COMMENTS ON REPORT LTD-45-57 (December 14, 1945)

I cannot agree entirely with the contents or conclusions contained in this report. We have tested the "one color" method of the Baton Rouge Laboratory thoroughly and we were so convinced of its advantages that we have incorporated this step in our routine method. We have made approximately 4,000 analyses with it and we are completely satisfied with the results.

1. We find no losses at low lead concentrations.

2. We find the final single color to be as stable as the mixed color which we used previously.

3. We find no losses due to phosphate in the final extraction even though citrate is not added. Experiments on this phase were carried out by us with quantities of phosphate up to 5 mg. This quantity is excessive and is unlikely to occur in the last extraction if good technique is employed in previous steps. Phosphate in KCN has been a topic of discussion for many years, but the amount in this reagent is so small that in our laboratory we have not bothered to remove it. More serious is entrainment of phosphate in the final step due to incomplete washing of extracts in the earlier extractions. We have stressed this point as well as the need for proper sequence in adding the reagents in the last step in several of our publications. The addition of citrate in the estimation extraction is unnecessary although we recommend its use in the initial extraction step.

4. I admit failure to understand the tests described on pages 4 and 5 under "Solubility of lead dithizonate at pH 11.4." We have tested this angle comparatively using 100 micrograms of lead and extracting with a single quantity of dithizone at pH 9.5 and 11.5. The aqueous phase was then analyzed for lead by extracting it with di-beta-naphthylthiocarbazone, which extracts completely at high pH values and is completely insoluble in the aqueous phase. Comparable quantities (1-2 micrograms) were found. We felt that this represented entrainment losses rather than solubility losses.

5. Accuracies of 7.5 per cent shown on page 4 are excellent for the range 0-5 micrograms, particularly in a 1 cm. cell. In most analytical work, including this type, errors up to ±20 per cent are permissible in the range 0-5 micrograms.

6. The comments on aging of reagents are generally recognized by analysts and all that is required is a blank determination in the final extraction so as to establish the zero value of the curve. The calibration curve is then drawn parallel to the original and the values of subsequent readings employing the same dithizone solution are taken from the corrected curve. This may be eliminated if the zero is established by setting the photometer to 100 with the blank in both cells.

7. It is a decided advantage to be able to use one dithizone solution for all extractions, initial and final colorimetric, and this feature attracted us to the method since it meant the elimination of bottling three distinctly different solutions which might go bad and which might delay analysis if they had to be made up and calibrated.

8. It should be admitted that the Baton Rouge method is applicable only to pure lead solutions. When applied to biological material, it must be modified to handle this more complex medium which may contain interfering elements, particularly bismuth. This has been done in our laboratory and the modified procedure discussing all of the points mentioned in the LTD-45-57 report will be published as a follow up to the paper by Snyder.

9. In connection with the TEL test, it should be pointed out that regardless of the compound which is formed with iodine and dithizone, it is interesting that this compound is different from lead dithizone as evidenced by the shift of the maximum to lower wave length (490 against 510). As used by Baton Rouge, the method is not a "single color" method but rather a "mixed color" because of the great excess of dithizone which is employed. This excess is important since if the amount of dithizone in the extracting solution is reduced to one-half (to conform to the original single color method); quantities of lead below 3 micrograms are not extracted.

10. On page 8, the statement is made that sensitivity was "lost due to the coincidence of the absorption maxima of the dithizone reagent and the organo-lead dithizonate." Dithizone transmits strongly at 490 mμ; in fact, it shows a transmission maximum at 505 mμ. Its absorption maxima occur at 445 mμ and 610 mμ.

11. It is recognized that the pH 11.5 extraction method is so contrary to what has been done with dithizone in the past that there may be some resistance to its use. We are convinced of its superiority over the older method, but also recognize that difficulties might occur in the application of the method to specific problems. It is understood therefore that each application should be thoroughly investigated and that certain modifications may become necessary.

J. Cholak

January 5, 1946