metals. By using a 1 per cent. (about 0.07 M) reagent solution, the extraction of aluminium was made effectively complete in one operation over a wide pH range.<sup>2</sup> The same conditions have been adopted by Westwood and Mayer<sup>3</sup> for the determination of cerium in cast iron. Lacroix,<sup>4</sup> who investigated the properties of the oxinates of aluminium, gallium and indium, used a 0.1 M solution of reagent (about 1.45 per cent.). The work of this author is of special interest for the valuable theoretical treatment given.

In the present work the 1 per cent. reagent concentration has been retained and the other conditions of extraction also follow those previously used for the extraction of aluminium, with the exception of a shorter time of shaking. The primary object of the investigation has been the establishment of the pH range for complete extraction of the several metals. As is to be expected, the results differ widely from those found by Moeller. Of special significance in the present work is the new method of photometric analysis offered by the extraction of stannic tin. In view of the paucity of good methods for the estimation of traces of tin, special attention has been given to this finding.

### EXPERIMENTAL

For each element a series of experiments was made at various pH values, extracting in each test 50 ml. of the aqueous solution, containing a fixed amount (50 or 200  $\mu$ g.) of the element, with 10 ml. of a 1 per cent. solution of 8-hydroxyquinoline in chloroform. After shaking for 1 minute, the chloroform layer was run off into a small flask containing about 1 g. of anhydrous sodium sulphate. A blank determination was made, omitting the element under investigation. AnalaR reagents were used where available. The acid buffer solutions were made from sodium acetate solution to which either hydrochloric or acetic acid was added, and the alkaline buffer solutions were prepared from mixtures of sodium hydroxide and bicarbonate. In the determination of some of the metals 10 ml. of 10 per cent. sodium potassium tartrate was included in the buffer solution. In order to keep the blank value at a low level it was found necessary to purify the solutions of sodium acetate, sodium bicarbonate and sodium potassium tartrate by the method to be described later.

The absorption of the chloroform solution was measured on the Spekker absorptiometer, using the mercury vapour lamp and a 1-cm. cell. The filter combination used was Ilford 601

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with Chance No. 8 (O.V.1), excepting for iron, for which Wratten 50 and Chance O.B.2 were used. The choice of filters was in accordance with the transmission curves reported by Moeller. In the determinations, the pH of the aqueous solution was measured with the glass electrode immediately after the separation of the chloroform layer.

### RESULTS

#### (a) ALUMINIUM—

The pH conditions for the extraction of aluminium in the absence of tartrate, which interferes, have been described previously.<sup>2</sup> For the sake of completeness the graphical representation of the results is included in Fig. 1.

Replacement of the Wratten No. 2 filter, previously used, by the Ilford 601 filter, together with the Chance No. 8 filter gave a linear calibration curve. The deviation from linearity previously reported was due to the transmission of some red radiation by the filter pair then used.

## (b) COPPER-

The results obtained with copper in the presence of tartrate are shown in Fig. 1. It can be seen that complete extraction of copper occurs in the pH range 2.8 to 14. Throughout this work the term "complete extraction" is used where at least 98 per cent. of the metal present has been extracted in one operation, as shown either by a second extraction or by comparison of the drum reading with results at other pH values.

### (c) IRON-

Ferric iron in the presence of tartrate can be completely extracted in the pH range 2.5 to 12.5 (Fig. 1). With a double or triple extraction the iron could be completely extracted from even more acid solution, say at pH 2, a fact of value in the separation of iron from other heavy metals.

### (d) MANGANESE-

On attempting the extraction of bivalent manganese in the presence of tartrate, it was found that, although extraction occurred in the alkaline range, the Spekker readings showed small but significant variations at slightly differing pH values. It was thought that these variations might be due to partial atmospheric oxidation of the manganese. Two series of experiments were therefore made, the first in presence of 5 ml. of 5 per cent. sodium sulphite solutions and the second in presence of 1 mg. of potassium ferricyanide. Under the latter oxidising conditions, complete extraction and constancy of drum readings were found in the pH range 7.2 to about 12.5. These conditions are therefore recommended for the photometric determination of manganese; but for the separation of manganese, the ferricyanide may be omitted.

#### (e) MOLYBDENUM-

The colour of the molybdenum hydroxyquinolinate extract was not so intense as for the other metals, and it was necessary to use 200  $\mu$ g. of molybdenum in each experiment. Tartrate interfered with the extraction, but in its absence molybdenum could be completely extracted in the pH range 1.6 to 5.6.

### (f) Nickel—

The complete extraction of nickel in the presence of tartrate was possible in the pH range 4.5 to 9.5 (Fig. 1).

It was found that stannic tin could be extracted from an acid solution, pH 2.5 to 5.5, to give a yellow chloroform layer. The transmission curve of the chloroform solution is shown in Fig. 2, from which the broad minimum at 3850 A. can be seen. This decided the choice of filters: Chance No. 8 and Ilford 601 transmitting the mercury 4078 and 4047 A. lines.

By the treatment of a series of solutions containing different amounts of tin, all at pH 3.5, a calibration curve was obtained. This was linear over the range examined, *i.e.*, up to  $280 \mu$ g., corresponding to a drum difference reading of 0.70. A 2-minute shaking period was used, and the extraction was made promptly after adjusting the pH of the solution,

<sup>(</sup>g) TIN----

as otherwise somewhat lower results were obtained. The presence of tartrate seriously interfered with the extraction of tin, but in the presence of 0.4 g. of ammonium oxalate 95 per cent. of the 200  $\mu$ g, of tin present could be extracted in the pH range 5 to 6.



(h) OTHER METALS-

Attempts to obtain conditions for the complete extraction of bismuth in one operation were unsuccessful, although partial extraction was possible in the pH range 5 to 12. Even in the absence of all tartrate and chloride, and using a bismuth sulphate solution and acetate buffers, the absorptiometer readings showed marked changes with pH.

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Cobalt, like manganese, gave peculiar results, thought to be due to oxidation by air in alkaline solution. Complete extraction of cobalt was possible in a pH range of about 5.7 to 9.5, but the drum readings showed variations larger than the expected experimental errors. Attempts to obtain constant readings under either oxidising or reducing conditions, as used for manganese, were not successful.

In view of the analytical association of arsenic, antimony and tin, the extraction of the first two elements was investigated under the conditions used for tin. Arsenic did not interfere but antimony could be extracted from acetate solutions to some extent over the range for the complete extraction of tin. Tartrate partially suppressed the extraction of antimony, whilst the presence of oxalate prevented extraction from solutions with a pH greater than  $5\cdot 0$ .

### DISCUSSION

As was to be expected, with the present conditions, the pH ranges for complete extraction differ markedly from those reported by Moeller.<sup>1</sup>

Where possible, tartrate has been added to the aqueous solution, to prevent precipitation of the hydrous oxides, which would otherwise occur. The presence of these hydrous oxides would considerably increase the extraction time necessary for the complete formation of the 8-hydroxyquinolinates. Molybdenum, tin and aluminium, however, cannot be extracted completely in the presence of tartrate. It is nevertheless possible to remove all but a negligible amount of aluminium in the presence of tartrate from a solution at pH 9.5 by using a triple extraction. Whether tartrate is added in a particular application will depend on the conditions required.

An example of the application of this method as a means of separating trace impurities is the determination of iron, nickel, cobalt, copper and manganese in very pure molybdenum trioxide. By double extraction with a chloroform solution of 8-hydroxyquinoline at pH 9 in the presence of tartrate the impurities from 5 g. of sample are separated from the molybdenum and concentrated into 10 ml. of chloroform solution. It is then a comparatively simple matter to determine the impurities by standard photometric methods on a microscale. It is possible by this means to determine the above-mentioned impurities in amounts down to 0.00002 per cent. in the molybdenum trioxide.

For the direct photometric determination of most of the elements investigated, chloroform extraction of the 8-hydroxyquinolinate has no advantages over other available methods, particularly in view of its non-selective nature. An exception to this is the determination of aluminium by the masking of interfering elements, a procedure described in a previous paper. A further exception is the photometric determination of tin, which is not easily determined in trace amounts by known methods. The application of the 8-hydroxyquinoline method is dependent on the ready separation of tin from other elements by distillation of the chloride or bromide. An accurate photometric estimation of tin in the distillate can then be made by the procedure previously described. Conditions of distillation must be carefully controlled to prevent the interference of antimony, but otherwise the method is specific among common elements.

This new method for the determination of tin has been applied to samples of tungsten and tantalum compounds with a considerable saving in time over the methods previously used.

A third general application of the extraction of the 8-hydroxyquinolinates is found in the removal of heavy-metal impurities from analytical reagents. This method is generally applicable to soluble salts of ammonium, the alkali metals or the alkaline earths, provided that the pH of the solution falls within the desired range, preferably from 4.5 to 9.5, as can be seen by inspection of Fig. 1. The procedure adopted is to shake the solution of the salt with a 1 per cent. solution of 8-hydroxyquinoline in chloroform, run off the chloroform layer, and repeat the process until the organic layer is colourless. Excess of 8-hydroxyquinoline can be removed from the aqueous solution by several extractions with chloroform. Finally, the chloroform dissolved in the solution can be removed by bubbling air through the solution. Experiments have shown that this procedure will reduce the heavy metal content of solutions to a very low level and the method is very suitable for the preparation of chemicals used in trace analysis.

### CONCLUSIONS

The work reported in this paper was originally undertaken as part of an investigation of analytical methods for the refractory metals, but the results are felt to be of more general interest. As a means of separation of trace impurities and as a method of reagent purification, chloroform extraction of 8-hydroxyquinolinates should have many applications. For the estimation of traces of tin, the direct photometric method using 8-hydroxyquinoline would seem to have some advantages over other methods and it should repay study.

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#### References

- Moeller, T., Ind. Eng. Chem., Anal. Ed., 1943, 15, 346.
  Gentry, C. H. R., and Sherrington, L. G., Analyst, 1946, 71, 432.
  Westwood, W., and Mayer, A., Ibid., 1948, 73, 275.
- Lacroix, S., Anal. Chim. Acta, 1947, 1, 260.

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