



## Double-bed-type extraction needle packed with activated-carbon-based sorbents for very volatile organic compounds

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### ABSTRACT

A novel needle-type sample preparation device was developed for the determination of very volatile organic compounds (VVOCs) in gaseous samples by gas chromatography–mass spectrometry (GC–MS). Two types of activated-carbon-based sorbents, Carbopack X and a carbon molecular sieve (CMS), were investigated as the extraction medium. A double-bed-type extraction needle showed successful extraction and desorption performance for all investigated VVOCs, including acetaldehyde, isoprene, pentane, acetone, and ethanol. Sensitive and reliable determination of VVOCs was achieved by systematically optimizing several desorption conditions. In addition, the effects of sample humidity on the extraction and desorption of analytes were investigated with the needle-type extraction devices. Only the CMS packed extraction needle was adversely affected by sample humidity during the desorption process; on the other hand the double-bed-type extraction needle was unaffected by sample humidity. Finally, the developed double-bed-type extraction needle was successfully applied to the analysis of breath VVOCs of healthy subjects.

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### 1. Introduction

Accurate and sensitive determination of volatile organic compounds (VOCs) has recently become the focus of research because of their adverse effects on human health, such as sick building syndrome and multiple chemical sensitivity [1]. The World Health Organization (WHO) defines VOCs with boiling points of 0 °C to 50–100 °C as very volatile organic compounds (VVOCs) [2]. VVOCs can also have adverse effects on human health because they can easily be emitted into environmental air.

Gas chromatography–mass spectrometry (GC–MS) is one of the most promising techniques for the analysis of VOCs because of its high selectivity and sensitivity. However, environmental VOCs typically occur at low concentrations; thus, some type of sample preparation process is necessary in most cases. Extraction of VOCs in gaseous samples with a needle-type sampling device is one of the most advanced techniques for the subsequent GC analysis because such device provide some advantages over conventional extraction methods [3,4]. These needle-type devices contain sorbent particles in a stainless steel needle, and the analytes are extracted on the sorbent when a gaseous sample is passed through the sorbent packed

section of the needle. The extracted analytes can then be thermally desorbed in the conventional GC injection port, typically without a desorption solvent [5–8]. Because this analytical technique requires no additional desorption instrument and/or cryogenic focusing process, the use of a needle-type device for VOCs extraction can be regarded as a simple and rapid sample preparation method. In addition, packing the extraction needle with a particulate medium allows a wide variety of extraction media to be used on the basis of suitability for the target analytes. Several applications have already been reported for determining trace levels of VOCs in gaseous environmental samples [9–12] and human breath samples [13–15]. Our research group has developed a series of extraction needles packed with polymer particles of divinylbenzene (DVB) for the extraction of fire-acceleration-related VOCs [10], a double-bed sorbent consisting of DVB and Shincarbon ST designed for indoor room air analysis [12], and polymer particles of methacrylic acid and ethylene glycol dimethacrylate for the extraction of breath acetone [14].

Because of their volatility, extracting gaseous VVOCs on sorbents is challenging [4,16]. The solvent extraction technique poses some problems, such as VVOC loss during reconcentration of the desorption solvent or overlapping of solvent peaks on analytes in the chromatogram. Some thermal desorption techniques for extracting VVOCs, have been reported, although cryofocusing has been used to effectively extract the analytes [17,18]. Some selected VVOCs have also been extracted by solid-phase microextraction (SPME) [19,20].

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Acetaldehyde, a VVOC classified as carcinogenic by the International Agency for Research on Cancer (IARC) [21], has typically been determined in chromatography by a derivatization process [22–25]. Hence, extraction of VVOCs including acetaldehyde with needle-type extraction device could have several benefits for the analysis of VVOCs. To extract VVOCs from gas phase, adsorbent having a stronger adsorption power is needed, although, water in the gaseous sample could be also extracted onto the adsorbent, and it might affect the analysis of VVOCs [26].

In this work, a novel needle-type extraction device was developed for the extraction of VVOCs such as acetaldehyde, isoprene, pentane, acetone, and ethanol in gaseous samples. The analytes were extracted on sorbent particles without cryofocusing or derivatization, and then were thermally desorbed in a conventional GC injection port. In addition, the effects of sample moisture on the VVOC analysis were investigated using needle extraction devices in the GC analysis. Finally, human breath VVOCs were successfully determined with the developed extraction needle.

## 2. Experimental

### 2.1. Chemicals

Acetone (>99.8%) and ethanol (99.5%) were purchased from Wako Pure Chemical (Osaka, Japan). Acetaldehyde (90%) was obtained from Nacalai Tesque (Kyoto, Japan). Isoprene (>99%) and pentane (>99%) were purchased from Tokyo Kasei Kogyo (Tokyo, Japan). To remove organic contaminants, nitrogen gas (>99.99% purity) used for the desorption of the extracted analytes and for the preparation of the standard gas sample were purified with a gas filter packed with a molecular sieve 5 Å.

### 2.2. Preparation of standard gas samples

Standard VVOC samples having the desired concentrations were prepared as follows. First, an appropriate amount of the analyte solution was injected into a 1.0 L decompressed vacuum glass vessel and evaporated therein. Next, pure N<sub>2</sub> gas, 1.0 L, was supplied to the glass vessel and the precise concentration was calculated. Then, a few milliliters of this gas sample was injected into a gas sampling bag (Smart Bag PA, GL Sciences, Tokyo, Japan), followed by dilution with pure N<sub>2</sub>. To obtain standard samples with lower concentrations, a similar dilution process was performed using another gas sampling bag. In this study, the standard VVOC sample is a mixture of acetaldehyde, isoprene, pentane, acetone, and ethanol, unless otherwise noted. The stability of the prepared standard gaseous sample in the sampling bag was confirmed up to 3 days for each analyte in preliminary study, where no permeation of the analytes was observed.

### 2.3. Needle-type extraction device

A stainless steel needle (85 mm × 0.5 mm I.D., 0.7 mm O.D. with a tip hole) was employed for all extraction processes in this study. To develop a novel extraction needle for the successful extraction of VVOCs, two types of activated-carbon (AC)-based sorbent particles were investigated: the graphite carbon absorbent Carbpac X (Supelco, Bellefonte, Pennsylvania, USA) (60/80 mesh) and a carbon molecular sieve (CMS) absorbent (Shinwa Chemical Industries, Kyoto, Japan) (70/80 mesh). A small amount of heat-resistant polymeric fibers consisting of Zylon filaments (Toyobo, Shiga, Japan) was packed at each end of the packed section to fix the packed sorbent. For sampling of gaseous samples, the extraction needle was attached to a commercially available vacuum sampling device (Komyo Rikagaku Kogyo, Tokyo, Japan). All the sampling was made at room temperature. After the extraction of the gaseous sample,

the extraction needle was attached to an injection syringe and then N<sub>2</sub> gas was collected via the extraction needle. The extraction needle was then inserted into the heated GC injection port and thermally desorbed VOCs were extruded into a column by N<sub>2</sub> gas.

### 2.4. Human breath samples

All breath samples used in this study were collected in the 1.0 L gas sampling bag after 3 s of breath holding by using a disposable straw. All volunteers were nonsmokers and prior to the test had abstained for at least 12 h from drinking alcohol or coffee, except during the alcohol drinking test.

### 2.5. GC–MS measurements

A Shimadzu QP5050A GC–MS system was used for all GC measurements. Helium (>99.999% purity) was used as the carrier gas. The head pressure and split ratio were set at 100 kPa and 15:1, respectively. The separation was performed with the capillary column HP-INNOWAX, 30 m × 0.2 mm I.D., 0.4 μm d<sub>f</sub> (J&W Scientific, Folsom, CA, USA). The column temperature was initially maintained at 40 °C for 2 min and then programmed to increase to 80 °C at a rate of 20 °C/min. The GC–MS interface temperature and ionization voltage were set to 250 °C and 70 eV, respectively. The mass spectrometer was operated in the selected ion monitoring mode (*m/z*: 44, 46, 57, 58, and 67).

## 3. Results and discussion

### 3.1. Development of a novel extraction needle for VVOCs

The extraction needles developed for the extraction of typical gaseous VOCs were initially used to investigate the extraction of gaseous VVOCs, but the extraction efficiencies were insufficient, especially for acetaldehyde and isoprene. In these preliminary experiments, relatively better extraction performance for VVOCs was obtained with the DVB/Shincarbon ST packed extraction needle because of the stronger adsorption power of Shincarbon ST. Therefore, use of strongly adsorbing AC-based extraction media was thought to hold promise for the novel extraction needle.

The extraction efficiency of the extraction needle for the analytes in this study was calculated as follows. Two identical extraction needles were connected in tandem, and the standard gaseous sample was introduced from the first extraction needle. The gaseous sample that passed through the first extraction needle was subsequently extracted by the second extraction needle. Then, the extracted analytes in each needle were separately analyzed by GC–MS. The extraction efficiency was defined as the ratio of the peak area for the respective analytes in each needle. The desorption efficiency was calculated on the basis of the ratio of the peak area obtained in the first desorption to the total peak area obtained in the first and second desorptions. Desorption conditions such as desorption temperature, volume of desorption gas, and desorption time were optimized for each extraction needle.

First, the CMS sorbent was investigated as the extraction medium. This sorbent has a surface area of approximately 1000 m<sup>2</sup>/g and is designed as one of the strongest absorbents for the extraction of typical VOCs in a gaseous sample. With the CMS packed needle, the extraction efficiencies for VVOCs were more than 99.9% for all investigated analytes. However, insufficient desorption was observed, especially the desorption rates of isoprene and pentane were approximately 90% and 86%, respectively. This was because the extracted analytes were so strongly adsorbed on the absorbent that they could not be desorbed successfully even at a desorption temperature of 300 °C. In addition, the peak shapes of isoprene and pentane were distorted owing to

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