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Synthesis and characterization of a novel cross-linking complex of β-cyclodextrin-*o*-vanillin furfuralhydrazone and highly selective spectrofluorimetric determination of trace gallium

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Abstract

A novel host inclusion complex of cross-linking-polymeric-β-cyclodextrin-*o*-vanillin furfuralhydrazone (β-CDP-OVFH) was synthesized and characterized with IR and ^{1}H NMR spectra to confirm its structure. A highly selective and sensitive fluorescent determination of trace amounts of gallium was proposed based on the reaction between Ga^{3+} with β-CDP-OVFH in acetic acid–ammonium acetate buffer medium of pH 4.10. The maximum excitation and emission wavelengths were 392 and 499 nm, respectively. The linear range of this method was 1.5–330 ng ml^{-1} with a detection limit of 0.44 ng ml^{-1}. The effect of interferences in the determination of gallium was investigated and the results showed that the same race elements such as Al^{3+} and In^{3+} did not interfere the determination of Ga^{3+} even when their concentration is 100 times of Ga^{3+}, the host reagent had quite high capacity of identifying Ga^{3+}. This method was successfully applied to the determination of trace amounts of Ga^{3+} in artificial and semiconductor samples.

Keywords: Cross-linking-polymeric-β-cyclodextrin-*o*-vanillin furfuralhydrazone (β-CDP-OVFH); Determination of gallium; Spectrofluorimetry; Synthesis and characteristic of host inclusion complex

1. Introduction

Gallium is one of the rare elements whose content is very little in earth, but it has the regulative function to the growth of plant especially for Chinese traditional and herbal drugs. In addition, gallium is very important in the production of semiconductor. At present, methods determining Ga^{3+}, such as atomic absorption spectrometry [1,2], spectrophotometry [3–5] and fluorimetry [6–8] have been often used. Compared with other methods, fluorimetry has the advantages of higher sensitivity, better selectivity, less amounts of samples, simpler and faster determination, so it has received more attention. Many reagents determining gallium, e.g. 8-hydroxyquinoline [9], butylrhodamine B [10] and lumogallion [11,12] have been used in fluorimetry, but the interference of the same race elements such as Al^{3+} and In^{3+} cannot be avoided. With characteristic structure, β-cyclodextrin (β-CD) has received much attention as a fine natural host reagent nowadays [13–19] and the formation of the inclusion complex can alter the photophysical properties of the guest molecules. The cross-linking complex of β-CD (β-CDP) has advantage over β-CD on including and identifying capacity and has a wide application foreground in the field of molecule identification [20]. In this paper, we synthesized the inclusion complex of β-cyclodextrin-*o*-vanillin furfuralhydrazone (β-CDP-OVFH), characterized its structure with IR and ^{1}H NMR spectra and studied the fluorescent reaction of β-CDP-OVFH with Ga^{3+}. The β-CD cavity in β-CDP-OVFH protected the single state molecule of the formative fluorescent complex from being quenched by water and soluble oxygen and improved the quantum yield, so the sensitivity was improved. The steric effect of β-CDP-OVFH made it difficult to include big molecules, so the selectivity was greatly improved. In

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the determination of gallium with β-CDP-OVFH, the linear range was 1.5–330 ng ml^{-1} with a detection limit of 0.44 ng ml^{-1}. The effect of interferences in the determination of gallium was investigated and the results showed that Al^{3+} and In^{3+} did not interfere the determination of Ga^{3+} even if their concentration is 100 times of Ga^{3+}. The host reagent has a quite high capacity of identifying Ga^{3+} so that the question existing in some references that the same race elements, such as Al^{3+} and In^{3+} seriously interfere the determination of Ga^{3+} by fluorimetry [21–23] was solved effectively.

2. Experimental

2.1. Apparatus

All fluorescent measurements were carried out on a Perkin-Elmer (Norwalk, CT, USA) LS-50 spectrofluorimeter, equipped with a xenon lamp and 1.0 cm quartz cells. The slit of excitation and emission were 5 and 4 nm, respectively. All pH measurements were made with a pHS-3C digital pH-meter (Shanghai Lei Ci Device Works Shanghai, China) with a combined glass-calomel electrode. The IR spectra were recorded on a PE-983 IR spectrometer (KBr discs cm^{-1}, Perkin-Elmer). Elemental analysis measurement was performed with a PE-240 CHN elementary analytical meter (Perkin-Elmer). The ^{1}H NMR spectra were recorded on a FX-90Q Nuclear Magnetic Resonance Spectrometer (DMSO as solvent, JEOL, Japan).

2.2. Reagents

β-Cyclodextrin was purified by recrystallization, a stock standard solution of gallium (5.0 μg ml^{-1}) was prepared from metal gallium by dissolving 0.5000 g of gallium in 3.5 ml of concentrated nitric acid, then the solution was diluted to 100 ml with doubly distilled water. Cross-linking complex of β-CDP-OVFH (5.0 × 10^{-4} mol l^{-1}) solution and OVFH (1.0 × 10^{-3} mol l^{-1}) solution were prepared in 100 ml of absolute ethanol. A buffer solution (pH 4.1) of acetic acid–ammonium acetate was used. All chemicals used were of analytical-reagent or higher grade and doubly distilled water was used throughout.

2.3. Synthesis of host molecule reagent

2.3.1. Preparation of formacylhydrazine

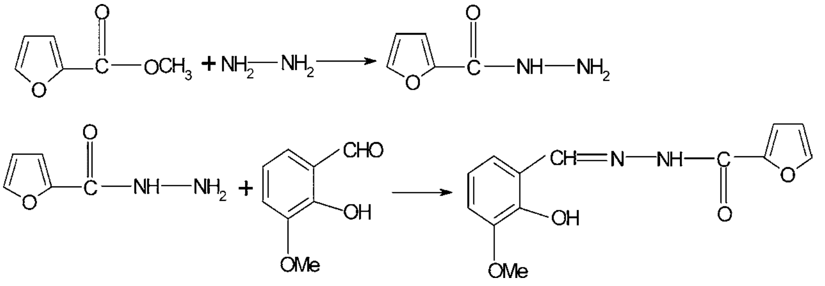
2.70 ml of methyl-furoate (about 0.025 mol) and 3.00 ml of 85% hydrazine hydrate (about 0.025 mol) were added into a 50 ml of flask, then 25.0 ml of 95% ethanol was added. The mixture was refluxed for 5 h in a water bath of 80–90 °C, then distilled under reduced pressure to eliminate ethanol and residual hydrazine hydrate. The red-brown and ropy liquid was obtained and cooled in ice water, then the white and pasty solid was obtained with a yield of 75%. The melting point of the solid was 75–76 °C.

2.3.2. Preparation of OVFH

1.26 g (0.010 mol) of formacylhydrazine was added into 40.0 ml of 95% ethanol and the mixture was heated until it was dissolved completely, 1.52 g (0.010 mol) of *o*-vanillin was added into 20.0 ml of 95% ethanol, then it was heated to dissolve. The solution of *o*-vanillin was added into the formacylhydrazine solution dropwise, then the mixture was refluxed for 2 h in a water bath of 90–100 °C, cooled and pumped out. The precipitate was recrystallized from ethanol and washed with 10.0 ml of 95% ethanol for three times, then 2.10 g of yellowish powder was obtained with a yield of 81%. The melting point of the powder was 147–148 °C. Elemental analysis gave a composition of: C 59.92%, H 4.61% and N 10.81%, which was in good agreement with the theoretical composition of OVFH: C 59.97%, H 4.65% and N 10.77%.

2.3.3. Preparation of β-CDP

10.5 g of β-CD was dissolved in 25.0 ml of NaOH (35%), then 8.50 ml of epichlorohydrin was added dropwise. The reaction mixture was kept at 90 °C for 5 min with stirring. After the solution was cooled to room temperature and neutralized with 6.00 mol l^{-1} of HCl, it turned into a transparent yellowish solution. This solution was dialyzed with a dialysis bag (molecular weight less than 3500) in order to eliminate NaCl and remnant material. The solution was concentrated to 50.0 ml. Twenty-five millilitres of the concentrated solution was freeze-dried under low pressure, then 4.30 g of β-CDP was obtained. The product decomposed at 240 °C. The average molecular weight of the complex was 5300, which was measured by gelatin chromatogram. It could be concluded that there were four β-CD units in one complex molecule [24].



2.3.4. Preparation of host molecule (β-CDP-OVFH)

0.200 g of *o*-vanillin furfuralhydrazone was dissolved in 5.00 ml of methanol and 6.00 ml of concentrated β-CDP solution was added. The color of solution changed from yellowish to brown and precipitation was observed simultaneously. The solution mixture was kept at 50 °C with stirring for 30 min, cooled and filtered under reduced pressure, then the precipitate was recrystallized from ethanol and washed with 10 ml of de-ionized water for three times. When dried, 0.290 g of brown crystal was obtained with a yield of 13%. The melting point was 181–182 °C.

2.4. Spectrofluorimetric determination of gallium

Into a 10 ml color comparison tube were added 1.00 ml of HAc–NH_4Ac buffer solution (pH 4.10), an aliquot of the standard or sample solution containing 0–3.30 μg ml^{-1} of gallium, 3.50 ml of ethanol and 0.50 ml of 5.0×10^{-4} mol l^{-1} β-CDP-OVFH (or 1.0×10^{-3} mol l^{-1}OVFH or 5.0×10^{-4} mol l^{-1} β-CDP and 1.0×10^{-3} mol l^{-1}OVFH), then it was diluted to volume. The solution was mixed thoroughly and equilibrated at room temperature for 10 min, then the fluorescent intensity was measured at $\lambda_{ex/em}$ = 392/499 nm against a reagent blank. A calibration graph was prepared under the same conditions for the determination of gallium.

3. Results and discussion

3.1. Confirmation of host molecule

3.1.1. The IR spectra of OVFH and β-CDP-OVFH

The peak shape of OVFH did not change after included by β-CDP, but the wave numbers of hydroxybenzene–OH, C=O, Ar–O and C=N all shifted to different extents. The IR spectra showed that the wave numbers of the function group increased 30 cm^{-1}(–OH), 19 cm^{-1}(–OH), 5 cm^{-1}(C=O), 5 cm^{-1}(Ar–O), 5 cm^{-1} (Ar–O) and 3 cm^{-1}(C=N), respectively (Table 1). Because hydroxybenzene–OH and Ar–O joined with benzene directly, C=O joined with furfuran ring directly, and benzene and furfuran rings enters into the cavities, the rich electron cavity of β-CDP increased the density of electron cloud and led to the increment of frequency. Although C=N did not join with benzene or furfuran directly, they formed a conjugated system with benzene and furfuran rings, which led to the increment of the density of electron cloud. The results of IR spectra showed that the new host reagent had formed.

Table 1
The IR spectra of OVFH and β-CDP-OVFH

Compound	ν Band and group (cm^{-1})			
	–OH	C=O	Ar–O	C=N
OVFH	3420, 3250	1660	1250, 1305	1612
β-CDP-OVFH	3450, 3269	1665	1255, 1310	1615
$\Delta\nu$[a]	+30, +19	+5	+5, +5	+3

[a] $\Delta\nu = \nu_{\beta\text{-CDP-OVFH}} - \nu_{OVFH}$.

3.1.2. The ^{1}H NMR spectra of OVFH and β-CDP-OVFH

In order to confirm if OVFH entered into the β-CDP cavities, the ^{1}H NMR spectra of OVFH and β-CDP-OVFH were obtained. The results are listed in Table 2. It was easy to see that the chemical shifts (δ) of all hydrogen atoms shifted to high field to different extents. The changes of Ar–OH, N–H, CH=N and Ar–OCH_3 were not obvious while the changes of phenyl and furan hydrogen were prominent. The results showed that the phenyl and furan rings of OVFH entered into the β-CD cavities. The rich electron β-CD cavities improved the electron cloud density of the hydrogens included, so the shield effect was increased, which made the chemical shifts of hydrogen nuclears included move to higher field. Because Ar–OH, N–H, CH=N and Ar–OCH_3 were located outside the cavities, their changes were not obvious.

3.2. Excitation and emission spectra

Under the selected condition, the maximum excitation and emission wavelengths were 392 and 499 nm, respectively (Fig. 1). We found that the complex of β-CDP-OVFH-Ga^{3+} had very strong fluorescent intensity while the reagent blank had low signal, which indicated that β-CDP-OVFH had a higher signal-to-noise than OVFH in the determination of gallium. With the driving force of hydrophobic interaction, van der Waals force and hydrogen bond, the OVFH molecule entered into the β-CD cavities and formed a supermolecular host reagent β-CDP-OVFH. Two β-CD units of the β-CDP cooperated to include phenyl and furan rings of OVFH, which improved the rigidity of the host reagent. The β-CD cavities in β-CDP-OVFH offered a non-polar microenvironment, the movement freedom of the formed fluorescent complex

Table 2
The ^{1}H NMR spectra of OVFH and β-CDP-OVFH

Compound	Function group (δ, ppm)						
	Ar–OH	N–H	Phenyl and furan	Ar–OCH_3	CH=N	>CH–O	C–OH
δ_{OVFH}	12.00	10.80	6.40–7.95	3.83	8.65		
$\delta_{\beta\text{-CDP-OVFH}}$	11.98	10.79	6.32–7.92	3.82	8.64	3.56–4.48	5.70
$\Delta\delta$[a]	−0.02	−0.01	−0.03 to −0.08	−0.01	−0.01		

[a] $\Delta\delta = \delta_{\beta\text{-CDP-OVFH}} - \delta_{OVFH}$.

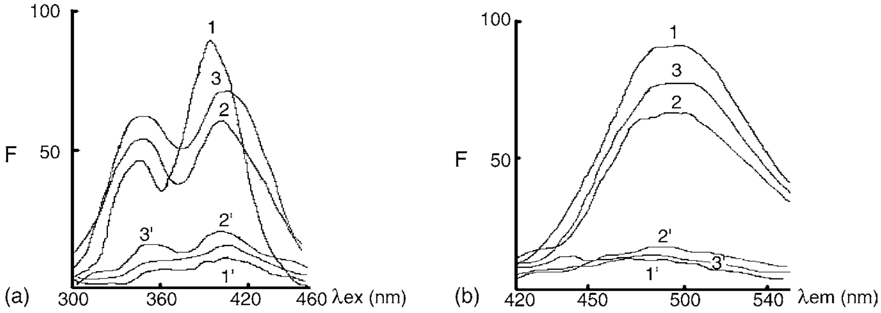


Fig. 1. (a) Excitation and (b) emission spectra: 1 and 1′ were the fluorescent spectra of β-CDP-OVFH-Ga^{3+} and blank, respectively; 2 and 2′ were the fluorescent spectra of OVFH-Ga^{3+} and blank, respectively; 3 and 3′ were the fluorescent spectra of β-CDP -OVFH-Ga^{3+} and blank, respectively. The concentration of reagents were: 2.5×10^{-5} mol l^{-1} of β-CDP-OVFH; 5.0×10^{-5} mol l^{-1} of OVFH; 2.5×10^{-5} mol l^{-1}β-CDP; and 300 ng ml^{-1} of Ga^{3+}.

molecule and the relaxation effect of the water molecule were both greatly depressed, which reduced the mutual collision of molecules and the non-radiative transition. Furthermore, the β-CD cavity could also protect the fluorescent single state molecule of β-CDP-OVFH-Ga^{3+} from the quenching of water and soluble oxygen.

If we simply added the same dosage of β-CDP and OVFH into the reaction system rather than β-CDP-OVFH, β-CDP could still offer a feasible microcircumstance of weaker polarity and stronger rigidity, so the quenching effect of water and soluble oxygen on the fluorescent single state molecule of OVFH-Ga^{3+} was reduced and the fluorescent intensity was improved, compared with the system without β-CDP. However, the steric effect of β-CDP restrained OVFH-Ga^{3+} from entering into the cavities of β-CDP, so the rigidity and plane of OVFH-Ga^{3+} could not be well improved. In β-CDP-OVFH, the steric effect made it easy to include with appropriate guest and the selectivity was greatly improved.

3.3. *Effect of pH*

The pH of the medium had a great effect on the fluorescent intensity of the β-CDP-OVFH-Ga^{3+} complex. The experimental results showed that the fluorescent intensity reached the highest value and remained constant between 3.80 and 4.40, so the optimum pH of 4.10 for the complex formation was selected.

3.4. *Effect of amount of buffer solution*

The influence of the amount of buffer solution (pH 4.10) on the relative fluorescent intensity of the solution containing 300 ng ml^{-1} of Ga^{3+} and 1.0×10^{-5} mol l^{-1} of β-CDP-OVFH was studied. The fluorescent intensity remained constant between 0.50 and 1.50 ml and decreased slowly thereafter. Thus, 1.00 ml of HAc–NH_4Ac buffer solution was selected throughout the experimental work.

3.5. *Effect of organic solvent*

The effect of organic solvent on the fluorescent intensity of the Ga^{3+}-β-CDP-OVFH complex was studied. The experimental results showed that the complex had stronger fluorescent intensity in ethanol than in any other organic solvent. The fluorescent intensity of the complex remained constant between 3.50 and 5.00 ml of ethanol. Therefore, 3.50 ml of ethanol was selected.

3.6. *Effect of amount of β-CDP-OVFH*

The influence of the amount of 5.0×10^{-4} mol l^{-1} β-CDP-OVFH on the fluorescent intensity of the complex was studied under the conditions established above (Fig. 2). The fluorescent intensity increased with the amount of β-CDP-OVFH up to 0.40 ml, remained constant between 0.40 and 0.60 ml and decreased slowly thereafter. A suitable amount of β-CDP-OVFH was advantageous to form fluorescent complex, while superfluous β-CDP-OVFH could decrease the fluorescent intensity of β-CDP-OVFH-Ga^{3+}. Thus, 0.50 ml of β-CDP-OVFH was selected throughout the experiment.

3.7. *Effect of temperature and time*

The influence of temperature was tested. The experimental results showed that higher temperature increased the collision of molecules, which made the collision probability

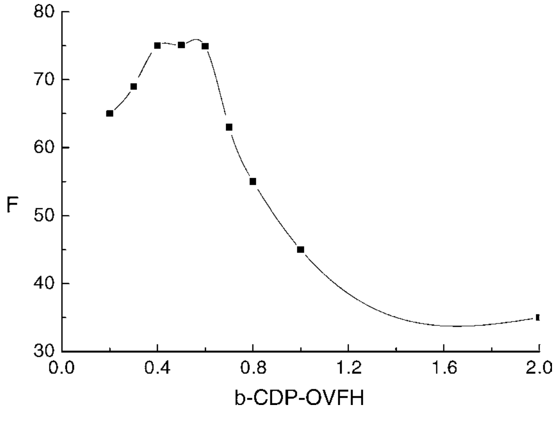


Fig. 2. Effect of amount of 5.0×10^{-4} mol l^{-1} β-CDP-OVFH on the fluorescence intensities of the complex.

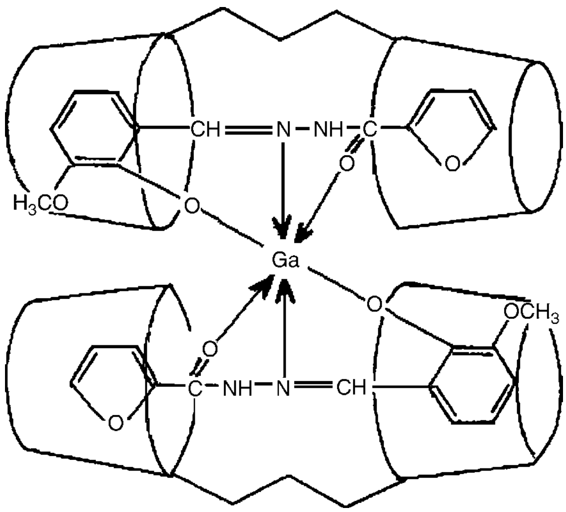


Fig. 3. Model structure of the complex.

of excited molecules and solvent molecules increase and resulted in the declination of fluorescent intensity. So, room temperature was selected. The fluorescent intensity reached a maximum after 10 min and remained constant for at least 1 h, then decreased slowly. Hence, all coordination reactions were kept for 10 min at room temperature.

3.8. Stoichiometry of the complex

The stoichiometry of the complex was studied under the established experimental conditions by the molar ratio and continuous variation methods. Both methods showed that the composition of the complex was 1:1(Ga^{3+}:β-CDP-OVFH). For the β-CD cavity is hydrophobic, it would reduce the stability of the complex if the guest has a greater polarity or electric charge, so the neutral host molecule is the best match to the β-CD cavity [25]. As described above, there were four β-CD units in one β-CDP molecule, so there were two OVFH molecules in one host reagent molecule. It was easy to see that the complex is neutral and suitable for the composition of the complex which was 1:1 (Ga^{3+}:β-CDP-OVFH). So, we concluded the model structure of the complex was as shown in Fig. 3.

3.9. Effect of interferences

A systematic study of the interferences in the determination of gallium (100 ng ml^{-1}) was carried out under the conditions established above. The criterion for interference was defined as an tolerable error not exceeding ±5.0% in the determination of Ga^{3+}. The results are shown in Table 3. From the results, we could see that Al^{3+} and In^{3+} in the same system (β-CDP-OVFH) with Ga^{3+} did not interfere the determination of Ga^{3+} even if their concentration is 100 times of Ga^{3+}, while Al^{3+} and In^{3+} had serious interferences in the OVFH-Ga^{3+} system. Therefore, the host reagent (β-CDP-OVFH) had a better selectivity and finer identifying capacity on the guest-Ga^{3+}.

3.10. Analytical characteristics

Under the optimum experimental conditions, there was a linear relationship between the fluorescent intensity and concentration of Ga^{3+} in the range of 1.5–330 ng ml^{-1} with a correlation coefficient (*r*) of 0.9982. The regression equation was $\Delta F = -4.607 + 0.858C$ (μg/10 ml). The detection limit, as defined by IUPAC [26], was determined to be 0.44 ng ml^{-1}. The relative standard deviation (R.S.D.) was 1.3% obtained from a series of 11 standards each containing 50 ng ml^{-1} of Ga^{3+}. The proposed method was compared with other common fluorimetric procedures (Table 4). As we could see, the proposed method had higher selectivity and good sensitivity than other fluorimetric methods, which composes the distinctive merits as well.

3.11. Determination of gallium in artificial and semiconductor samples

One millilitre of artificial sample was then determined fluorimetrically by the method developed above, the results are shown in Table 5.

One gram of semiconductor sample was put into a beaker and 3.3 ml of nitric acid and 10.0 ml of hydrofluoric acid were added, respectively. After the sample dissolved completely, it was diluted to 100 ml with doubly distilled water.

Table 3
Effect of interferences on the spectrofluorimetric determination of gallium (100 ng ml^{-1}) (tolerable error ±5.0%)

Tolerance ratio (*m*/*m*)	Interferences (β-CDP-OVFH-Ga^{3+})	Interferences (OVFH-Ga^{3+})
Over 3000	NH_4^+, I^-, NO_3^-, NO_2^-, Br^-, K^+, Na^+, F^-	NH_4^+, I^-, NO_3^-, Br^-, K^+, Na^+, Cl^-
2000	CO_3^{2-}, $C_2O_4^{2-}$, SO_4^{2-}, Ba^{2+}, Sn^{4+}	SO_4^{2-}, Ba^{2+}
1000	CH_3COO^-, Ti^{4+}, As(V)	CO_3^{2-}, CH_3COO^-
500	PO_4^{3-}, SO_3^{2-}, Cr^{3+}	SO_3^{2-}, F^-
200	Ca^{2+}	NO_2^-
100	Al^{3+}, In^{3+}	Co^{2+}
40	Co^{2+}	B^{3+}
20	Mo(VI), B^{3+}, Cd^{2+}	Mo(VI)
10	$Cr_2O_7^{2-}$, Cu^{2+}	In^{3+}, PO_4^{3-}
5	Zn^{2+}, V(V)	Zn^{2+}, V(V), Ca^{2+}
1	Be^{2+}, Fe^{3+}	Be^{2+}, Cu^{2+}, Fe^{3+}, $C_2O_4^{2-}$, Al^{3+}, Cd^{2+}, $Cr_2O_7^{2-}$

Table 4
Comparison of fluorimetric methods for gallium

Reagent	Linear range ($ng\,ml^{-1}$)	Detection limit ($ng\,ml^{-1}$)	Major interference	Ref.
Salicyladene-*o*-aminophenol	2–10	0.3	Al^{3+}, $Cr_2O_7^{2-}$	[6]
Lumogallion	0.3–6.1	–	Cu^{2+}, Fe^{3+}, $Cr_2O_7^{2-}$	[11]
Lumogallion	1.5–7.5	–	Al^{3+}, Cu^{2+}, Fe^{3+}	[12]
1,2,6,7-Trihydroxy-9-(*o*-chlorophenyl)fluorone	4–60	2.4	Fe^{3+}, In^{3+}, Sn^{4+}, V(V), Ti^{4+}	[23]
Calon-carboxylic acid	0.7–280	2.5	Al^{3+}, F^-, In^{3+}, Ca^{2+} Cd^{2+}, Cr^{3+}	[27]
β-CDP-OVFH	1.5–330	0.44	Be^{2+}, Fe^{3+}	This work

Table 5
Determination of gallium in artificial sample and semiconductor sample ($P = 0.95$)

Sample	Added value ($\mu g\,ml^{-1}$)	Measured value ($n = 6$, $\mu g\,ml^{-1}$)	R.S.D. (%)	Standard value
Artificial sample 1	0.025	0.024 ± 0.004	0.38	
Artificial sample 2	0.025	0.027 ± 0.005	0.48	
Semiconductor sample[a]		48.50 ± 0.36	0.34	48.20

Artificial sample 1 ($\mu g\,ml^{-1}$): NO_3^- 25; Al^{3+} 2.5; Ba^{2+} 3; Ca^{2+} 2.5; Co^{2+} 0.5; Ga^{3+} 0.025; artificial sample 2 ($\mu g\,ml^{-1}$): In^{3+} 2.5; NO_2^- 25; Ba^{2+} 3; Cd^{2+} 0.5; Zn^{2+} 0.05; Ga^{3+} 0.025.

[a] Semiconductor gallium arsenide doped with silicon containing 48.20% gallium unit ($g\,g^{-1}$).

The diluted samples were then determined fluorimetrically by the method developed above, the results are shown in Table 5.

The measured value was in good agreement with the standard value which indicated that the proposed method was reliable to determine trace amount of gallium.

4. Conclusion

In this paper, we applied β-CDP-OVFH as a host molecule to determine Ga^{3+} successfully. The question existing in some references that the same race elements such as Al^{3+} and In^{3+} seriously interfere the determination of Ga^{3+} by fluorimetry was solved effectively. The use of β-CDP-OVFH as a host molecule to determine small guest Ga^{3+} has the advantages of high sensitivity, good selectivity and stability. Therefore, the search of the new pattern of host molecule reagent using β-CDP as matrix has a widely applying foreground.

Acknowledgments

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