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Comparison of Analytical Methods for BTEX Determination in Gasoline-contaminated Soil

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Analytical methods for the determination of BTEX in soil sample using by gas chromatography / mass spectrometry (GC/MS) - direct injection, purge & trap and solid phase microextraction (SPME) were compared and described. The extraction of BTEX from soil sample was performed by ultrasonic agitation. The Carbopack C & B of BTEXTRAP™ as a trap was used for the concentration of BTEX in purge & trap-GC/MS analysis. In SPME analysis, a fused-silica fiber coated with 100 polydimethylsiloxane (PDMS) was used for the absorption of BTEX on the fiber, and the extraction of BTEX was performed by the headspace mode. For finding optimum conditions of BTEX analysis, experimental parameters of SPME such as extraction time, temeperature were investigated. For gasoline sample, 72 volatile compounds were identified by direct injection into GC/MS. The 65 compounds were observed in the analysis of cryogenic purge & trap-GC/MS, whileas 36 and 41 compounds were observed in non-cryogenic purge & trap-GC/MS and SPME-GC/MS, respectively. Although all volatile organic compounds (VOCs) were not observed by both purge & trap and SPME methods, BTEX was successfully determined by both methods.

Key words:

1. Introduction

Soil contaminations have a much lower probability of direct exposure to human beings than air and water. But the presence of air and water in soil causes the transportation of contaminants to groundwater and plants and finally it has an impact upon human beings.

Total petroleum hydrocarbons (TPH) are common soil contaminants and are divided into two classes : the gasoline-range organics (GRO) and the diesel-range organics (DRO), they frequently enter soil, sediments and groundwater because of accidental oil spills, leaking storage tanks. Among both classes of contaminants, GRO are more environmentally malignant because they have a larger percentage of the potentially more toxic aromatic compounds. Especially, BTEX of gasoline compounds are hazardous carcinogenic and neuro-toxic compounds and are classified as priority pollutants by the US Environmental Protection Agency (EPA).[1~2] Thus the analysis of BTEX is an important for monitoring of fuel contamination in soil.

Various methods for BTEX and other VOCs from environmental samples were reported in the literature which are based on methods such as solvent extraction, vacuum distillation and supercritical fluid extraction (SFE),[3] but the most commonly used methods are based on either static headspace or dynamic headspace.[4] But major problem of static headspace is that the sample matrix significantly affects the equilibrium. Matrix effects often result in loss of sensitivity for the analyte that show increased solubility in the sample matrix.

On the other hand, a dynamic headspace such as purge & trap overcomes the problem of static headspace. Even though the purge & trap has been often used as the recommended EPA method due to its high sensitivity, it has also some disadvantage of equipment complexity and limitation of injection volume depending on analytical concentration.[5] Because the

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high concentration samples may be the contamination of the system, they need the screening data for real samples. Therefore, a injection volume of purge & trap is determined by the screening data.

For the easier and more economical method, solid phase microextraction (SPME) has been applied to extract VOCs from the solid, liquid and gas matrix.6~8) The advantage of this method is fast, efficient, an environment-friendly means that does not require much of solvent for extraction from the various sample matrix.9~11) Additionally, it is possible to extract the analyte from the sample matrix without interferences in the case of using the headspace-SPME. But it is necessary for an equivalent extraction efficiency of purge & trap to optimize experimental parameters such as the extraction time, temperature, salting out effect an so on.

The alternative method for determining VOCs is a vacuum distillation. This method is the elimination of an adsorbent trap and direct interfacing of the apparatus to a gas chromatograph/mass spectrometer (GC/MS).12~13) Then it is eliminated a major source of problems that plagued VOCs determination. However, this method was cumbersome and required continuous operator activity. In addition, compounds with water solubilities and higher boiling point have lower recoveries.14~15)

Recently, membrane inlet mass spectromerty (MIMS) has been developed for a on-site, on-line, and rapid method of VOCs from environmental samples.16) Moreover, rapid analysis can be obtained by coupling dynamic headspace and membrane collection.17) In spite of the rapid analysis, the method has a limited selectivity since no chromatographic separation is used.18)

The purpose of this work is that an evaluation of different methods such as direct injection, purge & trap, and headspace SPME analysis for gasoline compounds. BTEX in gasoline-contaminated soil sample were mainly determined by two purge & trap and SPME methods. Furthermore, experimental parameters of SPME method were optimized for the extraction of BTEX from the soil sample, enable to give equivalent to purge & trap method. The effectiveness of these analytical methods for measuring BTEX in soil samples were compared in this paper.

2. Eeperimental

2.1. Samples

The granitic soils which is a common type in Korea were collected locally and then sieved in the range of between 850 μm and 2 mm. The homogenized mixture was washed several times with organic-free reagent water to remove debris. The washed sample was dried at 120°C and stored against moisture. The volatile organic compounds in the soil sample should not be observed at detectable levels of the target analytes before spiking. The 5g soil samples were spiked with BTEX in the range of between 0.2 / and 500 /, and then added methanol, shaken vigorously.

2.2 Standards and Materials

The analytical standards of BTEX and isotopically labeled 1,2-dichlorobenzene-d_4 as the internal standard were purchased from Supelco (Bellefonte, PA). The stock standard mixture was prepared with methanol at a concentration of 1/ and stored at 4?. Working standard solutions were prepared by methanol dilution. The gasoline was obtained from a gas station located in Seoul.

2.3. Purge and trap experiment

The 10 mL mixture containing 0.1 mL of methanol extract and 9.9 mL of organic free reagent water was purged and concentrated using a HP AS 16 autosampler and a Tekmar 3000 purge and trap device. The Carbopack C & B of BTEXTRAP ™ used as a trap was purchased from Supelco (Bellefonte, PA). The preconditioning of a trap was heated at for 60min prior to use. The analytes were desorbed from the trap at 270°C and started to run the GC/MS analysis. To improve chromatographic properties of volatile organic compounds, the liquid nitrogen cryogenic focusing was used for interface with gas chromatograph system, it was started after the end of desorption process.

2.4. SPME experiment.

The 2 mL mixture containing 0.1 mL of methanol extract and 1.9 mL of organic free reagent water in a 4 mL vial was sealed with a silicon septa. The SPME device and the fibers were purchased from Supelco (Bellefonte, PA). When a new fiber was conditioned for 1 hr in a GC injector port at 250°C before analysis. A fused-silica fiber coated with 100 polydimethylsiloxane (PDMS) was inserted and placed in the headspace. The sample was stirred by a 10 mm×3 mm magnetic stirring bar at 1000 rpm. After the sampling, the fiber was withdrawn and then transferred to a heated GC injection port.

2.5. Gas chromatography/Mass spectrometry

A Hewlett-Packard Model HP 6890 gas chromatograph equipped with a HP 5973 mass selective detector system was used. The GC separation column was a 30 m, 0.25 mm DB-5MS, with a 0.25 m film thickness, from J & W Scientific. GC conditions were as follows; injector temperature, 250°C inlet mode, splitless operation; linear velocity, 40 cms^{-1}. The oven program was a 5min isothermal time at 40°C followed by a 10°C/min ramp to 200°C where it was held for a 5min bakeout time. The mass spectrometer conditions were as follows; electron energy, 70 eV; ion source temperature, 180°C; scan mass range, 35~400(m/z). The selected ion mode was used to improve sensitivity in the analysis of BTEX.

3. Results and Discussion

3.1. Background of sample preparation

Generally, the adsorption processes of VOCs in environmental soil are as follows; (1) on the mineral grains (2) on the surface of the water layer on mineral grains, (3) on the organic material, and (4) on the micropores of particles. Furthermore, VOCs are partly dissolved in water film on the particles. All these factors affect the process of desorption from soil and then the extraction of VOCs from soil is more complicated process. The other considering of determination is to reduce the loss of VOCs from soil samples during the sampling, handling and analytical processes. For the reason a closed-system direct analysis by bulk sampling method has been used. However, the contaminants in soil for a long period of time have a tendency to be adsorbed in the micropores of soil particles instead of on the external soil surfaces.[19] So in the case of bulk sampling method it is not clear that the purge gas interacts with all parts of the sample because soil tends to be non-homogeneous micropores. While the methanol method is used, the methanol can be permeated into micropores of soil particles. Therefore, methanol can play an important role of preservation as well as extraction of VOCs from soil simultaneously. From recent literature review[20], even though the methanol extraction method can lead to a loss of BTEX between sample transport and analysis, but it can be more minimized than the bulk sampling method. In this study all samples were prepared by the methanol extraction method. The prepared spiking samples were added to 10 mL of methanol and stored at 4°C before analysis. The samples were shaken vigorously for 2 min and centrifuged in the speed of 4000 rpm for 5 min to settle the suspended soil particles. The supernatant were taken and analyzed by each method.

3.2. Identification of gasoline compounds

Gasolines are blended from several refinery process streams from direct distillation of crude oil, catalytic reforming processes, and from alkylation and isomerization of the light distillated streams. There are more than 300 individual compounds recognized to data in gasoline. Therefore, they had been identified and characterized in according to practical purposes. From the literature of ref 26. they described volatile alkenes which are unburn fuel compounds among gasoline.[26] Z. Wang *et al.*[21] focused on BTEX and C3-benzene in gasoline.

In this paper, the gasoline obtained from a gas station located in Seoul was identified and classified into 7 classes in according to their characteristics by direct injection and described the properties of different methods. In order to detect all compounds of gasoline, 1 *μl* of neat gasoline was injected to GC. Seventy-two compounds were detected and identified by direct injection-GC/MS analysis. Based on the correlated peak area, the content of each class was obtained as follow ; BTEX (52%), C3-benzene (14%), C4-benzene (2%), alkane (15%), alkene (5.6%), methyl-*t*-butyl ether (MTBE) (5.3%), cycloalkane (4%), cycloalkene (2%). As the result, major portion of gasoline are consist of BTEX. Therefore, it is possible to monitor gasoline-contaminated level in soil through the quantitative analysis of BTEX.

3.3. Determination of gasoline compounds by various analytical method

Four different methods were performed to compare with the selectivity of volatile organic compounds (VOCs) in gasoline. When the extraction of VOCs is performed using methanol solvent in direct GC/MS analysis, the highly volatile compounds with below boiling point than the extraction solvent were seriously affected by solvent peak. As a result, these compounds could not identify and quantify by direct injection mode. On the other hand, other three methods including non-cryogenic, cryogenic purge & trap and SPME could eliminate the effect of solvent through the concentration step and VOCs could easily concentrate, identify and quantify.

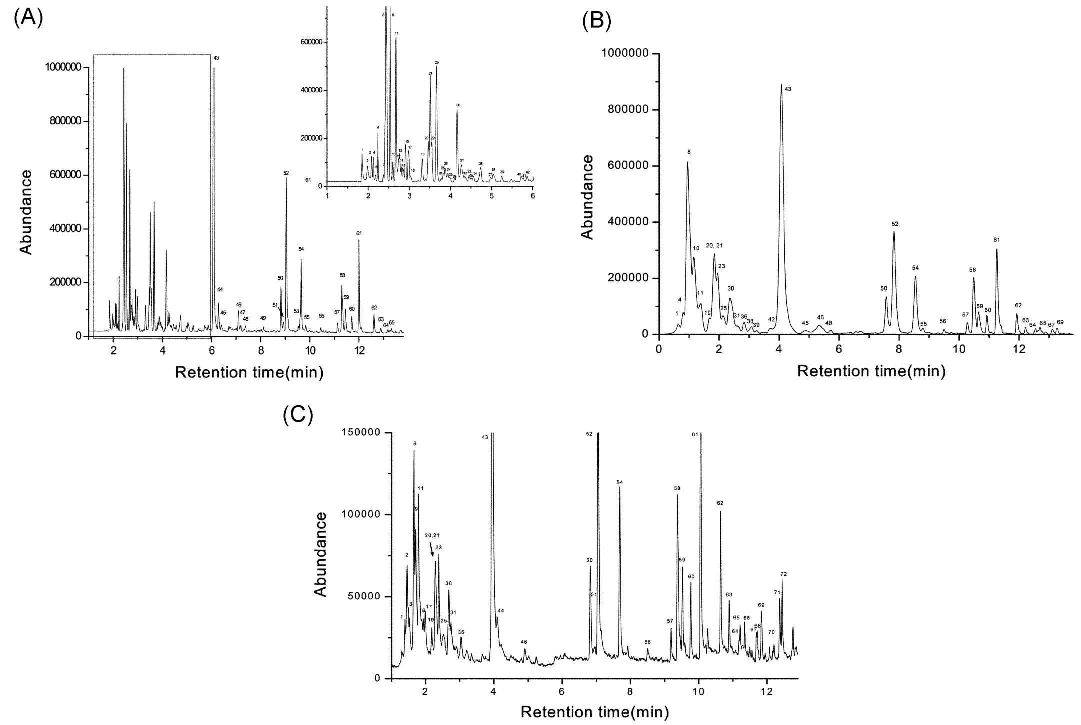

Fig. 1. Total ion chromatograms of VOCs in gasoline obtained by (A) Cryogenic purge & trap-GC/MS (B) Noncryogenic purge & trap-GC/MS and (C) SPME-GC/MS. Peak numbers : 1. 2-methylbutane, 2. 1,1-dime-thylcyclopropane, 3. n-pentane, 4. 2,2-dimethylbutane, 5. cyclopropane 6. 2,2-dimethylbutane, 7. 3-methylenepentane, 8. ethyl-t-butyl ether(MTBE), 9. 3-methylpentane, 10. 2-methyl-1-pentene, 11. n-hexane, 12. trans-2-hexane, 13. 2,3-dimethyl-1-butene, 14. 3-methyl-trans-2-pentene, 15. 2-hexene, 16. 3-methyl-trans 2-pentene, 17. methylcyclopentane, 18.2,3-dimethyl-2-butene, 19. 1-methyl-cyclopentene, 20. benzene, 21. 2-methyl-hexane, 22. 2,3-dimethyl-pentane, 23. 3-methylhexane, 24. 2,4- hexadiene, 25. 1,3-dimethyl cyclopentane, 26. 3-ethylpentane, 27. 3,3-dimethylcyclobutanone, 28. 2-cyclohexen-1-ol, 29. 1,1-dimethyl-cyclopropane, 30. heptane, 31. 2-methyl-2-hexene, 32. 2-heptene, 33. 3-methyl-2-hexene, 34. 4,4-dimethylcyclopentene, 35. cycloheptane, 36. methylcyclohexane, 37. 2,5-dimethylhexane, 38. 2,4-dimethylhexane, 39. 1,2,4-tri- methylcyclopentane, 40. 4,4-dimethylcyclopentene, 41. 1,3-heptadiene, 42. 2,3-dimethylhexane, 43. toluene, 44. 3-methylheptane, 45. 1,2-dimethylcyclohexane, 46. octane, 47. 2-methyl- 3-heptene, 48. 1,3,3,4-tetramethylcyclobutene, 49. 2,5-dimethylheptane, 50. ethylbenzene, 51. 2-methyloctane, 52. m,p-xylene, 53. 3-heptanone, 54. o-xylene, 55. nonane, 56. isopropyl- benzene, 57. n-propylbenzene, 58. 1-methyl-2-methylbenzene, 59. 1,3,5-trimethylbenzene, 60. 1-ethyl-2-methylbenzene, 61. 1,2,4-trimethylbenzene, 62. 1,2,3-trimethylbenzene, 63. 1- propenylbenzene, 64. 1,4-diethylbenzene, 65. 1-methyl-3-propylbenzene, 66. 1-ethyl- 3,5-dimethylbenzene, 67. 1,2-dimethyl-1,4-ethylbenzene, 68. 1-methyl-1-propylbenzene, 69. 1-ethyl-2,3-dimethylbenzene, 70. undecane, 71. 1,2,3,5-tetramethylbenzene, 72. 1,2,3,4- tetramethylbenzene.

Fig. 1 shows corresponding total ion chromatograms of gasoline obtained by these method. Most of compound in gasoline eluted within 14 min in GC-chromatogram. The different retention times of target analytes obtained by these methods were resulting in difference of analyte-entering time to GC/MS of desorbed compounds. The identified compounds in gasoline were given in order of elution as peak numbers in Fig. 1. As shown in Fig. 1, 65 peaks by cryogenic purge & trap *(A)*, 36 peaks by noncryogenic purge & trap (B) and 41 peaks by SPME (C) were detected in each chromatogram. All compounds in gasoline by GC/MS analysis could not get a complete GC separation because of coelution in chromatogram. As seen in Fig. 1, the major of peaks within 6 min were assigned as benzene and methyl-*t*-butyl ether (MTBE) that are used as oxygenates and octane enhancers in gasoline.[22] While all of 42 compounds were detected by cryogenic purge & trap within 6 min, 20 compounds were detected by non-cryogenic purge & trap and SPME compared with neat gasoline analysis. The coeluting compounds of MTBE [Peak no. 8] are 3-methylpentane [9], 2-methyl-1-pentene [10] and n-hexane [11] that are known to be relatively high Henry's law constants. While all compounds coeluted with MTBE were completely separated by using cryogenic purge & trap method. 2-Methyl-1-pentene [10] was not identified by SPME method and 3-methylpentane [9] and 2-methyl-1-pentene [10] were not identified by non-cryogenic purge & trap. Even though using cryogenic purge & trap, benzene [20] was not completely separated with 2-methylhexane [21]. Although these compounds were overlapped in chromatogram, they are easily identified using GC/MS-extracted ion monitoring. Toluene, ethylbenzene and xylenes were eluted between retention time 6 and 9 min.

Para- and meta-xylene isomers were not separated on the DB-5 column and these compounds were eluted at the identical retention time.[23] These compounds were always came out in GC chromatogram after the elution of C3-benzene isomers and C4-benzene isomers.

To sum up, cryogenic purge & trap for highly volatile compounds was shown to be more effective than SPME. It can be explained that highly volatile compounds are desorbed from the trap at high temperature and then refocussed by liquid nitrogen, before entering the GC column. Thus, the peak shape of these compounds could be greatly improved in the GC chromatogram. In addition, SPME was shown to be more favorable method compared with noncryogenic purge & trap. Besides, the sensitivity and selectivity of C3-benzenes and C4-benzenes by SPME were also more favorable than those of two purge & trap methods. These results reflected that the different extraction efficiency of each compound in gasoline was shown significant difference according to extraction.

3.4. Analysis of BTEX by direct injection, purge & trap

Total ion chromatograms as shown in Fig. 2 were obtained by direct injection, purge & trap and SPME. The separation of BTEX by all extraction method

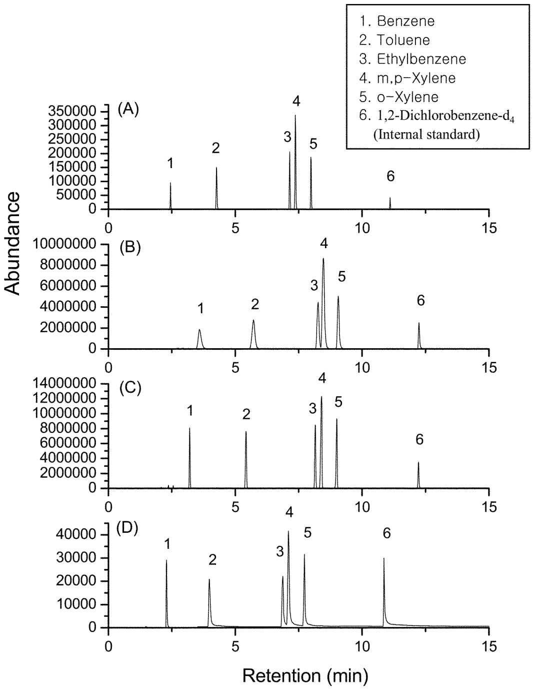

Fig. 2. Total ion chromatograms of BTEX obtained by (A) SPME- GC/MS, (B) Non-cryogenic purge and trap-GC/MS, (C) Cryogenic purge and trap-GC/MS and (D) Direct injection-GC/MS. Peak numbers : 1. benzene, 2. toluene, 3. ethylbenzene, 4. m,p-xylene, 5. o-xylene, and 6. 1,2-dichlorobenzene-d_4

was good. The linearities to verify were tested using five concentrations of BTEX. Calibration curves of BTEX was made by an internal standard method using isotopically labeled 1, 2-dichlorobenzene-d_4 as internal standard. Concerning the matrix effect, all the calibrations were carried out using the matrix spiked. Standard solutions of different concentrations of BTEX were spiked on to the soil matrix. As can be seen in Table 1, linear regression coefficients of BTEX were about above 0.995, showing successful linearity by both direct injection and purge & trap methods. Although direct injection method could not be applicable at lower concentration level (below 0.2 ppb) due to the limitation of injection, it can be used in wide range of concentration at 0.2~500 ppb. In the case of purge & trap, a calibration range of was limited between 0.2 and 20 ppb by an injection volume of 100 that was fixed. When the expected concentration of a soil sample is over the calibration range through the soil screening analysis, it should be diluted. SPME was performed in the same range of purge & trap. When using the standard solution for linearity without matrix, the equation is applied to quantify unknown samples as follow :

Concentration of each analyte (mg/kg)

$$= \frac{A_s X V_f X D}{W_d X V_i}$$

A_s : Amount(mg) obtained from standard solution

V_f : Methanol volume(mℓ)+moisture volume calculated on the basis of dry weight(mℓ)

D : Dilution factor

W_d: Dry weight of soil

V_i : Injection volume of sample

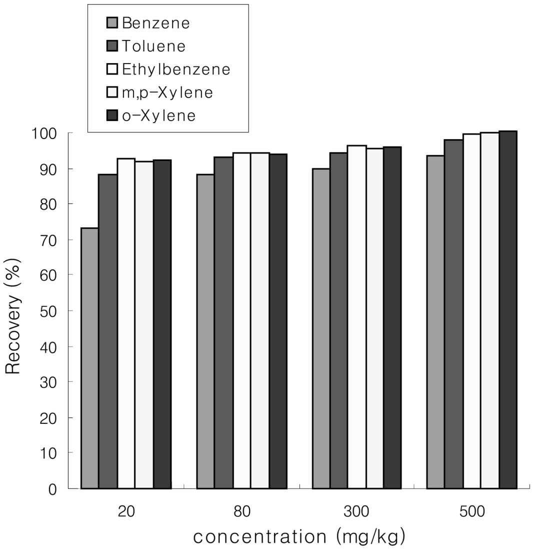

Fig. 3. Recoveries of BTEX spiked in soil samples at each concentrations by direct analysis.

Though each amount of analyte for the sample can be simply calculated without the above equation when using the matrix calibration. Additionally, the data has closer to real value containing the loss during the sample preparation, concentration and extraction step. The required blank soil has been obtained from a nearby sampling site for holding similar soil characteristics.

The efficiency of BTEX from soil by methanol extraction can be obtained with direct injection mode. As shown in Fig. 3, the extraction efficiencies according to various concentrations of BTEX were over 90 percent, except for benzene due to its high vapor pressure (95.2 mm Hg at 25°C).[24] Benzene may be loss occurred during the sample handling and workup.

Fig. 4 shows the extraction efficiency using purge & trap method. It contains the purging efficiency due to the aqueous solubility of each compound as well as the loss of former stated portion in case of direct injection.

Table 1. Calibration curves and linear regression of BTEX spiked in soil sample

Compound	Equation		Linear coefficient (R^2)	
	direct analysis	purge& trap	direct analysis	purge & trap
benzene	y=0.0911X+0.3505	y=0.0883x-0.0489	0.9979	0.9952
toluene	y=0.17X+0.4418	y=0.1652x-0.063	0.9987	0.9964
ethylbenzene	y=0.1944x+0.2759	y=0.1616x-0.0708	0.9987	0.9964
m,p-xylene	y=0.3651x+0.9623	y=0.3237x-0.1414	0.9982	0.9962
o-xylene	y=0.1883x+0.6663	y=0.148x-0.0641	0.9979	0.9964

As the solubility of compound increase, the purging efficiency is getting worse. Therefore, benzene has higher aqueous solubility (1800 mg/L)[24] and it causes the low purging efficiency than other compounds.

3.4. Optimization parameter of SPME

Headspace (HS)-SPME was performed to extract for high degree efficiency from matrix through the optimization such as extraction time, temperature, salt effect and headspace volume. The principle of SPME sampling is based on the partitioning of the analytes between the fiber coating and the sample matrix. When the partitioning comes to equilibration of the analytes between the fiber coating and sample, the adsorbed analytes in the fiber coating can be thermal desorption in high temperature GC injector. According to experimental parameters controlled properly, this method is can be relatively insentives to matrix effects. Moreover, many interference problems can be eliminated using HS-SPME, because the fiber is not in contact with the sample mixture.

Polydimethylsiloxane (PDMS) fiber was selected as concentration of BTEX from the literature review.[25] In general, a PDMS with 100 thickness fiber is well known to be suitable for the extraction of nonpolar compound with low molecular weight and high volatility.

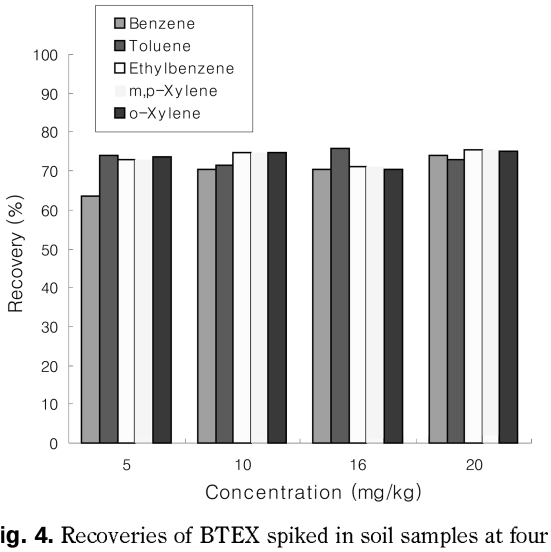

Fig. 4. Recoveries of BTEX spiked in soil samples at four concentration levels by purge & trap method.

As base on an equilibrium distribution process of SPME, sample stirring can reduce the required time to reach equilibrium by enhancing the diffusion of the analytes towards the fiber. Thus, samples were stirred with magnetic stirring at 1000 rpm. In this experimental condition, the final equilibrium was reached within 5min for BTEX, as shown in Fig. 5. Therefore, the extraction time was selected for 5 min.

The extraction temperature also enhances the diffusion of analytes towards the fiber from the matrix. However, the distribution constants of the analytes are decreased as increasing temperature for the same time. Thus, it is necessary to study the extraction temperature profile to find temperature effect on extraction of BTEX. As shown in Fig. 6, the extraction efficiency has shown negative effect on BTEX as the temperature increases. Thus, the extraction temperature was set at 30°C.

By adding a salt to the aqueous extraction sample, the ionic strength can be increased, thereby increasing the partitioning of organic compounds into the fiber. Furthermore, saturation of the sample can be achieved by the addition of an excess NaCl. However, the direct contact of NaCl solution with fiber can lead to significant degradation the fiber-surface, affecting on life-time of fiber. Thus, the addition of salting-out reagent to solution should be carefully used and is possible only using HS-SPME mode.

In HS-SPME, the situation is more complex compared to direct extraction since the analytes partition to the gaseous phase as well as to coating. The volume of

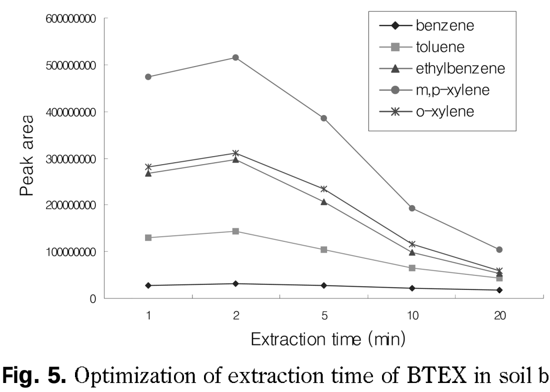

Fig. 5. Optimization of extraction time of BTEX in soil by headspace-SPME

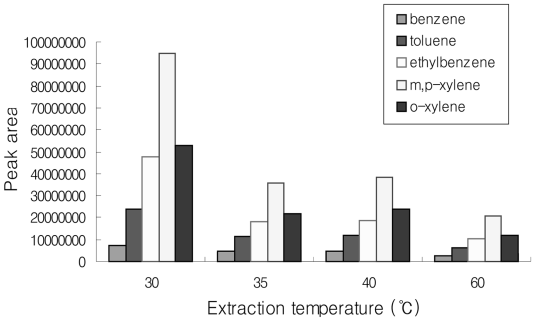

Fig. 6. Optimization of extraction temperature of BTEX in soil by headspace-SPME.

the gaseous phase should be minimized for high sensitivity in headspace extraction. In addition, when the headspace/sample volume ratio increases, volatile analytes have the loss of sensitivities. Aqueous volume which contain 100 of extracted sample were changed. As shown in Fig. 7, 3 mL of aqueous had better extraction efficiency.

Method detection limit (MDL) was performed on the basis of optimization condition. Table 2 shows the method detection limit (MDL) of each method obtained by analysis of seven times using the concentration which was expected the limit range. As shown in Table 2, MDL of direct injection was much higher because the injection volume of this is almost 1/10 1/100 fold much lower than other methods. HS-SPME had slight lower detection limit than purge & trap.

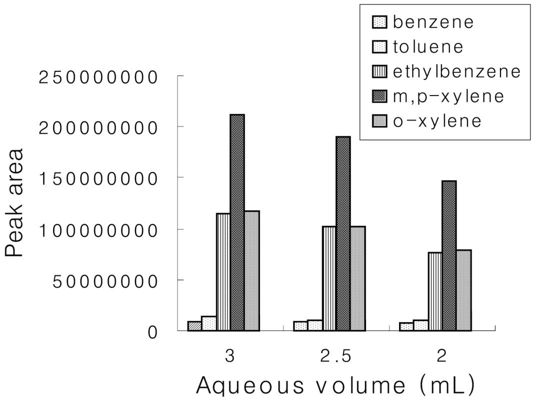

Fig. 7. Effect of aqueous volume of headspace-SPME

Table 2. Method detection limits of BTEX spiked in soil samples obtained by direct analysis, purge & trap method and headspace-SPME

Compound	Method detection limits (/)		
	direct analysis	purge & trap	headspace SPEM
benzene	119.8	0.80	0.62
toluene	96.3	0.49	0.47
ethylbenzene	71.8	0.28	0.15
m,p-xylene	79.0	0.55	0.52
o-xylene	87.8	0.24	0.13

4. Conclusions

This paper describes analytical method including direct injection, purge & trap and HS-SPME with GC/MS for determination in gasoline-contaminated soil with emphasis on BTEX.

Comparing with direct injection, 65 compounds in gasoline sample were observed by cryogenic purge & trap method while non-cryogenic purge & trap and SPME methods could detect 36 and 41 compounds extracted from gasoline. Purge & trap using cryogenic mode were effective method for highly volatile compounds that had within retention time 6 min. However, HS-SPME had more sensitivity and selectivity for C3-benzene isomers and C4-benzene isomers than non-cryogenic purge & trap method. However, the extraction efficiency of BTEX was shown to be equivalent results for both purge & trap and HS-SPME methods.

The linearities and MDL of BTEX by each method could obtain successful results to quantify BTEX in soil sample. In the case of HS-SPME, experimental parameters such as extraction time, temperature, salt effect and aqueous volume were optimized for the development of efficient BTEX analysis method. MDL obtained by direct injection method was over 100 fold higher than that by other methods. In addition, HS-SPME had shown a slight lower detection limit than purge & trap.

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