Microestimation of Cyanide with a Modified Epstein Procedure

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For microestimation of cyanide the methods of Alridge¹ and Epstein² seem to be the most sensitive and accurate³. Both of them use a preliminary formation of cyanohalogenide, which is then reacting with pyridine and benzidine (Alridge) or phenyl-methyl-pyrazolone (Epstein), thus giving a coloured compound for colorimetry. For further increase of sensitivity two principles can be applied: A preliminary concentration of the sample by distillation or aeration⁴ or concentration of the final coloured substance by extraction in e. g. butanol⁵.

In our work with the hemoglobin-cyanide complex we had some experience with the Epstein procedure, which we modified by altering the preparation of reagents. In this way we increased the sensitivity 5 to 6 times, and the method became more convenient to handle. Using 4 ml of sample with a cyanide concentration from 10^{-5} M to 10^{-6} M, the cyanide content could be determined with a standard deviation of $\pm 3\%$. The final extinction, read at 632 m μ , would vary from 1.0 to 0.1. Under these conditions Beers law is obeyed. The modification will be described here with a few comments.

Reagents. Chloramin-T, 0.5 % in water. Stable in the refrigerator for months. The concentration may vary from 0.25 to 1.0 %.

Pyridine. A. R. Stored in the refrigerator.

3-Methyl-1-phenyl-5-pyrazolone. Commercial product recrystallized to m. p. 127–128° C.

Bis-3-methyl-1-phenyl-5-pyrazolone. Can be prepared by boiling the monopyrazolone for several hours with phenylhydrazine but is more easily synthesized by gently refluxing 1 mole ethylacetoacetate with 3 mole phenylhydrazine for less than 0.5 h. The mixture will suddenly solidify. The solid bispyrazolone is boiled out three times with alcohol.

Mixed pyrazolone powder. A stock is made by mixing 5 parts mono- and 1 part bispyrazolone.

Pyridine-pyrazolone reagent. 150 mg mixed pyrazolone powder is dissolved in 25 ml pyri-

dine. This reagent is stable for one week when kept in the refrigerator. The solution of bispyrazolone alone in pyridine² is only stable for 2 days. The ratios of mono- to bispyrazolone and of pyrazolone to pyridine are chosen so that the final colour will be maximal. Small variations will cause no influence on the final result, so the preparation of reagents can be made easily. The chosen amount of powder is easily dissolved in the cold pyridine.

Standard cyanide solution.

Procedure. A 4 ml sample, with pH between 4 and 8, is chilled. 0.2 ml chilled chloramine solution is added and mixed by swirling. After 5 minutes in an ice bath 0.8 ml chilled pyridine-pyrazolone reagent is added. The mixture is left at room temperature for 80–90 minutes. The blue colour is read in a colorimeter or in a spectrophotometer at 632 m μ . A known standard is always run simultaneously.

5 minutes was found necessary for quantitative chlorination. As the reagent was stored cold, it was preferred to add it chilled. It was found of no advantage to control temperature with a thermostat during colour development. The final colour was only little influenced by the temperature used. Using room temperature, maximum intensity of colour is obtained after 75 min. and the colour is stable for at least 0.5 h.

If the sample contains other substances than cyanide, these of course may interfere and make it necessary to run blanks.

Many attempts to increase the sensitivity further by previous aeration with the technique of Boxer and Rickards⁴ and with modifications always failed to give satisfactory recoveries or reproducible results. On the other hand it was shown that extraction of the fully developed colour by butanol could increase the sensitivity at least 5 times, but as our experience with that method is only limited, a detailed description is omitted.

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