COMMENTS ON DR. BELKNAP'S METHOD

The pros and cons for the various lead methods used in biological work have been given so often in the past that a further discussion is not warranted. It suffices to say that the universal use of dithizone is sufficient evidence of the merits of this method and one is led to express amazement that the "Fairhall modification" method should be used in preference to simpler, more accurate and sensitive dithizone methods. The method which Dr. Belknap uses has a number of analytical pitfalls:

1. The ammonium hydroxide precipitation method does not remove all of the lead, and with this start, provided other losses or contaminations do not occur, the values should be low.

2. Losses may be increased by the filtration steps, due to absorption by the filter papers or by silica if present. In the dithizone method, these losses cannot occur since filtrations are not required.

3. On occasions, high results may be obtained due to contamination by lead from atmospheric dust. This source of contamination is much more serious in a method requiring several days of manipulative procedures than in one in which the analysis may be completed in a few hours' time.

4. Further addition of lead may arise from the many filtrations employed. We have found as much as 5 micrograms of lead in a single Whatman #40, 7 cm filter paper. If on occasion this is multiplied by six (the number of filter papers of various sizes used), an appreciable addition to the lead content is obtained.

5. High results may be obtained by the titration of extraneous chromate occluded by precipitates other than lead chromate. Such occluded chromate is tenaciously held by the precipitate and cannot be removed even by lengthy washings with hot water. Such precipitates may be due to iron or aluminum hydroxides formed in the neutralization step before precipitating the lead in the weakly acid solution. These metals should be absent from the test solution and the reagents used, and it is doubtful whether they can be removed from the test solution without employing the sulfate step which Dr. Belknap has omitted.

6. High results may be due to the formation of the double chromate. If this occurs the amount of thiosulfate required will be twice that for the normal chromate. On occasion, even mixtures of the salts may be present. As far as can be gathered from the details as given, this is a distinct possibility. Letonoff and Reinhold (Ind. Eng. Chem. Anal. Ed. 12, 280, 1940) obtained this double salt when the chromate precipitation was carried cut in a pH range extending from 7.4 to 6.6 and the pure single chromate did not occur by itself except in the pH region below 5.4. Comparison of the volumes of test solution and amounts of acetic acid used in this and Letonoff's method show that the conditions in the two procedures are about equal and suggest that the double salt formation is a distinct possibility.

If Dr. Belknap is willing to undertake a cooperative study, I believe that the pitfalls in the method employed by him can be demonstrated. It is proposed that a third disinterested party obtain a large volume of normal urine, and send to each laboratory a number of 500 ml samples to which known amounts of lead have been added.

The amounts added should not exceed 0.20 mg per liter of urine and the series should include specimens in the normal range. If the criticism and reply is to be published, the comparative results should also be published, as a note, otherwise the same argument will occur again.

J. C.