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Dual optoelectronic visual detection and quantification of spectroscopically silent heavy metal toxins: A multi-measurand sensing strategy based on Rhodamine 6G as chromo or fluoro ionophore

K.P. Prathish, D. James, J. Jaisy, T. Prasada Rao *

Inorganic and Polymeric Materials Group, National Institute for Interdisciplinary Science & Technology (CSIR), Industrial Estate (P.O), Pappanamcode, Trivandrum 695019, India

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ABSTRACT

A novel colorimetric chemo-sensor for the simultaneous visual detection and quantification of spectroscopically silent heavy metal toxins viz. cadmium, lead and mercury has been developed. This is based on the proposed sequential ligand exchange (SLE) mechanism of iodide from Pb–I^-–Rhodamine 6G ion associate with citrate (without affecting ion associates of Cd and Hg) and subsequently from Cd–I^-–Rhodamine 6G ion associate with EDTA (without affecting Hg–I^-–Rhodamine 6G). Multi-measurand detection and quantification by colorimetry is possible as the individual toxins gives identical bathochromic shifts in aqueous solution, i.e. from 530 to 575 nm on formation of ternary ion associates in singular, binary and ternary mixtures. The visual detection provides a simple, quick and sensitive detection method in addition to quantification via spectrophotometry with Sandell sensitivities of 1.1, 15 and 2.5 $\mu g\,dm^{-2}$ for cadmium, lead and mercury, respectively. The developed procedure has been successfully tested for the analysis of environmental (cast alkali, lead acid battery and zinc manufacturing industry effluents) samples. Furthermore, the multi-measurand quantification of the above-mentioned heavy metal toxins based on fluorescence quenching and use of Pyronine G as chromo-ionophore instead of Rhodamine 6G is also described.

1. Introduction

The toxicity of heavy metal in particular cadmium, lead and mercury is well known and the maximum permissible levels in drinking water as per USEPA [1], WHO and European water quality directives are 5, 15 and 2 $\mu g\,L^{-1}$, respectively. Sequential detection and quantification of the above-mentioned heavy metal toxins at $\mu g\,L^{-1}$ levels in presence of other coexisting metal ions is tedious task. Often multi-measurand pre-concentrative separation as a group is resorted to in conjunction with simultaneous multi-measurand quantification capability techniques like ICP-AES/ICP-MS/XRF/NAA/voltammetry [2]. However, all these techniques require expensive instrumentation, high maintenance costs and skilled technicians not only for operation of instrument but also for interpretation of results. Moreover, all these are laboratory based instruments necessitate tedious sampling and transportation protocols. On the other hand, colorimetry continues to be widely popular in view of its simplicity, rapidity, precision, common availability, and its facile visual detection. The chief limitation is selectivity, i.e. discrimination of one measurand in presence of several analogous co-existing metal ions. This was circumvented via (i) chemometric approaches [3,4], (ii) sequential extraction [5] and (iii) by employing higher order derivative spectrophotometric techniques [6]. Colorimetric or spectrofluorimetric procedures based on association of $[ML_x]^{n-}$ complexes with cationic dyes in general involves extraction into immiscible organic solvent prior to 1976 [7–9]. Ramakrishna et al. [10] have reported an aqueous procedure utilizing $[HgI_4]^{2-}$ (Rhodamine 6G)$_2$ colour system by taking advantage of bathochromic shift that occurs in aqueous medium on formation of ternary ion associate. This has triggered several colorimetric procedures for variety of metal ions and successfully applied to diverse complex real samples by taking advantage of masking or sequestering agents to eliminate deleterious effects of coexisting interferent ions, if any [7]. The concept of sequential ligand exchange (SLE) was advantageously utilized (though not mentioned) to improve selectivity by addition of EDTA to lead–bromopyrogallol red binary complex several decades back [11] and described recently by Balaji and Matsunaga [12] during fluoride quantification. To our knowledge, SLE concept has not been used and reported for successive determinations of binary or ternary analyte mixtures. This paper reports the findings pertaining to sequential detection and quantification of spectroscopically silent heavy metal toxins viz. cadmium, lead

* Corresponding author. Tel.: +91 471 2515317; fax: +91 471 2491712.
E-mail addresses: rao@csrrltrd.ren.nic.in, tprasadarao@rediffmail.com (T. Prasada Rao).

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and mercury in industrial effluent samples by using spectrophotometry.

2. Materials and methods

2.1. Apparatus and reagents

A Shimadzu UV-2401 PC controlled double beam spectrophotometer (Shimadzu, Japan), SPEX Fluorolog 3 Spectrofluorometer (Horiba Jobin-Yvon, Edison, NJ, USA), RF-5301PC Spectrofluorimeter (Shimadzu, Japan) and ELICO LI-120 digital pH meter were used for absorbance, fluorimetric and pH studies, respectively.

All chemicals used were of Analytical Reagent grade from E-Merck, Mumbai, India, unless otherwise stated and used as received. All solutions were prepared with deionized water. Individual stock cadmium, lead and mercury solutions were prepared by dissolving 0.1142, 0.1484 and 0.1618 g of cadmium sulphate, lead nitrate and anhydrous mercuric nitrate in 100 mL of water and were standardized with EDTA. Multi-measurand solution (MMS) containing 12.5, 125 and 25 $\mu g\,L^{-1}$ cadmium, lead and mercury, respectively was prepared by serial dilution. A 1 $mol\,L^{-1}$ (pH 5.0) hexamine buffer was prepared by dissolving 14.02 g of hexamine in 100 mL of water and the pH was adjusted to ~5 with dilute nitric acid. Similarly 0.4 $mol\,L^{-1}$ citrate buffer (pH 5.0) was prepared by dissolving 5.88 g of tri-sodium citrate in 40 mL of water and the pH was adjusted to ~5.0 using either HNO_3 or NaOH and diluted to 50 mL. EDTA solution of 0.05 $mol\,L^{-1}$ concentration was prepared by dissolving 1.86 g in 100 mL of water. Potassium iodide (10%), Rhodamine 6G (0.01%) (Aldrich Chemicals, Milwauke, WI, USA) and gelatin (1%) were prepared by dissolving 10.00, 0.01 and 1.00 g in 100 mL of water, respectively.

2.2. Procedure

An aliquot of sample solution (up to 15 mL) and 1.0 mL of hexamine buffer were taken in a 25 mL beaker and pH was adjusted to 5.2 ± 0.2 using HNO_3 or NaOH under a pH meter. The potassium iodide (2.5 mL) and Rhodamine 6G (5 mL) followed by gelatin (1 mL) were added, transferred to 25 mL volumetric flask and diluted to mark with water. The absorbances were measured at 575 nm in 10 mm quartz cells against a reagent blank (A_1). The solutions were transferred to 50 mL volumetric flasks and 1 mL of citrate buffer was added to sample as well as blank, i.e. total volume: 26 mL. The solutions were mixed and measured the absorbance (A_2) against the corresponding reagent blank solution. Again, the absorbance (A_3) was measured after the addition of 2 mL of EDTA to above blank and sample solution, i.e. total volume at this stage: 28 mL against the corresponding reagent blank. In first two stages after taking absorbance measurements, i.e. A_1 and A_2, the solutions in quartz cuvettes were transferred back to respective volumetric flasks in case of samples and blank as well. Calibration plots were constructed for (A_2–A_3), (A_1–A_2) and A_3 vs. volume of MMS for Cd, Pb and Hg, respectively. The heavy metal toxin content was arrived at by referring to the above calibration graphs. Optimal amounts selected eventually after optimization of various experimental variables viz. pH, potassium iodide, Rhodamine 6G, gelatin, λ_{max} and stability are summarized in Table 1.

2.3. Analysis of industrial effluent and natural water samples

The effluent samples (1 L) were collected in duly labeled PTFE bottles and are preserved by adding 1 mL of 10N ultrapure HNO_3 (70%) to bring the pH ~2. The effluent water samples collected from the vicinity of zinc metal, lead acid battery and chloralkali industry effluents and natural water samples were analysed by following the procedure described in Section 2.3, after adjusting the pH to 5.2 ± 0.2 in presence of 1.0 mL of 1.0 $mol\,L^{-1}$ hexamine buffer.

3. Results and discussion

Colorimetry and spectrofluorimetry are essentially based on the formation of binary, ternary or multi-component complexes with most inorganic species. The analysis in aqueous media employing ternary complexes are being preferred in green chemistry point of view and also the carcinogenity of most organic solvents [7–9,13]. Among these, colorimetric or spectrofluorimetric procedures based on ion-association offers superior selectivity in addition to highest sensitivity arising out of the fact that several masking agents can be used by proper choice of charged binary metal–ligand complex before associating with a chromophore usually a cationic or anionic dye [7] and high molar extinction coefficients of ionic dyes. We have taken one such system viz. metal–iodide–Rhodamine 6G or Pyronine G to demonstrate multi-measurand analysis capability of colorimetry by employing sequential ligand exchange (SLE) concept.

3.1. Absorption spectra and spectral characteristics

Fig. 1a shows the absorption spectra of 2 mL of 2×10^{-4} $mol\,L^{-1}$ Rhodamine 6G (Curve A) with 4 mL of MMS (Curve B) in presence of 2 mL 5% KI and 1 mL of 1% gelatin, in a final solution of 25 mL. It is evident from the figure that the interaction of iodo-complexes of chosen heavy metal toxins with Rhodamine 6G proceeds with an identical bathochromic shift, the pink ternary complexes absorbing at 575 nm compared with 530 nm of orange red coloured Rhodamine 6G dye, thus facilitating aqueous finish as the dye has negligible absorption at 575 nm. On sequential addition of 1 mL 0.4 $mol\,L^{-1}$ of citrate buffer and 1 mL of 0.1 $mol\,L^{-1}$ EDTA (Curves C and D, respectively) the absorbance at 575 nm diminishes corresponding to lead and subsequently cadmium. The absorption spectra of solutions representing Curves B, C and D measured against solution A (Blank) are depicted in Curves B′, C′ and D′, respectively. Masking of Pb on the addition of citrate buffer weakens the intensity of the absorption signal of Pb, Cd and Hg mixture on Curve B′ at 575 nm resulting in Curve C′ where the signal is purely of Cd and Hg. Further addition of EDTA masks signal due to Cd and give rise to Curve D′ of lower intensity.

3.2. Optimization of experimental conditions

Table 1 summarizes the results obtained on sequential variation of pH, KI, Rhodamine 6G and gelatin on the absorbance of the ternary ion-association complex at three different stages viz. direct, after addition of citrate and after further addition of EDTA along with the selected experimental condition for each parameter. The pH was varied in the range 2.0–7.0 in steps of 0.5 in all stages

Table 1
Effect of different parameters during multi-analyte determination of admixtures of cadmium, lead and mercury by colorimetry (0.5 $mol\,L^{-1}$ hexamine buffer (pH 5.0), 2.5 mL of 10% KI, 5.0 mL of 0.01% Rhodamine 6G and 1 mL of 1% gelatin (except when varied) total volume of 25 mL).

Parameter	Optimal range			Selected condition
	Stage I	Stage II	Stage III	
pH	4.0–5.5	5.0–5.5	5.0–5.5	5.2 ± 0.2
KI (10%) mL	2.0–3.0	2.0–2.5	2.0–2.5	2.5
Rhodamine 6G (0.01%) mL	≥5	≥5	≤5	5.0
Gelatin (%) mL	≥1	≥1	≥1	1.0
Stability (h)	30 min	15 min	15 min	15 min
λ_{max} (nm)	575	575	575	575