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Study and application on synergistic effect of double chromogenic agent between Eosin Y and butyl rhodamine B

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Abstract

In this paper, we researched the formation condition and application on ionic complex between Eosin Y (EY) and Butyl Rhodamine B (BRB). The ternary complex $GaCl_4BRB$ in toluene solvent was resolved by controlling the pH in water phase, $GaCl_4BRB$ was resolved into water phase, then add Eosin Y which was the same color as BRB into water phase, the ionic complex $(BRB)_2 \cdot EY$ was formed by electrostatic effect between BRB with positive charges and EY with negative charges. (Figure 1) Then the ionic complex $(BRB)_2 \cdot EY$ was extracted by toluene and was isochromatized by adding n-butanol catalyzed solvent, in that case, the determination sensitivity of Gallium was improved obviously because the addition effect of Double Chromogenic Agent in the ionic complex $(BRB)_2 \cdot EY$. The detect limit was decrease from 0.3 μg L^{-1} to 0.1μg L^{-1}. The method has been applied to determine Gallium in mineral with satisfactory results.

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INTRODUCTION

Gallium is used in the semiconductor industry as one of the doping elements. Its arsenide in air is considered a potential health hazard[1]. Increasing interest and importance of these metals in different fields has made it necessary to develop simple and selective methods for their determination[2]. Various analytical techniques used for determination of gallium in different types of matrixes include spectrophotometry[3-5], AAS [1, 6], XRF[7], ICP-AES[8, 9] and ICP-MS[10, 11].

In recent years, the application of the ternary com-plex in analytical chemistry was very wide; especially the ternary ionic complex was applied widely in elementary separation, enrichment and extraction spectrophotometric analysis. There are many reports about determination of metal ion by extraction spectrophotometric method with the ternary complex which was formed by metal complex ion with BRB or EY, but there is no report about determination of metal ion depending on synergistic spike effect between an acidic dye and an alkaline dye. In our paper, we discussed the isochromatic condition of BRB and EY and applied it to determine Gallium in mineral keeping the selectivity unchanged.
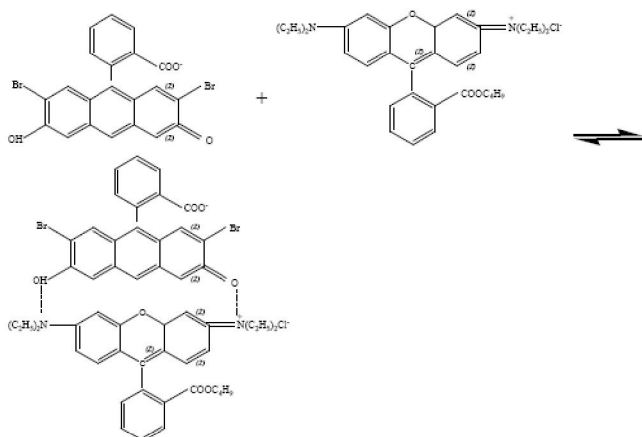
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Figure 1 : The electrostatic effect of (BRB)₂·EY.

EXPERIMENTAL

Apparatus

All fluorescence spectra were recorded by Shimadzu RF-540 spectrofluorophotometer; Absorption was measured with an UV-vis recording spectrophotometer (UV-265 Shimadzu Japan). All pH measurements were done with a pHS-3C acidity meter (Leici, Shanghai).

Materials

Gallium (Ga) standard solution: measure 1.0000 g (99.9999 %) Ga and add into 250 mL beaker, add 1: 1 hydrochloric acid 20 ~ 30 mL and drops of nitric acid, heat with water bath and make it solve, when cool, transfer it into 1.0 L volumetric flask.

Eosin Y (EY) was used as an aqueous 0.1 mM solution; Butyl Rhodamine B (BRB) was used as an aqueous 0.4 mM solution; NaOH-KH$_2$PO$_4$ buffer: pH =8.7. Above reagents were all analytical purity grades. Water for experiment was all de-ionized water.

Standard procedures

To a 30 mL separating funnel, add containing sample solution (not more than 1.5 μg Ga), 5 mL 13 M sulfuric acid, and 1.0 mL 0.4 mM BRB solution; 1.0 mL 10 M hydrochloric acid and 1.0 mL Titanium trichloride solution 15%, then extract the mixture with toluene, lay aside about 10 min, transfer the extract into another separating funnel, add 5.0 mL pH= 8.7 NaOH-KH$_2$PO$_4$ buffer, shake harmoniously, the extract in above layer was fade, then add 3 mL EY solution, shake for 1 min, when sepa-

rated, transfer the extract into 10.0 mL volumetric flask, add 5.0 mL n-butanol catalyzed solvent exactly and dilute to the mark with acetone. The fluorescence intensity of the solution was measured at $\lambda_{ex}/\lambda_{em} = 518/555$ nm against reagent blank prepared in the same way.

RESULTS AND DISCUSSION

The formation of complex between BRB and EY

To a 30 mL separating funnel, add the solution in the following order: 2.0 mL 1.0 μM BRB, 5.0 mL 10 μM EY and certain volume 0.05 M sulfuric acid or 0.1 M sodium hydroxide. And dilute to 10.0 mL with de-ionized water, shake harmoniously, add 5.0 mL toluene and extract for 1 min, lay aside and separate, transfer the extract into 10.0 mL volumetric flask, add 5.0 mL n-butanol catalyzed solvent exactly and dilute to the mark with acetone. The influence of acidity on the sys-
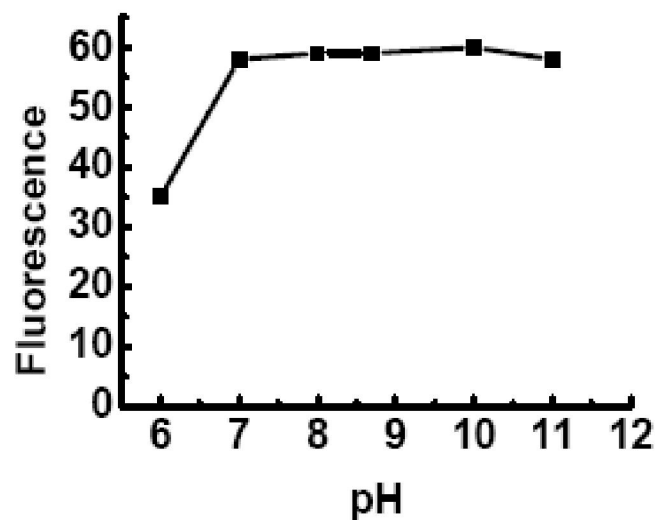

Figure 2 : Effect of pH on the formation of complex: EY: 10 μM, BRB: 1.0 μM.

tem was shown in Figure 2.

Because the solubility of acidic dye BRB in organic phase was better than that of alkaline dye EY, the EY was almost not extracted by toluene. In order to decrease the influence of blank value, we added superfluous acidic dye BRB to form complex. We could conclude the complex was formed and the fluorescence intensity was stable in pH range of 6.0 ~ 10.0.

The spectrum data of EY, BRB and (BRB)₂·EY was shown in TABLE 1. From TABLE 1, when the dye-pair was formed in toluene solvent, we can ob-

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serve a double peak whose height was the same in the fluorescence spectrogram, but in the toluene: n-butanol catalyzed =1: 1 solvent system, we could see a single peak at wavelength 555 nm, whose intensity was stronger than any other dye alone in the system, in other word, the ionic complex was formed between dyes, seen from Figure 3. Because of the synergistic spike effect of ionic complex between dyes, it made determi-
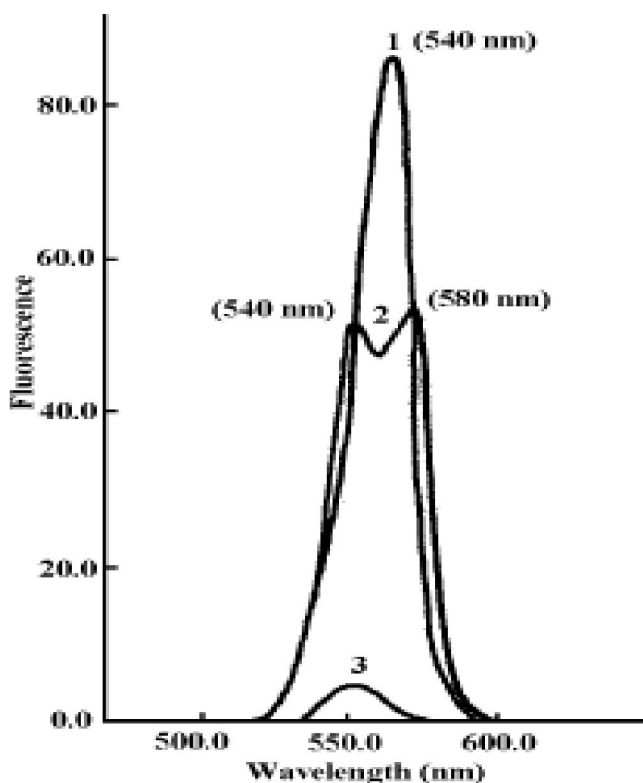

Figure 3 : The isochromatic spectra of $(BRB)_2 \cdot EY$: 1. the fluorescence spectra of $(BRB)_2 \cdot EY$ in toluene; 2. the fluorescence spectra of $(BRB)_2 \cdot EY$ in the toluene: n-butanol catalyzed= 1: 1 solvent system; 3. the blank solution

TABLE 1 : The spectrum data of EY, BRB and $(BRB)_2 \cdot EY$

| System | Water phase | | Toluene phase $\lambda_{ex}/\lambda_{em}$ | Toluene:n-butanol catalyzed $\lambda_{ex}/\lambda_{em}$ (nm) |
	λ_{ex} (nm)	$\lambda_{ex}/\lambda_{em}$ (nm)	(nm)	
BRB	564	562/578	540/ 570	518/ 565
EY	516	518/540		518/ 550
$(BRB)_2 \cdot EY$			518/540,580	518/ 555

nation sensitivity was improved obviously.

The forming condition of ternary complex $GaCl_4BRB$

According to the report[12], the optimum forming condition of $GaCl_4BRB$ was: 1.0 M hydrochloric acid; 6.5~ 8.0 M sulfuric acid; Titanium trichloride solution 15%; shaking time of extract with toluene was 1 min. the fluorescence intensity of the extract was stable within 24 hours, the formation of complex: Ga: Cl: BRB =1: 1: 1. In our experiment, we chose 6.5 M sulfuric acid, 1.0 M hydrochloric acid and titanium trichloride solution 15% as the optimum forming condition of $GaCl_4BRB$.

The resolving condition of $GaCl_4BRB$ and the forming condition of $(BRB)_2 \cdot EY$

The resolving pH of ternary complex $GaCl_4BRB$ was shown Figure 4. The ternary complex $GaCl_4BRB$ was formed in strong acid medium, while the $(BRB)_2 \cdot EY$ was formed when pH› 6.0. So we shook the ternary complex $GaCl_4BRB$ in toluene phase with NaOH-KH_2PO_4 buffer (pH= 8.7) adequately, here the $GaCl_4BRB$ was broken down, the dissociation substance was run into water phase, here we added EY into it. Because BRB was an alkaline dye with positive charges and EY was an acidic dye with negative charges. The ion-pair BRB·EY was formed easily depending on electrostatic attraction. According to equimolar series method, the formation of ion-pair was $(BRB)_2 \cdot EY$ (BRB: EY= 2: 1).
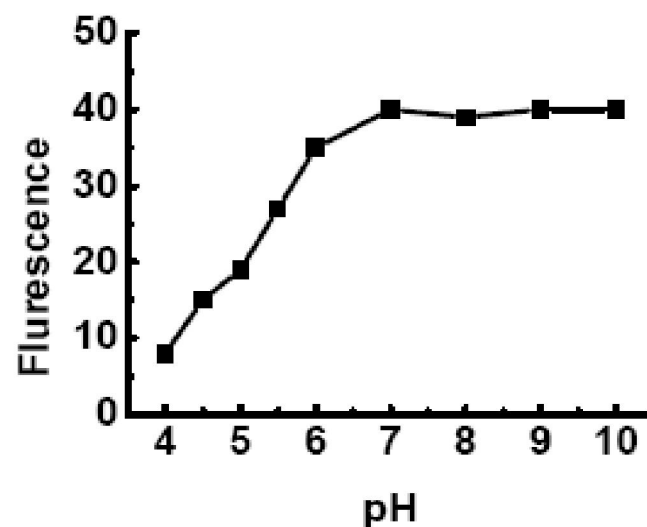

Figure 4 : The resolving pH of ternary complex $GaCl_4BRB$

The Concentration of EY

According to the proposed method, when the $(BRB)_2 \cdot EY$ was formed, the optimum value of EY: 3.0 mL 0.1 mM.

The calibration equation

According to the recommended procedure outlined above, standard calibration graphs were made. The spectrum data were processed by standard least squares treatment, and the calibration equation obtained was $\Delta F = 0.42345C$ (µg L^{-1})+0.40673, $R^2 = 0.9994$, where ΔF is the fluorescence intensity, C is the content of Ga and R^2 is the correlation coefficient. The concentration of Ga obeyed linear in the range of 0 ~ 150 µg L^{-1}, the detect limit of the method was 1.0 ng.

Interferences

According to the report[12], we determined 1.0 µg Ga in the medium of 1.0 mL Titanium trichloride solution 15% and 1: 1 hydrochloric acid: Al^{3+}, Ca^{2+}, Fe^{2+}, Zn^{2+} (100 mg); Cu^{2+}, Mg^{2+} (10 mg); V^{5+}, Bi^{3+}, W^{6+}, In^{3+}, As^{3+}, Mo^{6+}, Sn^{2+}, Re^{7+}, U^{6+}, Cr^{3+}, Te^{4+}, Ce^{3+} (1.0 mg); Au^{3+}, Tl^{3+} (100 µg); Sb^{3+} (50 µg); Hg^{2+} (40 µg) have almost no influence on the determination. The tolerance level was defined as an error not exceeding ±5% in the determination of the analyte.

Analytical application:Determination of Ga in mineral sample

Measure mineral sample (1.0000 g, containing standard value of Ga 0.0027%) to 50 mL plastic crucible, add 20 mL concentrated hydrochloric acid, 10 mL concentrated nitric acid, 10 mL fluorhydric acid and 5 mL perchloric acid, heat and dissolve on peltier panel, vaporize gradually until 1.0 mL left, dilute with 6.5 M sulfuric acid, transfer the solution into 100 mL volumetric flask, finally dilute to the mark with 6.5 M sulfuric acid, shake harmoniously. Fetch 2.0 mL form the volumetric flask and add it into separating funnel, add the solution in an order: 3.0 mL 13 M sulfuric acid; 1.0 mL 10 M hydrochloric acid; 1.0 mL 0.4 mM BRB and 1.0 mL Titanium trichloride solution 15%, shake harmoniously, record the

TABLE 2 : The results of sample analysis and recovery

Samples	Ga Measured (µg)	Ga added (µg)	Total Ga (µg)	Recovery (%)
	0.5400	0.5000	1.0400	100.2
	0.5518	0.5000	1.0518	102.6
Mineral Samples 2 mL	0.5255	0.5000	1.0255	97.3
	0.5650	0.5000	1.0650	105.2
	0.5124	0.5000	1.0124	94.7

fluorescence intensity as the recommended procedure outlined above, the results were shown in TABLE 2.

CONCLUSIONS

In our paper, we discussed the isochromatic condition of BRB and EY and applied it to determine Gallium in mineral keeping the selectivity unchanged. Because of the synergistic spike effect of ionic complex between dyes, it made determination sensitivity was improved obviously.

ACKNOWLEDGEMENTS

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