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CC: DR. R. A. KEHOE

August 8, 1944

Mr. J. I. Stecher
E. I. du Pont de Nemours and Co.
Wilmington, Delaware

Dear Mr. Stecher:

I am attaching hereto for your information copies of two letters of comments on Chambers Works Experimental Reports. The first of these, dated July 18, contains the comments of Mr. Gambrill of our Chemical Research Laboratory at Detroit on "Experimental Report No. TEL 44-8, Chambers Works Method for Lead Analyses by Dithizone". The second set of comments comes from Dr. Kehoe and is concerned with Report No. TEL 44-10, "Detection of Small Amounts of Lead in Air Spectrographically."

If you have any comments to make on these comments, I should be very glad to have them.

Yours very truly

J. H. Schaefer

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July 18, 1944

MEMORANDUM TO:

Dr. Calingaert

SUBJECT: Chambers Works Method for Lead Analyses by Dithizone.
Experimental Report No. TEL 44-8 - June 12, 1944

The method described is based on the method developed at the Kettering Laboratory of Applied Physiology for the determination of lead in biological samples. In this method (cf. Ind. & Eng. Chem. Anal. Ed 9. 493 - 1937) the solution of the Pb containing ammonium citrate and KCN is adjusted to pH 7.5. The Pb, and any Bi which may be present, is then extracted with dithizone-CHCl₃ solution. Iron and other metals which may be present are not extracted.

The CHCl₃ solution of the Pb and Bi is then extracted with dilute acid and the acid solution of Pb and Bi is adjusted to pH 2. Bi is then removed by dithizone-CHCl₃ extraction, and the aqueous phase after Bi removal is readjusted to pH 7.5 and again the Pb is removed by dithizone extraction. Again the Pb is removed from the CHCl₃ by extraction with a standardized amount of dilute acid. To this acid solution is added a standardized amount of NH₄OH-KCN solution to obtain a pH of 9.5. The Pb is then extracted by dithizone for color measurement, using standardized amount of pure dithizone in CHCl₃. The amounts of dithizone used depend on the amount of Pb present in the sample.

In the Chambers Works Method, the preliminary extractions, as mentioned above, to obtain the Pb free of interfering metals are not made. Rather the solution containing the Pb is adjusted to pH 2, then NH₄OH-KCN solution added to bring the solution to pH 7.8 and the color density of the Pb-dithizone complex obtained directly on the extraction from this solution.

According to Sandell (1), Hopkins and Williams (2), and Wichmann (3) only approximately 80% of the Pb is extracted at pH 7.8, unless a large excess of dithizone is employed. Generally when extracting Pb at pH 7.5, 5 ml. increments of the dithizone solution are used and drained each time from the aqueous phase until a green dithizone solution is obtained. Such an extraction procedure thus permits an estimate of the amount of Pb present, and the selection of the proper standard (see below) for the final color measurement of the Pb complex.

If Fe is present which according to the method is indicated by a brown color in the dried salts obtained by evaporating the I-KI solution used for absorbing the TEL, then a special extraction to remove Fe is suggested. This special extraction is actually the first extraction generally used by most workers to obtain the lead free from other interfering metals.

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given in the Chambers Works Method for adjusting the solution to pH 2. made regarding Bi, and if Bi is not to be considered then there is reason to adjust to pH 2 in the first place. Further, if Bi were present removed, the solution should be adjusted to pH 2.8-3.0, for as reported well as in LTD 42-19, the extraction of Bi at pH 2 does not give 100% the Bi (cf. also references 1 and 2).

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ment of the method, standard Pb solutions were used containing from 0-40 Pb, of them only 6 were reported for 0-12 micrograms of Pb and 5 for from 13-40 micrograms of Pb. The analysis of 8 spot samples (2.1 cu. ft.) however show 7 to have 3 micrograms of Pb and only one to contain above that or 7 micrograms is reason and for accuracy standard curves should be prepared for Pb to 10, 0 to 25, etc. micrograms of Pb. Attempting to estimate the Pb sample containing 0-10 micrograms of Pb from a 0-40 microgram Pb curve readings to be made in the most inaccurate portion of the curve.

Although the Chambers Works Method may be satisfactory, it does not seem that the best procedure has been used particularly for low Pb concentrations wherein an accuracy of 0.1 to 0.2 micrograms of Pb is desired for samples containing as little as 1 to 2 micrograms of Pb.

Note is also made that all glassware used in the manipulations shall be made lead free by treatment with concentrated HNO_3 . $\text{Pb}(\text{NO}_3)_2$ is insoluble in concentrated HNO_3 and for this reason voluminous washings with water must be made to completely remove any Pb contamination from the glassware. Dilute HNO_3 solutions are preferred for deleading glassware for dithizone Pb determinations.

The description of the Kettering Laboratory Method attached to the Chambers Works Method is in error in the paragraph on Preparation of the Sample. The addition of the $\text{NH}_4\text{OH-KCN}$ solution has been omitted. Therefore, according to the description given, only Bi would be extracted, no Pb would be removed.

- (1) Colorimetric Determination of Traces of Metals. E. B. Sandell, Interscience Publishers, Inc., New York, 1944.
- (2) Organic Reagents for Metals, 4th Edition, Research Staff Hopkins and Williams, Hopkins and Williams, Ltd., London, 1943.
- (3) Isolation and Determination of Traces of Metals, H. J. Wichmann, Ind. and Eng. Chem. Anal. Ed. 11, 66, 1939.