

A novel fluorescence reagent, 10-hydroxybenzo[*h*]quinoline-7-sulfonate, for selective determination of beryllium(II) ion at pg cm^{-3} levels

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A facile method has been developed for the highly sensitive and selective determination of ultratrace Be(II) ion using a new fluorimetric reagent, 10-hydroxybenzo[*h*]quinoline-7-sulfonate (HBQS), under extremely alkaline conditions, at pH 12.0. This reagent is quite suitable for the very small ion, Be(II), to form a 6-membered chelate ring, compatible with a high fluorescence yield. The stoichiometry of the chelate is 1:1 for Be–HBQS at pH 12.0. The calibration graph gave a wide linear dynamic range, 2–100 nmol dm^{-3} of Be(II) ion with the detection limit ($3s$ blank) of 0.52 nmol dm^{-3} , or 4.7 pg cm^{-3} . The excellent sensitivity and toughness toward the matrix influence were demonstrated using the artificial sample solutions for air-dust. Coupled with the simple masking procedure using EDTA, the method enables one to determine Be(II) ion at nanomolar levels in the presence of metals at the natural abundance levels in air–dust samples, typically Al, Ca, Cu, Fe, Mg, Pb, and Zn at 130, 150, 1.0, 70, 33, 3.0, and 8.0 $\mu\text{mol dm}^{-3}$, respectively, in the final solution. The proposed method was successfully applied to the determination of Be in urban air.

Introduction

Beryllium is a unique and valuable metal which plays important roles in nuclear, aerospace, and the electronics industries. However, Be and its compounds are very toxic, especially to the human lung and skin, and possibly cause cancer; Be is classified in Group 2A by IARC (International Agency for Research on Cancer).¹ In this connection, the allowable concentration of Be in workplace air is regulated in Japan at $<2 \text{ mg m}^{-3}$ for 8 h exposure,² which is about 100 times lower than that of other toxic metals, such as Cd or Pb.¹ Therefore, the monitoring of Be is a very important task for environmentalists and occupational hygienists.

Many methods for determination of a trace amount of Be have been reported: voltammetry,³ spectrophotometry,^{4–8} fluorimetry,^{9–12} atomic absorption spectrometry (AAS),^{11,13–18} inductively coupled plasma atomic emission spectrometry (ICP-AES),¹⁵ inductively coupled plasma mass spectrometry (ICP-MS),¹⁹ and gas chromatography with electron capture detection (GC-ECD).²⁰ However, most of the above mentioned methods do not seem to satisfy the requirements for environmental monitoring of Be in the terms of facility, sensitivity, matrix toughness and cost-effectiveness. The analytical techniques frequently employed for the ultratrace level determination of Be require some expensive and sophisticated instrumentation, such as electrothermal AAS or ICP-MS. Only a few laboratories, however, have access to such instruments and to the experienced operators required. In addition, even in those methods, preliminary separation and preconcentration processes are most often necessary to guarantee accuracy for the pg cm^{-3} range of Be in complicated matrixes such as environmental samples. Previously, we have reported the simple and cost-effective method for determination of ultratrace Be(II) ion: reversed-phase high-performance liquid chromatography (RP-HPLC) with photometric detection using 1-(2,4-dihydroxy-1-phenylazo)-8-hydroxy-3,6-naphthalene disulfonate (H-resorcinol) as a precolumn chelation reagent.²¹

An alternative approach to the sensitive detection of ultratrace Be with simplicity and cost-effectiveness is solution spectrofluorimetry. However, the existing fluorimetric methods do not seem to allow the requisite conditions for environmental analysis, detectability for the pg cm^{-3} range with compatibility to matrix toughness.^{9–12}

We have found that 10-hydroxybenzo[*h*]quinoline (HBQ) has excellent properties as a highly sensitive and specific fluorescence reagent for Be(II) ion due to the large π -electron system and the formation of a six-membered chelate ring, which is well-fitted to the extremely small Be(II) ion. However, the practical applicability seems to be limited because of the low solubility of this reagent in aqueous solutions where most analytical processes are performed. For this reason an attempt has been made to prepare the sulfonated derivative, 10-hydroxybenzo[*h*]quinoline-7-sulfonate, hereafter called HBQS (HL[−], Fig. 1), which is most probably compatible with the above-mentioned purpose of designing a fluorescence reagent.

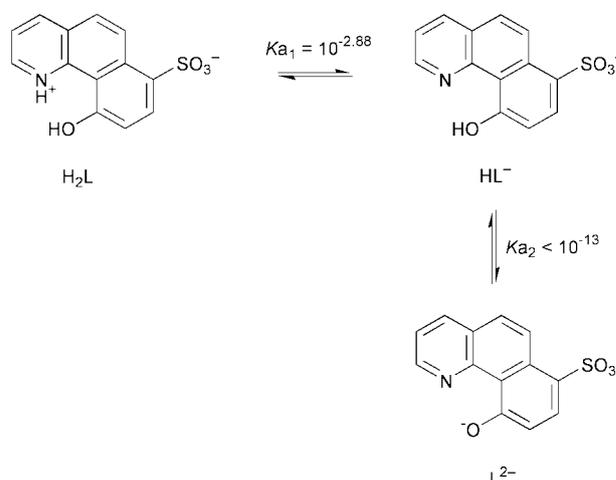


Fig. 1 Structures of 10-hydroxybenzo[*h*]quinoline-7-sulfonate with the acid dissociation constants at 298 K and $I = 0.10$.

This paper describes a facile method to determine ultratrace Be(II) ion using HBQS as the fluorimetric reagent; a 3s blank detection limit of 0.52 nmol dm⁻³, or 4.7 pg cm⁻³ in complicated matrixes, is readily accessible with no pre-concentration or preliminary separations. The method described here has advantages over any existing methods for Be in terms of sensitivity, specificity, and ease of operation.

Experimental

Apparatus

The fluorescence measurements were made with an Aminco-Bowman Model FA-257 luminescence spectrometer (SLM-Aminco, NY, USA) equipped with a 150 W xenon lamp and a 1 cm quartz cell at a bandpath of 4 nm for both excitation and emission. The pH of the solutions used was measured with a Model M-13 pH meter from Horiba Corp. (Kyoto, Japan).

Reagents and solutions

The standard solution of Be(II) ion (0.0100 mol dm⁻³) was prepared from anhydrous beryllium chloride (>99 % from Mitsuwa Pure Chemical Co., Tokyo, Japan) in 0.01 mol dm⁻³ hydrochloric acid solution. Other metal ion solutions (0.0100 mol dm⁻³) for the interference studies were prepared from the chlorides or the nitrates. The composition and concentrations of 17 metal ions in the artificial surrogate solution for air-dust samples are shown in Table 1. This solution contains the main metals found in air-dust digestion solution.²² The reagent, HBQS (HL⁻), was synthesized in a similar manner to that for 8-hydroxyquinoline-5-sulfonic acid;²³ 4 g of 10-hydroxybenzo[*h*]quinoline (from Tokyo Kasei Co. Ltd., Tokyo Japan) was gradually dissolved in a mixture which consists of 1.0 ml of fuming sulfuric acid (60%) and 10.5 ml of concentrated sulfuric acid at a temperature below 10 °C. After stirring for 24 h at 8 °C, the mixture was poured over 400 g of crushed ice. A yellow precipitate was filtered off, washed well with cold water and recrystallized from hot diluted hydrochloric acid (about 5%) several times. The final product was purified by column chromatography on a LiChrosorb RP-18 (Cica-Merck) with an eluent of 65:35 (m/m) water-methanol. The stock solution of HBQS was prepared by dissolving in slightly alkaline aqueous

solution to give a concentration of 1 mmol dm⁻³. Disodium EDTA from Dojindo Laboratories (Kumamoto, Japan) was used as the 0.01 mol dm⁻³ stock solution. Sodium hydroxide solution (0.10 mol dm⁻³) was prepared by dissolving the pellets in water. All other reagents and solvents used were of guaranteed reagent grade. Doubly distilled water was used throughout this study.

Recommended procedure

To a slightly acidic aqueous solution containing Be(II) ion, in a 25 cm³ volumetric flask, was added 5.00 cm³ of 0.01 mol dm⁻³ disodium EDTA solution, 1.25 cm³ of the HBQS solution (1 mmol dm⁻³), and 2.50 cm³ of 0.10 mol dm⁻³ NaOH solution in order to adjust the final pH value to 12.0. The solution was diluted with doubly distilled water to volume and allowed to stand for 15 min at room temperature. The fluorescence intensity was measured at 478 nm with excitation at 384 nm. All fluorescence data in this work were uncorrected for the light source and the photomultiplier response, these being represented in the arbitrary units for the instrument employed.

Application to air analysis for Be

Sampling was made at the air-monitoring station in the urban area of Sendai City, which was routinely controlled by Sendai Municipal Institute of Public Health (SMIPH). Airborne particulates (less than 10 µm in size) were collected on a quartz-fiber filter (Dylec 2500-QAST, 110 mm in diameter) attached to a low volume air sampler at the air suction rate of 20 dm³ min⁻¹ for 25 d; such long-term sampling was established by SMIPH for air surveillance depending on the relatively low sensitivity of routinely operated methods, such as AAS. The quarter of the quartz filter carrying airborne particulates was heated with 30 cm³ of HNO₃ (1 + 1) and 5 cm³ of H₂O₂ (30%) for 1 h. The solution was filtered and the residue was similarly treated with 20 cm³ of HNO₃ (1 + 1). All filtrates were collected and evaporated under heating, but avoiding dryness. The solution obtained was made up to 20.0 cm³ with a dilute HNO₃ solution (1 + 50). A 5.00 cm³ aliquot of this acid digestion solution was taken and analyzed for Be by the proposed method. The strong acidity of the sample solutions was neutralized with 5 mol dm⁻³ NaOH solution before the analysis.

Caution

Be and the compounds are very harmful so that handling of these compounds should be made in a ventilating hood. In addition, the waste solutions of the salt and the chelate should be stored in large polyethylene or Teflon bottles. At this stage physiological effects of HBQS are not known, hence careful handling of this compound is strongly suggested.

Results and discussion

Spectral characteristics of the chelate system

Excitation and emission spectra of the Be(II)-HBQS system are shown in Fig. 2 with those of HBQS. The excitation and emission maxima of the Be-HBQS chelate are at 384 nm and 478 nm, respectively. The emission maximum of the reagent, HBQS, is 575 nm with the excitation maximum at 360 nm. The reagent blank is considerably low due to the poor fluorescence yield of the reagent and the large shift of the emission peak from 575 to 478 nm on the chelate formation. It seems to be unusual that the emission peak is blue-shifted on chelate formation. The

Table 1 Composition and concentrations of the artificial surrogate solution containing main metals found in air-dust^a

Metal ion	Metal concentration in solution/µmol dm ⁻³	Metal concentration in solution/µg dm ⁻³	Metal concentration in air/ng m ⁻³
K(I)	5 000	200 000	4 000
Ca(II)	1 500	60 000	1 200
Al(III)	1 300	35 000	700
Fe(III)	700	39 000	780
Na(I)	400	9 200	180
Mg(II)	330	8 000	160
Zn(II)	80	5 200	100
Pb(II)	30	6 200	120
Mn(II)	20	110	2.2
Cu(II)	10	640	13
Ba(II)	10	1 400	28
V(V)	3.0	150	3.0
Ni(II)	1.4	82	1.6
Cd(II)	0.70	79	1.6
Co(II)	0.40	24	0.48
Se(IV)	0.30	24	0.48
Be(II)	0.0250	0.225	0.00450

^a Acidified with HCl (0.01 mol dm⁻³).

native fluorescence of 10-hydroxybenzo[*h*]quinoline at 585 nm in ethanol arises from the excited state with intramolecular proton transfer concomitantly with a fast interchange process between the keto–enol tautomers.²⁴ The complexation with the Be(II) ion, replacing the hydroxyl proton with the metal, most likely disturbs the four-level electronic state proposed by Sytnik and Kasha²⁴ for the native fluorescence emission, making the ordinary two-level system for the blue-shifted chelate emission. This is most probably also the case for the sulfonated analog, HBQS.

Optimum complexation conditions

The effects of pH on the fluorescence intensity of the Be(II)–HBQS system are shown in Fig. 3 with those of the reagent blank, HBQS alone. The fluorescence intensity increases with increasing pH at 4.7–12.0 and decreases over pH > 12.5 passing through a maximum at pH 12.0. The reagent blank signals are by contrast very low and nearly constant over the above pH range. The predominant species of HBQS present in solution over the pH range is HL[−], because the acid dissociation constants determined spectrophotometrically, $K_{a1} = ([H^+][HL^-])/[H_2L]$ and $K_{a2} = ([H^+][L^{2-}])/[HL^-]$ are $10^{-2.88}$ and $< 10^{-13}$ at 298 K and $I = 0.10$, respectively. In this work, the sample pH was adjusted to 12.0 with NaOH solution. Under the conditions described, the composition of the Be chelate is 1 : 1, being confirmed with both the continuous variation and the molar-ratio methods. The complexation reaction at room temperature is instantaneously completed on adjusting the

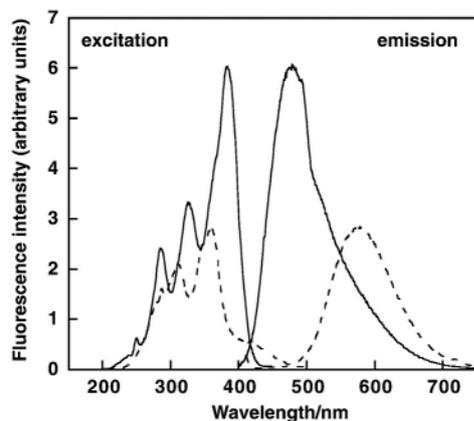


Fig. 2 Fluorescence spectra of the Be(II)–HBQS system at pH 12.0. Solid lines, the chelate spectra; $[HBQS]_T = 50.9 \mu\text{mol dm}^{-3}$, $[Be]_T = 0.500 \mu\text{mol dm}^{-3}$, $\lambda_{\text{ex}} = 384 \text{ nm}$, $\lambda_{\text{em}} = 478 \text{ nm}$. Broken lines, the reagent spectra at $50.9 \mu\text{mol dm}^{-3}$; $\lambda_{\text{ex}} = 360 \text{ nm}$, $\lambda_{\text{em}} = 575 \text{ nm}$.

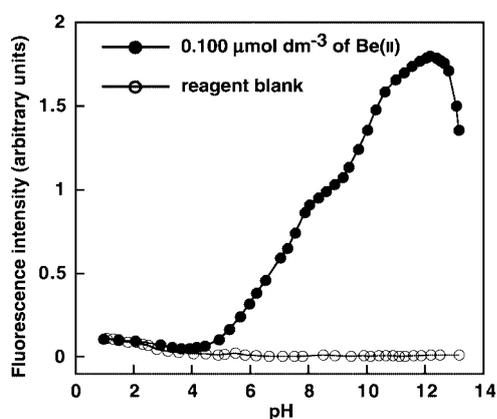


Fig. 3 Effects of pH on the fluorescence intensity of the Be(II)–HBQS system at $\lambda_{\text{ex}} = 384 \text{ nm}$ and $\lambda_{\text{em}} = 478 \text{ nm}$. $[HBQS]_T = 50.9 \mu\text{mol dm}^{-3}$. $[Be]_T = 0.100 \mu\text{mol dm}^{-3}$.

sample pH to 12.0. The fluorescence intensity is stable at least for 24 h.

Calibration graph and sensitivity

The calibration graph gave the wide linear dynamic range ($2\text{--}100 \text{ nmol dm}^{-3}$), which was expressed by the equation:

$$I = 0.0380 + (1.76 \times 10^7)C_{\text{Be}} \quad (r = 0.9999)$$

where C_{Be} is the total concentration of Be in the final solution. Without any preconcentration, the detection limit ($3s$ blank) for the Be ion was extremely low such as $0.52 \text{ nmol dm}^{-3}$, or 4.7 pg cm^{-3} . The limit of quantitation ($10s$ blank) was calculated to be 1.7 nmol dm^{-3} (16 pg cm^{-3}). This excellent sensitivity is due to the high fluorescence yield of the chelate and the sufficiently lowered reagent blank signals, which actually guarantee the low background noise for the detection of the ultratrace Be(II) ion. The detection limit reported here is far lower than those previously reported for fluorimetric methods.^{9–12} Moreover, the value is still lower than those obtained with routinely operated AAS (including graphite furnace AAS) and ICP-AES.^{11,13–18} Although the sensitivity in fluorimetry is

Table 2 Influence of interfering ions on the determination of Be(II) ion at 5 nmol dm^{-3}

Diverse ions	Concentration/ mmol dm^{-3}	Molar ratio to Be(II)	Be found/ nmol dm^{-3} $\bar{x} \pm s^a$	Recovery (%) $\bar{x} \pm s^a$
<i>Cations—^b</i>				
Al(III)	0.50	100 000	5.00 ± 0.07	100 ± 1.4
B(III)	0.50	100 000	5.98 ± 0.15	120 ± 3.1
	0.050	10 000	4.99 ± 0.10	100 ± 1.9
Ca(II)	0.50	100 000	5.01 ± 0.13	100 ± 2.6
Cd(II)	0.50	100 000	4.93 ± 0.07	99 ± 1.4
Co(II)	0.50	100 000	5.08 ± 0.07	102 ± 1.4
Cu(II)	0.50	100 000	4.87 ± 0.07	97 ± 1.5
Fe(III)	0.50 ^c	100 000	6.37 ± 0.01	127 ± 1.9
	0.050	10 000	5.08 ± 0.10	102 ± 2.0
Mg(II)	0.50	100 000	4.99 ± 0.13	100 ± 2.6
Mn(II)	0.50	100 000	4.91 ± 0.10	98 ± 1.9
Ni(II)	0.50	100 000	4.82 ± 0.11	96 ± 2.3
Pb(II)	0.50	100 000	4.94 ± 0.11	99 ± 2.2
V(V)	0.50	100 000	4.99 ± 0.13	100 ± 2.6
Zn(II)	0.50	100 000	5.05 ± 0.09	101 ± 1.7
<i>Anions—</i>				
Cl [−]	100	20 000 000	5.10 ± 0.14	102 ± 2.8
F [−]	100	20 000 000	5.19 ± 0.08	104 ± 1.7
NO ₃ [−]	100	20 000 000	5.10 ± 0.10	102 ± 2.0
PO ₄ ^{3−}	100	20 000 000	4.91 ± 0.12	98 ± 2.1
SO ₄ ^{2−}	100	20 000 000	4.87 ± 0.16	97 ± 3.1
SiO ₃ ^{2−}	10	2 000 000	4.96 ± 0.12	99 ± 2.4
Citrate	10	2 000 000	4.98 ± 0.10	100 ± 2.0
EDTA	10	2 000 000	4.90 ± 0.09	98 ± 1.9
Oxalate	10	2 000 000	5.11 ± 0.08	102 ± 1.6
Tartrate	10	2 000 000	4.86 ± 0.06	97 ± 1.2

^a $\bar{x} \pm s$: Mean \pm standard deviation, $n = 10$. ^b EDTA (2 mmol dm^{-3}) was added as masking agent. ^c The solution was turbid.

Table 3 Precision and recovery data of Be determination for the artificial surrogate solution for air–dust^a

Be spiked/ nmol dm^{-3}	Be total/ nmol dm^{-3}	Be found/ nmol dm^{-3} $\bar{x} \pm s^b$	Recovery (%) $\bar{x} \pm s^b$
—	2.50	2.49 ± 0.28 ($n = 10$)	100 ± 11 ($n = 10$)
2.50	5.00	5.27 ± 0.48 ($n = 3$)	104 ± 9 ($n = 3$)
7.50	10.0	10.3 ± 0.058 ($n = 3$)	103 ± 0.1 ($n = 3$)

^a 2.5 ml of the standard solution (Table 1) was taken; the dilution factor was 10. Final concentrations of other metal ions (in mol dm^{-3}): Al, 130; Ba, 1.0; Ca, 150; Cd, 0.070; Co, 0.040; Cu, 1.0; Fe, 70; K, 500; Mg, 33; Mn, 2.0; Na, 40; Ni, 0.14; Pb, 3.0; Se, 0.030; V, 0.30; Zn, 8.0. ^b $\bar{x} \pm s$: Mean \pm standard deviation.

Table 4 Analytical results of urban air for Be^a

Sample no.	Date	Be spiked in solution/ mmol dm ⁻³	Be found		
			In solution/nmol dm ⁻³	In air/pg m ⁻³	Recovery (%)
A	June 1990	—	3.89 ± 0.16 ^b	19.5 ± 0.8 ^b	
		5.00	8.77	18.9	98
		10.0	14.0	20.0	101
B	July 1990	—	4.14 ± 0.09 ^b	20.7 ± 0.4 ^b	
		5.00	9.26	21.3	102
		10.0	14.1	20.7	100
C	August 1990	—	4.88 ± 0.19 ^b	24.4 ± 0.9 ^b	
		5.00	9.69	23.5	96
		10.0	14.9	24.4	100

^a Sampling was made for 25 d at 20 dm³ min⁻¹ in the city area of Sendai. ^b Average values of five runs at the 95% confidence level.

largely determined by the instrument used and operating conditions, the minimal detectable concentration of 4.7 pg cm⁻³ is still comparable to those for ICP-MS (2.2 pg cm⁻³)¹⁹ and GC-ECD (5.1 pg cm⁻³).²⁰

Interference studies

The aromatic six-membered chelate ring system operated under the extremely alkaline conditions is doubtless responsible for the excellent specificity towards the Be(II) ion. This excellent specificity for the Be(II) ion is due to the proximity of two donor atoms which results in lowering of the formation constants with the other metal ions. Additionally, the extremely alkaline conditions also play an important role in this specificity; a large amount of hydroxide ion efficiently masks hydrolyzable cations, such as the Al(III) ion. Without masking agents, no reactions were found between HBQS and common cations given in Table 2, such as B(III), Al(III), and transition metal ions at pH 12.0. Actually, those cations, except for Mg(II), Ca(II), and Fe(III) ion, gave no interference up to the 10 μmol dm⁻³ level in the determination of the Be(II) ion at nanomolar levels with no masking procedure. The small alkaline earth cations, Mg(II) and Ca(II) showed slight interference even at the 10 μmol dm⁻³ level. Iron(III) ion gave an error because the sample solution became heavily turbid with the hydroxide precipitation under such alkaline condition, pH 12.0. Judging from the conditional equilibrium constants of Be(II), Mg(II), Ca(II), and Fe(III) ions with EDTA at pH 12.0, 10^{-3.9} for Be(II) and > 10⁸ for the other metal ions,²⁵ EDTA is most likely a suitable masking agent, having no effect on the Be determination. In the presence of a large excess of boron (for example 50 μmol dm⁻³), added as boric acid, it takes about 10 min to give the constant emission signals of the Be chelate; the fluorescent boron-HBQS chelate once formed in the slightly acidic conditions is destroyed during the steep pH-jump to the optimal conditions of pH 12.0. Therefore, standing at least for 10 min after sample preparation is recommended in the cases where a large excess of boron is present in the samples.

Table 2 summarizes the influence of diverse ions on the determination of the Be(II) ion in the presence of EDTA (2 mmol dm⁻³) as masking agent. Against 5 nmol dm⁻³ Be(II) ion, a 10 000 to 100 000-fold molar excess of cations were completely tolerated. Surprisingly, Al(III), B(III), Ca(II), and Mg(II) at sub-millimolar levels did not affect the fluorimetric detection of Be at 5 nmol dm⁻³. In addition, no interference from fluoride at 0.1 mol dm⁻³ was found, which suggests that the Be(II)-HBQS chelate is stable and undergoes no substitution reaction with the strong ligand, F⁻ ion.

Validation of the method for air analysis

The validation of the method was confirmed using the artificial surrogate solution for an air-dust sample. As shown in Table 3,

even in the complicated matrixes the method is very satisfactory in terms of reproducibility and recovery. Coupled with the simple masking procedure using EDTA, the method enables one to determine the Be(II) ion at the nanomolar levels in the air-dust digestion matrix without any separation procedures.

The proposed method was applied to the determination of Be in urban air. The results are presented in Table 4, together with the satisfactory recovery data obtained by the standard addition technique. It is noted that Be determined here is in the acid soluble fraction, not as total Be. Be in the silicate matrix most likely remains in the filtered residue. The levels of Be found were in the range of 19–25 pg m⁻³; those values seem to be reasonable in comparison with the other reported value, as 42 pg m⁻³ of Be because the latter was obtained using a high-volume air sampler for 24–48 h.²⁶ The filter blank of Be for Dylec 2500-QAST was not detected.

For the determination of Be at such extremely low abundance levels in air samples with no preconcentration or separation processes, any other existing methods are almost useless in the terms of sensitivity and robustness toward the complicated matrix influence. It is demonstrated that this fluorimetric method shows all requisite conditions encountered in air monitoring for Be. The highly practical ability of this method also encourages the extension of the applicability to the analyses of a wide variety of samples, such as natural water, biological fluids, and organs.

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