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FIA and Manual Batch Procedures for the Spectrophotometric Determination of Mercury Using Bromide and Crystal Violet as Reagents

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In the presence of a large excess of bromide, mercury(II) forms an ion-pair with Crystal Violet. The complex can be stabilized by addition of poly(vinyl alcohol). The calibration graph for measurements at 664 nm is linear in the range 3–45 μg of mercury per 25 ml of final solution, the molar absorptivity being 71 500 L/(mole.cm). The method can be successfully used with FIA purposes. The peak height is linear with mercury concentration over the range 0.2–4 $\mu\text{g}/\text{ml}$ using a single channel manifold. In this case an improvement on selectivity is obtained. The proposed methods have been applied to mercury determination on cleaning solutions for contact lenses with good analytical results.

KEY WORDS: Mercury determination, spectrophotometry, FIA, flow injection analysis, Crystal Violet.

INTRODUCTION

Mercury vapour and salts have important toxic effects, and as a consequence many articles have recently been published on the

determination of traces of mercury.¹⁻⁵ In environmental analysis the most frequently applied method is flameless atomic-absorption spectroscopy at ultra trace levels, but the spectrophotometric methods based on ion-pair formation are useful at trace levels.⁶⁻¹² The procedures so far described are sensitive, but as a general rule, extraction of the complex into an organic solvent is needed. An interesting alternative is due to the fact that some dyes show spectral shifts on formation of ion-association systems.¹³⁻¹⁷ If this occurs, the need for a solvent extraction process can be avoided and the spectrophotometric method can be carried out with minimum manipulation. In this way, we have examined the interaction of several basic dyes with mercury in the presence of large amounts of bromide, with the aim of developing a new method for the spectrophotometric determination of mercury without extraction. Our results showed that Crystal Violet offered the best possibilities.

In this work, the formation of an ion-association compound between Crystal Violet and mercury(II) in an excess of bromide is studied, the conditions for the spectrophotometric determination of mercury are established and the method is applied to the determination of this element in cleaning solutions for contact lenses.

On the other hand, the excellent characteristics of the method proposed here allow its use with flow injection techniques. Several FIA methods have been proposed for mercury determination using amperometric,^{18,19} atomic,²⁰⁻²² and fluorimetric²³ detectors. However, very few spectrophotometric methods²⁴ have been developed. In this way, the above reaction was studied in order to get a suitable FIA-spectrophotometric method for routine determination of mercury. As a consequence a very simple manifold for mercury determination is proposed. With this option a noticeable increase on selectivity is obtained from peak height measurements.

EXPERIMENTS

Apparatus

A Pye Unicam SP8-200 Vis-UV spectrophotometer with 10 mm glass cells and a Radiometer PHM62 were used for absorbance and pH measurements, respectively. The FIA manifold was made with a Gilson HP8 peristaltic pump, valve, tubing and connectors (Omnifit) and a Hellma 18 μ l flow cell.

Reagents

All inorganic chemicals used were analytical reagent grade and were used without further purification. Doubly distilled water was used exclusively.

Mercury(II) standard solution, 0.01 M.

Crystal Violet solution, 0.002 M.

Potassium bromide, 2.5 M.

Poly(vinyl alcohol) (PVA) solution, 1 %, m/V.

Sodium acetate–acetic acid buffer solution, 2 M, pH 5.

Preparation of reagent solution

The reagent solution for manual batch procedure (A) was prepared by mixing 100 ml of 0.002 M Crystal Violet solution, 100 ml of 1 % m/V solution and 100 ml of pH 5 sodium acetate–acetic acid buffer solution.

The reagent solution for FIA (B) was prepared by diluting 120 ml of above solution to 900 ml with distilled water. Then 40 ml of 2.5 M potassium bromide solution was added and diluted to 1000 ml with distilled water.

General procedures

A) *Manual batch procedure* Transfer up to 20 ml of sample containing no more than 45 μg of mercury into a 25 ml calibrated flask and dilute to 20 ml with water, if necessary. Add 1 ml of 2.5 M KBr solution, mix and add 3 ml of reagent solution A. Mix thoroughly and measure the absorbance at 664 nm after 15 min, against a reagent blank. Beer's law is obeyed over the concentration range 3–45 μg of mercury in 25 ml of solution.

B) *Flow injection analysis* Use the single-line manifold showed in Figure 5 and reagent solution B as carrier. In these conditions peak height at 664 nm is linear with mercury concentration between 0.2–4 $\mu\text{g}/\text{ml}$ (135 μl sample loop).

Procedure for the determination of mercury in cleaning solutions for contact lenses

Take a suitable volume (5 ml) of sample in a 50-ml calibrated flask,

add 5 ml of 10_N sulphuric acid, and dilute to 40 ml with distilled water. Add bromine vapour and let stand for 2 min, then pass air current through the solution for 5 min to eliminate the bromine. Adjust the sample to approximately pH 5 with 30% sodium hydroxide solution and dilute to volume with doubly distilled water. Treat a suitable volume according to the methods given above.

RESULTS AND DISCUSSION

The reaction of mercury(II) in the presence of a large excess of bromide and several triphenylmethane dyes was examined for shift in the spectral characteristics of the dye. With Crystal Violet the reaction proceeded very fast and the coloration was the best of all the dyes examined. However, the ternary complex that resulted on the addition of the dye to the aqueous solution of mercury containing bromide was unstable and a gradual precipitation on standing was observed. Stabilisation was achieved by the addition of the protective colloid PVA, which successfully retarded precipitation of the complex even on leaving to stand overnight.

Figure 1 shows the absorption spectra of Crystal Violet with different amounts of mercury in the presence of an excess of bromide solution in a pH 5 medium. It is evident that the interaction between the mercury bromide complex and Crystal Violet proceeded with a considerable bathochromic shift and that the complex showed maximum absorption at 664 nm, as against that of the reagent at 585 nm. All absorbance measurements were carried out at 664 nm.

Manual batch procedure

The effect of the pH was examined and the results are shown in Figure 2. The absorbance at 664 nm is maximal and constant over the pH range 4.5–7. A pH 5 adjusted with sodium acetate–acetic acid buffer solution is recommended. A final concentration of this buffer solution greater than 0.3 M produces a decrease in the absorbance due to mercury. So 1-ml of 2 M buffer solution is adequate to ensure the pH adjustment.

Figure 3 shows the effect of bromide on the absorbance at 664 nm; a 0.1 M potassium bromide concentration is optimal.

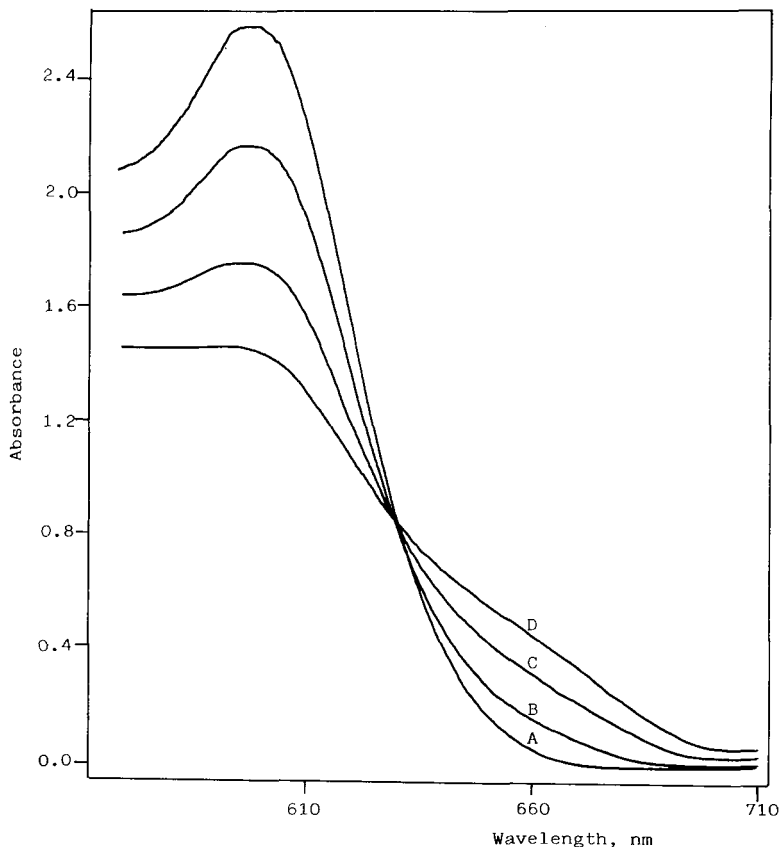


Figure 1 Absorption spectra, 5-mm cells. (A) 2×10^{-5} M Crystal Violet, 0.1 M bromide, 0.04% m/V PVA, pH 5; (B)–(D) as in (A) with the addition of 13, 32 and 44 μg of mercury(II).

As Figure 4 demonstrates, the use of 0.08 mM Crystal Violet concentration provides a low reagent blank and a high absorbance for the complex.

As indicated above, the poly(vinyl alcohol), PVA, plays an important role as stabilizing agent. Without PVA present, the colour fades gradually and the reproducibility (r.s.d.) is about $\pm 3\%$, whereas addition of PVA before, next or after the dye provides gradual development of the colour with better reproducibility. The best results are obtained when PVA is added next to the dye, as in the

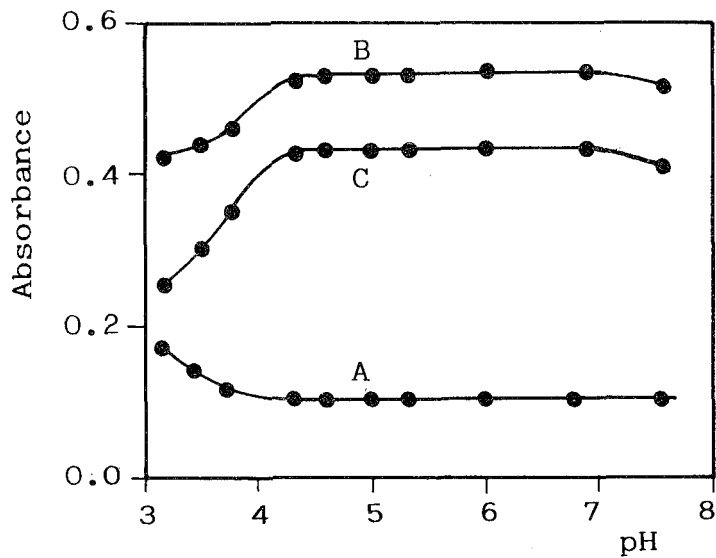


Figure 2 Effect of pH on absorbance at 664 nm. (A) reagent blank (reference water); (B) and (C) with $30 \mu\text{g}$ of mercury ((B) reference water and (C) reference reagent blank).

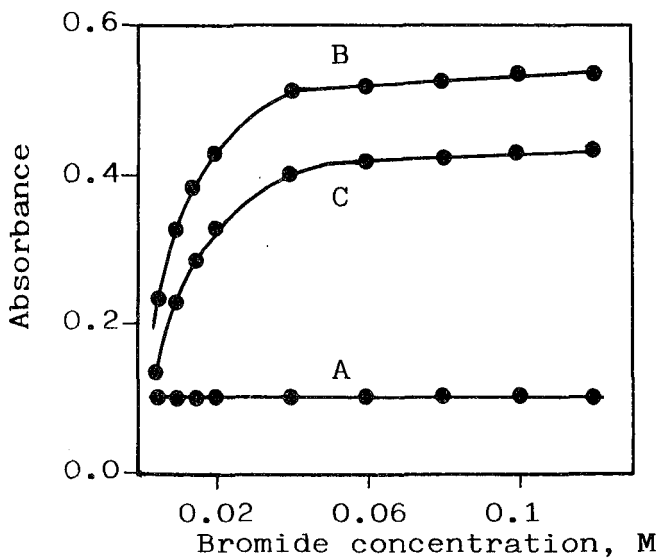


Figure 3 Effect of bromide concentration on absorbance at 664 nm. (A) reagent blank (reference water); (B) and (C) with $30 \mu\text{g}$ of mercury ((B) reference water and (C) reference reagent blank).

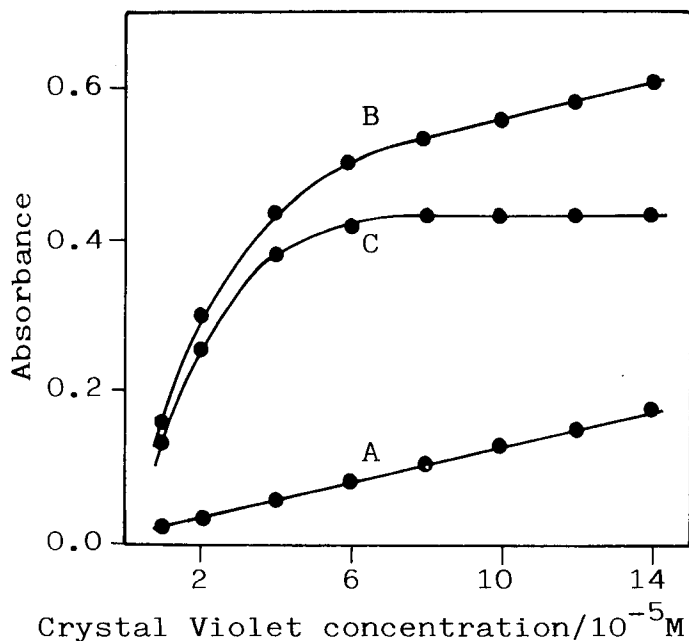


Figure 4 Effect of Crystal Violet concentration on absorbance at 664 nm. (A) reagent blank (reference water); (B) and (C) with 30 μ g of mercury ((B) reference water and (C) reference reagent blank).

Procedure. In order to simplify the experimental procedure the use of a mixture of Crystal Violet solution, buffer solution and PVA solution is recommended.

Nature of the complex

The ratio of mercury to Crystal Violet in the complex in presence of excess of bromide was established by the conventional continuous variations method. A Hg:Crystal Violet ratio of 1:3 was found. The ratio of mercury(II) to bromide was investigated by the Bent and French method in the presence of excess of Crystal Violet, and evidence for the formation of the pentabromomercurate(II) anion was found. Since the method uses a large excess of both bromide and dye, it is concluded that the neutral complex formed is $(R^+)_3(HgBr_5)^{3-}$ where R^+ represents the Crystal Violet cation.

Calibration graph, reproducibility and stability

Under the described conditions, Beer's law is obeyed over the range 3–45 μg of mercury(II) in a final volume of 25 ml. The molar absorptivity is 71 500 L/(mole. cm). For ten measurements of 20 μg of mercury(II) the relative standard deviation was $\pm 0.5\%$. The relative standard deviation of the reagent blank was $\pm 1.9\%$ and the quantification limit (given as ten times the r.s.d. of the blank in concentration units) 54 $\mu\text{g/L}$ of mercury. The absorbance of the complex is constant for at least 24 hr, at room temperature.

Effect of diverse ions

Numerous cations and anions were examined as potential interferences, by applying the method to a fixed amount of mercury in the presence of increasing quantities of the ion being studied. The results are given in Table 1, column A. The tolerance limit for the foreign ion was taken as the highest concentration which causes an error of no more than $\pm 3\%$ in the absorbance value.

An enhancement in the selectivity can be achieved by using the FIA option. In this case the kinetic effects produce an increase on selectivity as can be seen in Table 1, column B.

Table 1 Effect of diverse ions on the determination of mercury 2 μM

<i>Species added</i>	<i>Tolerance ratio (ion)/(Hg(II))</i>	
	<i>A</i>	<i>B</i>
Sulphate, bromate	10 000 ^a	10 000 ^a
Phosphate, citrate, fluoride, chloride, Ca(II), Ba(II), Mn(II)	2000	10 000
Nitrate, iodide, Mg(II), Al(III)	1 000	10 000
Oxalate, tartrate, Ni(II), U(VI)	700	5 000
Silicate, Fe(III), ^b Co(III), Pb(II), Cr(III)	300	5 000
EDTA, thiocyanate, Zn(II), Mo(VI)	100	2 000
Fe(III), Cu(II), Bi(III) ^c	50	500
Cr(VI), Th(IV), As(V)	10	500
Perchlorate, W(VI), Cd(II), Ag(I)	1	50

^aMaximum molar ratio tested.

^bWith fluoride added.

^cWith EDTA added.

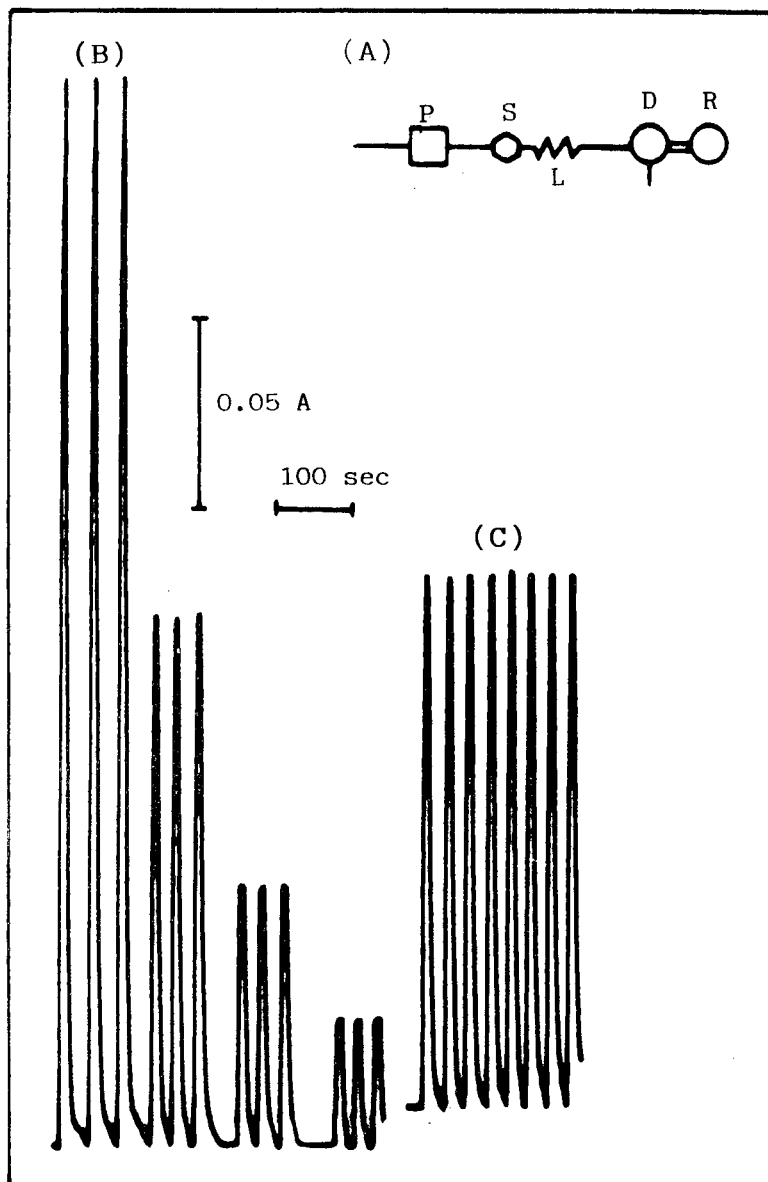


Figure 5 (A) Single-line FIA manifold where the carrier solution (see text for details) is propelled at 1.5 ml/min by a peristaltic pump, P; S, sample injector (135 μ l loop size); L, coil (0.5 mm i.d., 0.5 m length); D, Vis-UV detector at 664 nm; R, recorder. (B) Calibration graph for the FIA system. Concentrations: 2, 1, 0.5 and 0.25 μ g/ml of mercury(II) (from left to right). (C) Precision run for the FIA system. Eight successive injections of 1 μ g/ml mercury(II) solution.

Flow injection method

Due to very low absorbance value for the reagent blank and very fast rate of reaction the method here described is very adequate for the routine determination of mercury using FIA techniques.

A composition for the carrier solution similar to that used in the manual batch procedure containing also bromide solution leads to the best results. The mixture prepared as in the recommended

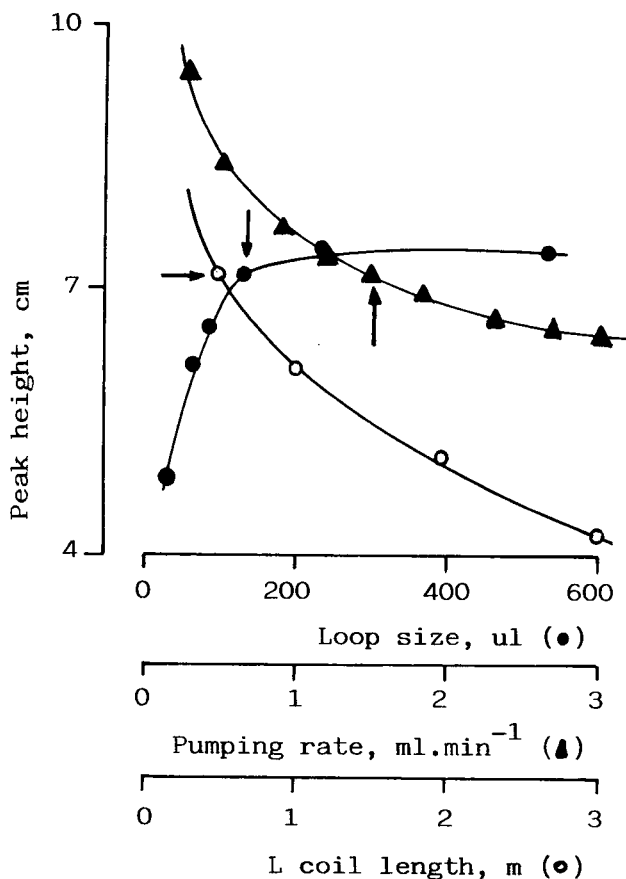


Figure 6 Effect of loop size (●), pumping rate (▲) and L coil length (○) on peak height at 664 nm. Sample injected 1 $\mu\text{g}/\text{ml}$ of Hg(II). The arrows remark the selected values for these parameters.

procedure (B) is stable for at least 3 months and it is ready for its use after mixing.

In order to find the optimal conditions for our purpose several experiments were carried out. Figure 5 shows the results obtained and the manifold used.

Figure 6 shows the effect of pumping rate, loop size and L coil length. From these results it seems clear that a minimum L coil length is the most adequate in order to avoid the decrease in sensitivity. Looking for a compromise between sensitivity and sampling frequency a $135\ \mu\text{l}$ sample loop and a $1.5\ \text{ml/min}$ flow rate were chosen as adequate.

At working conditions a sampling frequency of 180 samples/hour with a $\pm 0.6\%$ relative standard deviation for 20 injections of $1\ \mu\text{g/ml}$ of mercury(II) solution ($135\ \mu\text{l}$ sample loop) was obtained.

Determination of mercury in cleaning solutions for contact lenses

The method has been applied satisfactorily to the determination of mercury in solutions where it is present as an organomercurial compound. Table 2 shows the results obtained. In sample 1 mercury(II) appears as sodium ethylmercurithiosalicylate and in sample 2 as phenylmercury nitrate. In both cases the results for the mercury content agree with the label claim of pharmaceutical laboratories.

Table 2 Determination of mercury in cleaning solutions for contact lenses

Sample	Content, $\mu\text{g/ml}$	
	Found ^a	Label claim
1	20.37	20.34
2	19.88	20.03

^aAverage of three determinations.

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