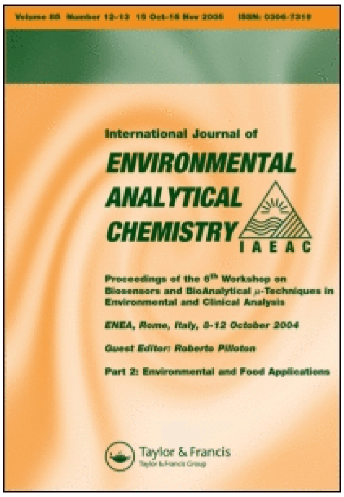

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FLUORIMETRIC DETERMINATION OF MERCURY(II) BASED ON ITS REACTION WITH IODIDE AND TRIPHENYLMETHANE COMPOUNDS

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A fluorimetric method for the determination of Hg^{2+} (5–100 ppb) was developed based on the reaction between triphenylmethane cations (Brilliant green, Malachite green and Crystal violet) and tetraiodomercurate(II). This reactioon gives ion-associated complexes with strong fluoresence at 521 nm after excitation at 256 nm.

Optimum concentrations for Brilliant green, Malachite green and Crystal violet were 15, 10 and 2 mg/l, respectively. The optimum pH for complex formation was 3.0 for Brilliant green and Malachite green, and 2.0 for Crystal violet. The detection limit for the method defined as $3 \times \sigma$ was found to be 0.72 μg/l of Hg^{2+}. Ions that interfere in the determination of mercury by the proposed method are Ag(I), Pt(II), Cd(II), Bi(III) and Ti(IV). Titanium(IV), Ag(I) and Bi(III) can be masked whereas the interference of Pt(II) and Cd(II) cannot be overcome as yet.

KEY WORDS: Fluorimetry, mercury, triphenylmethane compounds.

INTRODUCTION

Hazards associated with environmental mercury pollution are well documented and therefore there is an urgent need of analyzing and monitoring trace levels of the Hg in various materials. Traditionally, atomic absorption (cold vapour) has been widely used for the determination of Hg.[1] However, less tedious, simpler and at the same time accurate techniques are being sought. Ramakrishna *et al.*[2] suggested that spectrophotometric methods based on ternary complex formation would be a good alternative for this purpose. Indeed, three fluorimetric procedures based on ion-association complexes of tetraiodomercurate(II) ions with Rhodamine S, Butylrhodamine B and Rhodamine B, have been put forward.[3,4,5] More recently, Vijayakumar *et al.*[6] proposed an improved indirect fluorimetric determination of mercury(II) based on selective extraction of the ion-association complex of triiodomercurate(II) and Rhodamine 6G.

The objectives of this study were: (a) to study in detail the formation of complexes of Hg^{2+} with six cationic dyestuffs in the presence of an excess of KI,

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in a (weakly) acidic solution and, (b) to develop a method for the quantitative determination of Hg^{2+} based on the linear relationship of fluorescence intensity of the complex and amount of Hg^{2+} present.

EXPERIMENTAL

Apparatus

Fluorescence measurements were performed on a Perkin–Elmer Model 3000 fluorescence spectrometer with a xenon lamp using a 10 mm quartz UV cell. Wavelengths for excitation and emission, were 256 and 521 nm, respectively. The stoichiometry of the complexes was determined using a Varian Techtron Model 635 spectrophotometer. Comparative mercury(II) determinations were made using a Perkin–Elmer Model 503 atomic absorption spectrophotometer equipped with a mercury hydride system (MHS-1).

Reagents and Solutions

All reagents used were of analytical grade (BDH and Merck). A BDH stock solution of 1000 mg/l of Hg^{2+} was used for the preparation of the subsequent standards by proper dilution. The triphenylmethane derivatives used (Brilliant green, Malachite green, Crystal violet, Aluminon, Methyl blue, and Chrome azurol S) were each dissolved in water in concentrations of 1000 mg/l. Potassium iodide solution (5000 mg/l), sodium hydroxide (0.1 and 2 mol/l) and sulphuric acid (0.05 and 1 mol/l) were further used.

Procedure

An aliquot of the sample solution, adjusted to pH 3.0 with dilute H_2SO_4 or NaOH, containing 0.25 to 5 μg of Hg^{2+} was placed in a 50-ml volumetric flask. 1.0 ml of potassium iodide solution was added, followed by 0.75 ml of an aqueous Brilliant green solution (1000 mg/l). The flask was immediately swirled, brought to volume with distilled water, stoppered and shaken well to achieve complete mixing. Complex formation is instantaneous and since the fluorescence intensity at levels of 5–100 μg/l Hg^{2+} was found to be stable during the first 15 min, measurements were usually made 10 min after mixing the reagents. A linear calibration curve from 5 to 100 μg of Hg^{2+}/l was obtained in a similar manner.

RESULTS AND DISCUSSION

The experimental procedures of Ramakrishna *et al.*[2] and Ayyangar and Tilak[7] were followed for the formation of the tetraiodomercurate(II) complex dianion and the complex with the triphenylmethane cations, respectively. The former comples was formed in the presence of a large excess of iodide (1000-fold over mercury,

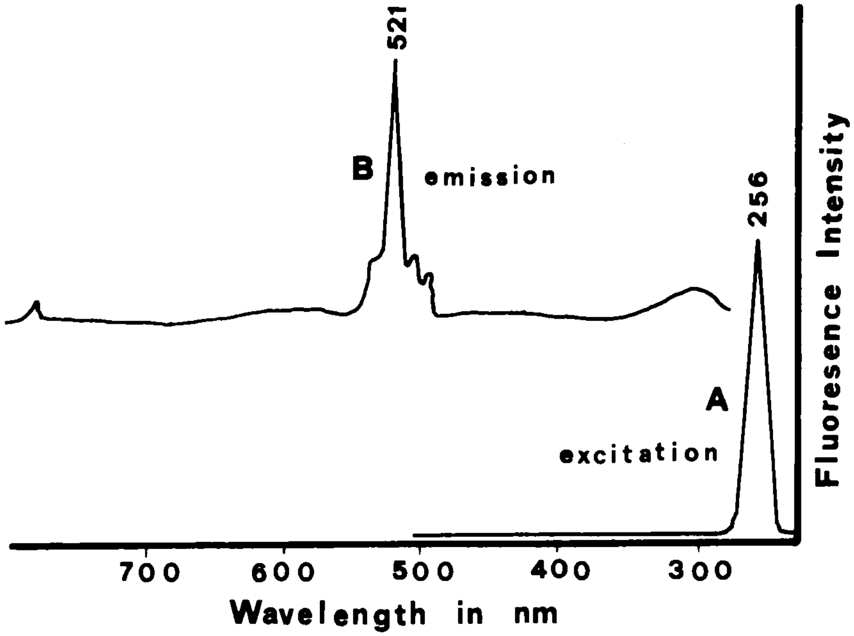

Figure 1 Excitation (A) and emission (B) spectra of the tetraiodomercurate(II)-Brilliant green complex; Hg^{2+}, 100 μg/l.

mass ratio). Under the experimental conditions tetraiodomercurate(II) dianions react with the cations with triphenylmethane structure leading to an instantaneous formation of the complex: R_2HgI_4 (where R represents the cation with triphenylmethane structure). Brilliant green, Malachite green and Crystal violet complexes were studied and gave identical results. Therefore, most of the discussion will be limited to Brilliant green.

The stoichiometry of the complexes was experimentally confirmed by the spectrophotometric "molar ratio"[8] method and found to be of the 1:2 type (R_2HgI_4). Ion-association complexes of this type exhibit a strong fluoresence, of which the intensity is proportional to the amount of Hg^{2+}. The excitation and emission fluoresence maxima of these complexes were found to be 256 and 521 nm, respectively (Figure 1).

The pH for maximum fluorescence intensity of the complexes was 3.0 for both the Brilliant green and Malachite green complexes (Figure 2; Table 1), and 2.0 for the Crystal violet complex (Table 1).

The optimum KI concentration of 100 ppm, as given by Ramakrishna *et al.*,[2] was confirmed by our experiments (Figure 3), whereas the optimum concentration was experimentally found to be 15 mg/l for Brilliant green (Figure 4), 2 mg/l for Crystal violet and 10 mg/l for Malachite green.

The stability of the fluorescence intensity was investigated by measuring a fresh portion of the solution at 5 min intervals. Fluorescence intensity was stable up to 15 min and decreased afterwards by approximately 10% up to 1 h. Therefore, all

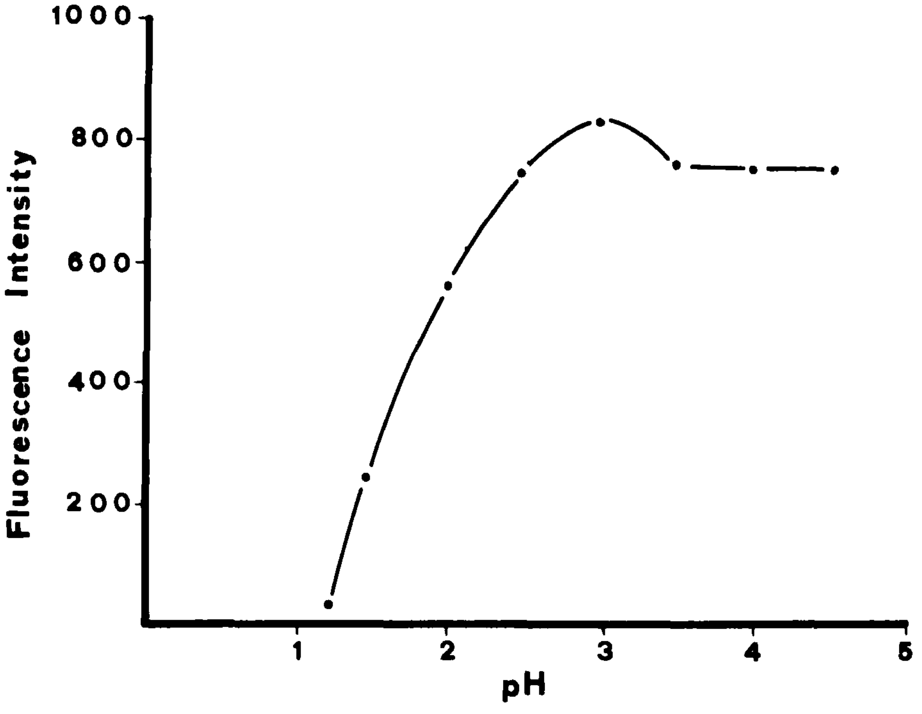

Figure 2 Effect of pH on the fluorescence intensity of tetraiodomercurate(II)-Brilliant green complex; Hg^{2+}, 100 μg/l.

Table 1 Optimum conditions for the formation of the fluorescence maximum intensities of the three triphenylmethane complexes with tetraiodomercurate(II) dianions

Conditions	*Brilliant green*	*Malachite green*	*Crystal violet*
pH	3.0	3.0	2.0
KI (mg/l)	100	100	100
Ligand (mg/l)	15	10	2
Time[a] (min)	15	25	20
Fluorescence intensity[b]	835	596	625
$\lambda_{excitation\,(nm)}$	256	256	256
$\lambda_{emission\,(nm)}$	521	521	521

[a] Refers to the time during which the fluorescence intensity of the complex was stable, decreasing afterwards.

[b] Hg^{2+} concentration is 100 μg/l. The numerical blank values of the fluorescence of intensity were 180 at the same wavelength. This was was consequently subtracted from the values obtained (standards and samples).

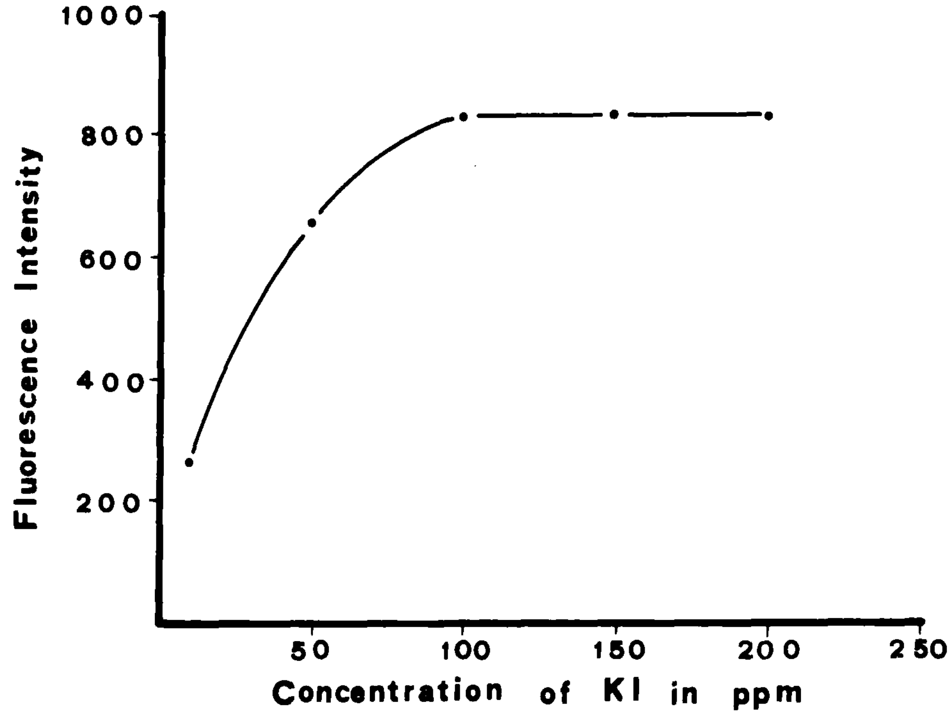

Figure 3 Effect of KI concentration on the fluorescence intensity of the tetraiodomercurate(II)-Brilliant green complex; Hg^{2+}, 100 μg/l.

measurements of the test samples were made within 15 min after the complex formation.

Three other triphylmethane compounds, Aluminon, Methyl blue and Chrome azurol S have been tested under the same experimental conditions. However, either no complexation with HgI_4^{2-} occurred or the resulting complex did not exhibit significant fluorescence.

Calibration Graph

The calibration graph of the tetraiodomercurate(II)-Brilliant green complex was obtained from 10 calibration points received from standard concentration measurements every 10 μg/l of Hg^{2+} (8 replicates of each standard concentration). The linear range was from 5 to 100 μg/l of Hg^{2+}, which is the concentration range studied, represented by the equation $y = 8.37x - 5.85$, with $r = 0.998$. Repeatability was satisfactory (coefficients of variation were 6% at 10 μg/l and 2.5% at 100 μg/l). The detection limit (calculated as $3 \times \sigma$ of six replicates of blank solutions)[9] was found to be 1.04 μg/l for the case of Brilliant green and 0.72 μg/l for Crystal violet. For the case of Malachite green the detection limit was too high.

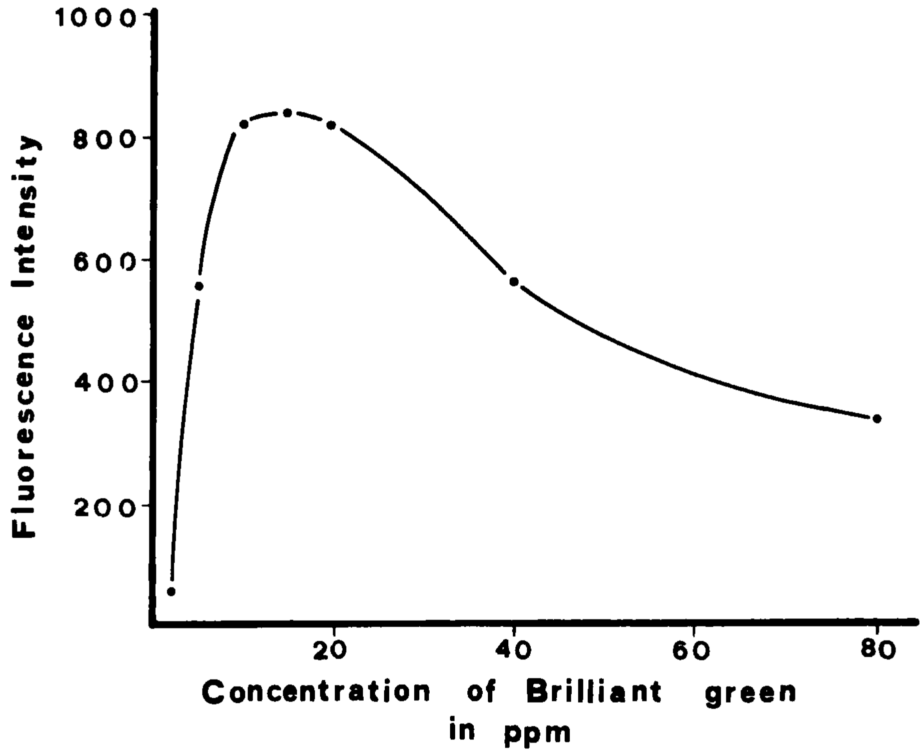

Figure 4 Effect of Brilliant green concentration on the fluorescence intensity of the tetraiodomercurate(II)-Brilliant green complex; Hg^{2+}, 100 μg/l.

Interferences

The interference of various ions on the determination of Hg^{2+} (100 μg/l) was examined. Cations such as Na(I), K(I), Li(I), NH_4(I) and Mg(II) in concentrations up to 10000 mg/l did not interfere. Similarly, no interference was observed for Ca(II), Mn(II), Fe(II), Co(II), Ni(II), Sn(II), Zn(II), Fe(III), Al(III) and As(III) up to 1000 mg/l and for Sr(II), Cu(II), Ba(II) and Sb(III) up to 200 mg/l. Anions such as Cl^-. Br^-, F^-, NO_3^-, and SO_4^{2-} up to 5000 mg/l did not interfere. There was a positive interference (ca. 10%) of PO_4^{3-} ions in concentrations of 500 mg/l. Also Ag(I), Pt(II), Cd(II), Bi(III) and Ti(IV) ions in concentrations of 100 μg/l showed a positive interference corresponding with 55%, 50%, 41%, 9%, and 7%, respectively, as calculated from the figures of Table 2. Interference by Ti(IV) and Bi(III) can be eliminated by adding 0.05 mol/l of EDTA and that of Ag(I) by Cl^- addition and filtration of the silver chloride formed. The Pt(II) and Cd(II) interferences present difficulties in the proposed analytical scheme of Hg^{2+} determination, because no satisfactory method for their removal is available; Cd(II) problem is now under study.

Table 2 Fluorescence intensity of the complexes of the interfering cations with triphenylmethane cations in the presence of iodide

Interfering cation (100 µg/l)	*Fluorescence intensity in presence of:*		
	Brilliant green	*Malachite green*	*Crystal violet*
Ti^{4+}	55	80	50
Ag^{+}	455	476	414
Pt^{2+}	415	590	478
Cd^{2+}	342	265	320
Bi^{3+}	75	58	66
Hg^{2+}[a]	835	597	625

[a] Mercury is given for comparison.

Table 3 Recovery[a] of added Hg^{2+} in two potable and in three other waters of different composition and origin

Origin of water	*Brilliant green*		*Malachite green*	*Crystal violet*	
			Hg^{2+} added (in µg/l)		
	25	*50*	*50*	*25*	*50*
Thessaloniki's potable	25.6	50.2	50.7	25.8	49.8
Nigrita's mineral	26.4	50.9	52.0	26.5	50.8
Souroti's mineral	27.0	50.2	51.7	26.8	50.7
Loutraki's potable	25.3	50.2	50.5	25.1	50.0
Sariza's potable	25.5	50.4	50.2	25.3	50.0
Thessaloniki's sea	26.0	50.8	50.7	25.8	50.9
Mean	26.0	50.5	51.0	25.9	50.4
C.V.[b]	2.5	0.6	1.4	2.6	1.0
E_r (%)[c]	4	1	2	4	0.8

[a] Data represent mean values of 20 determinations (replicates). For the: 25 ppb with Brilliant green, mean = 26.0, c.v.[a] = 2.5 and $E_r = 4\%$. 50 ppb with Brilliant green, mean = 50.5, c.v. = 0.6 and $E_r = 1\%$. 50 ppb with Malachite green, mean = 51.0, c.v. = 1.4 and $E_r = 2\%$. 25 ppb with Crystal violet, mean = 25.9, c.v. = 2.6 and $E_r = 4\%$. 50 ppb with Crystal violet, mean = 50.4, c.v. = 2.0 and $E_r = 0.8\%$.

[b] The c.v. has been calculated for one sample (20 replicates) of Thessaloniki's potable water.

[c] $E_r = \text{relative error} = \frac{(\text{Hg found-Hg added})100}{\text{Hg added}}$

Application

The proposed method was applied for the analysis of natural, potable and sea waters. However, mercury levels in these waters were below, the detection limit of the method (0.72 µg/l of Hg^{2+}). Therefore, only the recovery of added Hg^{2+} (25 and 50 µg/l) in such waters (Table 3) and the mercury content of cinnabar samples (Table 4) was studied. The content in sea waters was measured after removal of suspended material by passing the sample through a Millipore filter (0.45 µm pore size). Recovery of added mercury in potable, mineral and Thessaloniki's sea water was satisfactory (Table 3). These imply that mercury can be determined by the proposed method in polluted potable and sea waters, where

Table 4 Mercury determination[a] in three cinnabar samples using atomic absorption and fluorimetric techniques

Method	*Mercury (%, w/w) in samples from*		
	Spain	*Algeria (1)*	*Algeria (2)*
Atomic absorption (flame)	20.5	10.8	5.6
Atomic absorption (cold vapour)	21.8	11.5	6.1
Fluorimetric with Brilliant green	20.5	11.2	6.0
Fluorimetric with Malachite green	21.0	10.8	5.7
Fluorimetric with Crystal violet	20.8	11.0	5.8

[a] For the Spain cinnabar: (a) with Brilliant green, c.v. = 1.4 and $E_r = 5.96\%$; b) with Malachite green, c.v. = 1.7 and $E_r = 3.67\%$; (c) with Crystal violet: c.v. = 1.2 and $E_r = 4.59\%$. For the Algeria (1) cinnabar: (a) with Brilliant green, c.v. = 2.1 and $E_r = 2.61\%$; (b) with Malachite green: c.v. = 2.3 and $E_r = 6.09\%$; (c) with Crystal violet, c.v. = 1.8 and $E_r \approx 4.35\%$. For the Algeria (2) cinnabar: (a) with Brilliant green, c.v. = 2.5 and $E_r = 1.65\%$; with Malachite green, c.v. = 3.5 and $E_r = 6.56\%$; (c) with Crystal violet, c.v. = 3.5 and $E_r = 4.92\%$.

$$E_r = \frac{(\text{Hg found fluorimetrically}) - (\text{Hg found with A.A.S. cold vapour})}{\text{Hg (found with A.A.S. cold vapour)}}.$$

mercury exists in the same form as in the spiked samples. In case of polluted natural waters, where mercury exists in other forms (usually organic), conversion to inorganic forms may be necessary prior to its determination by the proposed method.[10, 11] Eight replicates of three cinnabar samples of varying mercury content were dissolved in *aqua regia* and the mercury content was determined by the proposed method and atomic absorption, flame and cold vapour, as well. The mercury content obtained by the latter technique served as a reference value (Table 4).

In addition to the direct fluorimetric determination of mercury, the method of standard addition was applied in all cases, to eliminate possible interferences. Both methods gave identical results.

The accuracy of the method in recovery studies in natural waters ranged from 0.8 to 6.5% and in cinnabar samples from 1.6 to 6.5%. Coefficient of variation of the measurements in natural waters ranged from 0.6 to 2.5%, and in cinnabar samples from 1.2 to 3.5%.

CONCLUSION

The proposed method provides a reliable means for the fluorimetric determination of Hg^{2+} at ppb level, based on the formation of a fluorescent complex between the tetraiodomercurate dianion and triphenylmethane cations ($\lambda_{exc.}$, 256 nm; $\lambda_{em.}$, 521 nm). The main features of the method are its simplicity and rapidity, since no extractions are involved. The complex is formed imediately after mixing of the reagents and hence the time required for one determination is less than 10 min. The low cost of the analysis is an additional advantage, since the reagents used are common and cheap. The detection limit is 0.72 μg/l; the method can be applied to water and mineral analysis.

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