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Analysis of volatile sulphur compounds in breath by gas chromatography–mass spectrometry using a three-stage cryogenic trapping preconcentration system

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Abstract

A method for the determination of trace volatile sulphur compounds (VSCs) including methanethiol, dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) at low ppbv (volume/volume) in breath has been developed using a large volume preconcentration technique prior to capillary GC–MS analysis. The breath sample was collected in a 6-l fused-silica-lined stainless steel canister and introduced into the three-stage cryogenic trapping preconcentration system by GC–MS in the total ion monitoring (scan) mode. The water condensation effect of breath sample inside the canister, which is due to the difference between human body temperature and laboratory temperature, was examined. The condensed water in the fused-silica-lined canister at 24°C did not affect the recoveries of VSCs within 12 h. As this three-stage cryogenic trapping preconcentration technique made it possible to remove excess water {relative humidity (RH) >95%} and carbon dioxide (3.8%) without loss of the VSCs, more than 400 ml of the breath sample could be concentrated. The detection limits of methanethiol, DMS and DMDS in a breath sample using this method were 0.13, 0.09 and 0.15 ppbv, respectively.

Keywords: Cryogenic trapping preconcentration; Canister sampling; Volatile sulphur compounds

1. Introduction

Although volatile sulphur compounds (VSCs) are detected as key compounds of the malodorant in human breath, it is very difficult to collect, store and analyze them at trace levels because of their highly adsorptive, reactive and very volatile properties. In addition, there are huge matrices such as water (RH>95%) and carbon dioxide (3.8%) in breath. In general, there are two approaches for the GC analysis of VSC in a gaseous sample. One is a direct injection of a sample into the GC using a sampling loop (0.5–5 ml) or gas tight syringe, the other is the enrichment of a large volume sample prior to the GC analysis. Tedlar bag sampling with the direct injection technique for the GC analysis of VSC has been widely used, however, the sensitivity is considered to be limited because of the small volume sampled in GC analysis with a sulphur selective detector such as FPD [1–3]. These methods were

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applied to the analysis of VSCs at sub-ppmv to ppmv level. In order to get a high sensitivity with the loop injection technique without the problem of matrix interference, capillary GC with a sulphur chemiluminescence detector (SCD) [4] or the selected ion monitoring (SIM) mode in GC–MS [5] were performed for the liquid petroleum gas (LPG) samples. The detection limits of VSCs by these methods were 5 ppbv for carbonyl sulfide [4], 1 ppmv for DMS and 10 ppmv for tert.-butanethiol, respectively [5]. In the only report at the time on the use of the loop injection technique for the analysis of ppbv level VSCs in breath, Blanchette obtained detection limit for methanethiol of 15 ppbv [6]. There are a variety of enrichment techniques for breath analysis such as thermal desorption GC–MS with a Tenax (2,6-diphenyl-*p*-phenylene oxide) adsorbent tube [7,8], and headspace GC–MS with Tenax [9]. However, these methods have not been suitable for very volatile compounds (in general, those with boiling points $<60^{\circ}C$) because of the small break through volume on Tenax. Although whole column cryogenic trapping with a fused-silica capillary [10] and canister-based method using cryogenic trapping [11] have been used for volatile organic compounds (VOCs) with higher vapor pressure, they only focused on non-polar VOCs such as halogenated hydrocarbons and aromatic hydrocarbons. The maximum sample volume available for a breath sample was 100 ml because of interference by the huge amount of carbon dioxide [11]. In this paper, a method for determining ppbv levels of VSCs including methanethiol, DMS and DMDS in breath has been developed by using a large volume (400 ml) enrichment of a sample with a matrix control technique. VSCs in breath were collected in a fused-silica-lined canister and introduced into a three-stage cryogenic trapping preconcentration system followed by GC–MS analysis in the scan mode.

2. Experimental

2.1. Chemicals and preparation of standard gases

Methanethiol standard gas (100 ppmv) in a 10-l aluminum cylinder with nitrogen (10 MPa) was purchased from Sumitomo Seika Chemicals (Tokyo, Japan). DMS and DMDS purchased from Tokyo Kasei Kogyo (Tokyo, Japan) were initially prepared at 100 ppmv each in a fused-silica lined canister with zero grade nitrogen (303 kPa). Then 100 ppmv of methanethiol, DMS and DMDS were dynamically diluted and mixed into a 6-l fused-silica-lined canister using an Entech 4620 dynamic dilution system (Entech Instruments Inc.) with humidified zero grade nitrogen. Concentrations of 1 ppmv per compound in the fused-silica-lined canister were obtained as stock standard gas mixtures. Ethanol, isopropanol, propanol, isobutanol, butanol, acetone, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate, diethyl ether, methyl tert.-butyl ether, ethanethiol, propanethiol, sec-butanethiol, tert.-butanethiol and butanethiol were purchased from Wako Pure Chemicals (Osaka, Japan). These standards were initially prepared at 100 ppmv each in a fused-silica-lined canister with zero grade nitrogen (303 kPa). Then 100 ppmv of mixtures were dynamically diluted and mixed into a 6-l fused-silica-lined canister using an Entech 4620 dynamic dilution system with humidified zero grade nitrogen. Concentrations of 1 ppmv per compound in the fused-silica-lined canister were obtained as stock standard gas mixtures. The US EPA TO-14 method reference standard gas mixtures (41 compounds including acrylonitrile and 1,3-butadiene, 1 ppmv) in a 10-l aluminum cylinder with nitrogen (10 MPa) was purchased from Sumitomo Seika Chemicals. The stock standard gas mixtures and the US EPA TO-14 method reference standard gas mixtures were used for the recovery test with the dynamic dilution system shown in Fig. 1. Final standard gas mixtures for the recovery test had concentrations of 2.5–10 ppbv per compound in an RH 70% nitrogen. To eliminate the adsorption of the test mixtures onto the interior surface of the sample paths in the dynamic dilution system, a fused-silica-lined stainless steel tube was used for all the sample paths.

The working standard gas mixtures of VSCs were prepared at 1 to 100 ppbv by the static dilution system using humidified zero grade nitrogen.

2.2. Apparatus

The 6-l fused-silica-lined and SUMMA canisters were purchased from Entech Instruments Inc. The

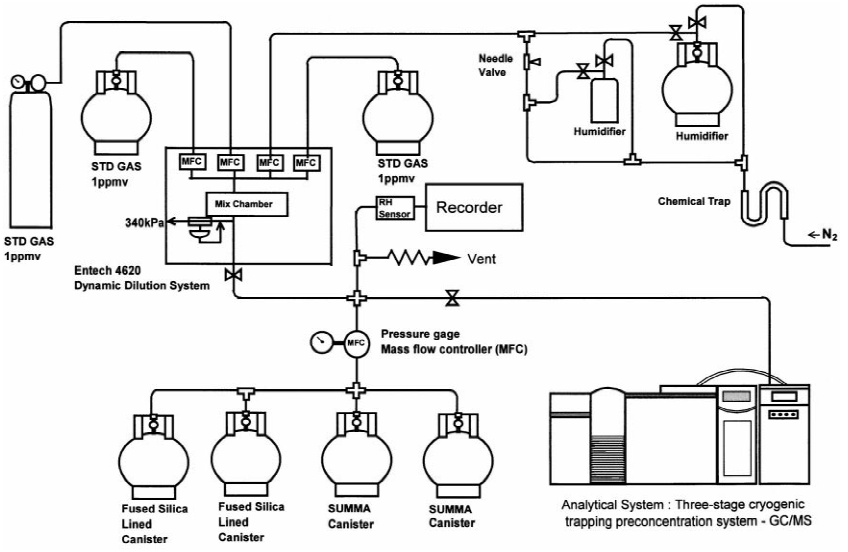

Fig. 1. Dynamic dilution system used to prepare test mixtures.

three-stage cryogenic trapping preconcentration and GC–MS analysis were performed using an Entech7100 preconcentrator and an Agilent 6890GC with a 5973 MSD from Agilent Technologies (CA, USA).

2.3. Sampling and preconcentration procedures

Several stainless steel canisters such as electro-polished, SUMMA polished, fused-silica-lined and multi-layer pretreated ones have been investigated to sample and store polar volatile organic compounds (VOCs) and VSCs [12–14]. The fused-silica-lined canister and the multi-layer pretreated canister that have a thinner, high-density fused-silica interior surface that showed good recovery for VSCs with any relative humidity in contrast to the traditional interior treated canisters such as electro-polished and SUMMA polished that have a metal surface [14]. A 6-l breath sample was collected in the fused-silica-lined canister via a quarter inch fused-silica-lined stainless steel tube (grab sampling). To eliminate the adsorption of the VSCs onto the interior surface of the sample paths in the three-stage cryogenic trapping preconcentration system, a fused-silica-lined stainless steel tube was also used for all the sample paths. After purging of the inlet line using high purity nitrogen, the breath sample was pumped from the canister into the system at the flow-rate of 100 ml/min as shown in Fig. 2. The 400 ml of breath sample were first concentrated to about a 0.5-ml volume in a glass bead cryogenic trap (M1) at −150°C. The trap was then heated to 20°C and was held there while slowly passing helium through it to transfer these compounds to a secondary Tenax trap (M2) held at −30°C. After transfer to M2, the VSCs could be back-flushed while heating to be further focused on a capillary focusing trap for rapid injection onto the analytical column.

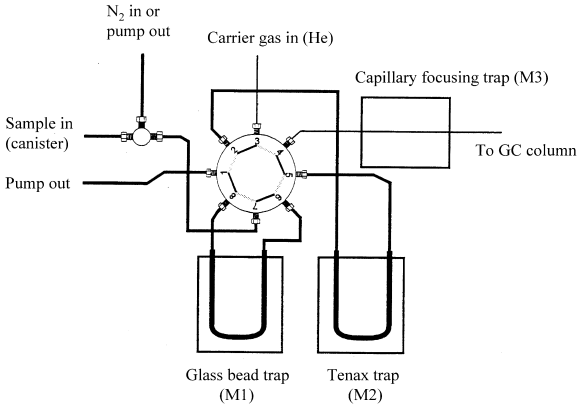

Fig. 2. Flow system for the preconcentration of VSCs from breath.

Table 1
Experimental conditions

Preconcentrator	Entech 7100
M1 (glass beads) trap temp.	−150°C
M1 (glass beads) purge temp.	20°C
M2 (Tenax) trap temp.	−30°C
M2 (Tenax) desorb temp.	180°C
M3 (capillary) trap temp.	−185°C
M3 (capillary) inj. temp.	75°C
Gas chromatograph	Agilent Technologies 6890
Column1	HP-1, 60 m length×0.32 mm I.D., 1.0 μm thickness
Column flow	1 ml/min constant flow mode
Oven temp.1	35°C (5 min)–5°C/min–220°C (5 min)
Mass spectrometer	Agilent Technologies 5973
Ionization mode	EI
Scan	m/z 29 to 300 in 0.45 s
Molecular ions used for determination	Methanethiol m/z 48, DMS m/z 62, DMDS m/z 94

2.4. GC–MS analysis

A HP-1 fused-silica capillary column (100% dimethylsilicone, 60 m length×0.32 mm I.D., 1.0 μm film thickness, Agilent Technologies) was used. The oven temperature was programmed from 35°C for 5 min, ramped at 5°C/min to 80°C, then with a second ramp of 15°C/min to 220°C for 5 min. The helium carrier gas was operated at a rate of 1 ml/min. The mass spectrometer was operated in the scan mode with the electron ionization (electron accelerating voltage: 70 V). The scan was set from m/z 29 to 300 in 0.45 s. For determination of the target compounds selected ion chromatograms over molecular ions (methanethiol: m/z 48, DMS: m/z 62 and DMDS: m/z 94) were used. All the analytical conditions are shown in Table 1.

3. Results and discussion

3.1. Canister sampling

It is generally recognized that certain minimum levels of relative humidity are necessary to effect good recoveries of VOCs from the stainless steel canister [15]. However, the breath sample has very high humidity (RH>95%) and higher temperature than normal ambient air sample. The normal laboratory temperature may cause condensation of liquid water within the canister. The compound that has sufficiently large water solubility may be partially absorbed into the aqueous phase and may not be recovered. The amount of condensed water in the 6-l canister at 24°C (laboratory temperature), which is generated from the 6-l breath sample at 36°C (human body temperature), is calculated by the ideal gas equation. Taking values of 44.569 mmHg (760 mmHg=101.3 kPa=1 atm) for saturated vapor pressure of water at 36°C, 22.375 mmHg for saturated vapor pressure of water at 24°C, 6 l for breath sample volume and 0.082 atm l/mol k for the gas constant, the moles of 6 l gaseous water which have saturated vapor pressure at 36°C and 24°C are calculated to be 0.01386 mol and 0.007242 mol, respectively. Consequently, the amount of condensed water in the 6-l canister at 24°C is calculated to be about 0.12 ml. We examined the effect of the condensed water in the canister for the recoveries of VSCs and VOCs from the high humidity sample. Evacuated 6-l fused-silica-lined canisters and 6-l SUMMA canisters were prepared by spiking 0.2 ml of water prior to the loading of the standard gas mixture. The test mixtures of standard gas, which has the concentration of 2.5–10 ppbv per compound for VOCs and VSCs in an RH 70% nitrogen, were introduced into the analytical system and the canisters (Fig. 1). After the test mixture analysis (pre-collection analysis), canisters were filled about to ambient pressure with the test mixture (RH 70%).

The amount of condensed water in each canister was calculated to be about 0.16 ml. Then the test mixture was reanalyzed (post-collection analysis). After 12 h equilibration, the samples were analyzed. The recovery of the test mixture compounds from canisters was determined by comparing the mean of the measured values to the mean of the pre- and post-collection analyses from the dynamic dilution system. For the fused-silica-lined canisters, the recoveries ranged from 90 to 105% for halogenated hydrocarbons, aromatic hydrocarbons and 1,3-butadiene, 86 to 102% for oxygenated hydrocarbons except all alcohol, 97 to 102% for VSCs and 36 to 54% for alcohol. For the SUMMA canisters, the recoveries ranged from 96 to 109% for halogenated hydrocarbons, aromatic hydrocarbons and 1,3-butadiene, 82 to 104% for oxygenated hydrocarbons except all alcohol, 90 to 97% for VSCs except all thiols and 42 to 76% for alcohol. All thiols were not recovered from SUMMA canisters. This is mainly due to adsorption onto the interior surface because the major difference between the SUMMA canister and the fused-silica-lined canister is the material of the interior surface. The SUMMA canister has a nickel-chromium oxide interior surface in contrast to the fused-silica-lined canister that has a thinner, high-density fused-silica interior surface. Thus the main drawbacks of canister sampling for thiol analysis using the SUMMA canister is the adsorption onto the metal interior surface rather than the effect of condensed water. Using the fused-silica-lined canister, about 0.16 ml of condensed water did not affect the recoveries of test mixture compounds except alcohol within 12 h. The recoveries of the test mixture compounds from the canisters and the Henry's law constants (k_H) [16–22] are shown in Table 2.

Table 2
The recoveries of the test mixture compounds from the canisters and Henry's law constants (k_H)

Compound	Recovery (%)		k_H[a] (mol/atm)
	FSL[b]	SUMMA[c]	
Dichloromethane	96	96	0.39 [16]
Chloroform	98	100	0.27 [16]
1,2-Dichloroethane	96	103	0.92 [16]
Benzene	97	102	0.18 [16]
Toluene	93	108	0.15 [16]
1,3-Butadiene	98	102	0.014 [16]
Ethanol	54	42	190 [17]
Isopropanol	38	56	130 [17]
Isobutanol	43	76	110 [17]
Acetone	86	82	26 [17]
Methyl ethyl ketone	98	98	18 [17]
Methyl isobutyl ketone	99	99	2.2 [18]
Ethyl acetate	97	96	6.5 [19]
Butyl acetate	102	104	3.5 [19]
Diethyl ether	98	92	1.2 [20]
Methyl t-butyl ether	100	100	1.6 [21]
Acrylonitrile	94	94	7.3 [19]
Methanethiol	97	ND[d]	0.39 [22]
Ethanethiol	99	ND	0.28 [22]
Propanethiol	101	ND	0.25 [22]
Butanethiol	102	ND	0.22 [22]

The test mixtures have a concentration of 2.5–10 ppbv per compound.
[a] k_H = Henry's law constants.
[b] FSL, fused-silica-lined canister.
[c] SUMMA, SUMMA canister.
[d] ND, not detected.

3.2. Preconcentration

The scan mode in the GC–MS analysis is useful to determine target compounds with any other sample matrix. However, in order to get enough sensitivity for the ppbv level analysis of VSCs in the scan mode, the preconcentration volume of the sample must be more than 100 ml. More than 100 ml of the breath sample preconcentration without water and carbon dioxide management will cause clogging of the cryogenic trap [10], or injection of a huge matrix into the GC–MS. The analytes that co-elute with these matrices will produce a serious problem such as poor peak shape and sensitivity suppression. A three-stage cryogenic preconcentration technique has been developed to analyze VOCs in humid air with a huge matrix management [23]. This made possible the removal of excess water and carbon dioxide from the ambient air sample without loss of the VOCs and polar VOCs. It is analogous to the purge and trap (P&T) used in water analysis, only on a much smaller scale between the cryogenic glass beads and Tenax traps. As the vapor pressures of the VOCs and water are roughly the same level at less than ambient temperature, the temperature during the purge process of a glass bead trap is set at ambient temperature. The vaporization rate of the VOCs and water are of the same order of magnitude even though total

amount is significantly different. Therefore, water is left in the glass bead trap held at ambient temperature, VOCs and carbon dioxide are easily purged by helium gas. One hundred ml of an ambient air sample would only yield less than 2 μl of water rather than the 5000 μl used in the water analysis. The distribution of the condensed water on the glass beads in the trap should further facilitate the transfer of VOCs and polar VOCs to the gas phase. Finally, the VOCs are trapped in the Tenax trap, while carbon dioxide breaks through the Tenax trap. Several parameters such as purge temperature, purge flow, purge volume and trap temperature on the recoveries and peak shapes of the VOCs were optimized with ambient air matrix [24]. Since the vapor pressures of the DMDS (DMDS has a lower volatility in the target VSCs) and water are almost the same at 20°C (3 kPa and 2 kPa, respectively), the purge temperature of 20°C was chosen. To make carbon dioxide (b.p. −78°C) pass through the Tenax trap without break through of the methanethiol (b.p. −6°C), the purge flow and trap temperature were set at 10 ml/min and −30°C, respectively [24]. The major differences between the ambient air and breath sample matrix are the amount of water (RH 95%) and carbon dioxide (3.8%). As the key parameter of the three-stage cryogenic trapping to eliminate these matrices in the breath sample is the purge volume, the purge volume during the preconcentration was optimized with the matrix-spiked VSCs standard gas mixture (400 ml samples, 40 ppbv each) in the canisters. Fig. 3 shows the influence of the purge volume on the purge efficiency of the VSCs with a high humidity (RH 100%). Only the purge volume of 10 ml was enough to reach the maximum yield and there was no degradation in the yield for the purge volume of 120 ml without effects by the water matrix on the GC–MS analysis. Fig. 4 shows the same influence under the same conditions except for a matrix spiking of 3.8% carbon dioxide. It can be seen that there were no responses of any of the VSCs between the purge volume of 1 ml and 5 ml in contrast with the carbon dioxide responses (plotted with 1/300 *Y*-axis scale). Carbon dioxide responses were dramatically decreased between the purge volumes of 5 and 20 ml. The peaks of methanethiol and DMS were still very small and broad at the purge volume of 10 ml (Fig. 5). As less than a 20-ml

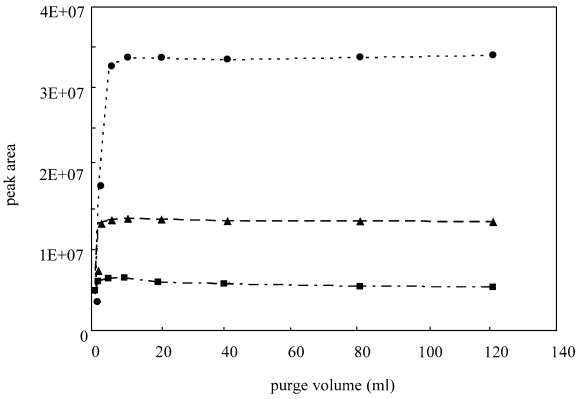

Fig. 3. Influence of purge volume on the purge efficiency with high humidity (RH 100%) matrix: ■, methanethiol; ▲, DMS; ●, DMDS.

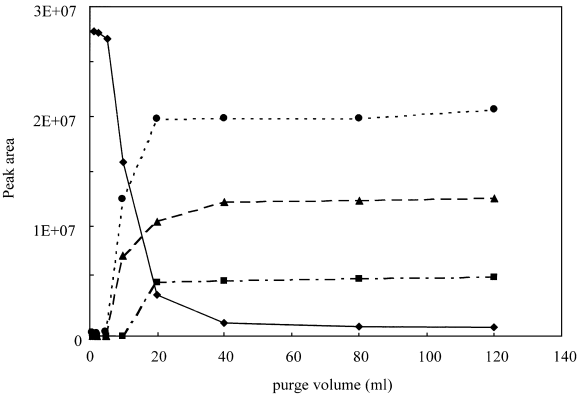

Fig. 4. Influence of purge volume on the purge efficiency with high humidity (RH 100%) and 3.8% carbon dioxide matrices: ♦, CO_2; ■, methanethiol; ▲, DMS; ●, DMDS.

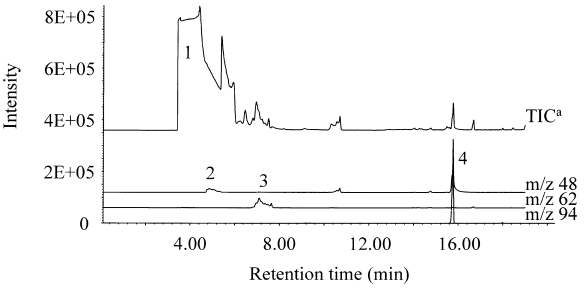

Fig. 5. The influence of carbon dioxide for VSC analysis with the three-stage cryogenic trapping using 10 ml of purge volume. (1) CO_2, (2) methanethiol, (3) DMS, (4) DMDS. Concentration of VSCs STD: 40 ppbv each. [a]TIC is multiplied by 0.1.

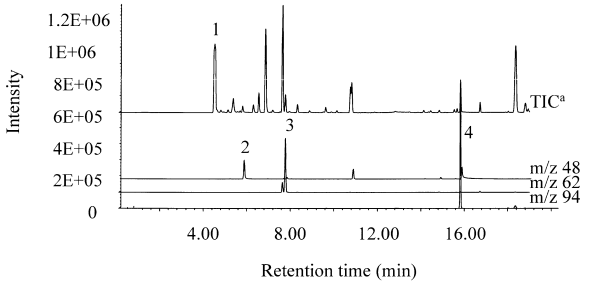

Fig. 6. Removal of carbon dioxide for VSC analysis with the three-stage cryogenic trapping using 80 ml of purge volume. (1) CO_2, (2) methanethiol, (3) DMS, (4) DMDS. Concentration of VSCs STD: 40 ppbv each. [a]TIC is multiplied by 0.1.

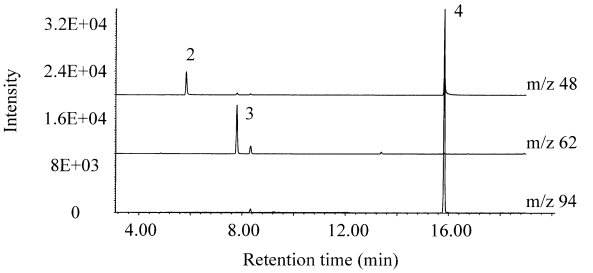

Fig. 7. Mass chromatograms of VSCs STD at 1 ppbv each. (2) Methanethiol, (3) DMS, (4) DMDS.

purge volume was not enough to remove the excess carbon dioxide from the secondary Tenax trap, a huge amount of carbon dioxide was introduced into GC–MS and caused signal suppression and serious chromatographic problems for methanethiol and DMS, which are early eluting VSCs. For DMDS, which has a lower volatility in the target VSCs, the purge efficiency was strongly affected by the huge amount of carbon dioxide on the glass bead trap. Consequently, more than 20 ml of purge volume was essential for the transfer of DMDS to the Tenax trap. The purge volume of 80 ml was chosen for further work. The total ion chromatograms (TIC) and mass chromatograms of the VSCs with huge matrices at purge volumes of 10 and 80 ml are shown in Figs. 5 and 6, respectively.

3.3. Method validation and determination of VSCs in breath

In order to validate the method, an ambient air sample (not including target VSCs) collected in a fused-silica-lined canister was prepared by spiking with VSCs and matrices such as high humidity (RH 100%) and carbon dioxide (3.8%) prior to the sample collection. The linearity, sensitivity and recovery of the method were tested and are shown in Table 3. The seven points for the calibration curves for the VSCs were linear over a range 1 to 100 ppbv (1, 2, 5, 10, 20, 50, 100 ppbv) with correlation coefficients better than 0.9988 and a relative standard deviation (% RSD) of response factors better than 7.4%. The mean recoveries of the VSCs at 10 ppbv within a day (24 h) were 83% (RSD 6.7%, $n=6$) for methanethiol, 98% (RSD 5.7%, $n=6$) for DMS and 88% (RSD 11%, $n=6$) for DMDS, respectively. By using these calibration curves, the replicate analysis of the lowest level (1 ppbv, $n=6$) and three times the standard deviation (3 SD) of these amounts, the detection limits of methanethiol, DMS and DMDS were calculated to be 0.13, 0.09 and 0.15 ppbv, respectively. Mass chromatograms of the VSCs at 1 ppbv are shown in Fig. 7. The developed method was then used for the breath sample. The 6-l breath samples ($n=6$) were collected from an examinee after using typical mouthwash solution that included a high ppm level of ethanol and flavor compounds such as menthol and mono-terpene (the examinee rinsed his mouth with 10 ml of mouthwash solution

Table 3
Method validation: correlation coefficients, detection limits and recoveries of VSCs

Compound	Correlation coefficient r^2 (1–100 ppbv)	Detection limit ppbv	Mean recovery % ($n=6$)
Methanethiol	0.9999	0.13	83 (RSD 6.7%)
DMS	0.9991	0.09	98 (RSD 5.7%)
DMDS	0.9988	0.15	88 (RSD 11%)

Detection limits were calculated by the replicate analysis of 1 ppbv ($n=6$) and three times the standard deviation (3 SD) of these amounts. The mean recoveries within a day (24 h) were examined by measuring spiked sample at 10 ppbv.

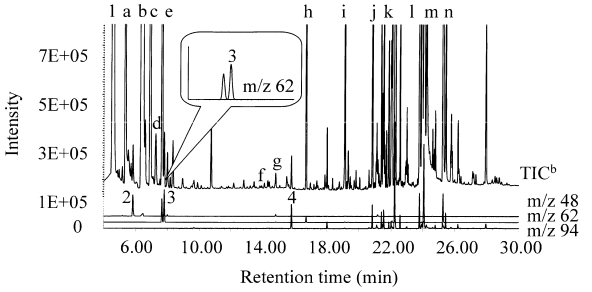

Fig. 8. Example of determination of VSCs in breath. (1) CO_2, (2) methanethiol, (3) DMS, (4) DMDS, (a) acetaldehyde, (b) ethanol, (c) acetone, (d) IPA, (e) isoprene, (f) allyl methyl sulfide, (g) methyl propyl sulfide, (h) toluene, (i) allyl isothiocyanate, (j) α-pinene, (k) sabinene, (l) menthone, (m) menthol, (n) anethol. [b]TIC is multiplied by 0.5.

for 20 s). A 400-ml breath sample was used for the analysis from the 6-l canisters. Typical chromatograms of the breath sample are shown in Fig. 8. Well-defined mass chromatograms of the VSCs were obtained without interference from carbon dioxide and the other matrix compounds. The concentrations of methanethiol, DMS and DMDS were calculated as 9.0 ± 0.7, 5.4 ± 0.4 and 1.1 ± 0.1 ppbv, respectively (mean$\pm$SD, $n=6$). Satisfactory reproducibilities were obtained for all the VSCs with an RSD value ($n=6$) for the peak areas of the mass chromatograms used for determination between 5.1 and 7.6%. The breath samples were also found to contain other VSCs such as allylmethyl sulfide, methylpropyl sulfide, allylisothiocyanate and other miscellaneous compounds.

4. Conclusion

A method for the determination of trace VSCs including methanethiol, DMS and DMDS at low ppbv in breath was developed. Although the water condensation of breath sample inside the canister occurred, the fused-silica-lined canister could be applied to the sampling of VSCs in breath. The combination technique of a fused-silica-lined canister and a three-stage cryogenic trapping system for sampling and preconcentration enabled a large volume injection of the breath sample into the GC–MS without loss of the VSCs. By the optimization of the purge volume of three-stage cryogenic preconcentration, the interference of huge matrices in breath such as high humidity (RH $>95\%$) and carbon dioxide (3.8%) was eliminated and more than 400 ml of breath sample could be concentrated. The detection limits of methanethiol, DMS and DMDS in breath using this method were 0.13, 0.09 and 0.15 ppbv, respectively. The detection limit of methanethiol was more than 100 times of the known method [6]. The method could successfully be applied to the analysis of VSCs at low ppbv levels in human breath. Furthermore, it was found that the breath samples contain allylmethyl sulfide, methylpropyl sulfide and allylisothiocyanate.

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