

conditions move cataphoretically as if the migration were due to a surface consisting of the pure protein.

2. Based upon this adsorption of protein by quartz, a method for studying the mobility of protein is presented.

3. The results for egg albumin for a variable hydrogen-ion concentration agree satisfactorily with the values given by Svedberg and Tiselius.

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## THE DETECTION OF TRACES OF BERYLLIUM AND THE COLORIMETRIC DETERMINATION OF THIS ELEMENT

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RECEIVED NOVEMBER 21, 1927

PUBLISHED FEBRUARY 4, 1928

Recently<sup>1</sup> it has been shown that adsorption indicators can be used advantageously for the detection and colorimetric determination of some elements. In a solution weakly acid with acetic acid and acetate ( $P_H$  about 5.5) aluminum, for example, gives a very nice and sensitive color reaction with 1,2,5,8-oxyanthraquinone. For magnesium, we found titan yellow to be an excellent reagent.<sup>2</sup>

In investigations on the solubility of the slightly soluble metal hydroxides it is of great practical advantage to have color reactions at our disposal with which we can determine traces of dissolved oxides. For the determination of the solubility of beryllium hydroxide (which is extremely small at the isoelectric point) at different hydrogen-ion concentrations we wanted such a method. As is well known, there are only a very few characteristic reactions for beryllium, and only two color reactions have been described in the literature.<sup>3</sup> For this reason we tried to detect and determine it by means of adsorption indicators. The beryllium hydroxide is precipitated at the proper  $P_H$  in the presence of some useful indicator and the color of the solution or the lake formed is observed.

**1,2,5,8-Oxyanthraquinone as Indicator**<sup>4</sup> (0.1% solution in alcohol).—To 10 cc. of the solution, 0.1 cc. indicator and 6 to 8 drops of 4 *N* ammonia

<sup>1</sup> Kolthoff, *Chem. Weekblad*, **24**, 447 (1927).

<sup>2</sup> Kolthoff, *ibid.*, **24**, 254 (1927).

<sup>3</sup> The aluminon (aurintricarboxylic acid), which forms a red lake with aluminum [Hammett and Sottery, *THIS JOURNAL*, **47**, 142 (1925); Lundell and Knowles, *Ind. Eng. Chem.*, **18**, 60 (1926)], is also suitable for the detection of beryllium [A. R. Middleton, *THIS JOURNAL*, **48**, 2125 (1926)]. According to the statements of Middleton, this reaction is not as sensitive as those described below in this paper.

<sup>4</sup> After writing this paper the author found that the reagent has been already applied by Hellmut Fischer, *Wissenschaftl. Veröffentl. Siemens Konzern*, **5**, 99 (1926); *Chem. Zent.*, 1927, I, 495, who determined the dyestuff in the lake in a colorimetric way. As no details are given in the abstract referred to, the practical statements made above may be of some value.

are added, the mixture is boiled and the color observed after five minutes' standing.

A solution containing 500 mg. of beryllium in a liter gives a flock with dark blue color; the supernatant liquid is colorless. With 50 mg. of beryllium per liter, the lake is violet blue; with 5 mg. of beryllium per liter no lake is formed; the solution has a blue-violet color.

A blank without beryllium gives a violet color; if the color of the unknown is compared with that of the blank, 0.5 mg. of beryllium per liter may be detected by the blue-violet color.

In the presence of ammonium chloride, the sensitivity is not changed, the lake formed settling out much sooner. Ten cc. of solution with 0.1 cc. of indicator, 1 cc. of 4 *N* ammonium chloride and 6 to 8 drops of 4 *N* ammonia are boiled and observed after five minutes. Five mg. of beryllium per liter gives a flock with a blue-violet color. More dilute solutions only give a blue-violet color (as without ammonium chloride); after standing overnight the lake flocculates with the same shade. In this way even 0.5 mg. of beryllium per liter can be detected. Aluminum, which very often occurs in the presence of beryllium, interferes. It forms a violet lake with the dyestuff and in the presence of excess aluminum the blue-violet color of the beryllium lake can no longer be seen. The aluminum has to be removed (see below).

Unfortunately, the blank without beryllium gives a solution with a violet color, and for this reason it is hard to apply the reaction described for a colorimetric determination of the element. Therefore a search was made for some other reagent more suitable for this purpose.

**Curcumin as Reagent** (0.1% solution in alcohol).—In weakly alkaline solution, this indicator is adsorbed by the beryllium hydroxide with the formation of an orange-red color.

To 10 cc. of solution are added 1 drop of indicator (no more), 0.5 cc. of 4 *N* ammonium chloride and 6 to 8 drops of 4 *N* ammonia.

A solution containing 50 mg. of beryllium per liter gives a flocculent precipitate with a red color; with 1 mg. of beryllium per liter the color is orange-red. If the color is compared with that of a blank, the sensitivity may be increased to 0.05 mg. of beryllium per liter. The color of the blank is yellow-brown.

The appearance of the solution changes on standing, as the lake flocculates. After standing overnight, the adsorption compound sinks to the bottom of the test-tube and may be detected by its color (orange-red).

The reaction is very suitable for the quantitative colorimetric determination of beryllium in concentrations between 1 and 0.05 mg. per liter. If the color is compared with solutions of known beryllium content after the *same time of standing*, the method gives good results. Not more than

0.5 to 1 cc. of 4 *N* ammonium chloride should be added to 10 cc. of solutions; otherwise the sensitivity is decreased.

Potassium, sodium, lithium, calcium and barium do not interfere. Magnesium decreases the sensitivity somewhat, but 1 mg. of beryllium per liter in the presence of 1 g. of magnesium per liter can be detected in the way described.

Aluminum has a disturbing effect as it also forms a colored lake. For the detection of aluminum this reaction, however, is not very suitable. If beryllium is to be detected in the presence of aluminum, the slightly acid solution is treated with an excess of sodium fluoride. The main part of aluminum precipitates in the form of  $\text{Na}_3\text{AlF}_6$ , and the rest in solution does not interfere. After standing for one hour, the liquid is filtered and the filtrate treated in the way described above. One mg. of beryllium per liter could be detected in the presence of 1 g. of aluminum per liter. We may remark here that sodium fluoride decreases the sensitivity of the reaction for beryllium somewhat.

Ferric iron interferes and can be made harmless in the same way as described for aluminum. Or, more easily still, the iron may be precipitated at room temperature with an excess of sodium hydroxide, and 1 drop of curcumin and an excess of ammonium chloride added to the filtrate. Two mg. of beryllium per liter in the presence of 1 g. of iron per liter could be easily seen.

It may be mentioned here that in strong alkaline solutions beryllium does not react with the curcumin (the beryllium hydroxide dissolves again). Under these conditions magnesium gives a distinct color reaction, however, not as sensitive as with titan yellow.

Ten cc. of solution with 1 drop of reagent and 1 cc. of 4 *N* sodium hydroxide gives an orange color with 10 mg. of magnesium per liter, an orange-yellow color with 5 mg. per liter and an orange-brown color (distinctly different from a blank) with 1 mg. per liter. Perhaps the curcumin is useful for determining amounts of magnesium between 1 and 10 mg. of magnesium per liter.

The tap water of Minneapolis, containing 16.5 mg. of magnesium per liter, gave a very distinct reaction.

### Summary

1. Curcumin is a very useful reagent for the detection and colorimetric determination of traces of beryllium.
2. The sensitivity extends to 0.05 mg. of beryllium per liter.
3. A method is described for the detection of beryllium in the presence of aluminum and ferric iron.