Efficient Detection of Trace Hg^{2+} in Water Based on the Fluorescence Quenching of Environment-friendly Thiol-functionalized Poly(vinyl alcohol) Capped CdS Quantum Dots Nanocomposite

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Using environment-friendly materials for sensing toxic metal ions has drawn significant attention in recent research. Herein, we present an aqueous synthesis of stable CdS quantum dots (QDs) using thiol-functionalized poly(vinyl alcohol) (PVA) as the unique capping ligand for the detection of trace Hg^{2+} in environmental water samples. The CdS QDs with an average size of 3.3 nm had good water-solubility and favorable fluorescence with a quantum yield of 32.8% and a longer luminescence lifetime of 31.9 ns. The fluorescence intensity of QDs aqueous solution in the 520 nm wavelength was quenched upon the addition of Hg^{2+} . Under the optimal conditions, the ratio of the blank fluorescence intensity to the quenched fluorescence intensity was linearly proportional to the Hg^{2+} concentration from 2 to 4000 nM with a detection limit of 1 nM. Also, many co-existing metal ions were not interfered with the detection of Hg^{2+} . This nanomaterial was successfully applied to the measurement of Hg^{2+} in water samples.

Keywords CdS quantum dots, environment-friendly polymer, mercury ions, fluorescence, detection

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Introduction

Recently, mercury has become widely used in many fields, such as thermometers, catalysts, mercury cell, and amalgams because of its specific chemical and physical properties. As we all know, mercury is one of the most dangerous pollutants among heavy metal ions, and water-soluble divalent mercuric ion (Hg^{2+}) is one of the most usual and stable forms of mercury pollution.¹ It has been demonstrated that Hg^{2+} can easily pass through the skin as well as respiratory and gastrointestinal tissues. Therefore, developing effective analytical methods for the sensitive detection of trace amounts of Hg^{2+} is an increasing demand, and is especially important.²

Up to now, considerable efforts have been devoted to develop methods for detecting Hg^{2+} based on different analytical techniques, such as inductively coupled plasma atomic emission spectrometry,³ atomic absorption spectrometry⁴ and surface-enhanced Raman scattering. However, these test methods often require complicated sample preparation steps, rigorous experimental conditions, sophisticated instrumentation, and well-trained individuals. In recent years, colorimetric methods involving using nanomaterials of gold (Au) or silver (Ag) noble

metal have been applied to detecting trace Hg^{2+} in actual samples.⁵ The fluorescence assay might be the best choice for Hg^{2+} detection due to its high sensitivity, reliability, fast analysis, low cost, being non-sample-destructing, and suitable for the real-time monitoring of anions and metal ions.⁶

Quantum dots (QDs) possess unique and excellent optical properties, such as high quantum yield of FL, tunable size-dependent emission and a longer fluorescence lifetime.⁷ In recent years, QDs have been used to detect various metal ions based on QDs quenching by analytes. Some studies involving water soluble QDs have been reported, but frequently with complex routes, toxic reagents or frequently using expensive precursors.⁸ Therefore, the development of facile and low-cost methods for producing water-soluble and environment-friendly QDs is an important key to improve the application of QDs in more extensive fields.

Poly(vinyl alcohol) (PVA) with excellent chemical and physical properties and low cytotoxicity is the largest synthetic water-soluble polymer in the world.⁹ PVA and its related products are good choices for preparing environment-friendly semiconductor nanocomposites due to its wide spectral range of optical transparency, biocompatibility and biodegradability, aiming at detecting environmental samples and biology applications.¹⁰ However, the relatively weak bonding ability of hydroxy groups with metal ions has significantly affected its stable conjugation with QDs, which will cause future

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nanoparticle aggregation. To solve the problem, a small molecule stabilizer needs to be added when PVA is used as a matrix for preparing QDs, which would lead to high cost, high toxicity and more complex steps. As stabilizer for the production of QDs, the use of chemically modified PVA with strong bonding ability is a good choice to avoid nanoparticle aggregation. -SH are strong bonding groups that bind IIB metal ions on the surface of commonly used nanocrystals, such as CdSe, CdS and CdSe/CdS core-shell nanocrystals.¹¹ However, the use of thiol-functionalized PVA as a stabilizer for the production of quantum dots nanomaterials is rarely unexplored.

Herein we report on the design and preparation of environment-friendly and water-soluble polymer-based QDs nanomaterials for the detection of Hg^{2+} . Thiol-functionalized PVA-stabilized CdS quantum dots (PVA-S-CdS) were synthesized based on the strong binding ability between cadmium ions and thiol groups in the aqueous phase. The structure, optical properties, and heavy metal response characteristics of PVA-S-CdS nanocomposites were studied. We investigated in detail the trace Hg^{2+} -sensing capabilities of a PVA-S-CdS aqueous solution. To the best of our knowledge, this is the first report to detect trace Hg^{2+} in water samples based on CdS nanocomposites using thiol-functionalized PVA as a capping ligand.

Experimental

Reagents and chemicals

PVA obtained from Aladdin Chemicals had a degree of polymerization of 1700 with a saponification value of 99% and an average molecular weight of 75000. It was washed with distilled water and then dried at 60°C before use. Mercaptoacetic acid was obtained from Kaixing Chemical Reagent Company in Tianjin. Acetic anhydride, cadmium acetate, sodium sulfide hydrate, and other analytical-grade chemicals were purchased from Beijing Chemical Works. All metal salts, except for Hg^{2+} , were adopted nitrate, and were of analytical-reagent grade or the highest available purity. All of the chemicals were used directly without further purification. Double-distilled deionized water was used throughout.

Apparatus

IR spectra were recorded on a Spectrum One NTS FI-IR spectrophotometer (PerkinElmer, USA). ^1H NMR experiments were performed on an AM-400 MHz BB Bruker. GPC measurements were performed at a GPCV2000 Gel Permeation Chromatography apparatus (Waters, USA). XRD data were collected on a D/max-III A X-ray diffractometer (Rigaku Corp., Japan). TEM images and energy dispersive X-ray (EDX) measurements were taken using a JEM-1200EX (JEOL, Japan). TG/DTA measurements were performed at a heating rate of 10°C min⁻¹ under nitrogen with a TG/DTA6300 (Japan). UV-vis spectra were acquired using a UV-2550 Vis-spectrometer (Shimadzu, Japan). FL measurements were performed with an LS-55 spectrofluorometer (PerkinElmer, USA), which was equipped with a Xenon lamp, a recorder, dual monochromators, and a quartz cell (1 × 1 cm). PL quantum yields (QY) was measured using rhodamine B in water, according to previously described methods.¹² All pH values were measured by using a pHs-3C digital pH meter (Shanghai, China). The time-resolved fluorescence decay was obtained with a high resolution Edinburgh Instruments FLS920 spectrofluorometer with a 360-nm laser as the excitation source.

Scheme 1 Synthesis of PVA-SH and PVA-S-CdS.

Procedure

At first, thiol-functionalized poly(vinyl alcohol) (PVA-SH) was prepared using a modified method described by Dominguez.¹³ Approximately 2.00 g of PVA (molar unity of ~44 g/mol) was added to 50 mL of redistilled water in a 100-mL flask. Then, the mixture was heated to (80 ± 5)°C under slow magnetic stirring and kept for 1 h when a clear solution was reached. A 36% acetic acid solution was obtained by adding 18 mL acetic acid into 32 mL of redistilled water.

A mixture of 10 mL of a 36% acetic acid solution, 18 mL of acetic anhydride [$\text{CH}_3\text{CO}_2\text{O}$], 0.2 mL of concentrated sulfuric acid (H_2SO_4) and 20 mL of mercaptoacetic acid (SHCH_2COOH) were put into a 250-mL flask and stirred to uniformity. The flask was then maintained at 30°C, while the clear PVA solution mentioned above prepared was added with a dropping funnel for 30 min. The reaction mixture was stirred at 30°C for 24 h. Then, the transparent colorless solution was allowed to precipitate in excessive alcohol to provide white deposit matter. After centrifugal settling, the solid was then put into a Soxhlet's extractor and extracted with methanol for at least 12 h to eliminate all non-covalently bounded mercaptoacetic acid in PVA. The desired product was ultimately synthesized *via* vacuum drying, as illustrated in Scheme 1. IR (KBr), $\tilde{\nu}/\text{cm}^{-1}$: 3330, 1663 (PVA-OH); 2940, 2910 ($-\text{CH}_2-$, $-\text{CH}-$); 1712, 1650 (acetate, C=O); 1150, 1096 (C-O). ^1H NMR (400 MHz, D_2O), δ : 1.5 – 1.8 (backbone, $-\text{CH}_2-$), 3.3 (thiol ester, $-\text{CH}_2-$), 3.8 – 4.1 (backbone, $-\text{CH}-$). The number of average molecular weight (M_n) of PVA-S-CdS was 57150 g/mol and the polydispersity index (PDI) was 2.92.

The synthetic route of PVA-S-CdS is shown in Scheme 1 and the procedure for the preparation of PVA-S-CdS is shown in Scheme S1 (Supporting Information). The details were as follows: 0.1 g of PVA-SH (molar unity of ~118 g/mol) was added to 50 mL of redistilled water in a 100-mL flask; the mixture was heated under slow magnetic stirring until a clear solution was obtained. Then, 0.0114 g of cadmium acetate [$\text{Cd}(\text{CH}_3\text{COO})_2$] was added into the prepared PVA-SH solution and stirred at room temperature for 24 h. Then, 0.012 g of sodium sulfide hydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) dissolved in 10 mL redistilled water was slowly added into the mixture and stirred under N_2 atmosphere for 5 h at 35°C. The ultimate solution was light yellow and transparent. The number of average molecular weight (M_n) of PVA-S-CdS was 79180 g/mol and the polydispersity index (PDI) was 1.69. PVA-S-CdS could emit bright-yellow light under UV irradiation whether in solution, granules and film states, as shown in Scheme S1 (Supporting Information).

The preparation method of PVS-S-CdS film was as follows: a glass substrate was immersed in EtOH ultrasonic for 10 min, rinsed extensively with ultrapure water and dried with nitrogen. A nanocomposite that could be film-forming was prepared from a clear, homogeneous solution by casting and drying the film on a glass slide and prepared high-performance PVS-S-CdS film.

Fig. 1 TEM micrographs of PVA-SH and PVA-S-CdS with different sizes.

Under the optimal condition, a fluorescence measurement for the detection of Hg^{2+} ions was obtained, as described in the *Procedure* part (Supporting Information).

Results and Discussion

Characterization and optical properties of PVA-S-CdS QDs

All changes in the FT-IR spectra of the PVA, PVA-SH and PVA-S-CdS QDs indicated that the hydroxyl groups of PVA were practically replaced by -SH. After adding Cd^{2+} and S^{2-} ions, no obvious spectral difference was observed, but the absorption band at 3330 cm^{-1} became narrower, which indicated a coordination reaction between PVA-SH and Cd^{2+} in Fig. S1 (Supporting Information).¹⁴ The recorded EDX spectrum of the PVA-SH displays a clear S line at around 2.2 keV, which indicated that the -SH group was successfully connected on the PVA. Besides C, O and S, no traces of other elements were found in the spectra, which confirmed the purity of the PVA-SH. Compared with the EDX spectrum of PVA-SH, there was a new peak for Cd in addition to C, O and S atoms in the EDX spectrum of the PVA-S-CdS in Fig. S2 (Supporting Information), which proved the conjugation of the quantum dots with PVA-SH. The peaks of "C" and "O" were corresponding to PVA-SH capping agent, which confirms the covering of CdS QDs with a polymer. In the XRD pattern of PVA-S-CdS, there are peaks with 2θ values of 26.6° , 31.5° , 43.9° and 64.2° , corresponded to the (111), (200), (220) and (400) crystalline planes of CdS in Fig. S3 (Supporting Information). These peaks could be indexed to cubic CdS, which are consistent with the literature data of JCPDS 10-0454.¹⁵ The results of the thermogravimetric analysis (TG) and the differential thermal analysis (DTA) of PVA-SH and PVA-S-CdS indicated that the incorporation of CdS nanoparticles significantly altered the thermal properties of PVA-SH in Fig. S4 (Supporting Information).

Figure 1 shows TEM images of PVA-SH and PVA-S-CdS with different sizes. Compared with the TEM images of pure PVA-SH, there are large numbers of nanoparticles on the images of PVA-S-CdS, which showed that the nano-CdS formed in the

Fig. 2 UV-vis spectra of PVA-SH and PVA-S-CdS. Inset, Optical band gap energy.

PVA-SH matrix. The particles are spherical, monodispersed and distributed with an average particle diameter of about 5 nm. The particles exhibit lattice fringes with d spacings of 0.333 nm, corresponding to (111) reflection of cubic phase CdS, which is consistent with the XRD results.

The UV-vis absorption spectra of PVA-SH and PVA-S-CdS QDs are shown in Fig. 2, respectively. The results showed that pure PVA-SH had no absorption within the measured range (250 – 600 nm). Apparently, the absorption between 250 and 500 nm for PVA-S-CdS was attributed to CdS nanoparticles formed on PVA-SH, and the polymer matrix did not change the optical characteristics of CdS. Moreover, the average size of semiconductor nanoparticles can be estimated by the optical band gap from absorption coefficient data as a function of the wavelength using the Tauc relation:^{16,17}

$$\alpha h\nu = A(h\nu - E_{g,\text{QD}})^{1/2}. \quad (1)$$

Fig. 3 Absorption spectra and fluorescence spectra of PVA-S-CdS in aqueous solutions and in film.

Here, A is a relative constant for the material, $E_{g,QD}$ (eV) is the optical band gap of the nanoparticles, α is the absorption coefficient and $h\nu$ is the photon energy. Hence, the values of optical band gap can be obtained from the plots of $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the straight portion of the graph to $h\nu$, i.e. at $\alpha = 0$ as shown in Fig. 2 (inset). It could be observed that the synthesized CdS QDs were with the calculated average band gap of $E_{g,QD} = 2.84$ eV, which was higher than the bulk value of 2.4 eV reported for CdS. Thus, the “blue-shift” of about 0.44 eV proved that the CdS quantum dots were successfully synthesized under these conditions. Next, the size of quantum dots was calculated according to Brus equation,¹⁸ an average diameter of 3.3 nm was obtained for PVA-S-CdS QDs, which indicated the quantum-confined effect.

Due to the light-emitting behavior of CdS nanoparticles at a specific wavelength,^{19,20} the formation of PVA-S-CdS QDs nanoparticles in this work could also be confirmed by fluorescence (FL) spectroscopy. Figure 3 shows excitation and emission spectra of the PVA-S-CdS in aqueous solution and in film, respectively. The PVA-S-CdS samples exhibit a sharp photoemission peak at 525 nm in aqueous solution and a broad peak at 500 nm in film at the excitation wavelength of 380 nm. Because pure PVA was no fluorescence at between 360 to 650 nm,²¹ the emission peaks of PVA-S-CdS are assigned to the electron-hole recombination of CdS, which clearly indicated the formation of CdS nanoparticles on the PVA-SH. Compared with the emission of PVA-S-CdS in aqueous solution, a blue shift of 25 nm was observed for PVA-S-CdS in film, which indicated the quantum confined effect of the PVA-S-CdS films.²² Furthermore, the quantum yield and the luminescence lifetime of PVA-S-CdS QDs were 32.8% and 31.9 ns, respectively. The longer decay time implies a better removal of quenching defects, possibly from uncoordinated S^{2-} sites, from the surface of CdS QDs capped with PVA-SH, resulting in a high quantum yield.²³ Considering the instability of samples at relatively high or low pH value, a neutral condition was selected in the present work in Fig. S5 (Supporting Information).

Determination of Hg^{2+} by fluorescence (FL) spectra

Figure 4 shows that the emission intensities of PVA-S-CdS are significantly weakened with the increase of the concentration of Hg^{2+} , indicating that the system could be used as a new fluorescence sensor for a sensitive determination of Hg^{2+} . In addition, the addition of different metal ions to a PVA-S-CdS solution does not cause any obvious changes of the fluorescence intensity, except for Hg^{2+} , which demonstrated that other

Fig. 4 Fluorescence spectra change of the system upon the addition of various concentrations of Hg^{2+} . The concentrations of Hg^{2+} (nM): (from 0 to 4000) are 0, 2, 8, 60, 100, 200, 400, 600, 800, 1000, 2000, 3000, 4000, respectively. Inset, Linear relationship between the relative fluorescence intensity (I_0/I) and the concentration of Hg^{2+} ($C_{Hg^{2+}}$).

divalent metal ions had no obvious interference on fluorescence detecting Hg^{2+} with PVA-S-CdS QDs in Fig. S6 (Supporting Information). Moreover, it was found that there is good linear relationship between the changes of the relative fluorescence intensity (I_0/I) and the concentration of Hg^{2+} ($C_{Hg^{2+}}$) from Fig. 4 (inset). The limit of detection (LODs) with 1.0×10^{-9} mol L^{-1} was obtained according to the general procedure. The linear range for Hg^{2+} was from 2.0 nM to 4000 nM and the coefficient of correlation was 0.9983. Table 1 shows that in a comparison of modified reagents, the linear range and detection limit of several selected fluorometric methods for Hg^{2+} detection with QDs as a probe are listed. It can be clearly found that this present method has a wider concentration linear range. Although a QDs probe modified by *N*-acetyl-L-cysteine also has a lower detection limit (1.0 nM), microwave-assisted synthesis is not a mild method compared with the soluble synthesis in ordinary temperatures. Some polymer, such as poly(dimethyldiallyl-ammonium chloride) and 2-(pyridin-2-ylmethyl)imidazo[1,5-a]-pyridine-3(2*H*)-thione, has been used as a modifier to determine Hg^{2+} , but these reagents are not more environment-friendly and expensive than poly(vinyl alcohol).

Table 1 Comparison of several selected fluorometric methods for the detection for Hg^{2+} with QDs as the probe

Modified reagent	Linear range/ $10^{-9} \text{ mol L}^{-1}$	LOD/ $10^{-9} \text{ mol L}^{-1}$	Ref.
Thioglycolic acid	62.5 – 2500	20.3	24
3-Mercaptopropionic acid	5 – 30	3.1	25
<i>N</i> -Acetyl-L-cysteine	5.0 – 1000	1.0	26
Denatured ovalbumin	8 – 300	4.2	27
Poly(dimethyldiallylammonium chloride)	10 – 1000	4.5	28
2-(Pyridin-2-ylmethyl)imidazo-[1,5-a]pyridine-3(2 <i>H</i>)-thione	0 – 400	6.5	29
Thiol-functionalized poly(vinyl alcohol)	2 – 4000	1.0	This present

Real sample analysis

Tap water without any pretreatment was directly used to prepare a Hg^{2+} contaminated stock solution for investigating the practical application of this fluorescence sensor. According to a spiked measurement, the recovery was determined three times, respectively, by adding the standard Hg^{2+} in real water samples. As shown in Table 2, the recovery values are satisfactory (93 – 108%), demonstrating that this fluorescence method is suitable for Hg^{2+} detection in real water samples.

Moreover, another experiment was carried out to determine Hg^{2+} in Yellow River in the Xigu area and the Annin area near our university (Lanzhou, China). As shown in Table 2, the concentration of Hg^{2+} was $4.1 \times 10^{-7} \text{ mol L}^{-1}$, and the recoveries values were in the range from 85 to 112% in the Xigu area. While the concentration of Hg^{2+} was $1.2 \times 10^{-7} \text{ mol L}^{-1}$, which is much lower than that in the Xigu area, and recoveries values were from 89 to 110% in the Annin area. The possible reason was that there was a large-scale industrial zone in Xigu and the large amount of discharging waste water lead to the higher content of Hg^{2+} than that in other areas. Furthermore, the recovery values of the testing concentration of Hg^{2+} in the Yellow River were broader than that in tap water, because there were many interfering ions and organic matter in the Yellow River. It can be seen that the results obtained by the present method were in good agreement with those determined by cold vapor atomic fluorescence spectrometry (CV-AFS). All of the results indicate that the present method could be applicable to the ultra-sensitive detection of Hg^{2+} in environmental samples and that is environment-friendly, simple, and rapid.

Analytical performance of PVA-S-CdS QDs and quenching mechanism

The interaction of PVA-S-CdS QDs with Hg^{2+} was studied in order to examine the selectivity. Experiments based on fluorescence measurements showed that, even at very low concentrations, Hg^{2+} was capable of reacting with the QDs, and gave rise to the observed fluorescence emission quenching phenomenon. This phenomenon arose from the binding of Hg^{2+} ions to the surface of QDs as an acceptor and changes the surface state of QDs, which could be described using the well-known Stern-Volmer equation,

$$I_0/I = 1 + K_{\text{SV}}[Q], \quad (2)$$

where I_0 and I are the fluorescence intensity in the absence and presence of the quencher (Hg^{2+} ions), K_{SV} is the Stern-Volmer quenching constant and Q is the concentration of the quencher. The fluorescence-quenching phenomenon could be used to

Table 2 Results for determinations in real water samples

Sample	$C_{\text{Hg}^{2+}}/\text{nM}$				Recovery, %
	Found	Added	Sum	CV-AFS	
Tap water	28.9	50.0	82.5	83.0	107.2
		150.0	191.4	192.3	108.3
		250.0	260.3	258.4	92.6
Yellow River (Xigu area)	414.2	50.0	456.4	452.8	84.4
		150.0	557.2	560.4	95.3
		250.0	694.1	700.3	111.9
Yellow River (Anning area)	123.6	50.0	170.8	168.2	94.4
		150.0	273.6	276.2	100.0
		250.0	347.2	351.5	89.4

determine the quencher if a linear relationship were to be established between the concentration of the metal ion of interest and the fluorescence quenching according to the Stern-Volmer equation. In this case, the slope of the linear relationship was proportional to K_{SV} if the intercept approaches closely to 1. Evidently, the sensitivity was directly related to the K_{SV} value, and the higher sensitivity is proportional to a greater K_{SV} value. In our work, the quencher interacts with PVA-S-CdS QDs according to the Stern-Volmer equation. A plot of I_0/I as a function of $[\text{Hg}^{2+}]$ was linear ($R^2 \geq 0.9983$) with 1.02 intercept and $K_{\text{SV}} = 6 \times 10^5$, which suggested that Hg^{2+} present in the medium acts as a quencher of the fluorophore.

Two different quenching mechanisms for electron-transfer process and ion-binding interaction have been used to explain the quenching phenomena of functionalized QDs.³⁰ Different from the mechanisms of the electron-transfer process, while the fluorescence of QDs was quenched by metal ions due to the ion-binding interaction, the emission wavelength exhibits an obvious red shift with changes in the fluorescence spectra profiles.³¹ Herein, no significant spectral shift was noted in the emission wavelength (emission band centred 525 nm with the excitation 380 nm) upon the addition of Hg^{2+} to the PVA-S-CdS solution. Thus, the quenching phenomenon in our case can possibly be attributed to the effective electron transfer from PVA-SH to Hg^{2+} . This indicates that the electron transfer from surface traps of PVA-S-CdS QDs to Hg^{2+} facilitates a nonradiative recombination of excited electrons (e^-) in the conduction bands and holes (h^+) in the valence band, which results in the fluorescence quenching of QDs.³²

Conclusions

In conclusion, a novel, water-soluble, and environment-friendly fluorescent polymer QDs (PVA-S-CdS), which exhibited excellent selectivity and sensitivity to Hg^{2+} in aqueous solution, was successfully designed and synthesized *via* a simple method. Based on the Stern-Volmer relationship between PVA-S-CdS and Hg^{2+} , the calibration graph was linear in the range of 2 – 4000 nM for Hg^{2+} , and the detection limit was 1 nM, which indicated that it could meet the selectivity requirements for environmental application, and also was sensitive enough to quickly detect trace Hg^{2+} exposure to the environment, such as in tap water and the Yellow River.

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Supporting Information

The procedure for the preparation of PVA-S-CdS and photographs of PVA-S-CdS in solution, granules and film states under UV irradiation, and fluorescence measurement for detection of Hg^{2+} ions, FT-IR spectra of the PVA, PVA-SH and PVA-S-CdS QDs, the X-ray diffraction patterns of PVA-SH and PVA-S-CdS, the thermogravimetric analysis (TG) and the differential thermal analysis (DTA) of PVA-SH and PVA-S-CdS, pH-influenced fluorescence emission, ion-selective sensing systems. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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