

A Spectrophotometric Study of Certain Methods for the Colorimetric Determination of Tin

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Introduction. Tin is usually determined by the separation of meta-stannic acid and subsequent ignition to the oxide which is weighed or by a titrimetric procedure. Neither of these methods is very satisfactory for the determination if the sample contains less than one percent of tin.

Several organic reagents are used for the qualitative detection of tin. Diazine green (S) (1), and cacotheline (2) seemed promising for use in a quantitative method.

Diazine green (S) forms a blue-green solution. Upon the addition of tin (II) in low acidic solution the color changes to deep red; in a highly acidic solution the color fades to a pale yellow. The latter reaction is more sensitive to slight changes in the concentration of tin.

Cacotheline forms an orange hued solution which changes to a red-purple upon the addition of a tin (II) solution.

Apparatus and Reagents. All measurements were made with a Beckman Quartz spectrophotometer using 2.00 ± 0.03 cm. cells. The band width varied from 1 to 5 mu.

A standard tin solution was prepared using 2.000 g. of reagent grade granulated tin dissolved in 100 ml. of concentrated hydrochloric acid and diluted to 2000 ml. with redistilled water.

A solution of cacotheline was prepared by dissolving 0.100 g. of solid reagent (E.K. 4396) in 250 ml. of redistilled water.

A solution of diazin green (S) was prepared by dissolving 0.100 g. of solid reagent (Janus green (s) E.K. 4444) in 250 ml. of redistilled water.

Concentrated hydrochloric acid cp and 30 mesh zinc, cp were used.

Reduction Procedure. Transfer an aliquot of the sample, free from nitrate ion, containing an amount of tin within the range of the particular method to be used to a 50 ml. volumetric flask. The volume of sample should be 5 ml. or less so that the reduction will proceed rapidly. Add 1.5 g. of 30 mesh zinc and 1 ml. of concentrated hydrochloric acid if the sample is not acidic. Stopper the flask loosely and place the flask on the edge of the steam plate for 2-3 minutes. After becoming warm, place the flask on the steam plate for 2-3 minutes more. Remove the flask and rapidly add the amount of hydrochloric acid required by the particular method, replacing the stopper loosely. Just before the last

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pieces of zinc disappear, force the stopper in tightly. Cool the solution to room temperature under a cold water tap taking care not to start with too cold water since the flask might break.

Diazin green method. To the sample just reduced, containing 23 ml. of hydrochloric acid and 8-20 ppm. of tin, add 5 ml. of reagent by use of a pipet with a cut off tip. The stopper is used to help shut off the mouth of the flask as the pipet drains. Immediately replace the stopper and mix by swirling. Color development requires 5-10 minutes. For low concentrations of tin use the five minute development time. Dilute the solution to volume with freshly boiled distilled water. Mix thoroughly and read the per cent transmittancy at once at 655 mu. Use distilled water in the reference cell. The oxygen from the air reoxidizes the reagent fairly rapidly hence the necessity for making the reading as soon as possible after dilution to volume.

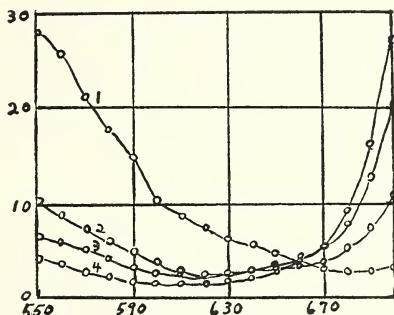


FIG. 1. Diazin Green method. Vertical scale is per cent transmittancy. Horizontal scale represents mu. Curve 1 represents 2 ml. reagent, 44 ml. HCl; curve 2 represents 2 ml. reagent, 25 ml. HCl; curve 3 represents 2 ml. reagent, 20 ml. HCl; curve 4 represents 2 ml. reagent, 15 ml. HCl.

When different concentrations of acid are used the per cent transmittancy curves show an isobestic point at about 655 mu. (Fig. 1). This happens to be the wavelength at which maximum sensitivity to concentration changes was observed hence it is convenient to measure at that wavelength as slight variations in the concentration of acid will have little effect upon the determination.

The reagent seems to be reasonably stable. However, transmittancies obtained for a given amount of tin and a given reagent solution are not usually the same on different days. Therefore, to use this reagent for quantitative determinations one must redetermine the calibration curve each day using standard samples.

This system does not follow Beer's law exactly. (Fig. 2, A). It can be used in the concentration range of 8-20 ppm. of tin.

Figure 3 shows a typical set of curves obtained using the concentration range specified.

Using 1:1 sulfuric acid and 2:1 phosphoric acid the same color change of blue-green to pale yellow was observed upon the addition of

tin (II) solutions. It was impossible to obtain complete reduction of the tin when these acids were used.

Cacotheline method. To the sample just reduced, containing 8 ml. of hydrochloric acid and 4-16 ppm. of tin, add 10 ml. of reagent by the use of a pipet with a cut off tip. The stopper is used to help shut off the top of the flask as the pipet drains. Immediately replace the stopper and mix by swirling. Then dilute to volume with freshly boiled distilled water. Mix thoroughly and read the per cent transmittancy at once at 560 mu. (Fig. 4). Use distilled water in the reference cell. The oxygen from the air reoxidizes the reagent fairly rapidly, hence the

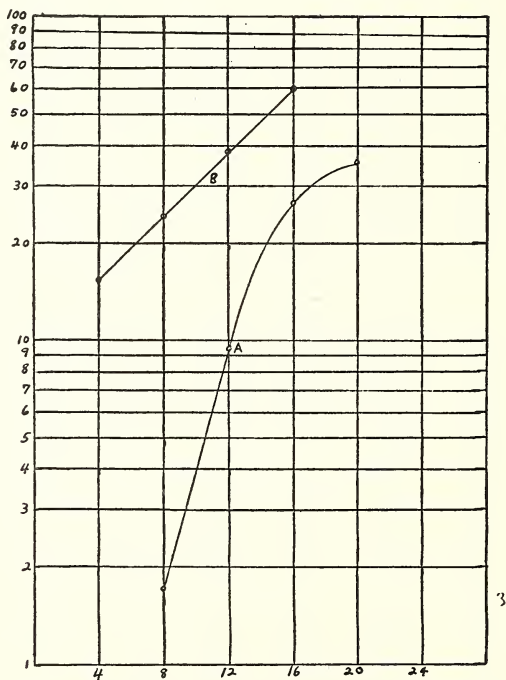


FIG. 2. Beer's Law curve. A, Diazin Green method. B, Cacotheline method. Vertical scale is per cent transmittancy, horizontal scale represents ppm. tin.

necessity for making the reading as soon as possible after dilution to volume.

This reagent seems to be unstable. An old solution will react to give a more dense color than one freshly prepared. Two freshly prepared reagent solutions will not give the same values. The calibration curve is a straight line so that it is necessary to check but one standard sample each day and draw a new line with a corresponding slope to the previously determined one. This system does follow Beer's law. (Fig. 2, B).

A combination of Corning filters No. 349 and No. 978 show a maximum transmittancy at about 560 mu. Consequently one could use the cacotheline method and with this filter combination make his measurements by use of a filter photometer.

Summary. Of these two methods the cacotheline method has given the best reproducibility. The concentration ranges are 8-20 ppm. of tin using diazin green (S) and 4-16 ppm. using cacotheline when using 2 cm. cells. The greatest difficulty with either method is the fact that re-oxidation of the reduced reagent is rapid upon exposure to the air. A lesser difficulty is the necessity for redetermining the calibration curves

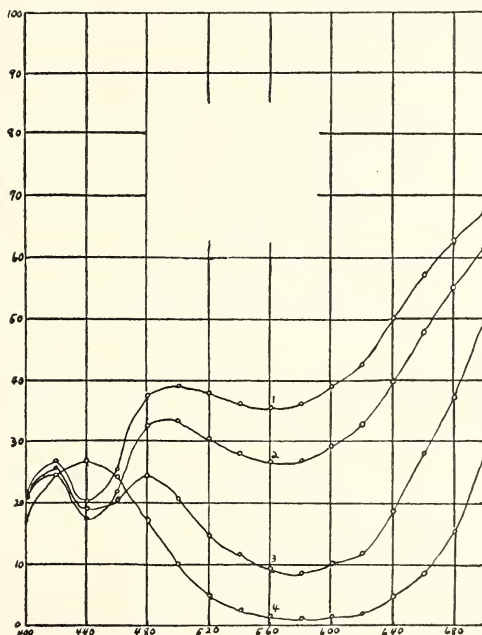


FIG. 3. Diazin Green method. Concentration curves. Vertical scale is per cent transmittancy. Horizontal scale represents mu. Curve 1 represents 20 ppm. tin; curve 2 represents 16 ppm. tin; curve 3 represents 12 ppm. tin; curve 4 represents 8 ppm. tin.

each day by analyzing standard tin samples. The usual precision of a colorimetric method, namely 1-3%, can be obtained by using the carefully controlled conditions described.

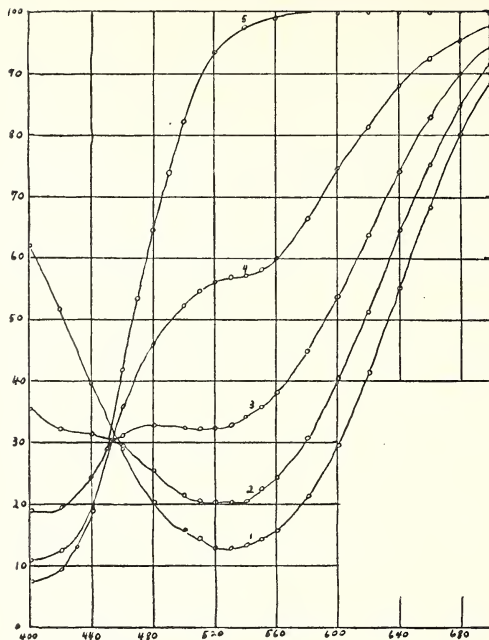


FIG. 4. Cacotheline method. Concentration curves. 10 ml. reagent and 10 ml. HCl. Vertical scale is per cent transparency. Horizontal scale represents μ . Curve 1 represents 16 ppm. tin; curve 2 represents 12 ppm. tin; curve 3 represents 8 ppm. tin; curve 4 represents 4 ppm. tin; curve 5 is the reagent curve.

Bibliography

1. Eegriwe, E., *Z. Anal. Chem.*, **74**:225 (1928).
2. Newell, I. L., Ficklen, J. B. and Mazfield, L. S., *Ind. Eng., Anal. Ed.*, **7**:26 (1935).
3. Beck, G., *Microchemica Acta*, **2**:9, 287 (1937).
4. Leuchs, H. and Leuchs, F., *Ber.*, **43**:1042 (1910).
5. Laidlaw, P. P., and Payne, W. W., *Biochem. J.*, **16**:494 (1922).
6. Korenman, I. M., *Pharm. Zentralhalle*, **70**:693 (1929).