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Fabrication of In-needle Microextraction Device Using Nichrome Wire Coated with Poly(ethylene glycol) and Poly(dimethylsiloxane) for Determination of Volatile Compounds in Lavender Oils

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A new needle-based device for headspace wire coated in-needle microextraction (HS-WC-INME) was fabricated using a nichrome wire coated with poly(ethylene glycol) (PEG) and poly(dimethylsiloxane) (PDMS) mixture. The proposed needle device was applied for the determination of volatile compounds in lavender and lavandin essential oils by gas chromatography. Fundamental parameters such as needle design, conditions of extraction and desorption were optimized along with the validation of the extraction and desorption efficiency. The optimal conditions were 30 min extraction at 50 °C and 2 min desorption at 240°C. The calibration curves showed good linearity with the suitable values of the coefficients of determination (r^2) greater than 0.99. The limits of detection for linalyl acetate, β-caryophyllene, linalool and (+)-limonene were 7.15, 9.04, 10.79 and 22.26 ng, respectively. Analytical recoveries were acceptable in the test samples, varying from 86.7% to 108.0%. The values of relative standard deviations for run to run showed range less than 0.9% while 3.9% through 7.2% for needle to needle. The proposed PEG-PDMS coating could be more suitable than PDMS coating to extract particular polar groups such as alcohols.

Key Words : In-needle microextraction, PEG-PDMS coating, Gas chromatography, Lavender and lavandin oils

Introduction

Recently, the new designs of devices and the developments of new sorbent phase for needle-based microextraction have attracted much attention. The solid-phase microextraction (SPME) introduced by Pawliszyn and his co-workers [1] has been one of the most successful approaches. The SPME is a convenient and solvent-free extraction technique which combines extraction, enrichment and sample introduction into a single step. However, conventional SPME has some disadvantages of the fiber fragility and the limited sorption capacity.[2,3] Alternative approaches such as in-needle capillary adsorption trap (INCAT) or in-tube SPME,[4,5] solid phase dynamic extraction (SPDE)[6,7] and a needle trap device (NTD)[8-10] were reported, respectively. Such a device contains sorbent in the stainless steel needle. The main advantages of NTD are solvent-free like the SPME, simple and fast sampling and short analysis times than most existing methods.[2,11] The drawbacks of NTD are relatively low sampling capacity, rapid breakthrough of the trap, possible dispersion of the elution zones of the analytes,[11] and the poor sampling flow reproducibility from needle to needle.[12] Jinno and his co-worker developed a fiber-packed needle[13] and an in-needle extraction device packed a copolymer of methacrylic acid and ethylene glycol dimethacrylate.[14] The most recently, we have reported an in-needle microextraction (INME) using a needle packed with poly(dimethylsiloxane) (PDMS) having a micro-bore tunnel.[15]

The common polymeric coating materials of SPME and SPDE are PDMS, PDMS/activated carbon, PDMS/OV 225, PDMS/phenyl-methylpolysiloxane, poly(ethylene glycol) (PEG) and PDMS, 7% phenyl, 7% cyanopropyl.[16] In general, polar coating materials are used for polar analytes and non-polar coatings for non-polar analytes as with conventional GC stationary phases. For a long time, PEG has been used as a polar stationary phase of GC column. The PEG phase which exhibits less hydrophobic attributes than PDMS, may provide enhanced retention for more polar analytes. These characteristics can be exploited in case where target analytes varying in octanol-water partition coefficient (log $P_{o/w}$) are to be separated. The durability of the coating often becomes a problem due to swelling and stripping, since PEG has a water-soluble property. Previously, the preparation of SPME fibers coated with PEG was studied by several researchers.[7,16-18]

In this study, we have designed and fabricated a new in-needle microextraction device using a nichrome wire coated with PEG modified with PDMS sorbent phase to improve effectively the extraction efficiency of both polar and non-polar compounds in a single experiment. The sol–gel technique[19,20] was used to prepare a nichrome wire coated with sorbent. It can provide a useful approach for synthesis of different sorbent with better homogeneity and purity as well as lower temperature of preparation, strong mixing abilities for multi-component systems, control of particle size, shape and properties, and better thermal stability for higher thermal desorption.[20] A nichrome wire coated with PEG and PDMS mixture was placed into a stainless steel extraction needle inside. The extraction needle after fabrication was hooked simply to a gas tight syringe barrel and a plunger then inserted and exposed into the HS over the sample. HS sampling prior

to GC or GC-MS separation was speeded up by suitable pulling-up and pushing-down cycles. After adsorption, the extraction needle was transferred to the heated GC injection port for thermal desorption and the simultaneous injection to the GC column. Optimizations, validation and application for the analyses of volatile compounds in lavender and lavandin essential oils as test samples have been studied to evaluate the headspace wire-coated in-needle microextraction (HS-WC-INME) efficiency. This sampling device has increased extraction speed and the practical merits of a durable stainless steel needle.

Experimental

Reagents, Materials and Samples. Analytical grade working standard of linalool (97%) was obtained from Fluka (Buchs, St. Gallen, Switzerland). Linalyl acetate (95%), (+)-limonene (95%) and β-caryophyllene (90%) were obtained from Tokyo Chemical Industry (Tokyo, Japan). The stock solutions of working standards were prepared in methanol of chromatographic grade obtained from Mallinckrodt Baker (Phillipsburg, USA) at a concentration of 10 mg/mL, respectively. Using these stock solutions a standard mixture was prepared in methanol with a concentration of 1 mg/mL each. The standard mixture was diluted with methanol for the appropriate concentrations.

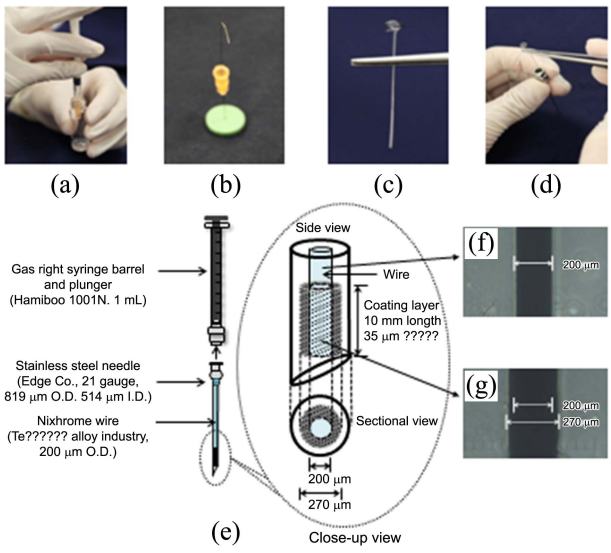
Essential oils of true lavender (Huile Essentielle de Lavande vraie, *Lavandula angustifolia* Miller) were purchased from Distillerie Vallon des Lavandes (Sault, France. Sample A), Terraroma (Valensole, France. Sample B), and Laboratoire Sainte Victoire (Chateau de Simiane la Rotonde, France. Sample C). Essential oil of lavandin Grosso (hybrid species of *Lavandula angustifolia* Mill. × *Lavandula latifolia* Medik) was obtained from Terraroma (Valensole, France. Sample D), Huile Essentieelle de lavandin from La Maison des Producteurs (Sault, France. Sample E), Huile Essentieelle Bio de lavandin clone super from Nature & Decouvertes (Paris, France. Sample F) and lavandin super from Laboratoire Sainte Victoire (Chateau de Simiane la Rotonde, France. Sample G), respectively.

Instrumentation. GC analyses were performed using an HP5890 II (Hewlett Packard) equipped with a flame ionization detector (FID). A DB624 capillary column of 30 m length, 0.25 mm I.D. and 1.4 μm film thickness of 6% cyanopropylphenyl-94%-dimethylpolysiloxane supplied by J&W Scientific (Folsom, CA, USA) was used for the separation of the analytes. The split/splitless injector was used in the split mode at a split ratio of 1:30 and operated at 240 °C. Nitrogen (99.99%) was used as a carrier gas at a flow rate of 1 mL/min. The temperature program of the GC oven began at 50 °C for 3 min, raised up to 240 °C at 5 °C/min kept finally at 240 °C for 3 min. Hydrogen and oxygen were used as a FID fuel gas at a flow rate of 30 mL/min and 300 mL/min, respectively. The FID temperature was operated at 250 °C.

GC/MS analyses were carried out on a Trace GC 2000 (Thermoquest) coupled with GC-Q ion trap mass spectrometer (Thermoquest). The separation column, oven temperature program, injector temperature, and split ratio were same as GC conditions. Helium (99.999%) was used as carrier gas at a flow rate of 1 mL/min. The electron impact ionization mass spectrometer was operated as follows: transfer line temperature, 230 °C; ionization voltage, 70 eV; ion source temperature, 200 °C; mass range (*m/z*) 50-500. The analytes were identified by comparing the retention time of the relevant chromatographic peaks with those of authentic standards and with spectra of the NIST and Wiley libraries.

Fabrication of a Needle Inserted Nichrome Wire Coated with Poly(ethylene glycol) and Poly(dimethylsiloxane). Extraction devices for WC-INME were prepared using nichrome wire (200 μm O.D.) obtained from Teikoku Alloy Industry (Tokyo, Japan), stainless steel needle (21 gauge, 819 μm O.D., 514 μm I.D., 39 mm length) with a bevel tip and a luer lock metal hub obtained from Edge Co. (Seoul, Korea), and 1 mL disposable syringe and a disposable bevel tip stainless steel needle (25 gauge, 25 mm length) with a removable plastic hub obtained from Hwajin Medical Co. (Seoul, Korea). Nichrome wire was straightened manually using a round pipe (6 cm O.D., 15 cm length) made of stainless steel, then it was cut to the same length of 10 cm using a cable cutting neeper. These pieces of wire were cleaned with methanol and heated in an oven (100 °C) for 3 min.

The schematic drawing for the fabrication of the WC-INME device is presented in Scheme 1. 0.500 g of 50% aqueous solution of PEG (number average molecular weight, Mn = 20,000) purchased from Aldrich (St. Louis, MO, USA), 0.500 g PDMS base solution (Sylgard 184A) and 0.050 g curing agent solution (Sylgard 184B) obtained from Dow Corning Inc. (Midland, USA) were weighed and mixed thoroughly in a 5 mL vial. A removable needle of a disposable syringe (1 mL) previously rinsed slightly with methanol was immersed into the 5 mL vial containing PEG-PDMS sol mixture for 15 s to pull the sol up to 0.4 mL by pulling plunger (Scheme 1(a)). Then, the disposable needle filled with the



Scheme 1. The schematic drawing for the fabrication of the HS-WC-INME device (Patent pending).

sol mixture was disassembled from the disposable syringe and pierced down vertically to a GC septum by the nichrome wire to make a coating on the wire surface (Scheme 1(b)). After drying and curing the disposable needle with the nichrome wire in an oven (100 °C) for 15 min, the nichrome wire was removed from the disposable needle to prepare a wire coated with PEG-PDMS gel layer (*ca*. 35 μm thickness). Then, a piece of the nichrome wire coated with PEG-PDMS layer (10 mm length) at the one end-side was adjusted by neeper-cutting (Scheme 1(c)). The other end of the nichrome wire uncoated was coiled up, ready to insert a 39 mm length of the straight wire part into inside of the stainless steel needle (Edge, 21 gauge, 819 μm O.D., 514 μm I.D., 39 mm length) with a bevel tip and a luer lock metal hub (Scheme 1(d)).

The prototype WC-INME device prepared as described above was hooked simply to a luer lock gas tight syringe barrel (Hamilton 1001N, 1 mL) and a plunger made of polytetrafluoroethylene (PTFE, Teflon) previously cleaned and dried (Scheme 1(e)). This nichrome wire coated with PEG-PDMS layer was confirmed using an inverted microscope (Nikon Eclipse, TS100, Q-imaging micropublisher 3.3 lens, 40 magnification (Scheme 1(f), (g)) and a field emission scanning electron microscope images (FE-SEM, Tescan, TUV Mira II-LMH, 50/60 Hz, 230-2200 VA). Thereafter the needle was conditioned before microextraction by inserting it in the GC injector for 30 min at 250 °C to remove the impurities and to reduce carry-over. This WC-INME device is reusable for multiple measurements.

Headspace Extraction and Desorption. A 50 mL vial containing 0.5 μL of lavender oil was kept tight with a mininut cap and the WC-INME needle prepared according to the previous section was inserted to be exposed in the HS of the vial at 50 °C for 30 min. HS sampling can be speeded up by sequential pulling-up and pushing-down of the Teflon plunger in the glass barrel (Hamilton 1001N, 1 mL) using a homemade automatic reciprocating piston (180 extraction cycles for 30 min) while microextraction needle was located in the HS of the vial. After the extraction was completed, the needle was removed from the sample vial and inserted directly into the heated injection port of the GC-FID or GC/MS for the thermal desorption for 2 min at 240 °C.

Results and Discussion

Optimization of the Headspace Wire Coated In-needle Microextraction (HS-WC-INME). Optimization of the parameters affecting method efficiency should be performed carefully, to enable efficient extraction of target analytes and to improve the sensitivity. The target analytes in this study were linalool, linalyl acetate, (+)-limonene and β-caryophyllene. The optimization process was performed using a stock solution of standard mixture containing all the analytes at a concentration of 1 μg/μL each. The standard mixture was diluted with methanol for the appropriate concentrations. Parameter optimization was determined based on the peak area that represented extraction efficiency. When a variable parameter such as the mixing ratio and the length of a coating phase, and extraction/desorption condition is optimized, its optimum value is fixed for further experiments.

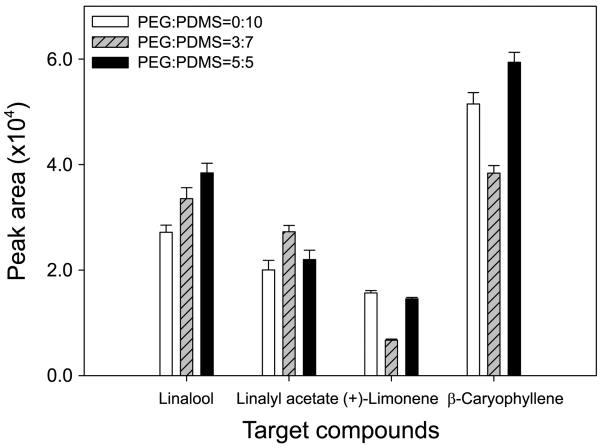


Figure 1. Effect of mixing ratio between PEG and PDMS on the peak area for the target analytes. Bars represent the standard deviation (n = 3).

The Mixing Ratio of PEG and PDMS as Coating Phase. In the present study, we select PEG-PDMS coating phase to increase the extraction efficiencies of both polar and non-polar volatile analytes in a single experiment. The proposed WC-INME technique, a nichrome wire coated with PEG-PDMS mixture (*ca*. 35 μm thickness, 1 cm length) was placed into the inside of a hypodermic stainless steel needle tube (21 gauge, 514 μm I.D., 819 μm O.D., 39 mm length).

The effect of the mixing ratios (wt:wt) between PEG and PDMS on the extraction efficiency of the HS-WC-INME was investigated in the range from 0:10 to 7:3. As can be seen in Figure 1, mixing ratio of 5:5 showed the greatest peak areas for linalool (log $P_{o/w}$ = 2.97, miscible with alcohol and ether, practically insoluble in water) and β-caryophyllene (log $P_{o/w}$ = 6.30, 1 mL soluble in 6 mL 95% ethanol, and insoluble in water). However, a little greater peak area of linalyl acetate (log $P_{o/w}$ = 3.93, water solubility of 30 mg/L) was observed at the mixing ratio of 3:7. In the case of (+)-limonene (log $P_{o/w}$ = 4.45, low solubility in water), the mixing ratio of 0:10 (PDMS coating only) showed a little greater or almost similar peak area to that of the mixing ratio of 5:5. However, in the range from 7:3 to 10:0 (PEG coating only), it was unable to make proper coating due to swelling, stripping and insufficient curing. Greater peak areas reflect the greater sensitivity, polarity and affinity of the analyte to the polar PEG. The results suggest that the PEG-PDMS (5:5) coating is more polar selective sorption system toward polar analytes, because the PEG is a more polar phase than the PDMS. Lavender essential oils have both polar and non-polar volatile analytes including linalool, linalyl acetate, (+)-limonene and β-caryophyllene, and most of the analytes are extracted well with the PEG-PDMS (5:5) coating. Therefore, the PEG-PDMS (5:5) coating layer was selected for providing the best possible combination of the extraction efficiency, sensitivity and durability.

The Length of PEG-PDMS Coating Layer. The effect

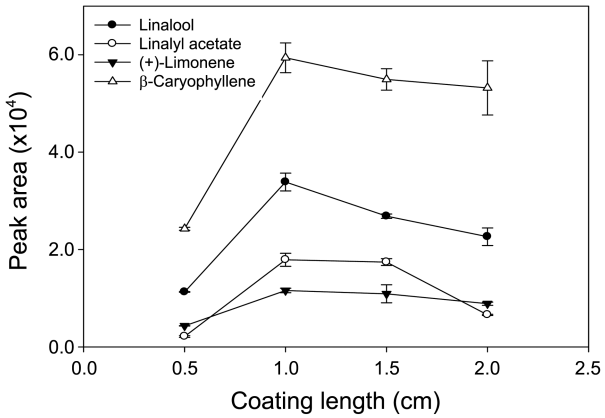


Figure 2. FID response (peak area) for various coating lengths. Bars represent the standard deviation (n = 3).

of the length of PEG-PDMS (5:5) coating layer on the extraction efficiency was evaluated in 0.5 cm intervals from 0.5 cm to 2 cm in length (Figure 2). The 1 cm length of PEG-PDMS layer coated on the wire surface showed the best effective results for all the analytes. The use of longer coating length than 1 cm may require a longer extraction time and higher extraction temperature.[15] It may be concluded that the most important feature determining the analytical performance of WC-INME are the physicochemical property, length and thickness of the coating material.

Extraction Conditions. The effect of the extraction temperature on the efficiency of HS-WC-INME was tested in 10 °C intervals from 30 °C to 70 °C. In this investigation, adsorption time was set at 20 min. As illustrated in Figure 3 (top), the peak areas of the most target analytes were increased with increased adsorption temperature from 30 °C to 50 °C and reached to the maximum at 50 °C. And then, peak areas were decreased by further increasing extraction temperature to 70 °C. Adsorption temperature of 50 °C was selected for further extraction methodology.

The effect of the extraction time on the extraction efficiency was also investigated by with and without an automatic reciprocating piston in the range from 5 min to 40 min. When using the automatic reciprocating piston for sequential pulling-up and pushing-down the plunger in the syringe barrel, the cycle number should be considered. A piston cycle is defined as the up and down movement of the plunger in the syringe barrel. It was designed to take 1 min for 6 cycles or 10 s for one cycle. The higher number of piston cycles means the longer adsorption time. The extraction time profile using the automatic reciprocating piston is shown in Figure 3 (bottom). It could be observed that analytes were equilibrated between PEG-PDMS coating layer and the headspace during the extraction time of 30 min (180 cycles). After 30 min of extraction time, the peak areas were decreased. Ulrich reported that the time of extraction in SPME is independent of the concentration of analyte in the sample.[21]

The relative extraction efficiency without using a reciprocating piston was compared. In contrast to the above

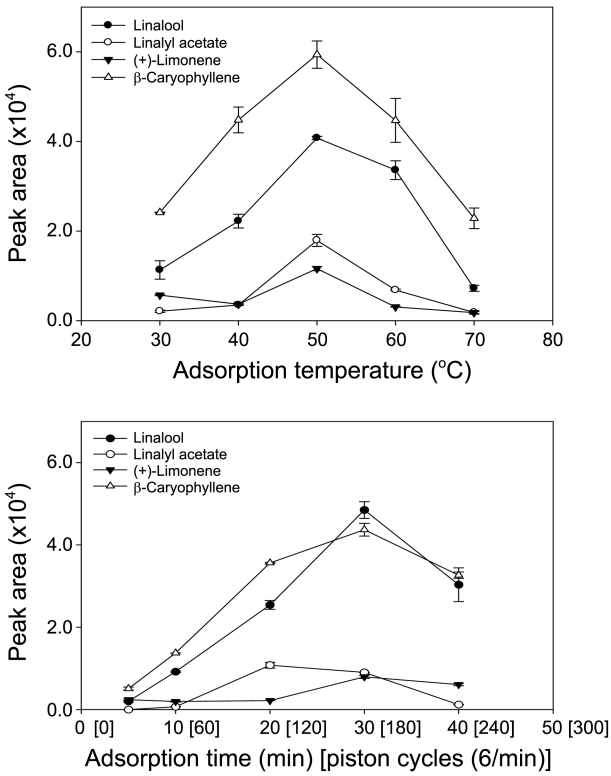


Figure 3. Effect of adsorption temperature on peak area of the target analytes (top). Effect of adsorption time and piston cycles on the extraction efficiency of target analytes (bottom). Extraction condition: adsorption time for 30 min, desorption temperature at 240 °C and desorption time for 2 min. Bars represent the standard deviation (n = 3).

successful results, it showed that the values of peak area were significantly smaller than those of analytes using a reciprocating piston. It demonstrates that the use of an automatic reciprocating piston was very important to shorten the extraction time and enhance the extraction efficiency, because the up and down movements of plunger accelerate the transport of volatile analytes into the very narrow needle inside from the headspace. From these results, in subsequent measurements, the optimum adsorption time using an automatic reciprocating piston at a speed of 10 s for one cycle was determined to be 30 min (180 cycles) at 50 °C.

Desorption Conditions. The effect of desorption temperature on desorption efficiency was investigated in the range from 150 °C to 250 °C. Stabilization of the chromatograms was observed and reproducible desorption efficiency were obtained at 240 °C for the most target analytes as shown in Figure 4 (top). Desorption efficiency was computed to evaluate desorption temperature and time using following equation.

$$\text{Desorption efficiency (\%)} = [A_{d1}/(A_{d1}+A_{d2})] \times 100$$

where A_{d1} is the peak area obtained from the first desorption and A_{d2} is the peak area obtained from the second desorption. From the equation indicated above, the adsorbed analytes are completely desorbed when the desorption efficiency reached at 100%.

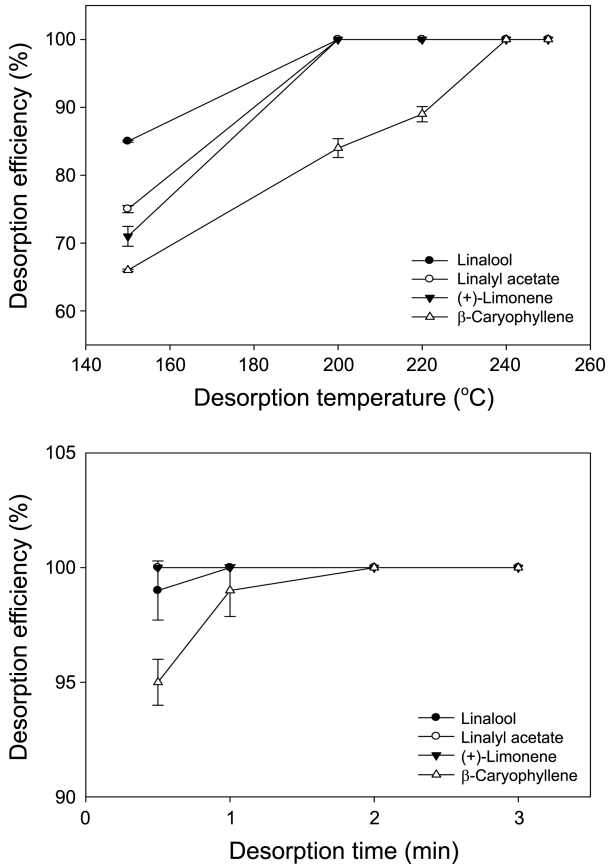


Figure 4. Effect of desorption temperature (top) and desorption time (bottom) on the desorption efficiency of HS-WC-INME analyzed by GC-FID. Bars represent the standard deviation (n = 3).

Desorption time for the target compounds were compared at four different times from 0.5 min to 3 min. Most target compounds were reached to about 100% reproducible desorption efficiency after desorption time of 2 min at 240 °C as shown in Figure 4 (bottom). In subsequent experiments sampling time in the GC injector was kept for 2 min at 240 °C.

Method Validation. The proposed HS-WC-INME method was validated in terms of linearity, the limits of detection (LOD), the limits of quantitation (LOQ), accuracy and precision by using the experimental setting at the optimized conditions. The linearity of the proposed methodology was evaluated by calculating the coefficients of determination (r^2) of the regression equations of calibration curves. A calibration curves was prepared at seven different levels for each analyte, triplicate measurements under the same extraction conditions. As shown in Table 1, calibration curves showed good linearity with the suitable values of the coefficients of determination (r^2) greater than 0.99 for all of the analytes. The values of LOD and LOQ were calculated based on the ratios of 3 (*s*/*m*) for LOD and 10 (*s*/*m*) for LOQ, respectively. Where, *s* is the standard deviation of peak area of the first lowest concentration of the 7-points calibration curve and *m* is the slope. LODs for linalyl acetate, β-caryophyllene, linalool and (+)-limonene were 7.15, 9.04, 10.79 and 22.26 ng, respectively. LOQs for linalyl acetate, β-caryophyllene, linalool and (+)-limonene were 23.83, 30.14, 35.97 and 74.21 ng, respectively. Dynamic ranges were varied in the range of 4 ng (lower value) ~ 3.0×10^4 ng (upper value).

The accuracy of HS-WC-INME method was investigated

Table 1. Validation data for the target compounds: calibration curve, linearity (r^2), the limit of detection (LOD), the limit of quantitation (LOQ) and dynamic range for linalool, linalyl acetate, (+)-limonene and β-caryophyllene

Calibration curve					
Compounds	Regression equation	r^2	LOD ng	LOQ ng	Dynamic range (ng)
Linalool	y = 17496.0(± 389) x + 5744.4(± 2439)	0.998	10.79	35.97	0.4 × 10 ~ 2.3 × 10^4
Linalyl acetate	y = 2670.4(± 97) x + 593.2(± 1036)	0.994	7.15	23.83	3.6 × 10 ~ 2.0 × 10^4
(+)-Limonene	y = 3239.5(± 91) x + 3300.7(± 1566)	0.995	22.26	74.21	2.3 × 10 ~ 3.0 × 10^4
β-Caryophyllene	y = 16892.0(± 187) x + 2683.5(± 1865)	0.999	9.04	30.14	4.6 × 10 ~ 2.0 × 10^4

Table 2. Validation data: recovery and reproducibility for linalool and linalyl acetate in lavender essential oil (sample A)

Recovery % (mean ± RSD%, n = 3)				
Sample	Compounds	100 ng spiked (lower level)	10 μg spiked (middle level)	100 μg spiked (upper level)
Lavender (sample A)	Linalool	86.7 ± 1.5	102.0 ± 11.0	102.1 ± 0.8
	Linalyl acetate	108.0 ± 16.5	107.4 ± 9.1	89.7 ± 8.5
Reproducibility % (RSD%, n = 10)				
Sample	Compounds	Intra assay (run to run, n = 10)	Inter assay (needle to needle, 5 needles × 10 measurements)	
Lavender (sample A)	Linalool	0.9	3.9	
	Linalyl acetate	0.8	7.2	

to determine the recovery by spiking the three levels (0.1, 10 and 100 μg) in triplicate using standards of linalool and linalyl acetate to lavender oil. Analytical recoveries were acceptable in the test samples, varying from 86.7% to 108.0% (Table 2).

The reproducibility for precision of the analytical method was investigated using linalool and linalyl acetate for lavender. The values of relative standard deviations (RSD) for the intra assay (run to run) in 10 replicate measurements showed range less than 0.9% while 3.9% through 7.2% for inter assay (needle to needle) in 10 replicate measurements using 5 different needles. Therefore, it can be concluded that the present method could be a suitable alternative to conventional approaches for the HS analysis of volatile components for facilitating the assessment of lavender essential oil quality.

Application of HS-WC-INME to Real Samples and Evaluation of Extraction Efficiency. The proposed HS-WC-INME followed by GC-FID or GC-MS without further clean-up step was successfully applied to the analyses of the real essential oil samples. Provence true lavender essential oils and lavandin oils were analyzed. Typical HS-WC-INME with GC-FID chromatograms were shown in Figure 5. Quantitative data were summarized in Table 3.

On the other hand, relative enrichment factor (*EF*) values of the characteristic aroma components in the true lavender and lavandin grosso essential oils extracted by two different coatings of WC-INME were compared and summarized in Table 4. Relative extraction efficiency was evaluated according to the previous reports.[15,22,23] *EF* was extraction efficiency of analyte that was evaporated from samples to the headspace and transferred to the adsorbent through extraction process. It was calculated by following equation.

$$EF = A_1/A_0$$

where A_1 is the peak area of components analyzed by the proposed HS-WC-INME, and A_0 is the peak area of linalool analyzed by static HS extraction, because most components showed very small or no sensitivity by static method.

Most relative *EF* values of the characteristic components by PEG-PDMS coating were higher than those by PDMS coating except camphor (m.w.: 152.23, b.p.: 204 °C, log $P_{o/w}$ = 2.089). Especially, *EF* values for polar linalool (m.w.: 154, b.p.: 198-199 °C, log $P_{o/w}$ = 2.97) and linalyl acetate (m.w.: 196.29, b.p.: 220 °C, log $P_{o/w}$ = 3.93) was significantly higher than non-polar monoterpene hydrocarbons such as α-phelandrene (m.w.: 136.24, b.p.: 171 °C, log $P_{o/w}$ = 4.4). The

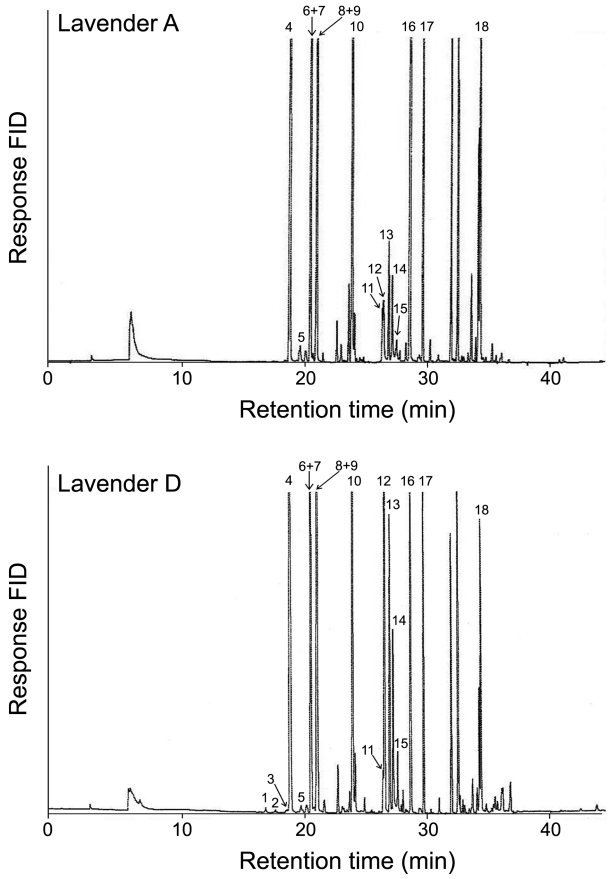


Figure 5. Typical chromatograms of lavender (sample A) and lavandin (sample D) essential oils obtained by HS-WC-INME and GC-FID. Peak identification: 1, α-Pinene; 2, Camphene; 3, β-Pinene; 4, β-Myrcene; 5, 3-Octanone; 6+7, (+)-Limonene + β-Phellandrene; 8+9, Cineol + Ocimene; 10, Linalool; 11, Camphor; 12, Lavandulol; 13, Terpinene-4-ol; 14, Borneol; 15, α-Terpineol; 16, Linalyl acetate; 17, Lavandulyl acetate; 18, β-Caryophyllene.

log $P_{o/w}$ value is usually employed to define the partition of a given analyte between water solution and PDMS coating (log $P_{o/w}$ $P_{PDMS/w}$).[24,25] Thus, linalool which has lower log $P_{o/w}$ value is more polar compound than monoterpene hydrocarbons. PEG-PDMS (5:5) coating was very effective in case of essential oils like lavender where target analytes varying in log $P_{o/w}$ are to be separated. Generally, linalool and linalyl acetate are the most abundant components in the essential oils of the true lavender or lavandin.[22,23] Therefore, it can be concluded that the present method by HS-WC-INME with

Table 3. Quantitation of linalool, linalyl acetate, (+)-limonene and β-caryophyllene in lavender and lavandin samples by HS-WC-INME and GC-FID

Essential oil	Concentration (mg/mL), mean ± RSD%, n = 3						
	Lavender A	Lavender B	Lavender C	Lavandin D	Lavandin E	Lavandin F	Lavandin G
Linalool	68.2 ± 7.74	107.0 ± 3.37	62.5 ± 10.83	67.7 ± 10.73	127.8 ± 3.91	132.4 ± 7.75	90.9 ± 5.59
Linalyl acetate	214.4 ± 15.53	275.8 ± 9.79	288.6 ± 13.06	290.1 ± 11.75	304.7 ± 3.62	449.8 ± 4.09	555.7 ± 4.32
(+)-Limonene	102.3 ± 4.46	91.1 ± 8.64	94.1 ± 6.67	79.1 ± 5.48	98.7 ± 7.83	96.6 ± 11.13	104.4 ± 13.50
β-Caryophyllene	17.5 ± 9.62	11.4 ± 8.30	12.5 ± 8.20	7.7 ± 6.27	5.9 ± 4.54	7.4 ± 10.43	6.3 ± 2.84

Table 4. Comparison of enrichment factors (*EF*) for characteristic components of lavender (A sample) and lavandin (G sample) essential oils by different coating methods

Components	log $P_{o/w}$	Enrichment factor (*EF*) (mean ± RSD%, n=3)			
		A: HS-WC-INME (PEG-PDMS coating)		B: HS-WC-INME (PDMS coating)	
		Lavender	Lavandin	Lavender	Lavandin
β-Myrcene	4.17	83.51 ± 8.51	76.91 ± 6.13	78.86 ± 6.26	74.07 ± 5.67
β-Phellandrene + (+)-Limonene	4.4 4.57	40.53 ± 5.48	39.88 ± 4.01	37.99 ± 9.21	39.15 ± 8.92
Cineol + Ocimene	3.13 4.17	71.93 ± 5.20	63.95 ± 4.97	64.33 ± 6.51	62.00 ± 8.48
Linalool	2.97	184.65 ± 10.73	146.40 ± 4.23	181.24 ± 7.16	131.64 ± 2.39
Camphor	2.089	2.50 ± 2.21	1.98 ± 1.36	2.05 ± 7.76	2.24 ± 1.38
Lavandulol	2.6	53.57 ± 7.84	5.15 ± 12.79	40.07 ± 5.39	4.69 ± 1.82
Terpinene-4-ol	3.33	22.43 ± 7.15	6.19 ± 7.12	20.15 ± 3.00	5.50 ± 3.03
Linalyl acetate	3.93	119.71 ± 11.75	60.49 ± 13.80	83.68 ± 4.84	52.48 ± 2.42
Lavandulyl acetate	3.6	24.84 ± 4.98	24.46 ± 9.06	20.39 ± 11.49	18.72 ± 10.01
β-Caryophyllene	6.30	28.88 ± 5.38	37.09 ± 5.96	16.97 ± 6.26	18.29 ± 10.70

PEG-PDMS coating could be more suitable to extract particular polar groups such as alcohols.

Conclusion

A new headspace wire-coated in-needle microextraction (HS-WC-INME) device was fabricated using a nichrome wire coated with 50% aqueous PEG-PDMS (5:5) mixture to improve the extraction efficiency of polar compounds. Fundamental parameters such as needle design, conditions of extraction and desorption were optimized along with the validation of the extraction and desorption efficiency. It was found that the proposed method was applied successfully to analyze volatile compounds in lavender and lavandin essential oils. The innovative design and improved method provided satisfactory validation results of analytical methods. Especially, enrichment factor for polar linalool was significantly higher than non-polar monoterpene hydrocarbons. This solvent-free and durable device is inexpensive to fabricate, simple to operate, reusable, fast and efficient for sampling of polar compounds in essential oils samples.

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References

1. Arthur, C.; Pawliszyn, J. *Anal. Chem.* **1990**, *62*, 2145-2148.
2. Alonso, M.; Godayol, A.; Antico, E.; Sanchez, J. M. *J. Sep. Sci.* **2011**, *34*, 2705-2711.
3. Bigham, S.; Medlar, J.; Kabir, A.; Shende, C.; Alli, A.; Malik, A. *Anal. Chem*. **2002**, *74*, 752-761.
4. McComb, M. E.; Oleschuk, R. D.; Giller, E.; Gesser, H. D. *Talanta* **1997**, *44*, 2137-2143.
5. Eisert, R.; Pawliszyn, J. *Anal. Chem*. **1997**, *69*, 3140-3147.
6. Lipinski, J. *Fresenius J. Anal. Chem*. **2001**, *369*, 57-62.
7. Bicchi, C.; Cordero, C.; Liberto, E.; Sgorbini, B.; Rubiolo, P. *J. Chromatogr. A* **2008**, *1184*, 220-233.
8. Lord, H. L.; Zhan, W.; Pawliszyn, J. *Anal. Chim. Acta* **2010**, *677*, 3-18.
9. Eom, I. Y.; Tugulea, A. M.; Pawliszyn, J. *J. Chromatogr. A* **2008**, *1196-1197*, 3-9.
10. Warren, J. M.; Pawliszyn, J. *J. Chromatogr. A* **2011**, *1218*, 8982-8988.
11. Qin, N.; Xu, X.; Polák, T.; Pacáková, V.; Štulík, K.; Jech, L. *Talanta* **1997**, *44*, 1683-1690.
12. Mieth, M.; Schubert, J. K.; Groger, T.; Sabel, B.; Kischkel, S.; Fuchs, P.; Hein, D.; Zimmermann, R.; Miekisch, W. *Anal. Chem.* **2010**, *82*, 2541-2551.
13. Saito, Y.; Ueta, I.; Ogawa, M.; Abe, A.; Yogo, K.; Shirai, S.; Jinno, K. *Anal. Bioanal. Chem.* **2009**, *393*, 861-869.
14. Saito, Y.; Ueta, I.; Kotera, K.; Ogawa, M.; Wada, H.; Jinno, K. *J. Chromatogr. A* **2006**. *1106*, 190-195.
15. Son, H. H.; Bae, S.; Lee, D. S. *Anal. Chim. Acta* **2012**, *751*, 86-93.
16. Wang, Z.; Xiao, C.; Wu, C.; Han, H. *J. Chromatogr. A* **2000**, *893*, 157-168.
17. Silva, R. G. C.; Augusto, F. *J. Chromatogr. A* **2005**, *1072*, 7-12.
18. Sungkaew, S.; Thammakhet, C.; Thavarungkul, P.; Kanatharana, P. *Anal. Chim. Acta* **2010**, *664*, 49-55.
19. Chong, S. L.; Wang, D.; Hayes, J. D.; Wilhite, B. W.; Malik, A. *Anal. Chem*. **1997**, *69*, 3889-3898.
20. Kumar, A.; Gaurav, M. A.; Tewary, D.; Singh, B. *Anal. Chim. Acta* **2008**, *610*, 1-14.
21. Ulrich, S. *J. Chromatogr. A* **2000**, *902*, 167-194.
22. Kim, N. S.; Lee, D. S. *J. Chromatogr. A* **2002**, *982*, 31-47.
23. Won, M. M.; Cha, E. J.; Yoon, O. K.; Kim, N. S.; Kim, K.; Lee, D. S. *Anal. Chim. Acta* **2009**, *631*, 54-61.
24. Bauld, T.; Teasdale, P.; Stratton, H.; Uwins, H. *Water Sci. Technol*. **2007**, *55*, 59-67.
25. Roldán-Pijuán M.; Alcudia-León, M. C.; Lucena, R.; Cárdenas, S.; Valcárcel, M. *J. Chromatogr. A* **2012**, *1251*, 10-15.