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Concerted derivatization and concentration method with dispersive liquid–liquid microextraction for liquid chromatographic analysis of 5-hydroxyindoles in human serum

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ABSTRACT

We developed a concerted derivatization and concentration method based on dispersive liquid–liquid microextraction (DLLME) for the liquid chromatography (LC) determination of 5-hydroxyindoles (5-HIs; serotonin, 5-hydroxyindole-3-acetic acid, *N*-acetylserotonin, and 5-hydroxytryptohol). Concerted derivatization and concentration could be affected by adding a mixture of an ionic liquid (1-hexyl-3-methylimidazolium hexafluorophosphate, extraction solvent), methanol (disperser), and water containing fluorescence derivatization reagents [benzylamine and potassium hexacyanoferrate(III)] into the sample. The resulting sedimented phase was injected into a reversed-phase LC column using a mixture of acetonitrile and 250 mM acetate buffer (pH 4.3) as the mobile phase for gradient elution, and the derivatives obtained were fluorometrically detected at excitation and emission wavelengths of 345 nm and 452 nm, respectively. The derivatization (reagent concentrations and pH) and extraction (extraction and disperser solvent type) conditions were optimized simultaneously. The limits of detection of the 5-HIs were in the range of 0.08–0.33 nM. The method was validated for 10 and 50 pmol/mL human serum levels, and the recovery of 5-HIs was between 66% and 98%, within a relative standard deviation of 9.5%. The proposed method is well suited for the highly sensitive analysis of trace amounts of 5-HIs in human serum samples.

1. Introduction

5-Hydroxyindoles (5-HIs) are metabolites of tryptophan, and they play biologically and physiologically important roles in the human body. Determining 5-HI levels in body fluids helps in the treatment of some diseases, such as depression or hyperactivity [1–4]. Various methods have been developed for the determination of 5-HIs by liquid chromatography (LC) with electrochemical [5–7], fluorescence [8,9], or mass spectrometry (MS) detection [10–12]. Our previously developed fluorescence derivatization with benzylamine (BA) is one of the most frequently used methods because of its good selectivity and sensitivity (Fig. 1) [13–19], although very high sensitivity is sometimes required for the analysis of trace amounts of 5-HIs in biological samples. Several sample pre-treatment/pre-concentration approaches with liquid–liquid extraction (LLE) and/or solid phase extraction (SPE) would be helpful for the sensitive analysis of analytes, but such conventional methods are time-consuming and labor-intensive and require large amounts of organic solvents and involve emulsion formation. Assadi and co-workers have recently developed a novel pre-concentration method, dispersive liquid–liquid microextraction (DLLME) [20], which is simple and inexpensive, allows for rapid operation, and has high recovery and a high enrichment factor. In past few years, DLLME has been extensively explored for the pre-treatment of not only organic but also inorganic compounds in various samples [21–24]. Furthermore, ultrasound-assisted DLLME [25,26], ionic liquid-based DLLME [27–29], DLLME based on solidification of a floating organic droplet [30,31], and incorporation with derivatization [32–35], which are modifications of the original DLLME, have been reported.

In this study, we found that DLLME accelerated the derivatization of 5-HIs with BA; hence, we developed a concerted derivatization and concentration method to improve the sensitivity of the said derivatization. Rapid injection of a mixture of a water–miscible solvent (for dispersion) and a water–immiscible solvent (for extraction) containing the derivatization reagents [BA and potassium hexacyanoferrate(III)] to aqueous biological samples including 5-HIs, followed by centrifugation and analysis of the sedimented phase by LC with fluorescence detection, enabled the highly sensitive and fast analysis of 5-HIs.

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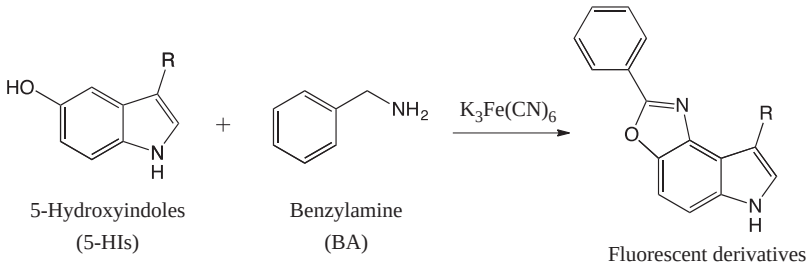

5-Hydroxyindoles (5-HIs) | Benzylamine (BA) | Fluorescent derivatives

5-Hydroxyindole	Abbreviation	R
5-Hydroxytryptamine (serotonin)	5-HT	$-CH_2CH_2NH_2$
5-Hydroxyindole-3-acetic acid	5-HIAA	$-CH_2COOH$
N-Acetylserotonin	NAS	$-CH_2CH_2NHCOCH_3$
5-Hydroxytryptophol	5-HTOL	$-CH_2CH_2OH$
5-Hydroxyindole-3-acetamide (IS)	5-HIA	$-CH_2CONH_2$

Fig. 1. Derivatization of 5-HIs with BA.

The analysis conditions were optimized using standards of the representative 5-HIs [serotonin (5-HT), 5-hydroxyindole-3-acetic acid (5-HIAA), 5-hydroxytryptophol (5-HTOL), and *N*-acetylserotonin (NAS)], and the method was applied to the analysis of human serum samples.

2. Experimental

2.1. Reagents and solutions

Standards of 5-HT hydrochloride, 5-HIAA, 5-HTOL, NAS, and 5-hydroxyindole-3-acetamide [5-HIA; internal standard (IS)] were obtained from Sigma-Aldrich (St. Louis, MO, USA). BA hydrochloride, 1-hexyl-3-methylimidazolium hexafluorophosphate ($HMIMPF_6$), and dodecyltrimethylammonium chloride (DTMA-Cl) were purchased from Tokyo Chemical Industry (Tokyo, Japan). Deionized water was purified using a Millipore EQG system (Billerica, MA, USA) and was used to prepare all aqueous solutions. All other chemicals and solvents from Wako Pure Chemicals (Osaka, Japan) were of analytical grade and used as received.

Respective stock solutions of 10 mM 5-HIs were prepared by dissolving an accurate amount of the compound in 10 mL of methanol, and working standard solutions were prepared by diluting the stock solution with deionized water to the required concentrations just before use. The solution for derivatization was prepared by dissolving BA hydrochloride and potassium hexacyanoferrate(III) in a mixture of methanol, water, and $HMIMPF_6$ (5:2:1, v/v) to final concentrations of 250 mM and 20 mM, respectively.

2.2. Concerted derivatization and concentration of 5-HIs with DLLME

To a 500 μL aliquot of the sample solution placed in a 1.5 mL screw cap tube, 100 μL of 10 mM CAPS buffer (pH 10.8), 100 μL of 10 mM DTMA-Cl, and 300 μL of 100 nM 5-HIA (IS) were added. Then, 160 μL of the derivatization solution was rapidly injected into the reaction solution by using a 500 μL glass syringe. The tube was tightly capped, and ultrasonication was performed for 5 min to induce derivatization and extraction. After centrifugation at 20,000*g* for 10 min at 4 °C, 30 μL of methanol was added to the obtained sediment phase (*ca.* 20 μL), and the resulting mixture (*ca.* 50 μL) was placed in the autosampler of the LC system.

2.3. Pre-derivatized 5-HIs with BA

Pre-derivatized 5-HIs with BA were prepared through a minor modification of a previously described procedure [19]. Briefly, a 250 μL aliquot of the 5-HI standard solution was placed in a 1.5 mL screw cap tube, and 250 μL of the BA solution [20 mM BA and 2 mM potassium hexacyanoferrate(III) in acetonitrile:125 mM NaOH:25 mM sodium tetraborate (2:1:1, v/v)] were added. The mixture was allowed to stand at room temperature for 5 min and then directly injected into the LC system.

2.4. Instrumentation and the required conditions

A Shimadzu (Kyoto, Japan) LC system consisting of an LC-10ADVP pump, an FCV-10ALVP low-pressure gradient unit, a DGU-12A online degasser, an SIL-10ADVP autosampler, a CTO-10ACVP column oven, and an RF-20AXL fluorescence detector was used. The fluorescence detector was operated at excitation and emission wavelengths of 345 nm and 452 nm, respectively. A reversed-phase XBridge™ shield RP18 column (150 × 4.6 mm ID, particle size 5 μm; Waters, Milford, MA, USA) was used. Solvent A consisted of a mixture of 250 mM acetate buffer (pH 4.3), water, and acetonitrile (50:40:10, v/v). Solvent B consisted of a mixture of 250 mM acetate buffer (pH 4.3) and acetonitrile (50:50, v/v). The gradient elution conditions were as follows: 0 min, 35% B; 0–20 min, linear change from 35% to 100% B; 20–25 min, 100% B; 25–25.01 min, linear change from 100% to 35% B; and run time, 35 min. 15 μL of the sample was injected automatically each time. The flow rate and column oven temperature were set at 1.0 mL/min and 40 °C, respectively.

2.5. Performance evaluation

To evaluate the efficiency of proposed concerted derivatization and concentration, the enrichment factor (EF), reaction efficiency (RE), and process efficiency (PE) were calculated using standard solutions of 5-HIs (50 nM). The EF was determined by comparing the responses of the extract from the pre-derivatized 5-HI solution with DLLME without any derivatization reagent and the pre-derivatized 5-HI solution without extraction. The RE was assessed by comparing the responses of the extract obtained from the concerted derivatization and concentration of 5-HIs with DLLME and the extract from the pre-derivatized 5-HI solution with DLLME without any derivatization reagent. The PE was evaluated by comparing the responses of the extract obtained from the

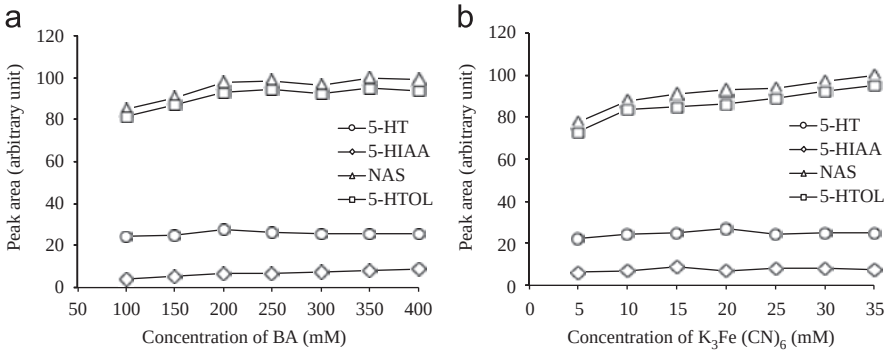

Fig. 2. Effects of the concentration of (a) BA and (b) potassium hexacyanoferrate(III) on fluorescence development of 5-HIs.

concerted derivatization and concentration of 5-HIs with DLLME and the pre-derivatized 5-HI solution. The EF, RE, and PE were calculated using Eqs. (1), (2), and (3), respectively.

$$EF = A/B \quad (1)$$

$$RE = C/A \quad (2)$$

$$PE = C/B = EF \times RE \quad (3)$$

where A is the response from the extract of the pre-derivatized 5-HIs with DLLME; B, the response from the pre-derivatized 5-HI solution without extraction; and C, the response from the extract obtained after the concerted derivatization and concentration of 5-HIs with DLLME.

2.6. Method validation

Peak areas were integrated automatically and used for the quantification of 5-HIs. Calibration solutions were prepared by diluting the stock solution of 5-HIs. The concentration range of the calibration standards was 0.5–100 nM (0.5, 1, 5, 10, 50, and 100 nM). The standards were subjected to the concerted derivatization and concentration procedure with DLLME after preparation. The concentrations of 5-HIs in the samples were calculated from the calibration curves by using the ratio of the peak areas of the BA-derivatized 5-HIs to that of 5-HIA (IS). The interday precisions of the method were estimated using the peak areas of the standard solutions (1 and 10 nM) obtained by repeated analysis six times each day. The limits of detection (LODs) were defined as the sample concentrations that gave a signal-to-noise (S/N) ratio of 3.

2.7. Human serum sample

Human serum sample (male) was purchased from Sigma-Aldrich and ultra-filtered by ULTRAFREE®-MC (5000 NMWL, Millipore), with centrifugation at 20,000g for 15 min. The filtrate (500 μL) was subjected to concerted derivatization and extraction using the procedure outlined above. For the recovery test, samples were spiked with 5-HIs standards containing 10 and 50 pmol/mL serum. The recovery rates were calculated as the ratio of the responses of derivatives obtained with standard spiked serum samples to those from equivalent amounts of 5-HIs.

3. Results and discussion

3.1. Optimization of procedure

The analysis conditions of the concerted derivatization and concentration method with DLLME were optimized for the sensitive analysis of 5-HIs.

3.1.1. Selection of extraction and disperser solvents

Screening of extraction and disperser solvents was performed using the pre-derivatized 5-HI solutions. For DLLME, solvents with higher density than water and non-polar solvents such as carbon disulfide, chloroform, and tetrachloromethane are selected as extraction solvents. However, such solvents could not be utilized in this study because of the low extraction efficiency of the BA-derivatized 5-HIs (data not shown). On the other hand, recently, ionic liquids have been often utilized as extraction solvents in DLLME because of their unique properties such as negligible vapor pressure, tunable viscosity, and high solubility for many compounds [36]. Four representative imidazolium hexafluorophosphate ionic liquids often employed for DLLME [27–29]—1-methyl-3-*n*-octylimidazolium hexafluorophosphate, 1-ethyl-3-methylimidazolium hexafluorophosphate, 1-butyl-2,3-dimethylimidazolium hexafluorophosphate, and $HMIMPF_6$—were evaluated as extraction solvents in the current study. $HMIMPF_6$ was chosen because of its adequate viscosity and suitable extraction capacity for the BA-derivatized 5-HIs.

The disperser solvent also affects the extraction efficiency of DLLME. The disperser solvent must show good miscibility with the non-polar extraction solvent and the aqueous sample solution. Among the disperser solvents examined for DLLME (acetone, acetonitrile, methanol, ethanol, and isopropanol), methanol was the most effective for solubilizing the derivatization reagent and extracting the 5-HI derivatives. Furthermore, deionized water was mixed with the extraction and disperser solvents for complete dissolution of the derivatization reagents. In this study, although BA hydrochloride and potassium hexacyanoferrate(III), which were added to the DLLME solvent mixture, dissolved more easily with increasing water content, high concentrations of water hindered dispersion in the reaction mixture. Therefore, a 5:2:1 (v/v) mixture of methanol, deionized water, and $HMIMPF_6$ was used as the optimum composition, and 160 μL of this solution was injected into 1 mL of the sample solution.

3.1.2. Optimization of derivatization conditions with DLLME

The derivatization of 5-HIs with BA is known to proceed under weakly alkaline conditions [13–19]. We tested the effect of pH of the reaction solution on the peak areas of the derivatives by using CAPS buffer in the range 10.0–11.2. A pH level of 10.8 was used as the optimal value. Furthermore, the effects of the concentrations

Table 1
Performance of the proposed method.

5-HI	EF[a]	RE[b]	PE[c]
5-HT	9.4	1.6	15
5-HIAA	0.34	8.0	2.7
NAS	9.8	1.9	19
5-HTOL	8.9	2.3	21

[a] Enrichment factor, ratio of response in extract of pre-derivatized 5-HIs with DLLME to that of pre-derivatized 5-HIs solution without extraction.
[b] Reaction efficiency, ratio of response in the extract obtained from the concerted derivatization and concentration of 5-HIs with DLLME to that of the extract of pre-derivatized 5-HIs with DLLME.
[c] Process efficiency, ratio of response in the extract obtained from the concerted derivatization and concentration of 5-HIs with DLLME to that of pre-derivatized 5-HI solution without extraction.

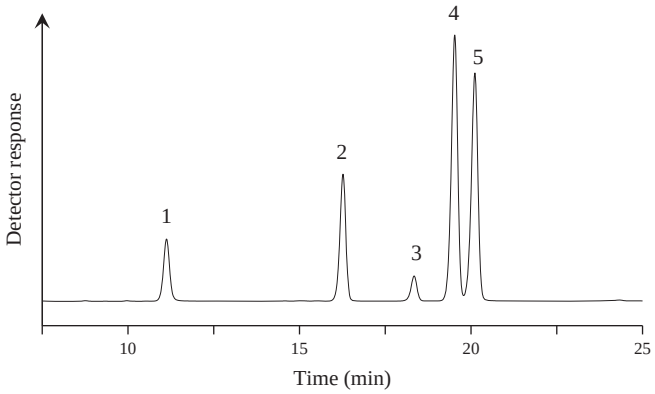

Fig. 3. A typical chromatogram obtained with the standard solution of 5-HIs (50 nM each). Peaks: 1, 5-HT; 2, 5-HIA (IS); 3, 5-HIAA; 4, NAS; and 5, 5-HTOL.

Table 2
Method validation.

5-HI	Linearity[a]	LOD[b] (nM)		RSD[c] (%) ($n=6$)	
		Present method[d]	Conventional method[e]	1 nM	10 nM
5-HT	0.9984	0.17	0.85	0.6 (2.2)[f]	0.4 (1.1)[f]
5-HIAA	0.9974	0.33	0.62	9.1 (21)[f]	2.2 (14)[f]
NAS	0.9998	0.08	0.35	1.8 (0.8)[f]	0.8 (0.5)[f]
5-HTOL	0.9997	0.10	0.48	1.0 (0.8)[f]	0.8 (0.6)[f]

[a] Correlation coefficient of the calibration curve of 5-HI in the concentration range 0.5–100 nM.
[b] Limit of detection, defined as the sample concentration giving a signal-to-noise ratio of 3.
[c] Relative standard deviation of peak area of BA-derivatized 5-HI.
[d] With DLLME.
[e] Without DLLME (see Section 2.3).
[f] Value in parenthesis is the RSD calculated from peak area obtained by the method without DTMA-Cl.

of BA and potassium hexacyanoferrate(III) in the DLLME solvent on the peak areas of fluorescent derivatives were examined (Fig. 2). By varying the concentration of BA over the range 100–400 mM, we found that the maximum and constant peak areas could be obtained for concentrations exceeding 200 mM BA. Therefore, the optimal concentration of BA was set at 250 mM. The reaction proceeded only to a negligible extent in the absence of potassium hexacyanoferrate(III), but high concentrations of this compound posed problems in dissolution in the DLLME solvent. The optimum concentration of potassium hexacyanoferrate(III) was found to be 20 mM. A derivatization and extraction time of 5 min in an ultrasonic water bath was required to obtain constant peak areas. An emulsification-enhancing surfactant dodecyltrimethylammonium chloride (DTMA-Cl) was added to the sample for better reproducibility, especially for 5-HIAA analysis (see Section 3.3), and its concentration was set at 10 mM.

3.2. Enrichment factor, reaction efficiency, and process efficiency

This method was designed to obtain high derivatization and extraction efficiencies of the 5-HI derivatives with BA (see Section 3.1). Under the optimal conditions, the EF, RE, and PE were calculated from Eqs. (1), (2) and (3) and found to be in the range of 0.34–9.8, 1.6–8.0, and 2.7–21, respectively (Table 1). Although the EF for derivatized 5-HIAA was very low, the RE was improved by the present method because this derivatization combined with DLLME could accelerate the reaction between 5-HIs and BA. Consequently, all the examined 5-HIs could be seemingly concentrated (PE > 1.0), thus highly sensitive analysis.

3.3. Analysis of the standards

The LC separation conditions were decided through a minor modification of a previously described procedure [19]. A typical chromatogram obtained from a standard mixture of 5-HIs is shown in Fig. 3. Under the present LC conditions, all the derivatives were eluted within 21 min. Validation data for the standard

Table 3
Determination results for human serum samples.

5-HI	Added concentration (pmol/mL serum)	Mean concentration (pmol/mL serum, $n=3$)	Mean recovery (%) ($n=3$)	RSD (%) ($n=3$)
5-HT	0	12	–	2.9
	10	22	96	0.8
	50	62	98	3.2
5-HIAA	0	5.5	–	6.0
	10	12	66	9.5
	50	41	70	2.4
NAS	0	ND[a]	—	–
	10	9.2	92	0.2
	50	47	94	0.9
5-HTOL	0	ND[a]	—	–
	10	9.1	91	0.7
	50	46	92	0.5

[a] ND—not detected.

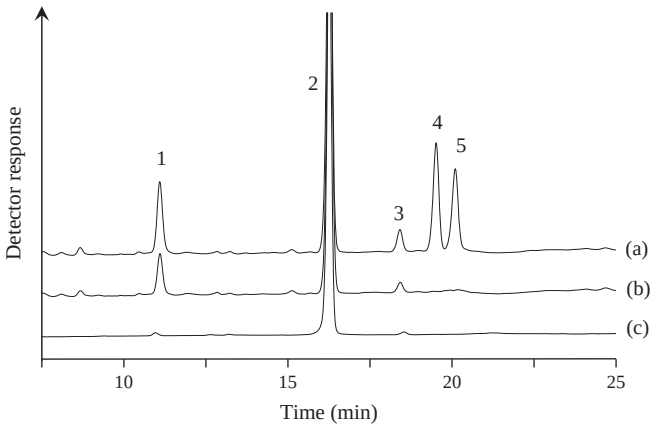

Fig. 4. Chromatograms obtained for (a) 10 pmol/mL serum spiked and (b) non-spiked serum samples treated with concerted derivatization and concentration, and (c) non-spiked serum sample treated with pre-derivatization with BA. Peaks: see Fig. 3. Concentrations (pmol/mL serum) of (b): 1 (12) and 3 (5.5).

solutions are presented in Table 2. The correlation coefficients of the calibration curves were greater than 0.9974. The LODs of 5-HIs in the present method were in the range from 0.08 to 0.33 nM. The relative standard deviations (RSDs) of the interday precision values of the peak areas of the derivatives were within 9.1%, as established by repeated determinations ($n=6$) using standard solutions of 5-HIs (1 and 10 nM). In contrast, the RSDs increased in the absence of DTMA-Cl, especially in the 5-HIAA analysis, probably because the acidic moiety of 5-HIAA was undesirable for extraction; DTMA-Cl aided the constant extraction of 5-HIs by enhancing emulsification.

3.4. Analysis of human serum

We investigated the feasibility of present method for application to human serum samples. The determination results and chromatograms of non-spiked and spiked (10 and 50 pmol/mL serum) human serum samples are presented in Table 3 and Fig. 4, respectively. Trace concentrations of 5-HT (12 pmol/mL serum) and 5-HIAA (5.5 pmol/mL serum) could be clearly detected from the non-spiked serum sample. Furthermore, the recovery values obtained for the spiked human serum samples were in the range 66–98%, within 9.5% ($n=3$) RSD. Thus, this method enables the sensitive as well as precise analysis of 5-HIs in biological samples.

4. Conclusions

A derivatization method with BA for 5-HIs based on concerted derivatization and concentration with DLLME, followed by LC fluorescence detection, was developed. 5-HIs were derivatized with BA, and the derivatives were extracted rapidly with an ionic liquid ($HMIMPF_6$) by DLLME. All the examined 5-HIs were successfully concentrated, and their derivatives were detected with high sensitivity by the fluorescence detector. Furthermore, this sufficient sensitivity enabled the determination of trace amounts of 5-HT and 5-HIAA in human serum. This method will be useful for the highly sensitive analysis for 5-HIs in various pharmaceutical and biological samples.

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