JOURNAL OF SEPARATION SCIENCE

15|2022
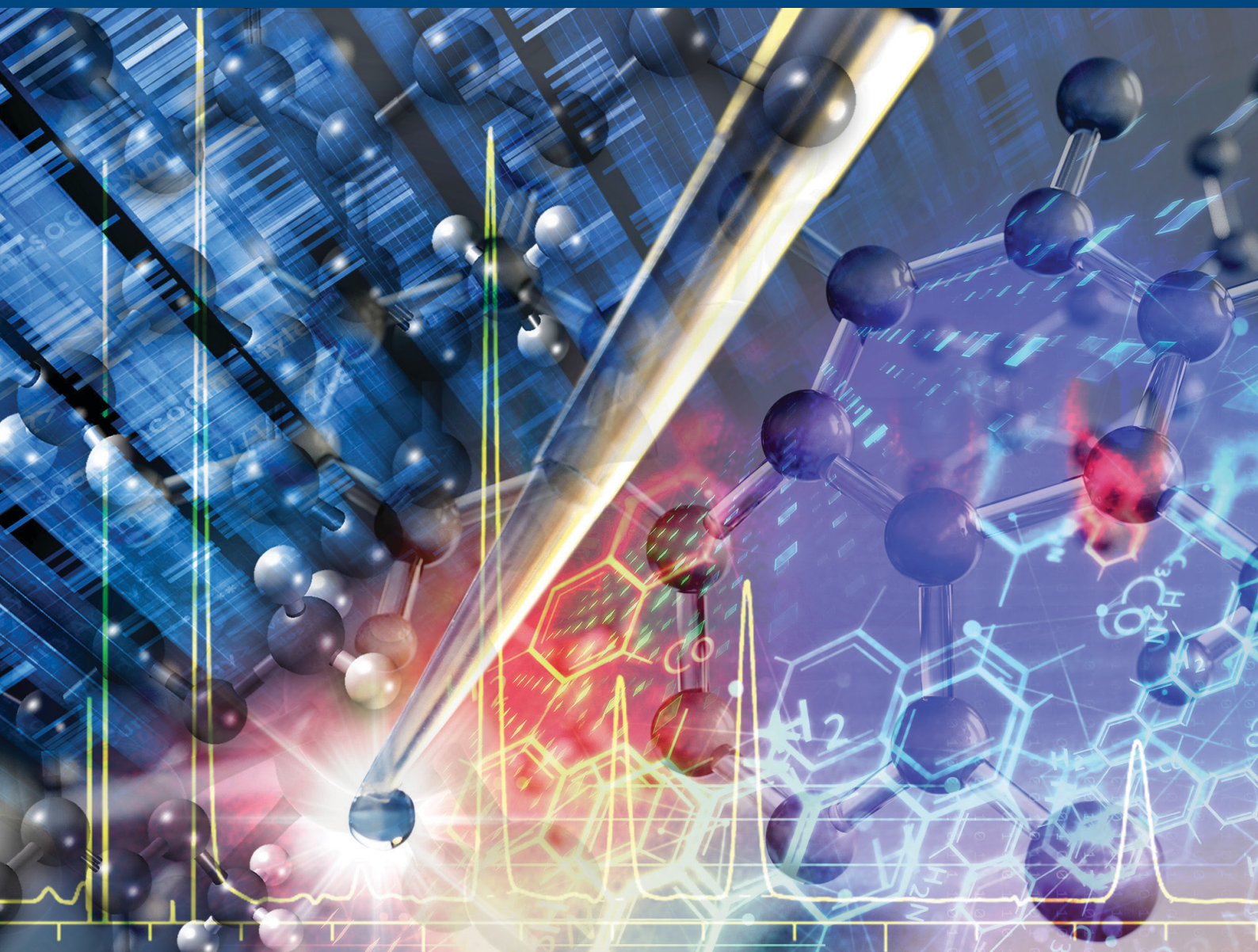
RESEARCH ARTICLE

JOURNAL OF
SEPARATION SCIENCE

The potential of thermal desorption-GC/MS-based analytical methods for the unambiguous identification and quantification of perfluoroisobutene and carbonyl fluoride in air samples

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Funding information
Swedish Ministry of Defence

The reactive gases perfluoroisobutene and carbonyl fluoride are highly toxic and difficult to analyze in air. For this paper, the available sampling and analysis methods involving gas chromatography/mass spectrometry were investigated for their potential to give unambiguous identification and quantification of perfluoroisobutene and carbonyl fluoride, for which no such methods exist. Although high concentrations of perfluoroisobutene could be analyzed directly by manual split injection, sorbent sampling followed by thermal desorption GC/MS allowed lower concentrations to be analyzed. However, a significant degradation of perfluoroisobutene observed after thermal desorption analysis inspired the use of derivatization of perfluoroisobutene with 3,4-dimercaptotoluene. The use of Tenax TA sorbent tubes spiked with 3,4-dimercaptotoluene and trimethylamine in a molar ratio of 1:8 proved successful for the quantification of a unique perfluoroisobutene derivative, and the method was validated for atmospheres in the range of 0.13–152 ppb with a relative standard deviation of less than 20% and an accuracy of 90%. Although carbonyl fluoride was less stable than perfluoroisobutene, direct analysis was possible at high concentrations but the response was not linear. The 3,4-dimercaptotoluene derivatization method developed was also applicable for quantification of carbonyl fluoride atmospheres.

KEYWORDS
carbon molecular sieve, chemosorption, derivatization, porous layer open tubular, thermal desorption

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1 | INTRODUCTION

Perfluoroisobutene (PFIB), carbonyl fluoride (COF$_2$), and carbonyl dichloride (phosgene, COCl$_2$) are all highly toxic gases that can cause irritation of mucous membranes, inflammatory responses, respiratory distress, and pulmonary edema [1–4]. It is understood that their primary toxicological activity results from acylation reactions with nucleophilic moieties such as thiols, hydroxyls, and amines in the respiratory epithelium. No antidotes are available and treatment is principally supportive and relies on management of the symptoms [1, 5].

PFIB and COF$_2$ may form during combustion of materials such as polyfluorinated organic compounds, batteries, and fluorinated fire suppressants or thermal degradation of such materials [6, 7], while phosgene may arise from the combustion of organochlorine compounds [8]. Thus, they are all potential health hazards in conjunction with fires in domestic and industrial buildings [9]. Phosgene is an industrial chemical and is used in the synthesis of aromatic di-isocyanates for the production of polyurethanes. PFIB and phosgene are both classified as chemical warfare agents and are included in the Chemical Weapons Convention (CWC) schedule 2 B and 3 B, respectively [10]. COF$_2$ is structurally related to phosgene but not included in the Convention. General data for these gases are shown in Table 1. Commercial detection techniques are available for the detection of hazardous levels of phosgene in industrial or occupational settings, but not for PFIB and COF$_2$. Since all three gases may be present in various occupational environments, and PFIB and phosgene are of interest during inspection under the CWC, both quantitative and qualitative methods are needed.

Although these reactive gases are corrosive and unstable, and thus difficult to analyze using GC, there are a few examples where PFIB and phosgene have been analyzed by direct analysis of gas samples [11–15]. However, due to their reactivity and instability, direct analysis or using sampling containers (canisters, Tedlar bags) may prove inadequate unless GC instrumentation is easily accessible at the sampling site. Another common approach for the
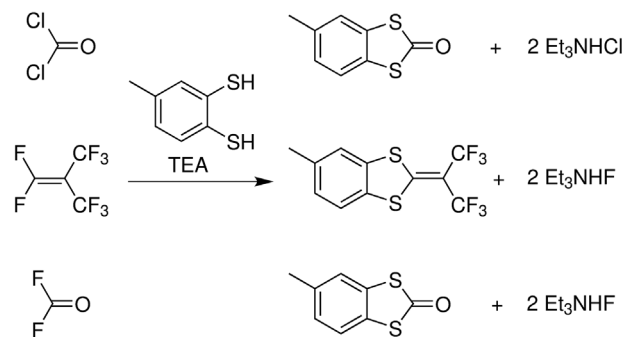

FIGURE 1 Formation of thermally stable derivatives of 3,4-dimercaptotoluene (3,4-DMT) with phosgene, perfluoroisobutene (PFIB), and carbonyl fluoride (COF$_2$). Triethylamine (Et3N, TEA) acts as a base and acid scavenger in the reaction

sampling of volatile organic compounds in general is the use of adsorbent tubes; however, as previously reported, this can be challenging for highly volatile and reactive compounds [15–18]. A more feasible approach for phosgene, allowing unambiguous identification, has been the use of nucleophilic derivatization agents spiked onto sorbents (for chemosorption sampling) or added to liquids (for impinger sampling) to form products that are both stable during storage and suitable for chromatographic separation and analysis [19–22]. The addition of the bis-nucleophile 3,4-dimercaptotoluene (3,4-DMT) in excess onto Tenax TA sorbent tubes, to form a cyclic product (Figure 1), followed by thermal desorption (TD) GC/MS was applied for the sampling and analysis of phosgene [23, 24]. Further improvements and a detailed validation demonstrated stability of the phosgene derivatization product on sampling tubes for up to 1 month [24], a useful feature when sampling in remote areas. Sampling on sorbent tubes has advantages compared to the use of sampling containers, one being that a larger volume of air can be sampled with more convenient sample handling, resulting in lower detection limits and lower variability [25]. The derivatization product of PFIB and 3,4-DMT was prepared in solution by Muir et al. [23], and it was shown that it

TABLE 1 Physical data and exposure limits for perfluoroisobutene, carbonyl fluoride, and phosgene

Compound	CAS	Molecular formula	Molecular weight (g/mol)	Boiling Point (°C)	Vapor pressure (kPa)	OELs (ppb)	AEGL 2, 8 h (ppb)
Perfluoroisobutene (PFIB)	382-21-8	CF$_2$C(CF$_3$)$_2$	200	7	232	10	14
Carbonyl fluoride	353-50-4	COF$_2$	66	−85	5613	2000	87
Phosgene	75-44-5	COCl$_2$	99	8	162-189	100	40

Note: CAS is the Chemical Abstract Service registry number, Vapor pressure is presented at 1 atm and 25°C; OEL denotes occupational exposure limit from GESTIS substance database. AEGL 2 denotes Acute Exposure Guideline Level 2, corresponding to a level where the general population could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

could be analyzed in spiked samples; however, no complete methodology for the analysis of air samples based on adsorption–derivatization has been presented for PFIB. Published analytical methods for COF_2 are scarce, and none has been found describing sorbent sampling of COF_2 followed by GC/MS analysis. COF_2 is expected to form the same derivatization product as phosgene using 3,4-DMT as the reagent (Figure 1).

In this study, the potential to determine PFIB and COF_2 unequivocally in air samples through GC/MS analysis was investigated, initially by direct analysis and adsorbent sampling in combination with TD. The chemical similarity between these gases and phosgene encouraged us to explore further the possibility of extending the use of 3,4-DMT as a derivatization agent on adsorbent tubes for sampling and GC/MS analysis of both PFIB and COF_2.

2 | MATERIALS AND METHODS

2.1 | Chemicals and materials

3,4-DMT was purchased from TCI Europe N.V. (Zwijndrech, Belgium). LC-graded methanol was obtained from Fischer Scientific (Loughborough, UK). PFIB (90 % purity) was obtained from Swedish Defence Research Institute Schedule I facility (Umeå, Sweden). COF_2 was obtained in a 1000 ppm gas cylinder (in N_2) from Linde Gas AB (Solna, Sweden). Triethylamine (TEA), toluene-d_8, phosgene (15 wt % in toluene), and chlorotriethylsilane were purchased from Sigma Aldrich (St. Louis, MI, USA). Other chemicals and materials for synthesis were purchased from Fisher Scientific GTF AB, Gothenburg, Sweden. All chemicals, except PFIB, were of analytical grade or higher.

Details of the synthesis of the 3,4-DMT-derivatisation products of PFIB and COF_2 are found in the supporting material.

Note that 5-L Tedlar bags were obtained from VWR (Radnor, PA, USA). Commercial stainless steel adsorbent tubes (6.35 mm od, length 89 mm) packed with Tenax TA (Supelco-25055, porous polymer resin based on 2,6-diphenyl-p-phenylene oxide), Carbosieve S-III (Supelco-25053, carbon molecular sieve), and Air Toxics (Supelco-25051, dual bed of medium strength graphitized carbon black backed up by carbon molecular sieve) were obtained from Perkin Elmer (Waltham, MA). Universal adsorbent tubes (C3-AAXX-5266, triple bed of Tenax TA, Carbograph 1TD, and Carboxen 1003) were obtained from Markes International Ltd (Llantrisant, Wales, UK).

Two TD cold traps, TurboMatrix Air Monitoring trap and Tenax trap, were obtained from Perkin Elmer (Waltham, MA) while a Tenax/molecular sieve cold trap was packed in-house. GC columns, DB 5MS (WCOT), DB 624 (WCOT) and GS-GasPro (PLOT), were obtained from Agilent J&W Scientific (Santa Clara, CA, USA). Air-sampling pumps of the type GilAir+ were obtained from Sensidyne, LP (St. Petersburg, FL, USA).

2.2 | Solutions

The synthesized PFIB and COF_2 derivatives were separately dissolved and diluted in methanol to suitable concentrations. An internal standard (IS) solution of toluene-d_8 (10 ng/μl) was prepared in methanol. Separate solutions of 3,4-DMT (2.5 μg/μl) and TEA (31 μg/μl) were prepared in methanol and stored at −20°C and +8°C, respectively.

2.3 | Generation of gas atmospheres

Typically, a PFIB atmosphere was generated by transferring 10 μl of PFIB(l) at −20°C using a pre-cooled (−20°C) 10 μl Gilson micropipette with capillary piston into a 1 L polytetrafluoroethylene canister containing dry $N_2(g)$, resulting in a PFIB concentration of 13.4 g/m^3. After 5 min equilibration in room temperature, 50 ml was transferred using a gas-tight syringe into a Tedlar bag containing 4.95 L $N_2(g)$, giving a primary PFIB atmosphere of 134 mg/m^3. A primary atmosphere of 40.5 mg/m^3 COF_2 in a 5-L Tedlar bag was prepared from a 1000 ppm COF_2 gas cylinder using mass flow controllers. A primary $COCl_2$ atmosphere of 277 mg/m^3 was prepared by injecting 10 μl of $COCl_2$ (15 % wt in toluene) into a 5-L Tedlar bag with N_2. Additional atmospheres in suitable concentrations were prepared in Tedlar bags by dilutions of the primary atmospheres.

2.4 | Calibration samples

Small aliquots (3−60 μl) of the PFIB derivative solutions were spiked onto Tenax tubes in the following amounts: 0.09, 0.15, 0.9, 9, 45, 90, 180, 360, 720, 1152, and 3000 ng, followed by addition of 5 μl of IS solution (50 ng). Thereafter, the tubes were purged with 600 ml of ambient air at a flow rate of 200 ml/min to remove excess methanol. Calibration samples of the COF_2-derivative were prepared in the same way in the following amounts: 1, 8, 16, 32, 64, 128, 250, and 500 ng. All calibration levels were prepared and analyzed in triplicate.

2.5 | Direct analysis of perfluoroisobutene and sorbent sampling without chemosorption

Extensive tests using direct analysis and analysis with sorbents (Carbosieve S-III, Air Toxics, Universal) using several commercially available columns (DB 624, DB 5 MS, GS-GasPro), and different settings (e.g., cryo) were performed for underivatized PFIB. The analytical settings are described in detail in Supporting Information Methods and Table S1.

2.6 | Chemosorption-based sampling procedure

Preconditioned (300°C, 50 ml N_2/min, 10 min) Tenax TA tubes were prepared, one at a time, by adding 5 μl of the IS solution (10 ng of toluene-d_8), 40 μl 3,4-DMT-solution, and 40 μl TEA solution (3,4-DMT:TEA molar ratio 1:8) followed by removal of excess methanol by purging the tube with 600 ml ambient air at a flow rate of 200 ml/min. Within 5 min after reagent addition, 500 ml of prepared gas atmosphere was pumped through the tube using a handheld air-sampling pump at a flow rate of 100 ml/min. In some experiments, sampling was carried out using two tubes in tandem (front and back-up tube) where both tubes were prepared as described above.

2.7 | Thermal desorption-GC/MS of derivatized samples

The derivatization products of PFIB, COF_2, and phosgene were analyzed with TD-GC/MS using two-stage desorption on a Turbomatrix 350 ATD-instrument (Perkin Elmer, Waltham, MA, USA). The following settings were used: primary desorption: 280°C (5 min, 40 ml/min), cold trap desorption: 5−300°C (40°C/min, 3 min hold), valve temperature: 280°C, transfer line temperature: 220°C, inlet split: 40 ml/min, and outlet split: 15 ml/min. The sample was introduced into a GC/MS (Agilent 7890A GC/5975C MSD) at constant column flow rate of 1 ml/min, giving an overall split ratio of 1:32. The temperature of the GC oven (column: DB 5 MS, 30 m × 0.25 mm id × 0.25 μm film thickness) was initially held at 40°C for 2 min, increased to 280°C at 15°C/min, and held for 5 min. The mass spectrometer (EI, 70 eV) was operated in synchronous selected ion monitoring (SIM)/scan acquisition using a full-scan range of m/z 29−400 and the following SIM ions: m/z 98 (toluene-d_8), m/z 134 (fluorotriethylsilane), m/z 154 and

m/z 182 (COF_2-derivative), and m/z 297 and m/z 316 (PFIB derivative).

2.8 | Data evaluation

The data were assessed using Enhanced Data Analysis (Agilent MSD Productivity ChemStation for GC and GC/MS systems, Santa Clara, CA, USA) software. Full scan data, in combination with the NIST mass spectral library, were used for initial identification of relevant compounds. For the chemosorption method, complete evaluation of data was based on IS normalized peak areas calculated by division of SIM ion peak areas for derivatives (m/z 316 and m/z 154) with the peak area of IS m/z 98. The sampled mass of the derivatives (calculated from calibration curves of derivative mass versus IS normalized peak area) was converted to mass of the analyte using the ratio of the molecular weight for the analyte and corresponding derivative. Finally, gas concentrations were calculated by dividing the mass of analyte by the sampled volume. Gas concentrations in mg/m^3 or μg/m^3 were converted to ppm or ppb based on the molar volume at 20°C (24.1 L).

3 | RESULTS AND DISCUSSION

3.1 | Direct analysis of perfluoroisobutene and sorbent sampling without chemosorption

For underivatized PFIB, it was concluded that relatively high concentrations could be analyzed using GC/MS directly, however with almost no retention, and that adsorbent sampling with Carbosieve S-III may allow a lower detection limit, thus potentially being useful for identification of PFIB in field conditions. On the other hand, this approach produced degradation of PFIB on the adsorbent necessitating prompt analysis and resulted in inadequate quantification. Further details are found in Supporting Information Materials.

3.2 | Chemosorption-based sampling of perfluoroisobutene

To enable quantitative analysis of expected levels in occupational environments and for trace level detection in authentic conditions, chemosorption utilizing derivatization was further investigated, with PFIB as the target for method development and validation. An extracted ion chromatogram (m/z 316, t_R = 12.13 min) and corresponding
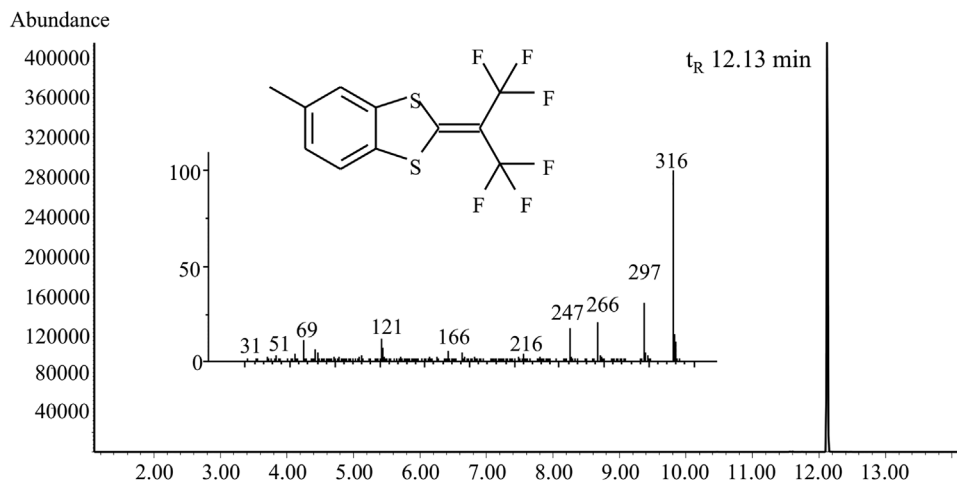
FIGURE 2 Extracted ion chromatogram (m/z 316) and mass spectrum of the perfluoroisobutene (PFIB)-derivative using chemosorption sampling of a PFIB atmosphere (1260 ng/L) followed by thermal desorption-GC/MS analysis

mass spectrum of the PFIB derivative from a PFIB atmosphere can be found in Figure 2.

3.2.1 | Molar ratio and amount of nucleophile base

The optimal theoretical ratio between 3,4-DMT and the hydrogen scavenger TEA is 1:2 for PFIB, COF_2, and phosgene, which forms cyclic derivatives with 3,4-DMT (see Figure 1). For PFIB, we investigated the ratios 1:2, 1:4, and 1:8 and found that 1:8 gave approximately twice as high a response of PFIB derivative compared to using 1:2. Furthermore, addition of different reagent solution volumes (10, 40, and 80 μl), while keeping the total amount of reagent constant, were tested. Based on these results, all subsequent sampling was carried out using adsorbent tubes prepared with 100 μg 3,4-DMT in 40 μl methanol and 1240 μg TEA in 40 μl methanol.

3.2.2 | Stability of reagents and sampling efficiency

3,4-DMT was found to form 2,8-dimethyldibenzo-(1,2,5,6)tetrathiocin (t_R = 20 min and retention index = 2644) (see Figure S3) in the presence of TEA after room temperature storage (>2 days) in solution. For this reason, separate solutions of 3,4-DMT and TEA were used in this study. It was also decided to investigate their compatibility when separately spiked on the sorbent material. Six freshly prepared tubes with matching back-up tubes were used to immediately (<5 min) collect 0.5 L of PFIB atmosphere (133 μg/m³) and, for six corresponding pairs of tubes, 30 ± 5 min was allowed between spiking

and sampling (Figure 3A). The total recovery of the PFIB derivative significantly decreased (p-value = 0.033 calculated with a Student's t-test) with increased time and the levels found in the back-up tubes increased (p-value = 0.006). A similar loss of recovery/derivatization efficiency was previously found for phosgene by Juillet et al. [24] and they recommended collecting samples within 5 min of spiking. The results using the present method, based on separate addition of 3,4-DMT and TEA at a molar ratio 1:8, show that the necessity of expeditious sampling after addition of reagents also applies to PFIB.

3.3 | Method validation

3.3.1 | LOD, LOQ, and desorption efficiency

When analyzing blank adsorption tubes prepared with 3,4-DMT and TEA, a background of PFIB derivative was observed. Therefore, calculation of the method LOD (MLOD) was based on repeated analysis of blank samples. Six tubes prepared with IS and reagents were individually used for sampling of 500 ml of N_2 and, thereafter, analyzed. MLOD was calculated as MLOD = X_{bl} + $3S_{bl}$, where X_{bl} is the analyte mass corresponding to the mean area of blank samples and S_{bl} is the standard deviation of the blank samples. This gave an MLOD for PFIB of 0.29 ng/tube, which corresponds to 0.07 ppb for a 0.5 L gas sample (Table S2). The instrumental LOD was found to be lower than the lowest point in the calibration curve (0.09 ng/tube; Figure S4), which corresponded to an S/N~100 for m/z 316. This S/N is 30 times higher than the common LOD definition, S/N = 3. The method LOQ (MLOQ) for PFIB was calculated to be 0.71 ng/tube (MLOQ = X_{bl} + $10S_{bl}$), corresponding to 0.17 ppb for a 0.5 L gas sample (Table S2). As analysis using
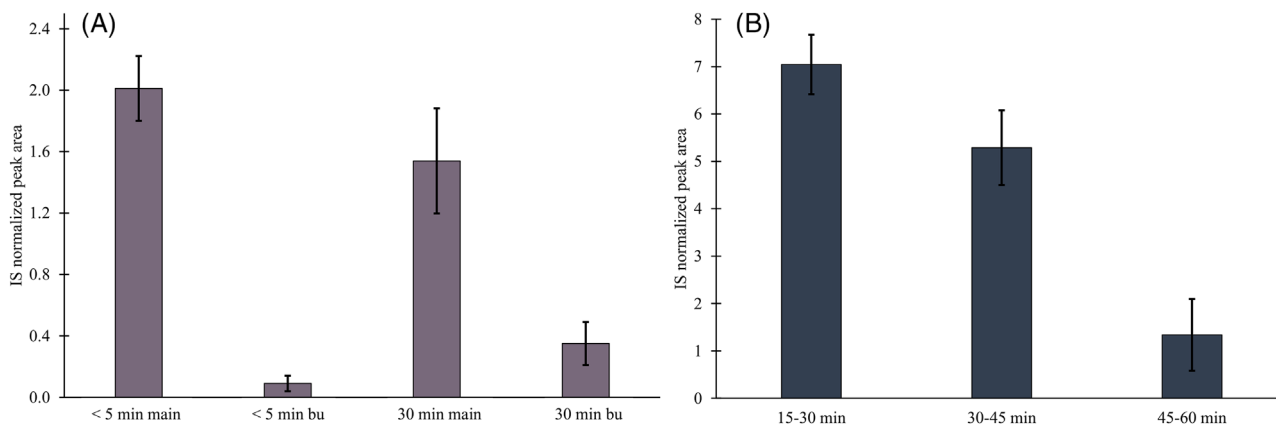
FIGURE 3 (**A**) Total recovery of perfluoroisobutene (PFIB) ($\pm$SD) from the main tubes ($n = 6$) and amount in back-up tubes (bu) when sampling PFIB atmosphere at 133 $\mu g/m^3$ within 5 min after addition of 3,4-dimercaptotoluene (3,4-DMT) and triethylamine (TEA), as compared to sampling after 30 min. (**B**) Total recovery ($\pm$SD) at different delay times between preparation of chemosorption tubes ($n = 3$) and sampling of 0.5 L of a 2750 ng/L carbonyl fluoride (COF_2) atmosphere

TD is to some extent susceptible to carry-over, MLOD may vary depending on the concentrations of previously analyzed samples. Empty tubes (without adsorbent) analyzed immediately after samples demonstrated a carry-over of PFIB derivative in the ATD system $\leq$ 1%. Re-desorption of samples demonstrated a desorption efficiency of typically 95%.

3.3.2 | Linearity, accuracy, and working range

Linearity was assessed in two ways. First, a calibration curve of the PFIB derivative was calculated based on analysis at 10 concentration levels in the range of 0.09–1152 ng per tube, with each level analyzed in triplicate. This gave a slope of 0.0115 and a regression coefficient (R^2) of 0.999 (Figure **S4**). One further calibration point at 3000 ng showed 18% deviation from the regression line, indicating a linear working range up to at least 1152 ng PFIB derivative per tube (corresponding to 180 ppb PFIB for a 0.5 L gas sample).

Second, a calibration curve was constructed from the TD-GC/MS analysis of PFIB atmosphere samples (0.5 L) at three concentrations, 1.1, 266, and 1260 $\mu g/m^3$ (0.13–152 ppb), with each concentration analyzed in triplicate. The corresponding R^2 was 0.989 and the slope was 0.0102, indicating a slight underestimation of concentrations. The accuracy was determined by calculating the deviation between theoretical concentrations of prepared PFIB atmospheres and measured concentrations calculated using the calibration curve for the PFIB derivative (Figure **S4**). An underestimation of 7%–19% was found (see Table **2**), which in part can be explained by an, on average 6 %, sample loss to back up tubes, which was confirmed by tests using tandem tubes.

3.3.3 | Repeatability and reproducibility

Repeated analysis of the PFIB derivative spiked on sorbent tubes gave an average RSD of 12% in the range 0.09–0.9 ng per tube and 2.0% in the range 9–1152 ng per tube (data from Figure **S4**). Repeated analysis of PFIB atmospheres carried out during the same day at concentration levels of 266 $\mu g/m^3$ and 1260 $\mu g/m^3$ gave an RSD of 9–13% (see Table **2**). Higher RSD of 20% was obtained at a lower concentration (1.09 $\mu g/m^3$). Between-day reproducibility, for the same PFIB atmosphere (1260 $\mu g/m^3$) over 2 days, was 17% (measured PFIB concentration of 1110 $\pm$ 102 $\mu g/m^3$ on day 1 and 1180 $\pm$ 288 $\mu g/m^3$ on day 2). Previous studies have reported reproducibility for phosgene using a similar methodology, with an RSD in the range of $\pm$10%–20% [23, 24].

### 3.4 | Chemosorption-based sampling of COF_2

As for PFIB, high concentrations of COF_2 could be analyzed directly using manual split injection (1000 ppm, 1 μl, 20 μl, 100 μl), giving a peak with almost no retention (DB5-MS column). However, the response was not linear. The chemosorption method developed for PFIB was also tested to see if it could confirm the presence of a COF_2 derivative when sampling prepared COF_2 atmospheres. Initial experiments, employing single adsorbent tubes prepared with 3,4-DMT and TEA for sampling of COF_2 atmospheres prepared at 100 $\mu g/m^3$ and 600 $\mu g/m^3$ in Tedlar bags, demonstrated the presence of the COF_2 derivative (m/z 154, $t_R = 12.56$) (Figure **4**). The necessity for expeditious sampling after addition of reagents seen for PFIB was confirmed also for COF_2, in a test using nine tubes prepared

TABLE 2 Comparison of theoretical perfluoroisobutene concentrations in prepared atmospheres ($C_{prepared}$) and measured concentrations after sampling

PFIB level	$C_{prepared}$ ($\mu g/m^3$)	$C_{mean\ front}$ ($\mu g/m^3$)	RSD %	$C_{mean\ front + bu}$ ($\mu g/m^3$)	RSD %	% diff$_{front}$	% diff$_{front + bu}$
Low	1.09	1.01 ± 0.20	20	n.a.	–	−7.2	–
Medium	266	236 ± 24	10	244 ± 26	11	−12	−8.4
High	1260	1020 ± 130	13	1110 ± 102	9.2	−19	−12

Note: $C_{mean\ front}$ refers to PFIB concentration calculated for front tube. $C_{mean\ front + bu}$ refers to the PFIB concentration calculated for the sum of front and back-up tube.

Abbreviations: n.a ., not applicable; PFIB, perfluoroisobutene.
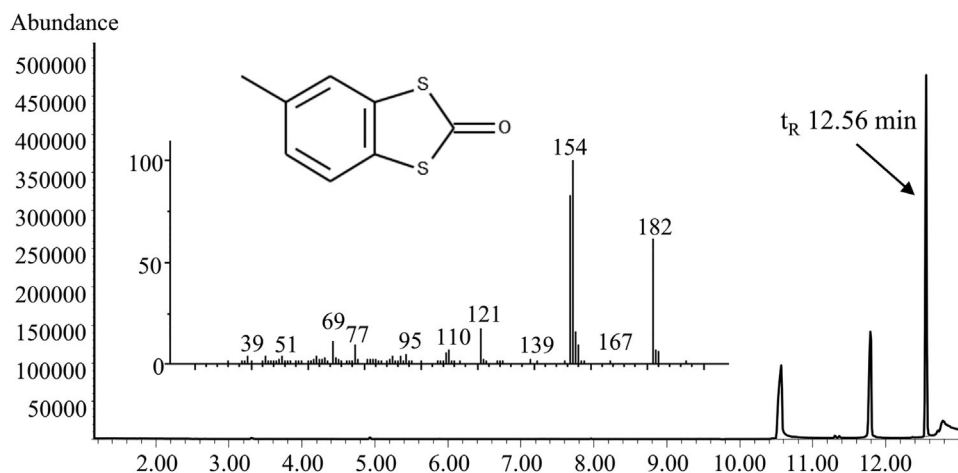
FIGURE 4 Extracted ion chromatogram (m/z 154) and mass spectrum of the carbonyl fluoride (COF_2)-derivative using chemosorption sampling of a COF_2 atmosphere (600 ng/L) followed by thermal desorption-GC/MS analysis

with TEA and 3,4-DMT. The tubes were consecutively sampled (0.5 L of 2750 ng COF_2/L) over a period of ∼ 1 h and showed a clear trend of declining responses with losses up to 80% (Figure 3B).

A calibration curve was calculated for the synthesized COF_2 derivative spiked onto tubes at eight levels in the range 1−500 ng per tube corresponding to COF_2 concentrations between 0.26 and 362 ppb for a 0.5 L gas sample (Figure S5). All calibration levels were prepared and analyzed in triplicate. The slope was 0.0087, intercept −0.0003, and the regression coefficient was 0.997. The average RSD was 8.1% within triplicates, although a larger RSD of 29% was observed at the lowest level (1 ng). Measured concentrations for the initial experiments calculated from the calibration curve revealed low recoveries (∼35%). Therefore, the stability of COF_2 in Tedlar bags was investigated by preparing a fresh COF_2 atmosphere that was sampled immediately and over a period of 4 days. After 1 day, the concentration had decreased 77%, and after 4 days, it decreased to 92%, necessitating the use of freshly prepared bags. Triplicate samples of a sequence of two tubes prepared with 3,4-DMT and TEA (front and a back-up) were

used to collect 0.5 L of freshly prepared COF_2 atmosphere (217 $\mu g/m^3$). The resulting concentrations, $C_{mean\ front}$ of 164 ± 34 $\mu g/m^3$ and $C_{mean\ front+ back\ up}$ of 196 ± 35 $\mu g/m^3$, showed a reasonable reproducibility, with 20% RSD and 18% RSD, respectively. The accuracy was 90% when including the amount found in the back-up tubes (∼20%). MLOD and MLOQ for COF_2 can be found in Table S2.

3.5 | Tests investigating the discrimination between carbonyl fluoride and phosgene

Since COF_2 and phosgene yield the same derivatization product after reaction with 3,4-DMT (Figure 1), a confirmatory test to identify remains of the corresponding halide (F^-) from COF_2 was explored. It was hypothesized that halide ions on the adsorbent would become volatile and suitable for detection with TD-GC/MS after reaction with a suitable derivatization reagent [26, 27]. A number of tests using small postsampling additions of chlorotriethylsilane, both as liquid (1 μl) and in the vapor phase

(≤250 μl headspace from the chemical bottle), demonstrated the production of fluorotriethylsilane. However, none of the tests was reliable in terms of specificity when comparing to blank N_2 samples or phosgene atmospheres. Fluorotriethylsilane was detected in each analysis of tubes prepared with derivatization reagent, indicating background contamination of fluorine. Repeated sampling of a COF_2 atmosphere demonstrated high variability of the fluoro derivative. Extensive cleaning of tubes and system (e.g., new trap and rinsing of split valves and tubing) did not eliminate the background contamination sufficiently. Some attempts were also made with pentafluorobenzyl bromide as the derivatization reagent, but the expected pentafluorobenzylfluoride was not detected.

It was concluded that unambiguous detection of fluoride produced on the adsorbent tube by the derivatization reaction could not be achieved based on the methods investigated in this study.

4 | CONCLUDING REMARKS

The potential to determine PFIB and COF_2 unequivocally in air samples using GC/MS analysis was investigated in this study. Direct analysis of high levels of PFIB was possible using manual split injection and standard GC/MS settings, with PFIB showing practically no retention on the column. Adsorbent sampling using different sorbent tubes proved inadequate for quantification, as degradation products of PFIB were observed after thermal desorption analysis. Of the tested adsorbents, Carbosieve S-III combined with an air monitoring trap showed the least degradation and could potentially serve for identification and semiquantification purposes up to 68 h after sampling. The use of the derivatization reagent 3,4-DMT and the base TEA, at a molar ratio of 1:8, spiked onto Tenax TA sorbent tubes proved successful for sampling and quantification of a unique derivative using TD-GC/MS. The method was validated for PFIB atmospheres prepared in Tedlar bags in the concentration range 0.13−152 ppb, and demonstrated a relative standard deviation below 20% and an accuracy around 90%. However, successful application of the method relied on the use of separately prepared solutions of 3,4-DMT and TEA and expeditious sampling after their addition to sorbent tubes. The chemosorption method was also applicable for quantification of COF_2, which was less stable and more reactive than PFIB. However, COF_2 forms the same derivatization product as phosgene, resulting in an ambiguous identification, highlighting a need to explore other unambiguous analytical techniques to discriminate low levels of those species in air samples.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the Supporting Information Materials of this article.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.