

Research Article

Nanoparticle-Incorporated PDMS Film as an Improved Performance SPME Fiber for Analysis of Volatile Components of *Eucalyptus* Leaf

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A new fabrication strategy was proposed to prepare polydimethylsiloxane (PDMS-) coated solid-phase microextraction (SPME) on inexpensive and unbreakable Cu fiber. PDMS was covalently bonded to the Cu substrate using self-assembled monolayer (SAM) of (3-mercaptopropyl)trimethoxysilane (3MPTS) as binder. To increase the performance of the fiber, the incorporation effect of some nanomaterials including silica nanoparticles (NPs), carbon nanotubes (CNTs), and carboxylated carbon nanotubes (CNT-COOH) to PDMS coating was compared. The surface morphology of the prepared fibers was characterized by scanning electron microscopy (SEM), and their applicability was evaluated through the extraction of some volatile organic compounds (VOCs) of *Eucalyptus* leaf in headspace mode, and parameters affecting the extraction efficiency including extraction temperature and extraction time were optimized. Extracted compounds were analyzed by GC-MS instrument. The results obtained indicated that prepared fibers have some advantages relative to previously prepared SPME fibers, such as higher thermal stability and improved performance of the fiber. Also, results showed that SPME is a fast, simple, quick, and sensitive technique for sampling and sample introduction of *Eucalyptus* VOCs.

1. Introduction

SPME developed by Belardi and Pawliszyn [1] is a solvent free, simple, relatively fast to execute, and easily automated method for direct immersion and headspace extraction of volatile and semivolatile chemicals from solid, liquid, and gas samples and has been successfully applied in numerous environmental, food, flavor, pharmaceutical, clinical, and forensic applications [2].

The sensitivity and selectivity of SPME is strongly dependent on its coating type and thickness. Several coatings are commercially available for SPME analysis. Commercial SPME fibers have a friable silica rod as substrate coated with polymers or copolymers and must be handled with great care and thus greatly limits the service life. The commercial SPME fibers in addition to the friability of the fibers present important drawbacks such as their relatively low

recommended operating temperature and stripping of the coatings [3], and finally, their extraction efficiency is low in some cases. However, most of these fibers are generally prepared by mere physical deposition or partial crosslink of the polymer coating on the surface of the fused-silica fibers. The lack of proper interaction between the polymer coating and substrate surface and their relatively high thickness may be responsible for their low thermal and chemical stability [3].

In the past 15 years, considerable effort has been invested in the development of new SPME coatings, which has recently been subject to the literature reviews [3, 4]. To improve the breakage of the fibers, metal wires such as Pt [5], Ni-Ti [6], Al [7], and Cu [8] wires have been used as an alternative to fused silica, and, for fiber coating, several approaches including sol-gel technology [6, 9], electrochemical procedures [10, 11], and ionic liquids [12] have been

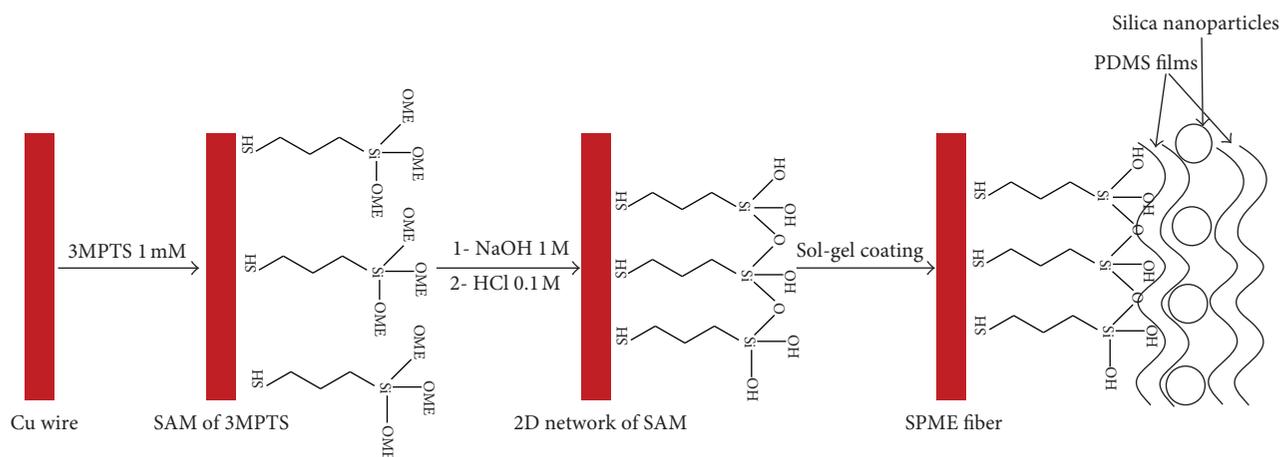


FIGURE 1: Schematic representation of substrate modification and coating deposition procedure.

TABLE 1: Volatile organic compounds (VOCs) of *Eucalyptus* leaf extracted by SPME-GC-MS.

No.	Chemical name	Formula	Retention time (min)	Relative area percent
1	Alpha-pinene	C ₁₀ H ₁₆	8.18	10.68%
2	Alpha-terpinene	C ₁₀ H ₁₆	9.97	0.64%
3	m-cymene	C ₁₀ H ₁₄	10.15	0.75%
4	Limonene	C ₁₀ H ₁₆	10.25	1.44%
5	1,8-Cineole	C ₁₀ H ₁₈ O	10.37	66.27%
6	Alpha-terpinolene	C ₁₀ H ₁₆	11.58	0.59%
7	Isopinocarveol	C ₁₀ H ₁₆ O	12.89	1.86%
8	Pinocarvone	C ₁₀ H ₁₄ O	13.40	0.80%
9	Calarene	C ₁₅ H ₂₄	19.08	0.32%
10	(+)-Aromadendrene	C ₁₅ H ₂₄	19.18	10.18%
11	Nealloocimene	C ₁₀ H ₁₆	19.61	1.95%
12	Beta-selinene	C ₁₅ H ₂₄	20.07	0.51%
13	Junipene	C ₁₅ H ₂₄	20.16	0.82%
14	(+)-Spathulenol	C ₁₅ H ₂₄	21.40	0.34%
15	Delta-guaiene	C ₁₅ H ₂₄	21.58	1.18%
Sum				98.33%

developed. Among the different approaches to stationary phase development for SPME fibers, sol-gel approach represents a promising direction in this important research with applicability in preparation of surface coatings for SPME fibers.

The principle of SPME is the distribution of the analyte(s) between solid or liquid coated film and the sample. In some cases, extraction capability is low because of limited adsorption sites on the fibers [13]. Using nanomaterials can overcome this problem. Nanomaterials offer a significant higher surface area to volume ratio that promises much greater extraction capability and efficiency compared with other materials used for SPME [14]. The applications of nanomaterials in SPME coatings have shown a remarkable growth in recent years. Carbon nanotubes [15], fullerenes [16], nanoporous silica [17], nanostructured metal oxides [18, 19], and Au nanoparticles [20] have been successfully used as SPME coatings.

In this study, silica sol-gel films chemically bonded on modified copper wire were presented as a novel technique for preparation of SPME fibers that have strong interaction between substrate and stationary phase. Also, to improve the extraction efficiency of prepared fibers, different nanomaterials were incorporated through the sol-gel film. The applicability of prepared fibers was evaluated through the extraction of volatile organic compounds (VOCs) of *Eucalyptus* leaf, and parameters affecting the extraction efficiency were optimized.

2. Materials and Methods

2.1. Chemicals. The (3-Mercaptopropyl)trimethoxysilane (3MPTS) (95%) was purchased from Fluka (Buchs, Switzerland). The Hydroxyl-terminated PDMS (OH-TSO), tetraethylorthosilicate (TEOS), trifluoroacetic acid (TFA, 98%), polymethylhydrosiloxane (PMHS), and Silica NPs (10–20 nm) were obtained from Aldrich (Steinheim,

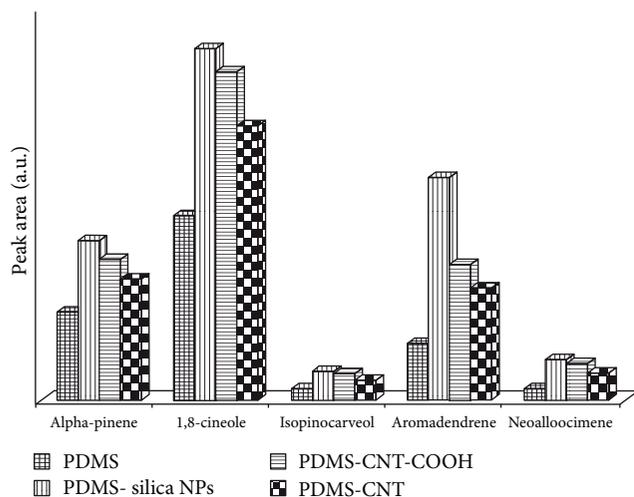


FIGURE 2: The effect of different nanomaterials incorporation on extraction capability of prepared fiber.

Germany). All these materials were used as received, except TFA which was diluted to 95% with water. Before use, all plastic and glassware were decontaminated overnight in 20% nitric acid and thoroughly washed with Milli-Q quality (Millipore, Billerica, MA) deionized water.

2.2. Instrumentation. A Hewlett-Packard (HP, Palo Alto, USA) HP 6890 series GC equipped with a split/splitless injector and an HP 5973 mass-selective detector (MSD) system were used to evaluate the SPME fibers. The MS was operated in the EI mode (70 eV). Helium (99.999%) was employed as carrier gas, and its flow rate was constantly adjusted to 1 mL·min⁻¹. The separation of VOCs was performed on a 30 m × 0.25 mm HP-5 MS column (0.25 μm film thickness). The column was held at 60 °C for 2 min and increased to 260 °C at a rate of 7 °C·min⁻¹. The injector temperature was set at 260 °C, and all injections were carried out on the splitless mode. The GC-MS interface was maintained at 280 °C.

The scanning electron microscope images were obtained by an FE-SEM S-4160 Hitachi.

2.3. Preparation of SPME Fibers

2.3.1. Modification of Cu Wire Surface. Cu wires with length of 2 cm and thickness of ~200 μm were prepared and cleaned by acetone, ethanol, and water solutions, respectively. To prepare a self-assembled monolayer (SAM) of 3MPTS, the copper wire was inserted in a solution containing 3MPTS 1 mM in ethanol for 3 hrs then washed with distilled ethanol and water, respectively, to eliminate physically deposited 3MPTS [21]. Then it was inserted in NaOH 1 M (30 min) and HCl 0.1 M (30 min), respectively. Then the 3MPTS-modified surfaces were abundantly rinsed with water and then allowed to air-dry.

2.3.2. Deposition of Coating on Modified Cu Wire. The detail of this procedure has been described elsewhere [22] with

some modifications; briefly, the sol-gel solution was prepared in a 1.5 mL PCR tube by mixing 300 μL TEOS, 180 mg OH-TSO, and 30 mg PMHS dissolved in 300 μL dichloromethane, and then 200 μL TFA (containing 5% water) was sequentially added to the resulting solution. Then the mixture was centrifuged at 12,000 rpm, 20 °C for 8 min. The Cu wire was vertically immersed (1 cm) inside the PCR tube containing the centrifuged sol-gel mixture for 30 min at room temperature. After that period, the fiber was carefully covered with a pile of nanomaterials: silica nanoparticles (NPs), carbon nanotubes (CNTs), or carboxylated carbon nanotubes (CNT-COOH) which were gently pressed against the sol-gel coating so as to stick the particles. The sticking of the particles was manually achieved, and its success depended on a great deal on the operator's experience gained after trial-and-microscopic inspection. Afterwards, it was left to stand for 24 h.

This coating process was repeated several times in the fresh sol solution and the same conditions until the desired fiber thickness was obtained. The prepared fibers were conditioned at 280 °C under Helium for 1 h in the GC injection port. After removal from the injector, the fiber was cooled to room temperature in a desiccator for use.

2.4. SPME Procedure. The extractions were performed in the headspace of a 50 mL glass vial containing 0.2 g powdered *Eucalyptus* leaf. The glass vial was inserted into the circulator bath for establishing of temperature. The vial was sealed with an aluminum cap with a PTFE-faced septum. The outside needle of the SPME fiber assembly penetrated to the vial septum, and the coated fiber was exposed in the headspace of the sample for extraction of analytes on the stationary phase. After extraction, the SPME fiber was retracted into the protective sheath, removed from the headspace, and transferred into the injector of the gas chromatograph for thermal desorption of the analytes at 250 °C for 4 min in splitless mode. At the same time, the GC/MS run was started.

3. Results and Discussion

3.1. Fiber Preparation and Characterization. Sol-gel technology is based on the hydrolysis and simultaneous condensation of metal alkoxides; this technique has been widely used to prepare SPME fibers. The films prepared by sol-gel technology do not have good adherence to the metal fiber surfaces and will be cracked and flaked off after deposition; therefore, commercial SPME fibers commonly have been prepared on friable silica fibers. To solve the problem of weak interaction of sol-gel films to metal substrates, there are some ways; at the first of them, the surface of metal oxide substrates should be activated (hydroxylated) through the NaOH treatment [23]. Another strategy to solve the problem is using an intermediate layer such as 3APTES [24] that can bind to the metal surface and, to the sol-gel film, on the other hand.

Sinapi et al. studies [21] show that 3MPTS chemisorbs on Cu surfaces through strong thiolate bonds forming a well-organized self-assembled monolayer (SAM) and is able to decrease the corrosion of the underlying copper substrate. In

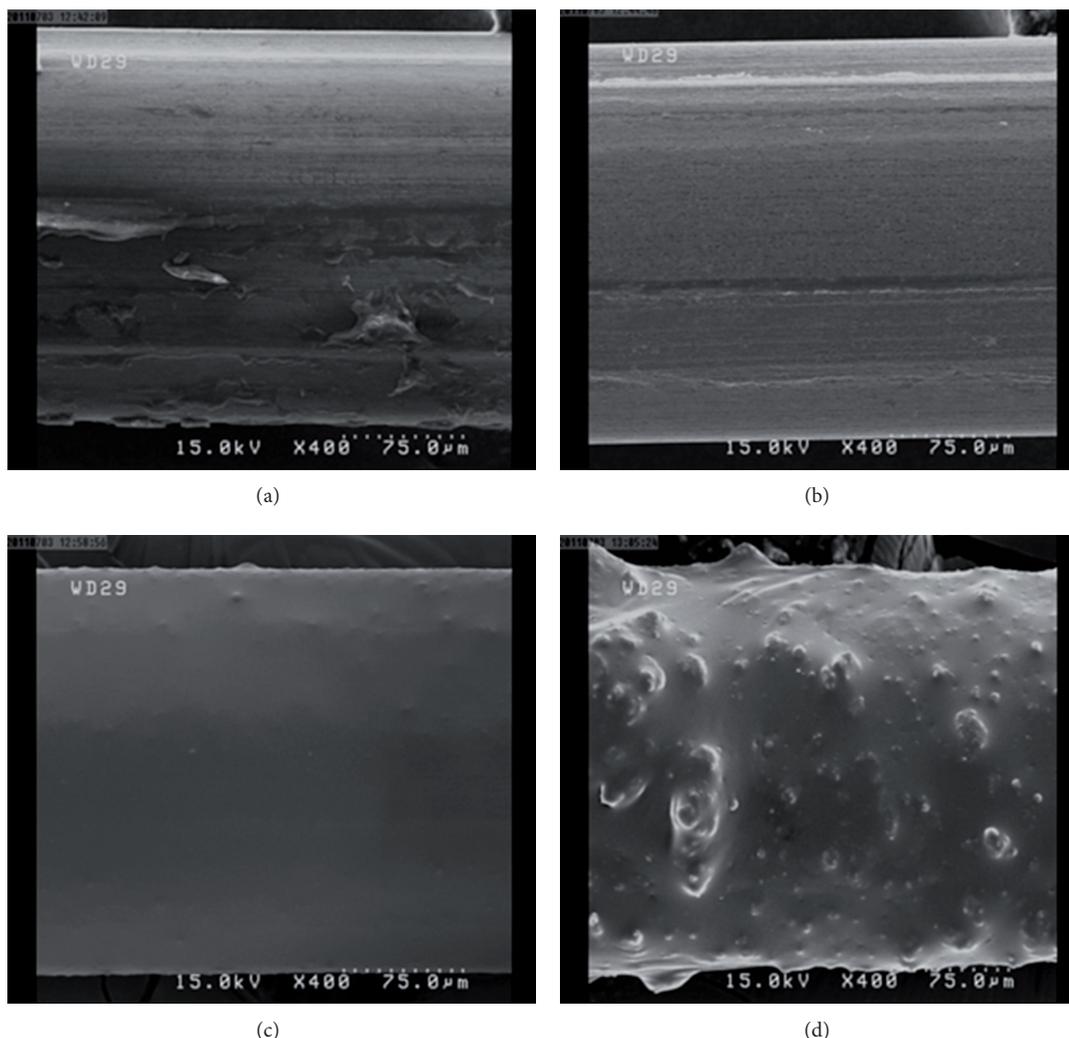


FIGURE 3: Scanning electron microscopy of (a) Cu wire, (b) Cu wire modified by self-assembled monolayer of 3MPTS, (c) PDMS coating on modified Cu wire, and (d) silica NPs-incorporated PDMS on modified Cu wire.

the present study, SAM of 3MPTS was used as intermediate layer to covalently bind the PDMS film to the copper substrate.

Figure 1 schematically shows the procedure of chemical bonding of PDMS coating on copper substrate and incorporation of nanomaterials in coating. At the presence of NaOH and HCl, the 3MPTS molecules that formed self-assembled monolayer on copper surface will be hydrolyzed and condensed to form a 2D network with some $-\text{Si}-\text{OH}$ functional groups as active sites to stick the sol-gel film.

The extraction efficiency of prepared fibers was evaluated through extraction of volatile organic compounds (VOCs) of *Eucalyptus* leaf. Table 1 shows VOCs of *Eucalyptus* leaf extracted by SPME-GC-MS. Five components of VOCs including alpha-pinene, 1,8-cineole, isopinocarveol, aromadendrene, and neoalloocimene were selected as model compounds.

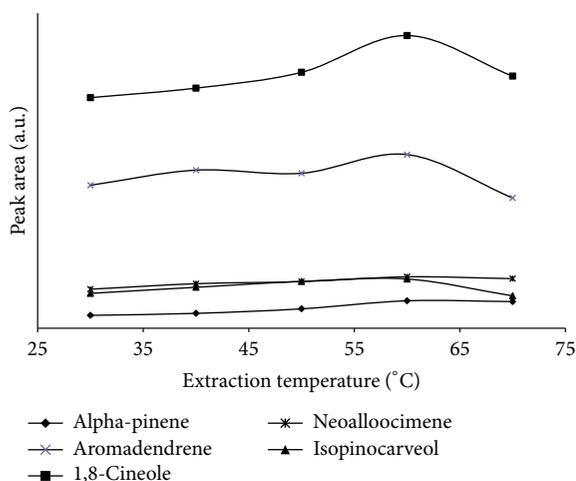
To increase the extraction capability of prepared fiber, the effect of incorporation of different nanomaterials including

CNT, CNT-COOH, and silica NPs in PDMS film was studied. As can be seen at Figure 2, the extraction capability of PDMS is increased at the presence of nanomaterials. The extraction capability of PDMS/CNT-COOH fiber is higher than PDMS/CNT, due to higher polarity of CNT-COOH to extract semipolar volatile components of *Eucalyptus* leaf. Also, the extraction capability of PDMS at the presence of silica NPs is higher than CNT and CNT-COOH-incorporated fiber, due to the higher surface area of NPs relative to the nanotubes.

The surface characteristics of Cu wire at different steps of coating were investigated by scanning electron micrograph (SEM) technique. The SEM image (Figure 3(b)) shows that no observable change was caused by SAM of 3MPTS on Cu wire surface, except smoother surface of Cu modified by SAM. As can be seen from Figures 3(c) and 3(d), the sol-gel film is coated on Cu substrate. Also, Figure 3(d) shows that silica NPs-incorporated sol-gel coating possesses a porous structure, which resulted in larger surface areas and higher extractive capability than PDMS coating without silica NPs.

TABLE 2: Repeatability and reproducibility using nanoparticle-incorporated PDMS fiber.

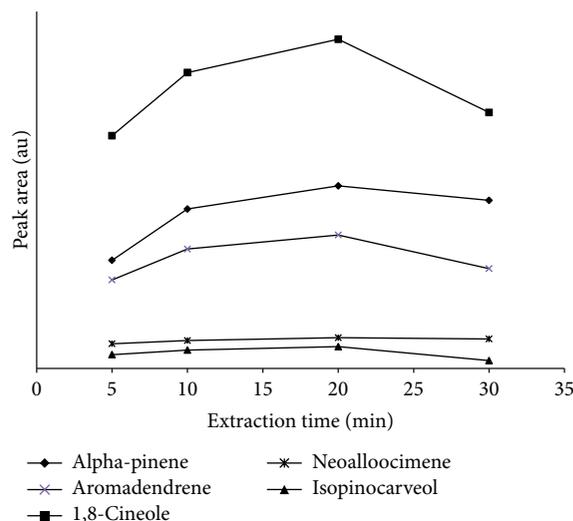
	Relative standard deviations (RSD)%	
	Reproducibility (fiber to fiber) ^a	Repeatability (single fiber) ^b
Alpha-pinene	6.8	5.7
1,8-Cineole	5.4	5.6
Isopinocarveol	9.4	7.9
Aromadendrene	7.7	6.1
Nealloocimene	10.8	8.4

^aRSD% for 4 fibers.^bRSD% for 5 replicates.FIGURE 4: Optimization of extraction temperature, 0.2 g powdered *Eucalyptus* leaf, and 20 min extraction time.

The coating thicknesses of each coating were estimated by SEM and found to be about 5 μm and 7 μm for the PDMS and silica NPs/PDMS fiber, respectively.

Commercial SPME fibers have low operating temperatures, due to weak interaction between the substrate and coating [3]. The thermal properties of the silica NPs/PDMS fiber were assessed by its TGA curve. Results show that the mass loss step begins above 320 °C, which can be assigned to the maximum practicable temperature of the sol-gel coating. The higher thermal stability of prepared PDMS fiber relative to commercial PDMS fiber is due to strong chemical bonding of coating to the Cu substrate provided by SAM of 3MPTS. Such high thermal stability can expand the SPME application range toward higher boiling-point compounds.

The performance of the developed fibers was also evaluated in terms of fiber-to-fiber (reproducibility) and batch-to-batch (repeatability) relative standard deviations (Table 2): RSDs lower than 10.8% were obtained for repeatability of sampling procedure and reproducibility of fiber preparation. The obtained results allowed assessing the feasibility of the proposed coating procedure in the development of thermally stable and efficient fibers.

FIGURE 5: Optimization of extraction time, 0.2 g powdered *Eucalyptus* leaf, and 60 °C extraction temperature.

3.2. Optimization of Extraction Parameters. To achieve the best extraction efficiency, effects of extracting parameters, including extraction temperature and extraction time, were systematically studied. It is generally accepted that temperature has adverse effects on the extraction; on one hand, at elevated temperatures, the higher mobility of molecules increases the extraction rate; on the other hand, it would decrease the distribution coefficient of analytes between the coating and sample solution, because extraction is an exothermic process. Therefore, the selection of a proper temperature is necessary for the extraction process.

The effect of the temperature in the present study was studied in the range of 30–70 °C. As shown in Figure 4, peak areas of all analytes reach the highest values at 60 °C, and hence, the extraction temperature was fixed at 60 °C for subsequent experiments.

SPME is an equilibrium-based technique, and the highest extraction efficiency is usually reached after equilibrium. To find the optimum extraction time, a time range from 5 to 30 min was investigated. Figure 5 shows the effect of extraction time on the extraction efficiency for five selected *Eucalyptus* leaf VOCs. As shown in Figure 5, for all components, the equilibrium was obtained after 20 min. Hence, 20 min was chosen as the optimum extraction time. Relatively short extraction times show that SPME of *Eucalyptus* volatile components using prepared fiber is a simple and quick sample preparation and sample introduction technique.

4. Conclusions

PDMS sol-gel film was chemically bonded to copper wire surface through self-assembled monolayer of 3MPTS as an intermediate. The thermogravimetric analysis showed that prepared fiber has higher thermal stability relative to commercial PDMS fiber. It was demonstrated that different nanomaterials including silica NPs, CNT, and CNT-COOH could be strongly attached to an inexpensive and unbreakable

Cu wire by making use of a sol-gel layer, allowing a novel way to prepare more efficient SPME fibers. The prepared silica NPs/PDMS fiber has higher extracting capability relative to CNT-incorporated PDMS fibers, due to the higher surface area to volume ratio of silica NPs. Also, results showed that SPME-based analytical method is simple, inexpensive, environmental friendly sampling, and sample preparation technique for analysis of volatile compounds in *Eucalyptus* leaf.

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