Needle-type Extraction Device Designed for Rapid and Sensitive Analysis in Gas Chromatography

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A needle-type extraction device is one of the promising sample preparation devices for the gas chromatographic (GC) analysis of various organic compounds. The most remarkable advantage of this device is a simple and rapid desorption of the analytes by direct insertion of an extraction needle into a conventional GC injection port. In this review, fundamental aspects of the needle-type extraction devices and its applications for the determination of trace organic compounds, especially volatile organic compounds (VOCs), in several sample matrices are described.

Keywords Sample preparation, extraction needle, volatile organic compounds, gas chromatography

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1 Introduction	105	Aqueous Samples	108
2 Fundamentals of the Needle-type Extraction Device	106	5 Conclusion and Future Prospects	109
3 Determination of VOCs in Gaseous Samples	106	6 Acknowledgements	109
4 Extraction of Organic Compounds from		7 References	109

1 Introduction

Sample preparation is an important step in modern chemical analysis, and it directly affects the accuracy, precision and sensitivity of the entire analytical method. However, this step is normally a time-consuming process, and therefore, development of a rapid and accurate sample preparation technique has been regarded as one of the most important objectives in the field of analytical science and the related research area.^{1,2}

Miniaturization of the sample preparation has also been widely studied in liquid-phase separations³⁻¹⁰ using precisely controlled extraction media such as prepared by molecular shape recognition concept¹¹⁻¹⁶ or computer simulation of interaction.¹⁷⁻²⁰

A large number of sample preparation methods have been developed for the extraction of volatile organic compounds (VOCs) in gas chromatographic (GC) analysis. For example, the extraction of VOCs using charcoal tubes is a traditional sample preparation technique, where the extracted VOCs were desorbed by an organic solvent, such as carbon disulfide, and

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Fig. 1 Typical extraction and desorption procedures of gaseous VOCs with the needle-type extraction device.

the resulting solution was analyzed by GC. The technique has been widely employed; however, there are some disadvantages, such as multi-step and complicated procedures along with a requirement for a long analysis time. The thermal desorption (TD) method is an alternative sample preparation technique of the above solvent desorption method. The conventional TD process enables a sensitive and fully-automated analysis, although relatively expensive specially-designed instruments are necessary.^{21–23} Solid-phase microextraction (SPME) is a simple and solvent-free sample preparation technique,^{24,25} which is based on the equilibrium between the sample matrix and the extraction phase that is immobilized on a solid support. This method has been widely applied to the analysis of VOCs; however, the extraction medium consisted of a fused-silica rod, which is quite fragile. The possibility of a problematic carryover must also be considered in the repeatable use.

The needle-type extraction device is one of the effective sample preparation methods for the analysis of VOCs.^{26–28} The fundamental concept of the needle-based extraction method was mainly developed in the early 2000s by several research groups, and many publications have appeared.²⁹ The device typically contains particulate extraction material(s) in a thin-wall stainless-steel needle. For specific target analyte(s), the type of sorbent packed in the needle can be easily optimized on the basis of relatively quick preliminary experiments, allowing a wide range of applications to the GC analysis of VOCs.

This review mainly focuses on the determination of VOCs by needle-type extraction devices in GC. Fundamental aspects of the needle-type extraction devices is reviewed along with the applications of several types of extraction needles that contain different types of sorbents for an effective extraction of respective target analyte(s) from both gaseous and aqueous samples.

2 Fundamentals of the Needle-type Extraction Device

In the needle-type extraction device, an extraction sorbent is packed inside of a stainless-steel needle. As extraction sorbents, porous polymer beads or activated carbon (AC) based particles have typically been employed for effective extraction/desorption of VOCs.³⁰ The diameter of the particulate medium is normally in the range from 150 to 250 μm . In order to effectively extract a wide range of VOCs, a multi-bed-type extraction needle,

containing more than one sorbents has also been introduced.³⁰ Most of the needle-type extraction devices have typically been designed for the active sampling of gaseous samples. The analytes are extracted on the packed sorbent when a gaseous sample is passed through the sorbent-packed section of the extraction needle. For the extraction of gaseous samples, the sample was introduced from the tip side of the needle typically using a syringe or pump. The limit of detection (LOD) of the analytes depends on the sampling volume, having a typical value of from 10 mL to 1 L. A sampling flow rate of lower than 20 mL/min is often preferable for the effective extraction of most air samples.^{31,32}

After the extraction of analytes, the needle is directly inserted into a GC injection port. The extracted analytes can then be thermally desorbed in the heated GC injection port, typically without a desorption solvent.^{31,33,34} For desorption of the extracted analytes from the sorbent, there are two types of desorption methods: one uses carrier gas flow as the desorption gas,^{32–37} while another way is not using a carrier gas. When not using a carrier gas, the flow of an inert gas, supplied from a gas tight syringe, was used as the desorption gas.^{31,38–44} More recently, a new desorption method using a water vapor stream, generated from packed alumina, was also reported.⁴⁵ Among these desorption techniques, the first method is suitable for automation; however, it often requires a special instrument or liner. The second method is a simple process, and it does not require any specific instrument or modification of GC, as typically shown in Fig. 1.

Because of the above simple extraction/desorption processes using a needle-type extraction device, the method has been regarded as being a fast, sensitive, robust, and repeatable extraction method. The needle-type extraction devices have been employed, especially for the analysis of VOCs in gaseous samples,^{39–43} and the devices have been applied to biomedical analysis, such as the determination of VOCs in human breath samples.^{44,45} The determination of VOCs in aqueous samples by needle-type extraction device was also reported.^{36–38,45–47}

3 Determination of VOCs in Gaseous Samples

Berezkin *et al.* reported on needle-type extraction devices packed with Tenax as the extraction sorbent.⁴⁸ The extraction needle was employed for the determination of benzene and toluene in tobacco smoke, and it was further applied to the determination of benzene, toluene, ethylbenzene and xylenes (BTEX) in aqueous samples. The group of Pawliszyn developed two types of needle extraction devices.³³ One is a multi-bed-type extraction needle containing polydimethylsiloxane (PDMS), divinylbenzene (DVB) and Carboxen, and another is packed with only Carboxen 1000. The LODs for benzene, ethylbenzene, and xylene using the latter extraction needle were 0.23, 2.10 and 1.12 ng/L, respectively, at a sampling volume of 25 mL. Alonso *et al.* compared two types of extraction needles packed with Carboxen X and Tenax TA.³² They applied the method to the analysis of VOCs in breath, indoor air and outdoor air samples, confirming several advantages of the needle-type extraction device.

To effectively extract several VOCs, Saito *et al.* developed co-polymer beads of methacrylic acid (MA) and ethylene glycol dimethacrylate (EGDMA) as the extraction medium.³¹ A gaseous sample was collected by a vacuum gas sampling device, and the extracted VOCs were determined by a flame ionization detector (FID) in GC. The results clearly indicated satisfactory extraction and desorption performances along with an excellent

storage performance of the extracted analytes in the extraction needle, typically up to 7 days, at room temperature. The extraction needle was then adapted for the evaluation of third-hand smoking,⁴⁰ where smoking-related VOCs evaporated from several types of fabrics to the environmental air were extracted and determined by mass spectrometry (MS). Third-hand smoking pollution in an automobile was also confirmed. In addition, a novel fire investigation technique was developed with a needle-type extraction device. For the determination of VOCs directly related to fire accelerants, such as gasoline or kerosene, a polymer particle of DVB was introduced as the extraction medium. The needle extraction was successfully applied to the determination of VOCs in simulated fires, as shown in Fig. 2.⁴¹

A novel double-bed-type extraction needle was developed for the determination of VOCs in indoor air environments.⁴² In this study, indoor air samples including a wide range of VOCs were collected for 30 min using a sampling pump. To determine an optimum extraction medium, several types of particulate sorbents were tested, and a double-bed-type extraction needle

containing DVB and AC particles showed excellent extraction and desorption performances for all of the investigated VOCs. The proposed extraction method was compared to the corresponding conventional solvent extraction method in the analysis of real indoor air samples. This double-bed-type extraction needle was then applied to an evaluation of the indoor air environment in school facilities,⁴³ suggesting the advantages of the needle-type extraction device for assessing indoor air environments.

On the basis of the above successful extraction performances of the needle-type extraction device for a wide range of VOCs having a different volatility and/or polarity, the extraction needle has been successfully applied to the determination of VOCs in human breath. Ueta *et al.* determined the breath acetone concentration for healthy subjects and type-2 diabetic patients by using a MA/EGDMA-packed extraction needle in the sample preparation step prior to the analysis in GC-MS.⁴⁴ For the diagnosis of diabetes, the glucose concentration and glycosylated hemoglobin level in blood, HbA1c%, have been used along with the concentration of the ketone bodies in urine. HbA1c% is the percentage of hemoglobin-sugar complex relative to total hemoglobin in blood, and that well represents an average amount of glucose level in blood over about the last two to three months. A higher HbA1c% value means a higher glucose concentration in blood, although the value is not affected by a short-term variation that might be induced by a meal, or other miscellaneous factors. The results well demonstrated that there is a clear correlation between the concentration of breath acetone and HbA1c% for type-2 diabetic patients. In addition, a high correlation between the breath and urine acetone concentrations during a fasting test was also confirmed for healthy subjects.

Mieth *et al.* introduced a multibed-type extraction needle for the on-site sampling of breath samples,³⁴ and applied the needle to the sample preparation of breath VOCs for subsequent analysis in a heart-cut GC/MS, and also comprehensive two dimensional GC-time-of-flight mass spectrometry (GCxGC/TOF-MS).³⁵ Trefz *et al.* investigated the sample flow rate and sample volume, along with the effect of humidity for breath analysis using a MA/EGDMA-packed needle and a triple-bed extraction needle.⁴⁹ They reported that the triple-bed extraction needle was not affected by the humidity. Determinations of VOCs in gaseous or breath samples by needle-type extraction devices are summarized in Table 1.

In order to extract high-volatile VOCs, several VOCs should be derivatized before chromatographic analysis. With a fiber-packed extraction needle, derivatization reactions were introduced. The extraction needle was packed longitudinally

Fig. 2 Typical chromatograms of extracted VOCs in two simulated fire scenes. (A) Simulation of an arson fire and (B) simulation of misfueling of gasoline into kerosene heater. Peaks: (a) 1-ethyl-2-methylbenzene, (b) 1,2,4-trimethylbenzene, (c) 1,2,3-trimethylbenzene.

Table 1 Needle-type extraction device for the determination of VOCs in gaseous samples

Packed sorbent	Analyte	Sampling volume/mL	Detection	LOD/ng L ⁻¹	Ref.
Tenax	Benzene, toluene				48
Tenax TA	10 VOCs	1000	MS	0.002 - 0.01	32
Carboxen 1000	Benzene, ethylbenzene, xylene	25	FID	0.23 - 2.10	33
MA/EGDMA	Hexane, acetone, ethyl acetate, toluene	50	FID	1000	31
MA/EGDMA	Tobacco related VOCs	50	MS	0.5 - 5.0	40
DVB	Fire accelerants related VOCs	50	MS	0.03 - 0.1	41
DVB/AC	Indoor air VOCs	600	MS	0.004 - 0.02	42
DVB/AC	VOCs in school facilities	50/600	MS		43
MA/EGDMA	Breath acetone	50	MS	1.2	44
Tenax/Carbopack X/Carboxen 1000	Breath VOCs	25	MS	0.4 - 8.3	34
Tenax/Carbopack X/Carboxen 1000	Breath VOCs	20	MS		35
DVB/Carbopack X/Carboxen 1000	Breath VOCs	10 - 100	TOF-MS		49

with a bundle of Zylon filaments (12 μm o.d.),^{50,51} which were also surface-coated with polymeric materials, as illustrated in Fig. 3. Taking advantage of a good heat-resistant property along with the stability to organic solvents and reagents,⁵⁰⁻⁵⁶ a Zylon-packed needle could be employed in the sample preparation process using a derivatization reaction of target compounds. For the extraction of volatile aldehydes and ketones, a derivatization reaction with 2,4-dinitrophenylhydrazine (DNPH) was introduced.⁵⁷ After loading of the DNPH solution into the needle extraction device, a gaseous sample was collected through the fiber-packed needle. During the sampling, analytes were reacted with the derivatization reagent on the packed filaments at room temperature, and the derivatives were simultaneously extracted on the polymer coating of the fiber. The extracted derivatives were then desorbed by injecting acetonitrile and N_2 gas through the needle in the GC injector. Volatile aldehydes were also derivatized by *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) using the fiber-packed needle.³⁹ This method was further applied to the determination of gaseous ethylene oxide (EO),⁵⁸ where an aqueous solution of HBr was used for the derivatization of EO

in the needle. As the desorption solvent, methanol was used for an effective desorption of the extracted derivative, 2-bromoethanol, from the needle. Successful applications to the analysis of EO in tobacco smoke and automobile exhaust were demonstrated in the report.

4 Extraction of Organic Compounds from Aqueous Samples

The amounts of organic compounds, including VOCs, in tap water or drinking water, are typically on the order of $\mu\text{g/L}$ to ng/L . To determine trace levels of organic compounds in these water samples, an effective sample preparation is needed. The extraction of the VOCs in aqueous samples by a needle-type extraction device showed significantly higher extraction amounts than SPME.⁵⁹ The representative publications for the determination of organic compounds in aqueous samples by needle-type extraction device are tabulated in Table 2. For the extraction of BTEX in aqueous samples, a novel extraction needle was developed.⁴⁵ An extraction needle contained Porapak Q and wet alumina; they could work as the sorbent and the source of water vapor for the desorption of the extracted target analytes, respectively. In this method, aqueous samples were directly passed through the needle. BTEX in aqueous samples was also analyzed by a purge and trap (PT) technique using a Carbowack X-packed extraction needle.⁴⁶ Crom *et al.* also reported the determination of BTEX in aqueous samples using a Carbowack X-packed needle, where several experimental parameters were systematically optimized.³⁶ Additionally, the same research group compared two techniques, headspace and PT, for the analysis of VOCs in aqueous samples using a needle extraction device. They concluded that PT analysis showed a better sensitivity.³⁷ Lou *et al.* determined formic and acetic acids in aqueous sample using a DVB-packed extraction needle in GC-FID.³⁸

Ueta *et al.* demonstrated an effective analysis of 23 VOCs in aqueous samples by PT with a multibed-type extraction needle, as illustrated in Fig. 4.⁴⁷ As the extraction medium, DVB, AC particles, and carbon molecular sieve (CMS) particles were used. The technique does not require any desorption solvent for the analysis of VOCs in aqueous samples. The limit of quantifications of all the investigated VOCs reached 10-times lower than its reference values. The method was applied to the analysis of real tap-water samples, and some trace VOCs were successfully detected.

A fiber-packed extraction needle was applied to the dynamic extraction of aromatic compounds in aqueous samples.⁶⁰ The extraction was made by pumping the sample solution into the extraction needle, and the subsequent desorption was carried out using a desorption solvent of dichloromethane. The fiber-

Fig. 3 Determination of VOCs with derivatization reaction using a fiber-packed needle.

Table 2 Needle-type extraction device for the determination of organic compounds in aqueous samples

Packed sorbent	Analyte	Sampling method	Sample volume/mL	Detection	LOD/ng L ⁻¹	Ref.
Porapak Q/alumina	BTEX	Dynamic extraction	5	FID	430 – 830	45
Carbowack X	BTEX	PT	50	FID	50 – 70	46
Carbowack X	BTEX	Static HS		FID	10000 – 25000	36
Tenax TA/Carboxen 1000	18 VOCs	Static HS	5	MS	10 – 60	37
DVB	Formic and acetic acids	PT	20	FID	87200 – 234800	38
DVB/AC/CMS	23 VOCs	PT	20	MS	10 – 300	47
Polymer-coated fiber	Aromatic compounds	Dynamic extraction	0.16	FID	200 – 2000	60
Polymer-coated fiber	Bisphenol A	Dynamic extraction	0.16	MS	< 500	61

Fig. 4 PT analysis of VOCs in an aqueous sample by a multibed-type needle extraction device.

packed needle was also employed for the determination of bisphenol A in water samples using the derivatization reaction with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA).⁶¹ After the extraction of bisphenol A onto the polymer-coated fiber by pumping aqueous solution into the needle, the remaining water in the needle was completely eliminated by N₂ gas flow, aspiration by a vacuum pump, and heating. Then, BSTFA was introduced into the needle, and reacted with the analyte by heating. The derivative was successfully desorbed with a desorption solvent of dichloromethane.

5 Conclusion and Future Prospects

The development of a miniaturized and effective sample preparation method is one of the important objectives in the field of analytical science;^{62,63} it should be continuously studied to construct a simple and effective analytical method in the next generation. The extraction of organic compounds by a needle-type extraction device showed a simple and sensitive extraction method, and actually several applications have been reported, including the sample preparation of gaseous and aqueous samples. Further applications of the extraction needle could be performed, such as the determination of organic compounds in food and drink, soil or biomedical samples. In addition, the needle-type extraction device could be hyphenated with other types of separation techniques, such as liquid chromatography or capillary electrophoresis.

Techniques developed related to the needle-type extraction devices include a precise packing process of the fine particles into the capillary tube, which have been applied to the development of packed-capillary columns.⁶⁴⁻⁶⁶ A wide variety

of additional applications of the needle-type extraction devices coupled with the packed-capillary column will be expected,⁶⁷⁻⁷⁰ along with further developments of miniaturized separation techniques, while offering many advantageous features.

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