SUMMARY (RG/93/C/02)

Title : Development of a kinetic analytical method for the determination of trace amounts of mercury.

Research Institute : Sri Jayewardenepura University

Chief Scientific Investigator : Dr. Jayantha H. Wimalasena

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Pollution of the environment by mercury is a matter of concern because of its toxic effects. As such, a knowledge of the amounts of mercury present in environmental samples is important in order to minimize the pollution of the environment. Thus, methods for the determination of mercury are important.

Among the available methods some demand sophisticated instruments and some other methods are not sensitive enough to detect trace amounts of mercury. Sri Lanka being one of the most poorest countries in the world can not afford expensive sophisticated instruments. As such, in this study an attempt was made to develop an analytical method for the determination of trace amounts of mercury with the use of unsophisticated simple instruments any poor country can afford to buy.

The highly sensitive and selective kinetic spectrophotometric method using the catalytic effect of mercuric ions on the indicator reaction of hexacyanoferrate(II) and nitrosobenzene has been used in developed countries for the determination of mercury. The method requires the measurement of the absorbance of the product at 520 nm at extremely short times (milli second) in the presence of different amounts of Hg(II).

The inverse of the time required to increase the absorbance by a constant amount or the absorbance at a fixed time and the concentration of mercuric ions were assumed to be linearly related for calibration purposes. In this work it was shown theoretically that the above assumption is correct only if the fixed time is extremely short. However, Sri Lanka being a poor country can not afford expensive instruments to perform kinetic experiments at such short times. As such, a different method of calibration is required if one wants to use this kinetic method in Sri Lanka with its available resources.

The aim of this project was to completely modify the existing kinetic method to arrive at a different calibration equation derived from kinetic experiments performed at longer times. Experiments were carried out keeping hexacyanoferrate(II) in excess compared to nitrosobenzene with varying amounts of mercuric ions.

The pH of the solution was kept at 4.5 using an acetic-acetic buffer. It was observed that the reaction rate is highest at this pH. The rate of reaction was followed by monitoring the absorbance of the product at 520 nm for about 5-7 minutes. When the ratio of the concentrations of hexacyanoferrate(II) to nitrosobenzene is higher than 40 the reaction was found to be zeroth order is hexacyanoferrate and first order is nitrosobenzene. Appropriate theory was derived and a rate parameters, $k_1 = (k_a + k_b [Hg^{2+}])$, was determined. The values of k_a and k_b at 30oC were found to be 9.40×10^{-5} s^{-1} and 39.94 dm^3 mol^{-1} s^{-1}. As such, the linear relationship between k_1 and $[Hg^{2+}]$ can ben used to determine the concentration of mercuric ions in an unknown sample.

Mercuric ion concentrations down to about 2.0×10^{-6} mol dm^{-3} could be determined using this method. The only instrument this method requires is a simple colorimeter.

A linear relationship between a rate parameter and the concentration of mercuric ions is considered for calibration, thus deviating from conventional analytical methods. The method developed is sensitive and selective and the results are reproducible.

Papers published

1. Kinetic spectrophotometric method for the determination of trace amounts of Hg.

   Proceedings . Sri Lanka Association for the Advancement of Science 212, 1993.

2. Kinetics of the mercuric ion catalyzed reaction of hexacyanoferrate(II) and nitrosobenzene.

   Proceedings Sri Lanka Association for the Advancement of Science 237, 1994.