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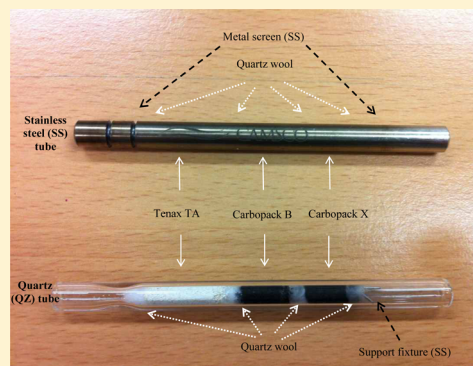
Extent of Sample Loss on the Sampling Device and the Resulting Experimental Biases When Collecting Volatile Fatty Acids (VFAs) in Air Using Sorbent Tubes

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S Supporting Information

ABSTRACT: Not all volatile organic compounds (VOCs) are suitable for sampling from air onto sorbent tubes (ST) with subsequent analysis by thermal desorption (TD) with gas chromatography (GC). Some compounds (such as C2 hydrocarbons) are too volatile for quantitative retention by sorbents at ambient temperature, while others are too reactive – either for storage stability on the tubes (post-sampling) or for thermal desorption/GC analysis. Volatile fatty acids (VFAs) are one of the compound groups that present a challenge to sorbent tube sampling. In this study, we evaluated sample losses on the inner wall surface of the sorbent tube sampler. The sorptive losses of five VFA (acetic, propionic, *n*-butyric, *i*-valeric, and *n*-valeric acid) were tested using two types of tubes (stainless steel and quartz), each packed with three sorbent beds arranged in order of sorbent strength from the sampling end of the tube (Tenax TA, Carboxpack B, and Carboxpack X). It showed significantly higher losses of VFAs in both liquid phase and vapor phase when using stainless steel tube samplers. These losses were also seen if vapor-phase fatty acids were passed through empty stainless steel tubing and increased dramatically with increasing molecular weight, e.g., losses of 33.6% (acetic acid) to 97.5% (*n*-valeric acid). Similar losses of VFAs were also observed from headspace sampling of cheese products. Considering that stainless steel sampling tubes are still used extensively by many researchers, their replacement with quartz tubes is recommended to reduce systematic biases in collecting VFA samples or in their calibration.



A wide array of gas chromatographic (GC) methods have been developed and refined for the quantification of volatile organic compounds (VOCs) including volatile fatty acids (VFAs) in biological media such as blood and rumen fluid.^{1,2} Interests in the analyses of VFAs (~C6) have grown steadily since they were identified as important malodorous compounds or as the source of energy conversion (sewage and waste treatment plants).^{3,4} Several VFAs have also been designated as the target of removal, because of their nuisance.^{4,5} If the VFAs with their relatively low volatility and high reactivity are to be analyzed by GC, their recoveries must be validated.⁶ Thus, it is important to employ the sampling method that should warrant a reliable recovery in VFA analysis.

There are many pretreatment options for the sampling and analysis of VFA in air or water, which include derivatization, solid-phase microextraction (SPME), bag sampling, sorbent adsorption, and solvent absorption. For many of these options, their reliabilities are yet to be validated, while some methods are proven to be very problematic. For instance, the use of bag sampling method (e.g., Tedlar bag) for gaseous VFAs is found to be subject to significant sorptive losses relative to aromatic hydrocarbons.^{7,8} Of the range of available options, the use of sorbent tube (ST) sampling coupled with thermal desorption (TD) technique is the most recommendable option,⁹ because of simplicity, detectability, and recovery.^{10,11}

As recommended in international standard methods for sorbent tube-thermal desorption-GC/(MS) analysis (e.g., EN ISO 16017, ASTM D61960, ISO 16000-6, etc), analyte recovery should always be assessed to minimize experimental uncertainties. The use of glass, quartz, or inert (quartz)-coated steel sorbent tubes is reported, although stainless steel (SS) has been the most common choice for sorbent tube sampling of stable gaseous VOCs (e.g., benzene, toluene, and xylene (BTX)).¹² Nonetheless, the reliability of tube materials used to hold or pack sorbent is poorly documented for less-stable compounds.¹³ Hence, quantitative information on the extent of analyte loss due to sampling tube materials and associated apparatus is worth evaluating in detail.

In this study, the sorptive loss of VFAs due to the tube material was first evaluated against the most common sorbent holding material (SS) and then extended to quartz (QZ) tubes for comparison between different materials. Their sorptive loss was also examined with respect to sorbent tube sample loading techniques (e.g., between direct injection (D) and vaporization (V) approaches). Hence, the effects of the two variables (tube material types and standard loading methods) were investigated

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simultaneously to understand the mechanism of VFA losses during sampling and overcome such problems.

MATERIALS AND METHODS

The sorptive loss pattern of VFAs was investigated from three experimental stages described below (Table 1). The basic experimental scheme developed in this study is illustrated in

Table 1. Three Types of Experimental Schemes To Explore the Adsorptive Loss of Volatile Fatty Acids (VFAs) Using TD-GC-TOF MS

A. Basic Experimental Design for the Comparative Analysis of VFA Loss on Tube Sampler			
pretreatment methods			exp code
[A] Exp Stage 1: Combination between tube type and loading approach			
1-1. Direct injection (D) – sorbents tube made of stainless steel (SS)			D-SS
1-2. Direct injection (D) – sorbents tube made of quartz (QZ)			D-QZ
2-1. Vaporization (V) – sorbents tube made of stainless steel (SS)			V-SS
2-2. Vaporization (V) – sorbents tube made of quartz (QZ)			V-QZ
[B] Exp Stage 2: collection of vaporized VFA by quartz (QZ) after passing two types of empty tube materials			
1. Vaporization: stainless steel (S) → sorbents tube made of quartz (QT)			S-QZ
2. Vaporization: quartz (Q) → sorbents tube made of quartz (QT)			Q-QZ
[C] Exp Stage 3: analysis of VFA released from cheese sample			
1. Impinger system (I) – sorbents tube made of stainless steel (SS)			I-SS
2. Impinger system (I) – sorbents tube made of quartz (QZ)			I-QZ
B. Information of Pretreatment Methods and Samplers			
	(a) direct injection	(b) vaporization	(c) impinger system
[A] Pretreatment Methods			
1. Experiment code	D	V	I
2. Target materials	liquid VFA standards	liquid VFA standards	cheese volatiles
3. Purge (or sweep) gas	nitrogen (>99.999%)	nitrogen (>99.999%)	nitrogen (>99.999%)
4. Purge (or sweep) flow rate	100 mL min ^{−1}	100 mL min ^{−1}	100 mL min ^{−1}
5. Purge (or sweep) loading time	5 min	5 min	5 min
6. Purge (or sweep) loading volume	500 mL	500 mL	500 mL
7. Purge (or vaporization) temperature	25 °C	180 °C	25 °C
[B] Samplers			
1. Sorbent material ^a	Tenax TA + Carbowack B + Carbowack X (each 50 mg)		
2. Sorbent tube size	(1) SS tube: length, 89 mm; OD, 6 mm; and ID, 5 mm (2) QZ tube: length, 89 mm; OD, 6 mm; and ID, 4 mm		
C. Information Regarding the Preparation of Environmental (Cheese) Samples Used for VFA Analysis			
cheese			
1. Sample weight		32.2 g	
2. Sample size		2 cm × 2 cm × 1 cm	

^aQuartz wool was packed between each adsorbent.

Figure 1S in the Supporting Information (SI). Information concerning the experimental procedures covering the preparation of liquid standard and instrumental setups) are provided in sections 2.1 and 2.2 of the SI, respectively. In addition, the detailed descriptions of the standard/sample injection approaches (direct injection vs vaporization) for our sorbent-tube-based analysis is also provided, along with explanations for the experimental schemes used in section 2.3 of the SI.

Basic Scheme for the Quantification of VFA Loss Patterns. *Exp Stage 1.* A series of calibration experiments was made by both direct injection (D) and vaporization injection (V) of the liquid VFA standard on the two types of tube (stainless steel (SS) and quartz (QZ)) packed with identical sorbents. This matching generated four datasets that could be used to assess analyte losses: V-QZ, D-QZ, V-SS, and D-SS (Table 1A). The results were thus compared in terms of signal size (response factor, RF (ng⁻¹)) for each VFA under the different matching conditions.

Exp Stage 2. The VFA standards were vaporized and passed through the empty sample tubes to evaluate the impact of the tube material alone, without sorbent present. Having passed through the empty tubes, the vapors were then trapped using quartz tubes packed with sorbent, because of its better performance (refer to stage 1).

Exp Stage 3. The relative recovery between stainless steel and quartz was tested using real samples (headspace sample of 32.2 g of cheese^{14,15}). Nitrogen gas was supplied to sweep vapors released from the cheese sample (cheddar, extra mature; Alvis Bros., Ltd., U.K.) placed in the impinger (at 25 °C) onto each sorbent tube.

Target Compounds, Standard Preparation, and Experimental Setups. The calibration and the basic tests for quality assurance/quality control (QA/QC) were assessed using the liquid working standards (L-WS). Five VFAs were selected as representative target analytes for this study: (1) acetic acid (ACA), (2) propionic acid (PPA), (3) butyric acid (BTA), (4) isovaleric acid (IVA), and (5) *n*-valeric acid (VLA). In addition, six aromatic hydrocarbons including benzene (B), toluene (T), *p*-xylene (*p*-X), *m*-xylene (*m*-X), *o*-xylene (*o*-X), and styrene (S) were included as reference components. The liquid working standards were prepared by gravimetric dilution of the primary-grade chemicals using methanol (see Table 1S in the SI). For the reader's reference, the odor thresholds of all target compounds are also presented in Table 1S in the SI, since most of them belong to a list of offensive odorants¹⁶ with low odor thresholds.^{3,17–20}

For the analysis of VFA, a GC system (Agilent Model GC 7890A, USA) equipped with time-of-flight mass spectrometry (TOF-MS) (Bench TOF-dx, Almsco UK) was interfaced with a thermal desorption system equipped with an electrically cooled focusing trap (UNITY, Markes International, Ltd., U.K.). The sorbent tube for VOC sampling was prepared as a three-bed type (50 mg of Tenax TA, Carbowack B, and Carbowack X) to induce optimal adsorption of target VOCs; breakthrough was not observed under the experimental setups tested in this study.⁶ The thermal desorber focusing trap was packed with an equivolume ratio of Tenax TA and Carbowack B (see Table 2S in the SI).

RESULTS

The chromatograms obtained from each of all three experimental stages are presented in Figure 1. In Table 3S in the SI, the calibration results (e.g., response factor (RF) and

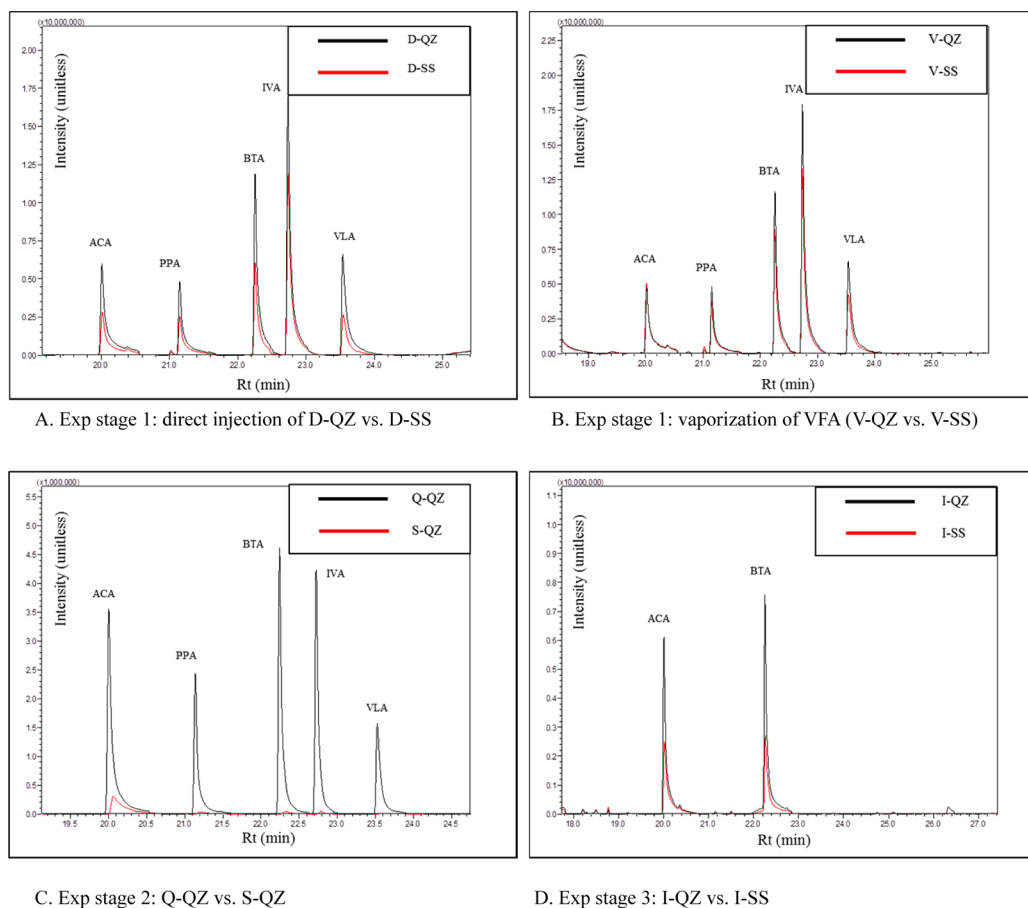


Figure 1. Volatile fatty acid (VFA) chromatograms of Exp Stages 1, 2, and 3: (A) Exp stage 1, direct injection of D-QZ vs D-SS; (B) Exp stage 1, vaporization of VFA (V-QZ vs V-SS); (C) Exp stage 2, Q-QZ vs S-QZ; and (D) Exp stage 3, I-QZ vs I-SS. (1) Exp stage 1 and 2: concentration = $54.2 \text{ ng } \mu\text{L}^{-1}$ and injection volume = $1 \text{ } \mu\text{L}$ and (2) Exp stage 3: sampling volume = 50 mL and sampling flow rate = 100 mL min^{-1} .

coefficient of determination (R^2)) are summarized, along with the basic quality assurance (QA) parameters (e.g., method detection limit (MDL) and relative standard error (RSE)). In the case of BTXS, response factor values of each compound are highly comparable between both injection approaches and between both tube types. The percent difference (PD, %) in RF values was calculated for each analyte, relative to the response factor for vaporization or the response factor for quartz (see Table 2).

$$\text{PD (\%)} = \frac{(\text{RF(V)} - \text{RF(D)})}{\text{RF(V)}} \times 100$$

(1 and 2) for D vs V (1)

$$\text{PD(\%)} = \frac{(\text{RF(QZ)} - \text{RF(SS)})}{\text{RF(QZ)}} \times 100$$

(3 and 4) for SS vs QZ (2)

Unlike the case of BTXS, the response factor patterns of VFAs were substantially different. In case of VFA, the mean response factor values of the stainless steel were significantly lower than those of quartz: (1) response factor (D-QZ) = 299 ± 252 and (2) response factor (D-SS) = 192 ± 87 . Consequently, the computed percent difference value of $37.2\% \pm 9.77\%$ (between D-SS and D-QZ) suggests a significant loss of VFA on stainless steel (relative to quartz) with direct injection (Table 2). Similarly, vaporization

experienced the loss of VFA, although less significant than direct injection. Refer to the results under the different conditions (Figure 2).

The results of comparative analysis of real sample (cheese) between quartz and stainless steel (exp stage 3) are summarized in Table 4S in the SI. The concentration (ppb) of VFAs from the cheese product was quantified by the calibration data of both tube types and both sample loading methods for comparative purposes. The results of both tube types consistently showed the existence of acetic acid and butyric acid among five target VFAs (and all reference BTXS). If gaseous BTXS from cheese was quantified by each of the two calibration results (direct injection and vaporization), their concentrations are highly consistent, regardless of criteria: direct injection (I-SS ($8.08 \pm 13.8 \text{ ppb}$) and I-QZ ($7.84 \pm 13.2 \text{ ppb}$)) or vaporization (I-SS ($7.61 \pm 12.8 \text{ ppb}$) and I-QZ ($7.21 \pm 12.1 \text{ ppb}$)). In contrast, their VFA counterparts exhibited moderate distinctions for each criterion. In case of acetic acid, the values are 365 (I-SS(D)), 363 (I-QZ(D)), 348 (I-QZ(V)), and 269 (I-SS(V)), while their butyric acid counterparts were 259, 261, 245, and 182, respectively. The loss patterns of VFA from real samples are thus somewhat comparable to those derived by the liquid working standard.

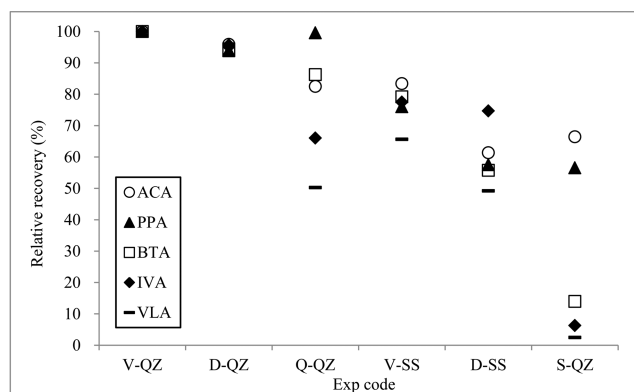
DISCUSSION

Quality Assurance (QA) of VFA Analysis with the Sorbent Tube Method. In this study, the basic quality

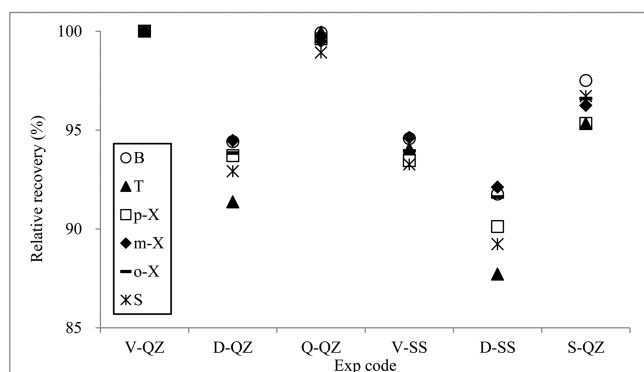
Table 2. Comparison of Relative Performance between Different Sampling Modes in Exp Stages 1 and 2

A. Percent Difference (PD, %) of Response Factors (RF, ng ⁻¹) of VFA between Injection Method and Sampler Types (Stainless Steel (SS) Tube vs Quartz (QZ) Tube) in Exp Stages 1 and 2 ^a																
order	exp code	Compounds														
		ACA	PPA	BTA	IVA	VLA	mean	SD	B	T	p-X	m-X	o-X	S	mean	SD
[A] Different injection approaches (D vs V), Exp stage 1																
1	D-SS vs V-SS	26.4	24.3	29.6	3.61	25.0	21.8	10.4	2.97	6.74	3.57	2.66	2.48	4.32	3.79	1.59
2	D-QZ vs V-QZ	4.08	5.99	6.13	4.30	4.03	4.91	1.06	5.58	8.63	6.29	5.53	6.17	7.09	6.55	1.17
[B] Different tube materials (SS vs QZ), Exp stage 1																
3	D-SS vs D-QZ	36.0	38.8	40.6	21.9	48.7	37.2	9.77	2.81	4.00	3.83	2.50	2.37	3.97	3.25	0.77
4	V-SS vs V-QZ	16.6	24.0	20.8	22.5	34.4	23.6	6.60	5.43	5.95	6.55	5.38	6.06	6.74	6.02	0.56
[C] Different empty tube materials (S vs Q), Exp stage 2																
5	S-QZ vs Q-QZ	19.5	43.2	83.8	90.5	95.1	66.4	33.3	2.42	4.63	4.29	3.26	3.17	2.23	3.33	0.97
B. Relative Recovery (RR, %) and the Sorptive Loss (%) of RF for Each VFA between All Six Exp Codes Tested in Exp Stages 1 and 2 ^b																
order	exp code	Compounds														
		ACA	PPA	BTA	IVA	VLA	mean	SD	B	T	p-X	m-X	o-X	S	mean	SD
[A] Relative recovery (RR, %)																
1	V-QZ	100	100	100	100	100			100	100	100	100	100	100		
2	D-QZ	95.9	94.0	93.9	95.7	96.0	95.1	1.06	94.4	91.4	93.7	94.5	93.8	92.9	93.5	1.17
3	Q-QZ	82.5	99.6	86.3	66.1	50.3	76.9	19.1	99.9	99.95	99.6	99.5	99.7	98.9	99.6	0.38
4	V-SS	83.4	76.0	79.2	77.5	65.6	76.4	6.60	94.6	94.1	93.5	94.6	93.9	93.3	94.0	0.56
5	D-SS	61.4	57.6	55.8	74.7	49.2	59.7	9.47	91.8	87.7	90.1	92.1	91.6	89.2	90.4	1.73
6	S-QT	66.4	56.6	14.0	63.0	2.47	29.2	30.0	97.5	95.3	95.3	96.2	96.6	96.7	96.3	0.85
[B] Sorptive loss (%)																
1	V-QZ	0	0	0	0	0			0	0	0	0	0	0		
2	D-QZ	4.08	5.99	6.13	4.30	4.03	4.91	1.06	5.58	8.63	6.29	5.53	6.17	7.09	6.55	1.17
3	Q-QZ	17.5	0.40	13.7	33.9	49.7	23.1	19.1	0.08	0.05	0.39	0.51	0.25	1.08	0.39	0.38
4	V-SS	16.6	24.0	20.8	22.5	34.4	23.6	6.60	5.43	5.95	6.55	5.38	6.06	6.74	6.02	0.56
5	D-SS	38.6	42.4	44.2	25.3	50.8	40.3	9.47	8.24	12.28	9.88	7.89	8.39	10.8	9.58	1.73
6	S-QT	33.6	43.4	86.0	93.7	97.5	70.8	30.0	2.49	4.68	4.66	3.75	3.41	3.29	3.71	0.85

^aRefer to equations used for derivation of PD values for the datasets of [A], [B], and [C]. For [A]: $(D \text{ vs } V) = \{RF(V) - RF(D)\}/RF(V) \times 100$. For [B]: $(SS \text{ vs } QZ) = \{RF(QZ) - RF(SS)\}/RF(QZ) \times 100$. For [C]: $(S \text{ vs } Q) = \{RF(Q) - RF(S)\}/RF(Q) \times 100$. ^bThe RR and sorptive loss of six exp codes were calculated as the RF values of all exp codes were normalized against those of V-QZ. $RR(\%) = \{RF(n)/RF(V-QZ)\} \times 100$. Sorptive loss $(\%) = \{RF(V-QZ) - RF(n)\}/RF(V-QZ) \times 100$.



A. Five VFAs



B. Six aromatic compounds

Figure 2. Comparison of the relative recovery (%) of VFA and aromatic compounds (BTXS) after normalization to the RF value of V-QZ between all six experimental approaches tested in this study (Exp stages 1 and 2).

assurance of sorbent tube sampling method for the application to VFA analysis was assessed primarily in terms of relative standard errors (RSE (%)) and method detection limits (MDL) for each tube type (stainless steel and quartz). The relative standard error values of the stainless steel and quartz tube were calculated using triplicate analyses of liquid working standard prepared for the third point calibration (mean $51.2 \pm 3.50 \text{ ng } \mu\text{L}^{-1}$) through the direct injection approach (analytical volume = $1 \mu\text{L}$) (see Table 3S in the SI). According to this analysis, six aromatics had fairly good reproducibilities with relative standard errors of <2% for both stainless steel and quartz: $\text{RSE(D-SS)} = 1.24\% \pm 0.28\%$ and $\text{RSE(D-QZ)} = 0.79\% \pm 0.23\%$. In the case of VFAs, their mean RSE values differed greatly between the stainless steel ($8.13\% \pm 0.97\%$) and quartz tube ($0.96\% \pm 0.72\%$). As such, the analytical reproducibility of VFA seems greatly influenced in the case of stainless steel, because of sorptive reaction on the inner wall material.

The method detection limit values were determined by seven repeat analyses of the diluted liquid working standard (mean = $2.56 \pm 0.18 \text{ ng } \mu\text{L}^{-1}$), which was made by 2-fold dilution of the first-point calibration standard (Table 1S in the SI). The method detection limit of BTXS from exp stages 1 and 2 was $0.063 \pm 0.028 \text{ ng}$ ($n = 36$). Regardless of criteria, their method detection limit fell in a narrow range of $0.061 \pm 0.028 \text{ ng}$ (V-QZ) to $0.067 \pm 0.032 \text{ ng}$ (D-SS). In contrast, the method detection limit values of VFAs were affected more sensitively by the type of tube material than by the injection method. In Exp stage 1, method detection limit results of all quartz tubes (D-

QZ and V-QZ) were almost identical for each VFA but were generally smaller than their stainless steel counterparts (D-SS and V-SS) (see Table 3S in the SI).

Assessment of the Sorptive Loss Patterns for VFA under All Different Sampling Conditions. In Exp stages 1 and 2, four types of ((1) D-SS, (2) D-QZ, (3) V-SS, and (4) V-QZ)) and two types of experimental data ((1) S-QZ and (2) Q-QZ) were obtained, respectively (see Table 3S in the SI). Accordingly, the sorptive loss of VFA can be compared to determine the combined effects of injection approaches and tube material types. In case of exp stage 1, the recovery of VFA was higher in the vaporization than in the direct injection, so does the quartz tube over the stainless steel tube. For example, the response factor values of acetic acid decreased on the order of $\text{V-QZ}(327,922) > \text{D-QZ}(314,552) > \text{V-SS}(273,496) > \text{D-SS}(201,281)$. These relative RF ordering was seen consistently from all other VFAs without any exception. The sorptive patterns of VFA on the inner wall of the empty tubes (Exp stage 2) indicate that such a loss systematically increased as the molecular weights increased. In the case of the lightest compound (acetic acid), differences in RF values between Q-QZ and S-QZ were moderately small (19.5%) (see Table 3S in the SI). However, such dominance (Q-QZ over S-QZ) increased dramatically with molecular weight propionic acid (~2), butyric acid (~6), isovaleric acid (~10), and *n*-valeric acid (~20 times).

To assess the overall patterns of VFA sorptive loss, the results from both exp stages 1 and 2 are pooled together and plotted in reference to six aromatics in Figure 2. Because the V-QZ yielded the highest response factor (or the least loss of VFA), the results of all different modes were normalized against those of V-QZ. As shown in Figure 2B, the results of aromatics were fairly comparable throughout all exp codes with good relative recoveries (RR) of $90.4\% \pm 1.73\%$ (D-SS) to $99.6\% \pm 0.38\%$ (Q-QZ). In all six modes, the relative recovery values of individual aromatic hydrocarbons are close enough to show significantly small losses: $94.7\% \pm 4.82\%$ (T) – $96.4\% \pm 3.33\%$ (B).

$$\text{RR}(\%) = \frac{\text{RF}(\text{exp code})}{\text{RF}(\text{V-QZ})} \times 100 \quad (3)$$

If such comparison is extended to VFA, their relative recovery values contrasted greatly across six exp codes. In case of the quartz, the RR value of D-QZ ($95.1\% \pm 1.06\%$ ($n = 5$)) was slightly low relative to the V-QZ. In contrast, the relative recovery of Q-QZ dropped with large variations between VFAs ($76.9\% \pm 19.1\%$ ($n = 5$)). For instance, *n*-valeric acid had the largest loss (relative recovery = 50.3%), while propionic acid had the smallest loss (relative recovery = 99.6%). It is worth noting that the recovery of vaporization method is superior to that of the direct injection method, regardless of tube type. We suspect that direct injection into tube may cause more loss of VFA due to direct contact of liquid with sorbent or its capping material, while transfer of scattered vapor (vaporization method) may reduce such possibilities. For the reader's reference, VFA residues were not detected from the repeated desorption of stainless steel tube used in our study, to possibly reflect their strong sorption with such material.

Comparison of the Sampling Performance between Tube Materials against Real Sample (Cheese). The gaseous VFA released from cheese products were collected by the two tube types (stainless steel and quartz).²¹ All six

Table 3. Overview of the Pretreatment Information for VFA Analysis

order	ref	medium	sampler material	adsorbent	detector ^a	target VFAs (number) ^b
1	Koziel et al. ²⁸	sorbent tube	stainless steel	Tenax TA	GC-MS	ACA, PPA, IBA, BTA, IVA, VLA, and HXA (7)
		SPME (Cx/PDMS) ^c			GC-MS	ACA, PPA, IBA, BTA, IVA, VLA, and HXA (7)
		container	polyvinyl fluoride (Tedlar)		GC-MS	ACA, PPA, IBA, BTA, IVA, VLA, and HXA (7)
		container	PET		GC-MS	ACA, PPA, IBA, BTA, IVA, VLA, and HXA (7)
		container	canister		GC-MS	ACA, PPA, IBA, BTA, IVA, VLA, and HXA (7)
2	Trabue et al. ⁷	sorbent tube	Ni ^d	Tenax GR	GC-MS-O	ACA, PPA, IBA, BTA, IVA, VLA, IHA, HXA, and HPA (9)
		bag	polyvinyl fluoride (Tedlar)		GC-MS-O	ACA, PPA, IBA, BTA, IVA, VLA, IHA, HXA, and HPA (9)
3	Sun et al. ⁵	sorbent tube	glass	multisorbent ^e	GC-MS	ACA, PPA, IBA, BTA, IVA, VLA, HXA, and HPA (8)
4	Trabue et al. ²⁷	sorbent tube	glass	Tenax TA	GC-MS	ACA, PPA, IBA, BTA, IVA, VLA, IHA, HXA, and HPA (9)
		sorbent tube	glass	Carbotrap 300 ^f	GC-MS	ACA, PPA, IBA, BTA, IVA, VLA, IHA, HXA, and HPA (9)
		sorbent tube	glass	CP-X ^g	GC-MS	ACA, PPA, IBA, BTA, IVA, VLA, IHA, HXA, and HPA (9)
5	Parker et al. ²⁹	sorbent tube	stainless steel	Tenax TA	GC-MS	ACA, PPA, IBA, BTA, IVA, VLA, and HXA (7)
6	Zhang et al. ³⁰	sorbent tube	stainless steel	Tenax TA	GC-MS	ACA, PPA, IBA, BTA, IVA, VLA, HXA, and HPA (8)
7	Idris et al. ³¹	bag → sorbent tube	nalophan → quartz	Tenax TA	FID	ACA, PPA, IBA, BTA, IVA, and VLA (6)
8	Ahn et al. ⁸	sorbent tube	stainless steel	Carbopack X	GC-MS and FID	PPA, BTA, IVA, and VLA (4)
		bag	polyvinyl fluoride (Tedlar)		GC-MS and FID	PPA, BTA, IVA, and VLA (4)
		glass bead tube	glass	alkali beads	GC-MS and FID	PPA, BTA, IVA, and VLA (4)

^a(1) GC, gas chromatography; (2) MS, mass spectrometry; (3) O, olfactometry; and (4) FID, flame ionization detector. ^b(1) ACA, acetic acid; (2) PPA, propionic acid; (3) IBA, *i*-butyric acid; (4) BTA, *n*-butyric acid; (5) IVA, *i*-vaeric acid; (6) VLA, *n*-vaeric acid; (7) IHA, *i*-hexanoic acid; (8) HXA, *n*-hexanoic acid; and (9) HPA, heptanoic acid. ^cCarboxen/PDMS 75 μ m. ^dNo information available. ^eCarbopack C and Carbopack X (1:2 ratio v/v). ^fCarbotrap C, Carbotrap B, and Carbosieve S-III. ^gCarbopack C and Carbopack X (1:2 ratio v/v).

target aromatic compounds (BTXS) were detected from cheese samples by both I-SS and I-QZ. Their concentrations were quantified using the calibration results obtained by both injection approaches (direct injection and vaporization): the mean concentrations of six BTXS = (1) 8.08 ± 13.8 ppb (I-SS(D)), (2) 7.61 ± 12.8 ppb (I-SS(V)), (3) 7.84 ± 13.2 (I-QZ(D)), and (4) 7.21 ± 12.1 ppb (I-QZ(V)) (see Table 4S in the SI). It confirms strong compatibilities for BTXS between different approaches, as the basic qualities of the data are not affected much by the main variables for VFA. It is worth noting that the concentrations of toluene (>30 ppb) released from the cheese products are significantly high to exceed all other aromatics (<5 ppb). The occurrence of such excess toluene is however unlikely to reflect the effect of any pollution or experimental bias, according to some previous studies.^{22–24}

In the case of VFAs, their recovery and analytical stability were greatly altered by the combined effects of both variables. The VFAs from the cheese samples were also quantified using the RF values of the direct injection and vaporization approaches. The direct injection-based concentrations of acetic acid were 365 (I-SS(D)) and 363 ppb (I-QZ(D)), while their butyric acid counterparts were 259 and 261 ppb, respectively. As such, comparison based on direct injection indicates the

strong compatibility with low percent difference values of 0.57% (acetic acid) and 0.86% (butyric acid).

$$\text{PD (\%)} = \frac{\text{ABS}[\text{concentration(I-QZ)} - \text{concentration(I-SS)}]}{\text{concentration(I-QZ)}} \times 100$$

for I-SS vs I-QZ (4)

Although there was a large gap ($40.3\% \pm 9.47\%$) in calibration results between D-SS and V-QZ (Exp stage 1), their effect may not produce any bias in the computation of concentration for the cheese sample: different loss patterns for each material seem to systematically cancel out between sample and standard.

In contrast, if the VFA values were quantified using the RF data of vaporization method, their results yielded significantly different percent difference values (between I-SS and I-QZ) = 22.8% (acetic acid) and 25.6% (butyric acid)). In the case of I-QZ, the V-QZ results (348 ppb (acetic acid) and 245 ppb (butyric acid)) were similar to those of D-QZ, as the performance of those two quartz approaches was comparable enough (Figure 2) to yield relatively small percent difference values of 4.08% (acetic acid) and 6.13% (butyric acid).

$$\text{PD (\%)} = \frac{\text{ABS}[(\text{concentration (by D)} - \text{concentration (by V)})]}{\text{concentration (by D)}} \times 100$$

(by D) vs (by V) (5)

However, the VFA concentrations of I-SS, if quantified by V-SS, decreased 26.4% of acetic acid (269 ppb) and 29.6% of butyric acid (182 ppb), relative to D-SS, as their difference was reflected directly. Hence, if VFAs from cheese were quantified using the stainless steel calibration data, the reliability can be distinguished more effectively by the sample loading approaches. However, we suspect that the observed compatibility in stainless steel and quartz is unlikely to occur consistently. For instance, unlike cheese products, the concentration of VFA in common environmental sources cannot be significantly high. Under such circumstances, the VFA loss on stainless steel can yield highly erroneous data (e.g., values below detection or negative values). As such, the quantification of VFAs from environmental samples requires much caution. Hence, one should perform sampling and calibration as consistently as possible to maintain the least bias. Thus, it is recommended to use suitable tube material (such as quartz) for both sampling/calibration of VFA, if one intends to reduce the sources of bias in their quantitation.

It was experimentally demonstrated that the loss of VFA can occur from the selected sampling tube material. However, this type of bias has been well-known for many other reactive compounds, such as reduced sulfur compounds (RSC). Kim et al.²⁵ investigated the sorptive loss patterns of RSCs between six tubing materials ((1) stainless steel, (2) silicosteel, (3) silicone, (4) copper, (5) Teflon, and (6) tygon) using standards of H₂S, CH₃SH, dimethyl sulfide, and dimethyl disulfide. Accordingly, most tested materials that included stainless steel were subject to sorptive loss, while its extent was the largest for the lighter RSCs, such as H₂S. Although copper tubing showed more loss selectively on the lighter RSCs, silicone tubing had such loss from all reduced sulfur compounds. Hayes et al.²⁶ analyzed 62 VOCs using a GC-time-of-flight-MS system. The relative recovery of each VOC was measured by passing standard gas through four tubing materials ((1) Nylon (Nylaflow), (2) polyetheretherketone (PEEK), (3) fluoroethylene propylene (Teflon), and (4) low-density polyethylene (polyethylene)). All tubing materials (except polyethylene) had significantly high relative recovery values of BTXS, in range of 91% (benzene, PEEK) to 117% (styrene, Nylaflow). In case of polyethylene, low relative recovery values in the range of 55% (*o*-xylene) to 89% (styrene) was recorded. In contrast, polyethylene had a high relative recovery value (100%) of acetone, while acetone had low recoveries from others 58% (PEEK) to 87% (Nylaflow). Similarly, the sorptive loss of BTXS, observed to be fairly stable in this study, can also be subject to a significant loss, if the sampling approach is not properly set for such consideration.

To learn more about the potential bias occurring from the sampling device, we conducted a comprehensive survey of common sampling approaches for VFA in previous studies (Table 3). Although the use of bag sampling is likely to be subject to the largest bias, such application is still found in many instances. The use of glass tube for the collection of VFAs has also been reported. Although its performance may be comparable to quartz tube, no specific data to support its selection (or replacement with stainless steel) were provided.^{5,27} Interestingly, the use of stainless steel tube for VFA can be found commonly in both early studies²⁸ and recent

studies.^{29,30} Moreover, there is a modified approach in which samples are initially collected in the bag and later recollected by quartz tube sorbent sampler.³¹ However, such modification is likely to induce a large bias due to the significant loss at the initial bag sampling. As such, many previous data should contain certain biases due to the lack of proper consideration on this sample loss problem.

CONCLUSIONS

The collection of volatile fatty acids (VFAs) in air is a highly delicate task, because they are prone to significant sorptive loss in the sampling stage, because of their strong sorptive reactivity. Although the need for accurate quantitation for VFAs grows, the experimental reliability of their sampling method is still poorly validated. To conduct reliable measurements of VFAs in air, it is imperative to employ a sampling method that warrants reliable recovery. Among the many available options, thermal desorption analysis coupled with sorbent tube sampling has been recommended as the optimal pretreatment method for VFAs. To validate the reliability of sorbent tube–thermal desorption method for VFA analysis, the sorptive loss of VFAs was analyzed on a quantitative basis, using the most common material (stainless steel (SS) tube) and its alternative material (quartz (QZ) tube). In addition, comparison was also made for the injection method of liquid standard onto the sorbent tube between direct injection (D) and vaporization (V).

The experimental results of VFAs between stainless steel and quartz tubes showed that the former had a significantly high loss of VFAs, relative to the latter. If the sorptive loss of VFAs by stainless steel tube was assessed relative to the V-QZ data, the extent of VFA loss was higher on all the stainless steel tube data for each loading method by ~20% (V-SS) and ~40% (D-SS). Furthermore, if the sorptive loss of vaporized VFAs was measured after they passed through the empty stainless steel tube, the relative loss of VFAs increased systematically with increasing molecular weights, such as from 33.6% (acetic acid) and 97.5% (*n*-valeric acid).

To validate the loss patterns of VFA from real samples, the VFAs emitted from some cheese products were collected by both stainless steel and quartz tubes. The results showed that they experience a loss of VFAs in a pattern comparable to those validated by liquid standards. Experimental bias due to sample loss can be minimized by employing the sampling and calibration consistently, but the optimal results should be obtained by the most stable sampling method (e.g., the use of quartz tube). Furthermore, for quantitative analysis of highly reactive compounds such as VFAs from environmental media, the material types of tube sampler and calibration methods should be considered simultaneously to maintain the least bias. In this respect, our study can provide practical grounds to establish reliable measurement techniques for gaseous VFAs. However, for future study, the choice of sorbent is also one of the interesting areas to investigate further to improve the collection efficiency or performance of VFA analysis.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

- (1) ACA = acetic acid
- (2) B = benzene
- (3) BTA = butyric acid
- (4) GC = gas chromatography
- (5) IVA = isovaleric acid
- (6) L-WS = liquid working standard
- (7) MDL = method detection limit
- (8) MFC = mass flow controller
- (9) *m*-X = *m*-xylene
- (10) *o*-X = *o*-xylene
- (11) PD = percent difference
- (12) PPA = propionic acid
- (13) *p*-X = *p*-xylene
- (14) QA = quality assurance
- (15) QC = quality control
- (16) QZ = quartz
- (17) R^2 = coefficient of determination
- (18) RF = response factor
- (19) RR = relative recovery
- (20) RSE = relative standard error
- (21) S = styrene
- (22) SS = stainless steel
- (23) ST = sorbent tube
- (24) T = toluene
- (25) TD = thermal desorption
- (26) TOF = time-of-flight
- (27) VFA = volatile fatty acid
- (28) VLA = *n*-valeric acid
- (29) VOC = volatile organic compounds

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