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Flow Chemiluminescence Determination of Antimony(III,V) Using a Rhodamine B-Cetyltrimethylammonium Chloride Reversed Micelle System Following Liquid–Liquid Extraction

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A flow chemiluminescence (CL) method combined with a liquid–liquid extraction technique is proposed for the indirect determination of antimony in aqueous samples using rhodamine B (RB). In the liquid–liquid extraction process, the antimony(V) chloro-complex anion, $[SbCl_6]^-$, was extracted from an aqueous acidic solution into toluene *via* ion-pair formation with the protonated RBH^+ ion. Upon mixing the extract with a reversed micellar reagent solution of cetyltrimethylammonium chloride (CTAC) in 1-hexanol–cyclohexane/water (0.60 mol dm^{-3} H_2SO_4) containing cerium(IV), uptake of the ion-pair by CTAC reversed micelles occurred easily, followed by an oxidation reaction of RB with Ce(IV) in the CL process. The CL signal produced was then measured. Using a flow injection system, the detection limits (DL) of 0.25 μmol dm^{-3} Sb(III) and 0.20 μmol dm^{-3} Sb(V), and linear calibration graphs with dynamic ranges from the respective DLs to 16 μmol dm^{-3} for Sb(III) and Sb(V) were obtained under optimized experimental conditions. The proposed method was successfully applied to a mixture of Sb(III) and Sb(V), where total antimony, Sb(III) + Sb(V), was measured using ceric sulfate as an oxidant to oxidize Sb(III) to Sb(V) prior to extraction, Sb(V) was determined directly without the use of an oxidant, and Sb(III) was calculated by difference.

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Introduction

Antimony and its compounds are widely used in a variety of products, and industrial and commercial materials including various alloys, ceramics, glasses, plastics and synthetic fabrics. It is known that antimony is one of the toxic metals; the toxicity of antimony depends on the oxidation state. In order to determine low concentrations of antimony, many methods based on different principles have been proposed.[1-6] However, most of the reported methods lack either selectivity or sensitivity.

The unique applications of chemiluminescence (CL) in analytical chemistry have made the most of the advantages presented by the method's high sensitivity, wide dynamic range, and simplicity of instrumentation. Application of CL has been extensively reported in fields of drug analysis, organic contamination determination, inorganic ion assay, peroxide and amino acid determination, *etc*.[7,8] Especially, analytical methods based on CL reaction of only a few CL reagents such as luminol are famous for their inherent simplicity, speed and high sensitivity.[9] However, many inorganic anions like the antimony(V) chloro-complex anion, $[SbCl_6]^-$, do not cause luminol CL and thus applications of flow injection CL methods for anion determination have been limited.[10] In order to extend the use of the CL method for practical analysis, on the other hand, rhodamine compounds as a series of xanthene dyes are attracting increasing attention as highly sensitive and selective CL reagents. As is well known, rhodamine B (RB) has been applied in analytical chemistry,[11,12] mostly in spectrophotometry[13] and fluorescence analysis.[14] It has been reported recently that CL emission could be generated by the oxidation of RB. The behavior of a new CL system, cerium(IV) with RB in an acidic medium, was investigated.[15]

The utility of micelles and microemulsions and their analytical applications are numerous.[16-18] In the reversed micellar solution, the surfactant molecules encompass tiny water droplets, surrounded by surfactant polar heads, and are converted into homogeneously distributed micelles in the organic bulk. Acting as microreactors,[17] the reverse micelles possess unique properties. When reversed micelles are incorporated into the CL detection system, several advantages, including sensitivity and improved selectivity, are achieved.[18-27,29] It is believed that the reversed micellar-mediated CL (RMM-CL) reactions occur at water-surfactant interfaces of the reverse micelles.[18,19,23] We have pointed out that the uptake of CL-active species or CL reagents by reversed micelles into their water pools is significant in the RMM-CL process.[20,21,24,25,27-29] In our previous work, the RMM-CL behavior of RB was investigated using the acidic water pool containing the Ce(IV) oxidant in the reversed micellar medium of cetyltrimethylammonium chloride (CTAC) in 1-hexanol–cyclohexane.[29] When the reversed micellar solution of Ce(IV) was mixed with the RB solution in 1-hexanol–cyclohexane using a flow injection (FI) system,

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stronger CL emission from RB was observed compared with that in the usual aqueous solution.

To improve selectivity of the CL methods, various separation techniques such as chromatography, gas generation, and membrane separation are usually incorporated into the flow CL detection systems.[30,31] Liquid–liquid extraction is one of the most effective separation methods. We have developed new hybrid analytical methods based on the combination of extraction procedures with the RMM-CL detection system.[19,22,25,26] For the liquid–liquid extraction of Sb(V), an ion-pair formation between the protonated rhodamine B, RBH^+, and the negatively charged Sb(V) chloro-complex, $[SbCl_6]^-$, was described earlier by Ramette and Sandel.[32] The technique has come to be regarded as an efficient analytical method for Sb(V) detection. The same principles are extended to the present work, where the above RMM-CL detection using a RB-Ce(IV) reaction is applied to the indirect determination of Sb(V) extracted from aqueous sample solutions. To the best of our knowledge, no investigation of the utility of RB, not only as an extracting reagent but also as a CL reagent, has been reported so far for a hybrid method based on the combination of liquid–liquid extraction with a CL detection system. In this work, the feasibility of using RB as both reagents was examined for the proposed method, where CL active conditions compatible with the extraction should be selected. Furthermore, validation of the present method was confirmed by applying it to a speciation analysis of Sb(III, V), where a reaction process using the Ce(IV) oxidant was added for oxidizing Sb(III) to Sb(V) prior to extraction.

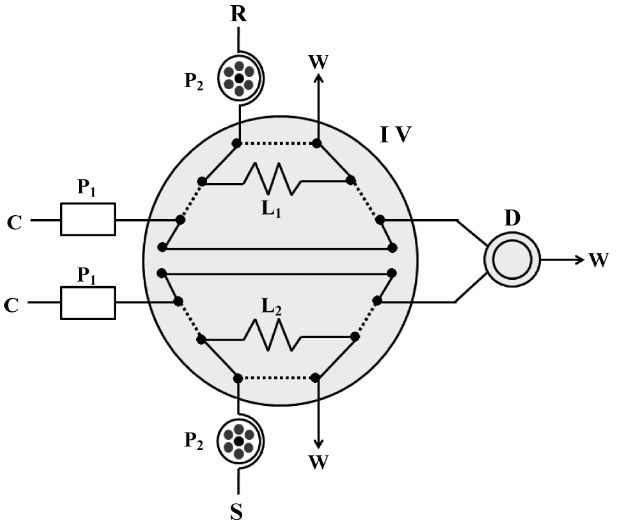

Fig. 1 Schematic flow diagram for the RMM-CL determination of antimony. C, carrier; L_1, reagent loop (100 mm^3); L_2, sample loop (100 mm^3); P_1, plunger pump (2.5 cm^3 min^{-1}); P_2, peristaltic pump; R, reversed micellar oxidant reagent; S, sample; D, detector; IV, injection valve in the load (—) and injection (···) positions; W, waste.

Experimental

Chemicals and reagents

Rhodamine B, ceric sulfate tetrahydrate, hydroxylamine hydrochloride and hydrochloric acid were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Cyclohexane, 1-hexanol, toluene and metal standard solutions used for interference studies were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). Potassium pyroantimonate and sulfuric acid were obtained from Katayama Chemical Industries (Osaka, Japan). The surfactant CTAC was obtained from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). All other reagents used were of analytical reagent grade. All chemicals were used without purification. All aqueous solutions were prepared with deionized water purified with a Millipore Milli-Q system (Merck Millipore, Milli-Q integral 3). A 5.0 mmol dm^{-3} RB stock solution was prepared in water. The oxidant solution of 0.10 mol dm^{-3} Ce(IV) was made by dissolving ceric sulfate tetrahydrate in 0.60 mol dm^{-3} sulfuric acid. Also, a 1.0 mol dm^{-3} solution of hydroxylamine hydrochloride was prepared in 3.0 mol dm^{-3} HCl for use as a reductant. A commercially available 1000 mg dm^{-3} standard of Sb(III) (Merck, Darmstadt, Germany) in 2.0 mol dm^{-3} HCl was used as a stock standard solution. A 1000 mg dm^{-3} Sb(V) stock solution was prepared by dissolving potassium pyroantimonate in conc. HCl. Working solutions of Sb(III) and Sb(V) were prepared daily by serial dilution of the standard stock solutions with 6.0 and 3.0 mol dm^{-3} HCl, respectively. Both standard solutions were also used for preparation of mixed sample solutions containing Sb(III) and Sb(V) in 6.0 mol dm^{-3} HCl. All glassware was soaked in 20% nitric acid and thoroughly cleaned before use.

Apparatus

For the FI-CL measurements, as illustrated in Fig. 1, a multi-component instrument composed of a Hitachi (Tokyo) Model K-1000 FI analyzer equipped with a 16-port rotary programmed automatic injection valve, a Tosoh (Tokyo) Model CCPD computer-controlled pump unit, and a Niti-on (Funahashi) Model LF-800 photometer with spiral flow cell (70 mm^3) was used as previously reported.[29] PTFE tubing of 0.5 mm i.d. was used throughout the flow system. A Shimadzu (Kyoto) Model C-R6A computer-controlled recorder was used to record CL signals.

Absorption measurements were recorded with a Hitachi (Tokyo) Model U-3900 UV-visible spectrophotometer, equipped with 1 cm quartz cells thermostatted at $25.0 \pm 0.1°C$, unless otherwise indicated.

Liquid–liquid extraction procedure

In the extraction procedure for Sb(V), an aqueous sample solution (10 cm^3) of Sb(V) in 3.0 mol dm^{-3} HCl, to which 5.0 mmol dm^{-3} RB stock solution (0.10 cm^3) was add as an extraction reagent, was placed in a separating funnel and 10 cm^3 of toluene as a solvent for extraction was added to it. The mixture was shaken for approximately 5 min and was allowed to stand (*ca.* 5 min) until the two phases were separated out. The upper organic layer was then subjected to CL analysis as mentioned below.

In the procedure for Sb(III), Sb(III) must first be converted to Sb(V) using an oxidizing agent.[32] Cerium(IV) is one of the few suitable oxidizing agents and causes rapid oxidation at room temperature. As only a slight excess is needed, 0.50 cm^3 of the Ce(IV) solution (0.10 mol dm^{-3}) was added to 5.0 cm^3 of the aqueous sample solution of Sb(III) in 6.0 mol dm^{-3} HCl, then diluted to a final volume of 10 cm^3 with water. After the oxidation of Sb(III), only a slight excess (10 mm^3) of the hydroxylamine hydrochloride reductant (1.0 mol dm^{-3}) is added to the sample solution for reducing excess Ce(IV), which otherwise would oxidize RB and thus interfere with the extraction. For the resultant sample solution, the subsequent extraction procedure was conducted in the same manner as mentioned above for Sb(V). The same procedures for oxidation with Ce(IV), reduction of excess Ce(IV), addition of RB and

Table 1 Optimum experimental and instrumental operating conditions

Solvent extract system	
HCl concentration	3.0 mol dm^{-3}
Rhodamine B concentration	50 µmol dm^{-3}
Aqueous/organic volume ratio	1:1
Mixing and phase separation time	5 min, each
Oxidizing agent Ce(IV) concentration	5.0 mmol dm^{-3}
Reducing agent $NH_2OH{\cdot}HCl$ concentration	1.0 mmol dm^{-3}
RMM-CL system	
[Ce(IV)] in the CTAC reversed micellar solution	1.0 mmol dm^{-3}, calculated on a final volume total solution basis
[H_2SO_4] in the Ce(IV) oxidant solution	0.60 mol dm^{-3}
R_w (= [H_2O]/[CTAC])	5.0
[CTAC] in the reversed micellar bulk organic solvent	0.11 mol dm^{-3}
Reversed micellar bulk solvent	1-Hexanol–cyclohexane (X_h = 0.10)
Flow system	
Sample and reagent loop size	100 mm^3, each
Carrier	1-Hexanol–cyclohexane (X_h = 0.10)
Flow rate	2.5 cm^3 min^{-1}

toluene extraction were also performed for the determination of total antimony, Sb(III) + Sb(V), in the mixed sample solutions that contained variable concentrations of Sb(III) and a constant concentration of Sb(V) in 6.0 mol dm^{-3} HCl.

CL measurement

Certain volumes of the oxidant solution of 0.10 mol dm^{-3} Ce(IV) were dispersed in a reversed micellar bulk solvent of 1-hexanol in cyclohexane (the mole fraction of 1-hexanol X_h = 0.10) containing 0.11 mol dm^{-3} CTAC to prepare their reversed micellar solutions. The Ce(IV) concentration in the CTAC reversed micellar solution, calculated on a final volume total solution basis, was 1.0 mmol dm^{-3}. A water-to-surfactant molar concentration ratio, R_w (= [H_2O]/[CTAC]) of 5.0, was used in the present work. The FI system used was based on a merging-zone technique (Fig. 1). Peristaltic pumps were used to suck the ion-pair extracted solution and the reversed micellar oxidizing reagent solution of Ce(IV) into their respective 100 mm^3 loops in the load position (straight line in Fig. 1), which were then inserted simultaneously into the respective carrier streams of 1-hexanol–cyclohexane (X_h = 0.10) by switching the rotary injection valve to the injection position (dotted line in Fig. 1). Both the carrier streams were driven at the flow rate of 2.5 cm^3 min^{-1}. The reversed micellar solution of Ce(IV) was mixed with the ion-pair extracted solution in a 70-mm^3 spiral-flow cell mounted in front of a phototube of the photometer, and the resultant CL signal was recorded. An aqueous solution of 1.0 mg dm^{-3} Sb(V) or 8.2 µmol dm^{-3} Sb(V) was used to optimize experimental and chemical parameters. The optimum experimental conditions used for the FI-CL detection in this work are given in Table 1.

Results and Discussion

Ion-pair extraction and RMM-CL system

Numerous analytical procedures based on the formation of ion pairs between protonated organic compounds and negatively charged metal complexes extractable into organic solvents have been reported.[33,34] Also, the application of the ion-pair formation between protonated RB and $[SbCl_6]^-$ to liquid-liquid extraction had been established earlier,[32] and was employed in this work. The RB is first protonated in an acidic medium and is then associated with a negatively charged counterion containing antimony(V). Because ion pairs in slightly polar organic solvents are more stable than in aqueous solutions, the ion pairs are then quickly and efficiently extracted into a slightly polar solvent, *e.g.* benzene or toluene. As toluene is more suitable for extracting ion pairs in terms of safety and low-cost, toluene was selected as the extractant in this work. However, toluene is not suitable for the stability of the CTAC reverse micelles. When the extract containing the ion-pair ($RBH^+[SbCl_6]^-$) was mixed with the reversed micellar solution of Ce(IV), the RMM-CL emission resulting from the oxidation reaction of RB was observed. In this work, we demonstrated that the compatibility of the extractant and reversed micellar bulk solvent is not necessarily important for obtaining sharp and reproducible CL signals. The CL intensity obtained from the oxidation of RB with Ce(IV) in the reverse micelles, as reported previously,[28,29] is proportional to the amount of RB extracted one-on-one with antimony(V), and thus the present procedure permits the indirect quantitative determination of antimony(V).

Optimization studies

A series of experiments were performed to establish the optimum analytical conditions as to those given in Table 1. Especially, the extractability of the ion-pair depends on the HCl concentration in aqueous sample solutions and the CL emission is affected by the molar ratio, R_w (= [H_2O]/[CTAC]), in the reversed micellar system; these are described below in detail. In our previous paper,[29] it was noted that when the mole fraction of 1-hexanol in the reversed micellar bulk solvent used was 0.045, the problem of turbidity was caused in the R_w range from beyond 5 up to over *ca.* 10. In the present procedure, a higher mole fraction of 1-hexanol (X_h = 0.10) was used to overcome this problem, and transparent and homogenous solution of the CTAC reverse micelles was made without suppressing the CL emission. The other experimental parameters related to RMM-CL detection were close to those reported earlier.[29]

Effect of the HCl concentration

The formation of the $[SbCl_6]^-$, as well as the protonation of the RB and, consequently, ion pair formation depend on the HCl concentration in aqueous sample solutions. The absorbance at the maximum wavelength (564 nm) of $RBH^+[SbCl_6]^-$ in toluene, obtained by the above extraction procedure, was recorded as being a function of the HCl concentration in the aqueous sample solution, and is shown in Fig. 2. With an increase in the concentration of HCl, an increase in the absorbance was observed, reaching a maximum around 3.0 mol dm^{-3}, beyond which the absorbance declined.

The amounts of generated $RBH^{2+}([SbCl_6]^-)_2$ and $RBH^{2+}Cl^-[SbCl_6]^-$ increase in stronger concentrations of HCl, but they do not compensate for the decreased extraction of $RBH^+[SbCl_6]^-$. Consequently, the total fraction of antimony extracted decreases with increasing acidity. An acid concentration of 3.0 mol dm^{-3} HCl was selected as an optimum value.

Effect of the [H_2O]/[CTAC] molar ratio

The molar ratio, R_w, significantly affects the physiochemical properties of the reverse micelles. By varying R_w, one can modify the size of the reversed micellar water pool.[17,18,35] The

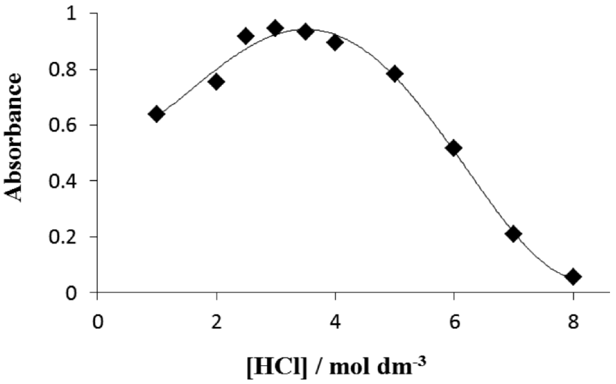

Fig. 2 Effect of HCl concentration in aqueous sample solutions on the absorbance of the RB species in the extract. Experimental conditions are given in Table 1.

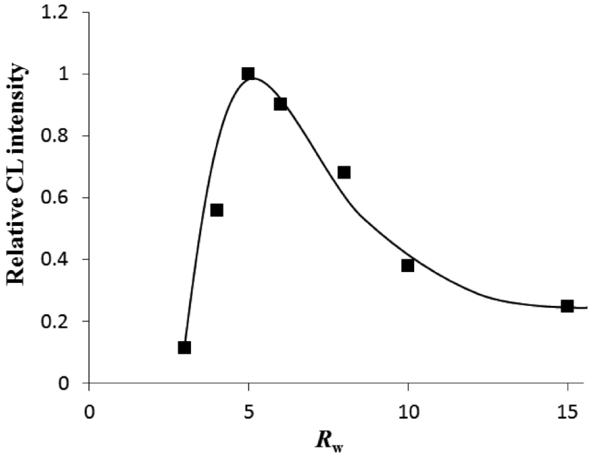

Fig. 3 Variation of CL intensity with the molar concentration ratio of water to surfactant, $R_{\rm w}$, in the reversed micellar solution of 0.11 mol dm^{-3} CTAC in 1-hexanol–cyclohexane ($X_{\rm h}$ = 0.10). Experimental conditions are given in Table 1.

$R_{\rm w}$ value was varied by changing the water concentration at a fixed amount of CTAC surfactant ([CTAC] = 0.11 mol dm^{-3}) in the reverse micellar solution. As shown in Fig. 3, the CL signal increased with an increase in the $R_{\rm w}$ value. A maximum CL intensity was attained around $R_{\rm w}$ value of 5.0, which was chosen as an optimum $R_{\rm w}$ value. Similar behavior in the variation of the RMM-CL intensity with $R_{\rm w}$ was observed in our previous work.[29] Increasing the $R_{\rm w}$ value caused an increase in the size of the reversed micellar water pools. It can be supposed that due to a decrease in the Cl^- concentration in the water pools with an increase in volumes, the suppressing effect of the Cl^- ion on the Ce(IV) activity in the pools is weakened and thus RB-Ce(IV) CL emission is enhanced. Meanwhile, after reaching the optimum $R_{\rm w}$, the ability of the reversed micellar microenvironment for the CL enhancement is lowered in larger pools, where the properties of water may be similar to those of the usual bulk water.[17,18,35]

Analytical performance

An analytical CL signal was taken as the difference in the observed peak heights for the analyte and the blank. However, the blank signal was negligibly small. Thus, the detection limit (DL) was given as the analyte concentration for which the analytical signal was three times higher than the noise level of the base line. Under optimized instrumental and chemical conditions, DLs of 0.25 µmol dm^{-3} Sb(III) and 0.20 µmol dm^{-3} Sb(V) were achieved. The DL values are superior to those attained (29 µmol dm^{-3} Sb(V)) by a flow method using absorptiometric detection following ion-pair extraction.[36] The linear calibration graphs for Sb(III) and Sb(V) were obtained with dynamic ranges from the respective DLs to 16 µmol dm^{-3}. The relative standard deviations (n = 6) obtained at the Sb(III) concentration of 4.1 µmol dm^{-3} and the Sb(V) concentration of 8.2 µmol dm^{-3} were 2.2% and 1.1%, respectively.

Table 2 Metals tested for possible interfering behavior in liquid-liquid extraction and CL determination of Sb(V)

Metal	Relative CL intensity[a]		Metal	Relative CL intensity[a]	
	10[b]	100[b]		10[b]	100[b]
Sb(III)	101	103	Cu(II)	102	100
Au(III)	960	—	Pb(II)	110	102
Fe(III)	93	100	Sn(II)	98	98
Ga(III)	101	106	Hg(II)	101	101
Al(III)	98	99	Zn(II)	97	100
As(III)	105	97	Ni(II)	95	95
Cr(III)	97	99	Co(II)	98	101
Bi(III)	109	104	Ag(I)	104	96

a. All CL intensities are relative to the CL signal (= 100) for 8.2 µmol dm^{-3} Sb(V) alone.
b. Metal-to-Sb(V) weight ratio.

Interference effects

The effect of some common metals, *e.g.* Au(III) and Ga(III),[37,38] which can be given red or violet compounds of the type $RBH^+[M^{III}Cl_4]^-$, and other metal ions were examined to check possible interference. For the interference studies, 8.2 µmol dm^{-3} Sb(V) solutions containing the individual interfering species were used. The results obtained are summarized in Table 2. None of the species tested, except for Au(III), interfered with the CL determination of Sb(V) when present at an interferent-to-Sb(V) weight ratio of 10 and 100. Because an ion-pair of $RBH^+[AuCl_4]^-$ in HCl solution (3.0 mol dm^{-3}) can be considerable readily extracted into toluene, the presence of Au(III) caused an enhancement in the CL emission.

Differential determination of antimony(III)/antimony(V)

In the present extraction–CL detection system for mixed sample solutions containing Sb(III) and Sb(V), the crucial process of oxidizing Sb(III) with Ce(IV) was added prior to the extraction. When the concentration of Sb(III) alone was changed while keeping the content of Sb(V) constant in the sample solutions, a linear calibration graph for the total antimony, Sb(III) + Sb(V), measured as the peak height was obtained using the oxidant, while almost the same CL signals were produced without use of the oxidant, as shown in Fig. 4. This indicates that Sb(V) alone is transferred to the organic phase and thus the effect of Sb(III) on the CL signals is negligibly small. As such, Sb(III) determination is easily possible from the difference.

Conclusions

An ion-pair formation and liquid–liquid extraction method

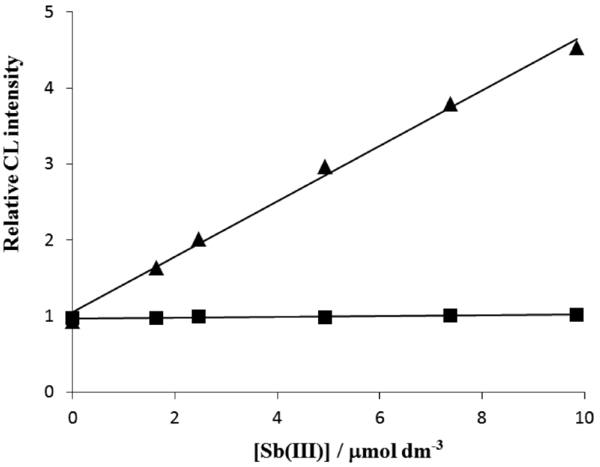

Fig. 4 Variation of the CL intensity with the concentration of Sb(III) in mixed sample solutions of Sb(III) and Sb(V) in the absence (■) and presence (▲) of 5.0 mmol dm^{-3} Ce(IV).

coupled with CL detection based on the reversed micellar-mediated oxidation of RB with Ce(IV) was developed for the determination of Sb(V), where RB was used not only as an extracting reagent but also as a CL reagent. With a simple experimental setup using low-cost instrumentation, the proposed method is undoubtedly fast and sensitive. Modification of this technique provided for analyses of Sb(V) only, Sb(III) + Sb(V), or Sb(III) and Sb(V) in the same sample using Ce(IV) oxidant cycling. However, before this method can be applied to samples of a biological and environmental nature, analytical efforts are certainly needed to identify potential interferents such as Au(III). Moreover, to provide automated, rapid and reproducible analyses of the aqueous samples of antimony using an on-line extraction-CL detection system, further studies are being undertaken to incorporate a membrane phase separator into the flow system.

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