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Development of a whole headspace injection method for the determination of volatile organic compounds in water

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Abstract

A whole headspace injection method was devised and evaluated. In the conventional static headspace method, only a part of headspace gas is introduced into the separation column. The amount of volatile organic compounds in a whole headspace calculated using Henry's constants was shown to be enough for the measurement using gas chromatography–mass spectrometry. Therefore, we have designed a device which allows the whole headspace gas to be sampled from a vial, and the volatile organic compounds in it are brought into a micro-trap, and then into a gas chromatographic–mass spectrometry system. Using this method, sensitive headspace analysis has been achieved.

Keywords: Water analysis; Headspace analysis; Purge-and-trap methods; Large-volume injection; Environmental analysis; Volatile organic compounds

1. Introduction

Purge-and-trap (P&T) analysis or static headspace (SHS) analysis are used for the measurement of volatile organic compounds (VOCs) in water. P&T analysis has a predominantly higher sensitivity than SHS analysis, but aerosols formed by the purging induce the adhesion of inorganic and organic compounds in the sample, such as inorganic salts, silicate, humus, etc., to the pipes and valves. These substances have a carry-over effect on later measurement and may produce mechanical troubles.

On the other hand, SHS analysis has the advantage that it is applicable to various types of water, such as those that produce foam by purging, those with high

viscosity or those containing sludge or solid material. However, in the conventional static headspace method, only a part of the headspace gas is introduced into the separation column. Therefore, if a whole volume of an equilibrated gas-phase in a SHS can be injected into a gas chromatographic (GC) system, the method would be ideal for the analysis of VOCs from the viewpoint of sensitivity and adaptability. We named this method the whole headspace injection (WHSI) method. The WHSI method developed has been applied successfully to the measurement of 23 kinds of VOCs added in the drinking water standard in Japan.

Let us assume as follows: A sample solution of volume V_L and a VOCs concentration of C_L^0 (solute mass M_L^0) is put into a closed vial of volume V_T . Then the vial is led to a gas–liquid equilibrium at

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constant temperature T ($^{\circ}\text{C}$). The VOC concentration in the liquid and gas phases become C_L (solute mass M_L) and C_G (solute mass M_G) respectively. The volume of the gas-phase (the headspace) is V_G . Under these conditions, distribution coefficient K of the solute is given by Eq. (1):

$$K = \frac{C_G}{C_L} = \frac{M_G}{V_G} \cdot \frac{V_L}{M_L} \quad (1)$$

Masses and volumes are in the following relationships.

$$M_L^0 = M_G + M_L \quad (2)$$

$$V_G = V_T - V_L \quad (3)$$

M_G is presented from Eqs. (1) and (2).

$$M_G = \frac{K \cdot V_G}{K \cdot V_G + V_L} \cdot M_L^0 \quad (4)$$

The solute quantity M_G which exists in gas-phase is shown by Eq. (5) derived from Eqs. (3) and (4):

$$M_G = \frac{K \cdot (V_T - V_L) \cdot V_L \cdot C_L^0}{K \cdot (V_T - V_L) + V_L} \quad (5)$$

The distribution coefficient of carbon tetrachloride (CCl_4) is the largest of the compounds in the drinking water standard and bromoform (CHBr_3) is the smallest. The mass of VOCs in gas-phase in a vial (V_T : 14.227 ml) calculated from Eq. (5), in the case of 1 ng/ml of those compounds, at 20°C was presented in Fig. 1. There are maximal points of M_G in the curves and they move toward a larger sample volume as the distribution coefficient of the species increases. The sample volume which gives the maximal point of M_G is 7.05 ml for CCl_4 , and 1.98 ml for CHBr_3 . If sample volume can be chosen near the maximum point for every VOC, maximum sensitivity will be expected.

Table 1 shows the solute quantity in the gas-phase that is calculated from the distribution coefficients when 5 ml of sample is put into the vial. If a whole volume of the gas-phase can be introduced into a capillary column, it is possible to measure the

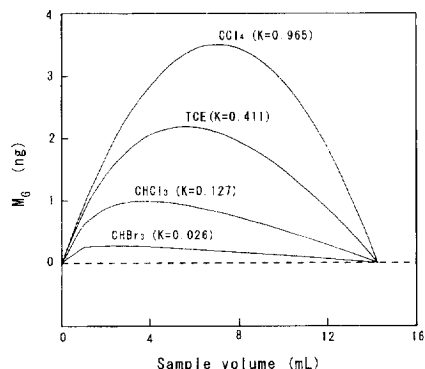


Fig. 1. Effect of sample volume on the VOC amounts in gas-phase with different distribution constants. Vial volume: 14.227 ml; initial concentration C_L^0 : 1 ng/ml

analytes down to $1 \mu\text{g/l}$ or even less by a GC–mass spectrometry (MS) system.

2. Experimental

2.1. Reagents

Reagent water obtained from a water purification system (Yamato WAU-12, Tokyo, Japan) was boiled for more than 15 min in a conical flask to eliminate any traces of volatile interference, and while the water was still hot, an activated carbon trap was connected to the flask. For preparing standards solutions of VOCs, trihalomethane-grade methanol (Wako, Osaka, Japan) was used. Twenty-three kinds of VOCs standard stock solutions (1000 mg/l) and an internal standard stock solution (1000 mg fluoro-benzene/l) were prepared according to JIS K 0125 [5] using methanol as the solvent. Ampoule of 1,1-dichloroethylene in methanol (1000 mg/l) was obtained from Kanto (Tokyo, Japan). The mixed VOCs and internal standard solution were diluted with methanol by 100 times just before use. Sodium chloride (Kanto) of special grade was used without further purification. Tenax TA of 177–250 μm in diameter (GL Sciences, Tokyo, Japan) was used as the adsorbent. Ultra-high-purity helium, 99.9999%, with a total hydrocarbon content of less than 0.01

Table 1
Calculated amounts of compounds in the gas-phase at 20°C

No.	Compound	Abbreviation	Distribution coefficient	Amount in gas phase (ng)	M_G/M_L^0
1	1,1-Dichloroethylene	1,1-DCE	0.857 [1] ^a	3.06	0.612
2	Dichloromethane	DCM	0.071 [1]	0.58	0.116
3	<i>trans</i> -1,2-Dichloroethylene	<i>t</i> -DCE	0.300 [1]	1.78	0.356
4	<i>cis</i> -1,2-Dichloroethylene	<i>c</i> -DCE	0.152 [1]	1.09	0.218
5	Chloroform	CHCl ₃	0.127 [2]	0.95	0.190
6	1,1,1-Trichloroethane	1,1,1-TCA	0.299 [2]	1.78	0.356
7	Carbontetrachloride	CCl ₄	0.965 [2]	3.20	0.640
8	1,2-Dichloroethane	1,2-DCA	0.046 [2]	0.39	0.078
9	Benzene	Benz	0.180 [2]	1.25	0.250
10	Trichloroethylene	TCE	0.411 [2]	2.16	0.432
11	1,2-Dichloropropane	1,2-DCP	0.082 [11]	0.66	0.131
12	Bromodichloromethane	CHBrCl ₂	0.095 [3]	0.75	0.150
13	<i>cis</i> -1,3-Dichloropropene	<i>c</i> -DD	no data		
14	Toluene	TOL	0.217 [9]	1.43	0.286
15	<i>trans</i> -1,3-Dichloropropene	<i>t</i> -DD	no data		
16	1,1,2-Trichloroethane	1,1,2-TCA	0.032 [2]	0.28	0.056
17	Tetrachloroethylene	PCE	0.823 [2]	3.01	0.602
18	Dibromochloromethane	CHBr ₂ Cl	0.035 [3]	0.30	0.060
19	<i>p</i> -Xylene	<i>p</i> -XYL	no data		
20	<i>m</i> -Xylene	<i>m</i> -XYL	0.169 [9]	1.19	0.238
21	<i>o</i> -Xylene	<i>o</i> -XYL	no data		
22	Bromoform	CHBr ₃	0.026 [2]	0.23	0.046
23	<i>p</i> -Dichlorobenzene	<i>p</i> -DCB	0.110(25°C) [4]	0.84	0.168

Distribution coefficients were calculated from each Henry's constant at 20°C in the articles.

Initial concentration: 5 ng VOCs in 5 ml. Vial volume: 14.227 ml.

^a Numbers in brackets are the reference numbers.

volume ppm reduced as methane was used to purging and GC.

2.2. Apparatus

A V-10B vial (capacity is 14.227 ml, S.D. is 0.127 at $n = 15$) obtained from Nichiden (Kobe, Japan) was used for the headspace sampling. A reciprocal shaker (SR-II) from Taitec (Tokyo, Japan) was used for complete dissolution of sodium chloride and faster equilibration of the analytes in the two phases in contact. The shaking frequency was adjusted to 200 times/min.

A Hewlett-Packard Model 5890 Series gas chromatograph equipped with a Model 5971A mass selective detector and a single flame ionization detection (FID) system was used. When the mass selective detector was used, the interface temperature was 280°C. MS data were collected and handled by

the HP G1034CJ MS Chemstation data management system. When FID was used, the injector temperature was 180°C. The detector temperature was 220°C. GC data were collected and handled by the Shimadzu C-R4A data management system.

GC separation columns used were Supelco Vocol, 60 m × 0.32 mm I.D., with a 3.0 μm film thickness for GC-MS and 30 m × 0.53 mm I.D., with a 3.0 μm film thickness for the sample equilibration study.

A P&T GAS-20 with automatic-sampler (DKK, Tokyo, Japan) was modified and assembled as shown in Fig. 2. The P&T system was equipped with a micro-computer controller for purging time. A sampling needle and a helium inlet needle were used for taking out the whole headspace gas (Part A in Fig. 2). Both needles were able to be simultaneously pierced into the septum of a vial. The sampling needle was connected to the micro-trap (Part B in Fig. 2) through stainless-steel tubing (0.5 mm I.D. ×

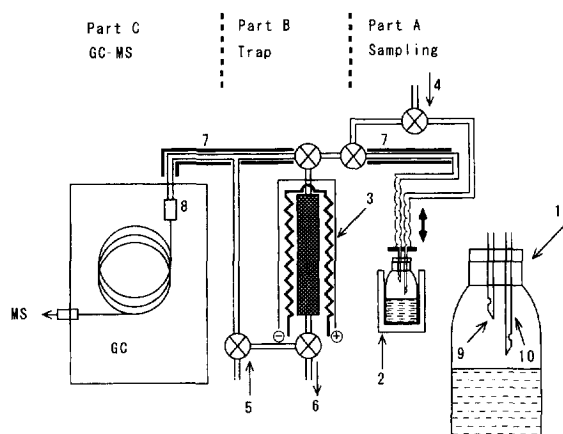


Fig. 2. Schematic diagram of WHSI system. 1=Sample vial; 2=aluminium block (20°C); 3=Tenax trap unit; 4=He for carrier; 5=He for desorption and carrier gas; 6=vent; 7=heated stainless-steel transfer line; 8=capillary connector; 9=sample needle; 10=outlet needle for helium.

1.58 mm O.D.). The other end of the micro-trap was connected to the capillary column (Part C in Fig. 2). The micro-trap was able to introduce adsorbed compounds into GC-MS. The micro-trap was a small column made of stainless-steel (11 cm×2.17 mm I.D.×3.17 mm O.D.) packed with 70–72 mg of Tenax TA [6].

2.3. Analytical procedure

All the operations were carried out in temperature-controlled rooms at 19–22°C. Initially, 2 g of sodium chloride was added to the sample vial. Then 5 ml of sample water and 5 μ l of internal standard fluorobenzene solution were added. The vial was tightly closed with a silicone septum covered with a PTFE sheet and an aluminum perforated cap and it was shaken for more than 10 min. The vial was placed in the aluminum block in the automatic-sampler for 1 h at 20±0.2°C before analysis. Then, piercing the septum with the sampling and helium inlet needles VOCs were carried with helium to the micro-trap for 3 min at the flow-rate of 20 ml/min. For the GC-MS analysis, the trap was heated up rapidly to 260°C (holding 2 min) and VOCs desorbed were introduced to the capillary column. The transfer lines and valves were about 70°C.

GC was operated as follows: isothermal operation at 35°C for 4 min, then heated with a linear temperature mode to 160°C (6 °C/min), and then isothermal operation at 160°C for 13 min. After desorption, the trap was baked at 260°C for 12 min to prepare for the next analysis. The carrier gas was helium and its flow-rate was 1 ml/min.

The GC-MS in the single-ion monitoring (SIM) mode was chosen to get the highest analytical sensitivity. Two ions were selected for each compound. The ion chosen for quantitation was usually the base peak. The ion employed for quantitation, the secondary ion and the retention times of the target VOCs were the same as those in previous paper [6].

3. Result and discussion

3.1. Time required for taking gas out

First, the time required for taking a whole gas out was measured. 1, 5 or 10 ml of water were put into the vials and closed. Then, 62, 44 or 20 μ l of methane were injected with a gas-tight syringe into each closed vial. The outlet of the sampling needle was directly connected to the FID trap by way of a deactivated fused-silica capillary (length 0.7 m×0.53 mm I.D.). After piercing the septum with the needles, methane exhausted was measured by GC-FID.

After about 0.1 min, the response of methane starts to appear and it decreases exponentially with time. When the needles were handled manually the reproducibility becomes poor, but it is acceptable when an automatic-sampler was used, because of needle piercing points are fixed appropriately. An approximate equation of the response line was calculated by least squares fitting and the time required for 99% recovery of methane was calculated by the integration of the formula. The time was found to be proportional to the volume of gas-phase as shown in Fig. 3. Three min at 20 ml/min was chosen to be appropriate for the sample volume of 5 ml. In that case, time required is short enough to prevent breakthrough from micro-trap. The chromatograms obtained have no problem for quantitative measurements.

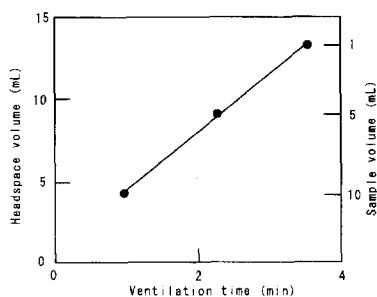


Fig. 3. Time required for 99% ventilation of headspace air.

3.2. Sample equilibration

The time and procedure used to equilibrate the sample will affect chromatographic response [10]. The measurement of equilibration rate was performed for $5 \mu\text{g}$ VOCs/5 ml standard solution by SHS using GC-FID. Equilibration times were 5, 10, 20 and 60 min. Agitation with mechanical shaker makes equilibrium complete within 5 min as shown in Fig. 4. In this case, the coefficients of variation of the relative responses for 23 compounds were 2.8% as the average four different equilibration times and 6.8% as maximum. However, equilibration with no shaking was very slow. Even after 1 h, equilibration was far from complete when vials were not shaken. In actual procedure, after sodium chloride was added to sample in a vial, it was shaken for more than 10

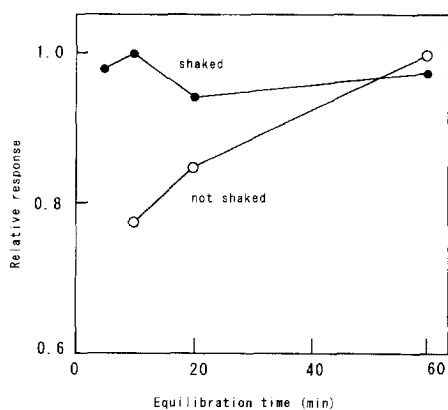


Fig. 4. Effect of equilibration time on the relative response of tetrachloroethylene. Concentration of analyte: $5 \mu\text{g}/5 \text{ ml}$.

min to dissolve the sodium chloride completely and get faster equilibration, then it was placed in the automatic-sampler at $20 \pm 0.2^\circ\text{C}$.

3.3. Transfer of the VOCs from liquid-phase to gas-phase during headspace purge

According to the mass transfer theory in gas-liquid film, variation of the VOCs concentration in water with time is presented by Eqs. (6) and (7) [7,8]:

$$m = -\frac{dC_L}{dt} \cdot V_L = K_L \cdot A \cdot C_L \quad (6)$$

$$\frac{C_L'}{C_L^0} = \exp\left(-K_L \cdot \frac{A}{V_L} \cdot t\right) \quad (7)$$

Where, m is the amount of mass transferred, C_L^0 is the initial concentration in the liquid phase, C_L' is the concentration in the liquid phase at time t (h), A is a gas-liquid contact area (m^2) per unit volume and K_L is a mass transfer coefficient (1/h) of the liquid film. Because the gas-liquid equilibrium is broken by the helium blowing, transfer of VOCs from the water phase to the gas-phase occurs to following Eq. (7). This phenomenon was observed by the experiments with different headspace purging time. The results obtained by changing the purging time from 1 to 15 min for three compounds with different distribution coefficients are shown in Fig. 5. Carbon tetrachloride, which has the largest distribution coefficient,

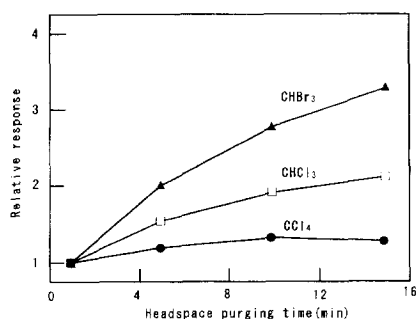


Fig. 5. Effect of headspace purging time on the relative responses of the compounds with different distribution coefficient. Sample volume: 5 ml; amount of analyte: 50 ng.

cient, show a little increase of response with time. Following Eq. (7), the response is increased logarithmically with time. The effects of purging time on the quantitation can not be satisfactorily discussed, because the transfer rate of VOC from static water surface to a stream of gas has not been fully studied yet. Since the working curve for WHSI method is a straight line in the range of 0.5 to 50 ng/5 ml standard solutions, we assume that K_L will be independent of VOC concentration in the case of dilute solution.

The errors originating from the variation of headspace purging time were measured on ± 0.02 or ± 0.04 min for the purging time, 3.00 min. The results obtained for 50 ng/5 ml of each target VOC errors are -5.8% – 1.8% . The errors are not correlated with distribution coefficients of VOCs.

3.4. Salting-out effect

Mineral salts have been added to increase the distribution coefficient in SHS analysis of VOCs [9,10]. Compare to other salting-out reagents, solubility of sodium chloride is rather constant with temperature. In other words, saturated concentration of it does not change so much with temperature.

To study salting-out effect, 50 ng of VOCs and different amounts of sodium chloride (0, 0.5, 1.0, 1.5, 1.7, 1.9, 2.1, 2.3 g) were added to 5 ml water in each vial separately. Results obtained are shown in Fig. 6. It is shown from the figure that near the saturated concentration increased peak areas for all VOCs are obtained. Responses, however, could not be increased even when more sodium chloride was

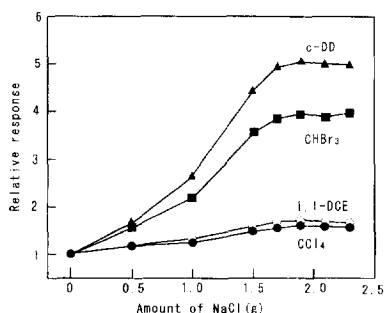


Fig. 6. Effect of NaCl amount on the relative response. Concentration of analytes: 50 ng/5 ml.

added. Addition of more sodium chloride leads to decrease of gas-phase volume and hence the amount of VOCs in gas-phase changed according to Eq. (5). In the analytical procedure, 2 g of sodium chloride was added to sample water (5 ml) to increase chromatographic response.

Reproducibility was studied on the 5 ml sample water added with 0.5 ng of each VOC. Quantitative data is presented in Table 2. It is shown that the ratios of signal heights to average noise height for 0.1 μ g VOCs/l are 11.3 to 193.5 and WHSI method have enough sensitivity for the measurement of 0.1 μ g VOCs /l solution.

In Fig. 7, chromatograms of 1 μ g VOCs/l standard solution by WHSI and SHS methods are compared. It is clearly shown in the figure that WHSI method is superior in signal to noise ratio to SHS method for very diluted solution under usual operating condition.

3.5. Application to environmental samples

Measurements of VOCs in waters which contains sludge or solid material are difficult with usual P&T method. Recovery of VOCs was studied on aerobically treated water of night-soil which is one of the difficult samples to analyze with a P&T method. Five milliliters of sample was added with 50 ng of each VOC and measured six times repeatedly by WHSI method. Table 2 shows the results including the reproducibility of the recovery. As can be seen, the reproducibility for each VOC is also excellent as in the case of pure water sample.

4. Conclusions

We have proposed a whole volume injection method for headspace gas analysis. It could be thought to be the only method suited for the determination of VOCs with excellent sensitivity and reproducibility. It can be applied to various types of liquid samples which can not be measured by P&T because of forming by purge, or of high viscosity, or of containing sludge or solid. WHSI method has a potential use in the field of environmental measurements.

Table 2
Determination of signal to noise ratio for 0.1 μg VOCs/l and recoveries of VOCs spiked to aerobically treated night-soil

No.	Compound	Pure water ^a		Night-soil ^b	
		RSD (%)	S/N (p/p)	Recovery (%)	RSD (%)
1	1,1-DCE	1.85	67.2	100.6	4.18
2	DCM	3.13	91.6	101.1	3.70
3	<i>t</i> -DCE	1.89	71.9	99.6	3.75
4	<i>c</i> -DCE	0.82	20.9	99.4	3.66
5	CHCl ₃	2.64	127.7	99.0	3.69
6	1,1,1-TCA	1.38	78.8	99.8	3.87
7	CCl ₄	1.26	83.4	100.0	3.93
8	1,2-DCA	1.83	17.8	97.9	3.89
9	Benz	1.84	100.5	100.0	3.75
10	TCE	0.82	193.5	99.7	3.81
11	1,2-DCP	0.97	41.4	98.7	3.96
12	CHBrCl ₂	2.88	37.7	98.0	3.86
13	<i>c</i> -DD	1.16	41.7	96.4	3.81
14	TOL	1.80	193.3	99.4	4.00
15	<i>t</i> -DD	3.83	27.4	95.2	3.96
16	1,1,2-TCA	4.14	11.3	97.3	4.09
17	PCE	1.23	158.0	99.5	4.13
18	CHBr ₂ Cl	4.79	27.8	97.2	4.12
19	<i>m</i> + <i>p</i> -XYL	3.21	90.4	98.0	4.54
20	<i>o</i> -XYL	4.66	32.7	97.7	4.56
21	CHBr ₃	5.72	48.4	97.6	4.20
22	<i>p</i> -DCB	4.83	56.2	95.6	6.70

^a Spiked 0.5 ng VOCs in 5 ml pure water. Signal to noise ratios (S/N) was calculated from the peak height of quantitated ion and average height of baseline noise of 6 replicate runs.

^b Spiked 50 ng VOCs in 5 ml aerobically treated night-soil. All values are calculated from the peak area of 6 replicate runs.

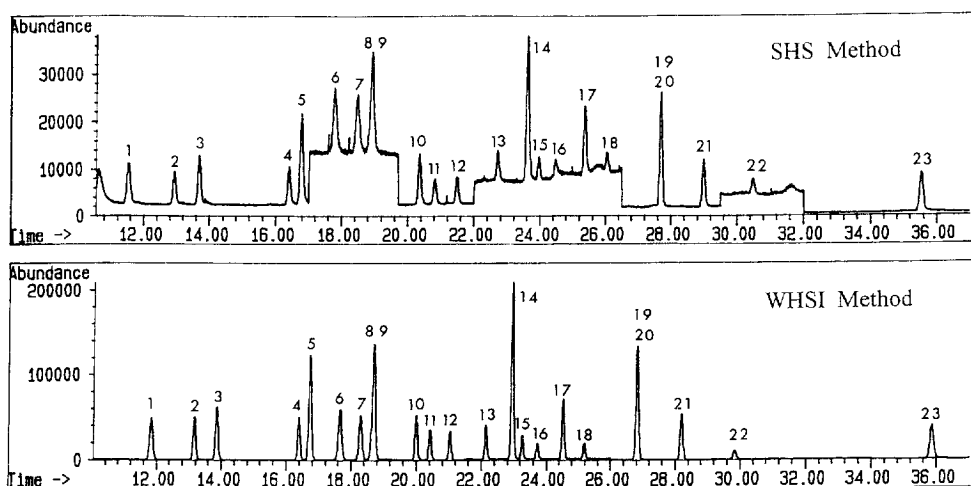


Fig. 7. Chromatograms of 1 $\mu\text{g}/\text{l}$ standard solution by SHS and WHSI. SHS measurements were as follows: sample temperature, 60°C; vial volume, 22.5 ml; sample volume, 10 ml; NaCl, 4 g; injection volume, 500 μl ; split ratio, 1:10; head pressure, 70 kPa; others, same as WHSI.

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