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Characterization of biogas and biomethane trace compounds: A critical review of advances in in situ sampling and preconcentration techniques

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1 **Characterization of biogas and biomethane trace compounds: A critical review of advances**
2 **in *in situ* sampling and preconcentration techniques**

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13 **ABSTRACT**

14 Worldwide, the valorization of biogas, landfill gas and biomethane is gaining momentum as circular econ-
15 omies and energy transitions are triggered. Nevertheless, to sustainably integrate those gases into today's
16 energy mix, their quality must be controlled regarding their major, minor and trace constituents to preserve
17 the integrity of infrastructures wherein they are burned, transported or stored. Field gas sampling is the first
18 and most critical step in the analytical chain to characterize the composition of such gases. A large array of
19 gas sampling techniques is available, yet choosing the most suitable technique is complex, especially when
20 targeting trace compounds ($< \text{ng}\cdot\text{Nm}^{-3}$ to $\text{mg}\cdot\text{Nm}^{-3}$) which often require a preconcentration step to be de-
21 tectable. Sampled trace compounds must be kept stable (no loss, degradation or contamination can occur)
22 during the storage phase between sampling and analysis, and all materials in the sampling chain that contact
23 the gas potentially influence this stability.

24 This paper aims to review the available gas sampling and preconcentration techniques for determining trace
25 compounds in biogas, landfill gas and biomethane. Techniques reviewed include 1) whole gas sampling
26 methods (gas sampling bags, gas cylinders, canisters) and 2) gas sampling methods with preconcentration
27 on solid media (sorbent tubes for physisorption or chemisorption, amalgamation, solid phase microextrac-
28 tion); preconcentration in liquid media (absorption in impingers); and cryogenic preconcentration. These
29 techniques are reviewed for the sampling of nonmetal(loid) volatile organic trace compounds (aliphatic,
30 aromatic, halogenated and oxygenated species; organic silicon compounds (siloxanes, silanes), and (in)or-
31 ganic sulfur compounds) as well as for volatile (in)organic metal(loid) compounds. The suitability of all
32 presented sampling and preconcentration methods for given families of trace compounds regarding storage
33 stability issues, is discussed as well as considerations regarding the ease of field implementation, ad-
34 vantages and disadvantages. This review highlights the intricate complexity of sampling trace compounds
35 in biogas, landfill gas and biomethane. The different trace compounds indeed display extremely diverse
36 physicochemical properties (volatility, polarity, reactivity...) which results in different stabilities in given
37 sampling units so that no sampling method along can trap and recover all families of trace compounds.

38 The review finishes with a list of recommendations to select proper sampling units, materials and parame-
39 ters and to apply suitable sample transport and storage conditions to safeguard the integrity of samples.

40	KEYWORDS
41	Biogas and biomethane
42	Trace compounds
43	Whole gas sampling
44	Preconcentration
45	Volatile organic compounds
46	Volatile metal(loid) compounds

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84

85 **LIST OF ABBREVIATIONS**

86	AD	Anaerobic Digestion
87	AES	Atomic Emission Spectrometry
88	BTEX	Benzene; Toluene; Ethylbenzene; <i>o</i> -, <i>m</i> -, <i>p</i> -Xylene
89	CT	Cryotrapping
90	D3	Hexamethylcyclotrisiloxane
91	D4	Octamethylcyclotetrasiloxane
92	D5	Decamethylcyclopentasiloxane
93	D6	Dodecamethylcyclohexasiloxane
94	DMDEL	Dimethyldiethyllead
95	DMDS	Dimethyldisulfide ((CH ₃) ₂ S ₂)
96	DMS	Dimethylsulfide ((CH ₃) ₂ S)
97	DNPH	2,4-Dinitrophenylhydrazine
98	DVB	Divinylbenzene
99	FAAS	Furnace Atomic Absorption Spectroscopy
100	FEP	Fluorinated Ethylene Propylene
101	FID	Flame Ionization Detector
102	GC	Gas Chromatography
103	HPLC	High Pressure Liquid Chromatography
104	HVOC	Halogenated Volatile Organic Compound
105	ICP	Inductively Coupled Plasma
106	ID	Internal Diameter
107	L2	Hexamethyldisiloxane
108	L3	Octamethyltrisiloxane
109	L4	Decamethyltetrasiloxane
110	L5	Dodecamethylpentasiloxane
111	LOD	Limit of Detection
112	MS	Mass Spectrometry
113	MSW	Municipal Solid Waste
114	MTEL	Methyltriethyllead
115	OD	Outer Diameter
116	PA	Polyacrylate

117	PDMS	Polydimethylsiloxane
118	PEA	Polyester Aluminum
119	PEG	Polyethylene glycol
120	PET	Polyethyleneterephthalate
121	PTFE	Polytetrafluoroethylene
122	PVDF	Polyvinylidenedifluoride
123	PVF	Polyvinylfluoride
124	RH	Relative Humidity
125	SPME	Solid Phase Microextraction
126	TD	Thermal Desorption
127	TEL	Tetraethyllead
128	TMA	Trimethylarsine
129	TMEL	Trimethylethyllead
130	TML	Tetramethyllead
131	TMS	Trimethylsilanol
132	VMS	Volatile Methyl Siloxane
133	VOC	Volatile Organic Compound
134	VSC	Volatile Sulfur Compound
135	VSIC	Volatile Silicon Compound
136	WWTP	Wastewater Treatment Plant

137 **1. Introduction**

138 Biogas is a flammable gas generated by the anaerobic digestion (methanization) of humid organic matter
139 ('feedstocks' such as agricultural and food-processing residues, manure, organic municipal and household
140 wastes, sewage sludge) in controlled digesters [1]–[5] or spontaneously in landfills ('landfill gas'). In ad-
141 dition to its two major constituents CH_4 (≥ 50 %_{vol}) and CO_2 (< 50 %_{vol}) and depending on the production
142 conditions, biogas contains minor constituents such as H_2O , H_2S , H_2 , N_2 , CO , O_2 (~ 1 – 5 %_{vol}), and traces of
143 volatile compounds ('trace compounds') from various families including alcohols, aldehydes, alkanes, al-
144 kenes, aromatics, esters, ethers, halogenated organic compounds, ketones, terpenes, (in)organic sulfur- and
145 organic silicon-compounds and (in)organic metal(loid) species. The variations in the nature and proportions
146 of feedstocks and in production conditions among biogas production plants causes biogas to exhibit a highly
147 variable biogas composition, especially regarding trace compounds [3]–[13]. Biogas is valorized by com-
148 bustion in boilers, fuel cells or engines to generate heat and power, or by separating the CO_2 and CH_4
149 fractions to upgrade the gas to 'biomethane'. This purified methane fraction of biogas exhibits the same
150 calorific value as that of natural gas and is intended to be injected in the existing natural gas infrastructures,
151 provided that it satisfies the natural gas quality standards stipulating maximal levels of given chemical
152 compounds.

153 The analysis of trace compounds in biogas, landfill gas and biomethane is complex due to the low concen-
154 trations ($< \text{ng}\cdot\text{Nm}^{-3}$ to $\text{mg}\cdot\text{Nm}^{-3}$), the variability in trace compound composition and the complex nature of
155 these gas matrices, which may contain condensate phases and a relatively high water content [14]–[17].
156 Specific preconcentration operations are often needed for trace compounds to reach higher concentration
157 levels and surpass the limits of detection of available analytical apparatuses. Determining the most appro-
158 priate preconcentration technique is a delicate task considering that the complex mixtures of volatile (in)or-
159 ganic and metallic trace compounds have different physicochemical behaviors (polarities, volatilities, re-
160 activities etc.) [4], [14], [15], [18], [19]. Gas sampling is the first and most decisive step in the analytical
161 chain toward determining trace compounds (analytes). Indeed, any sampling method involves at least one
162 element in the sampling line through which targeted analyte loss or sample contamination is possible (ana-
163 lyte or ambient air permeation through the container walls, leaks at valves, analyte condensation, sorption
164 of analytes on sampling lines or on container walls, chemical reactions between sampled analytes inside
165 the container that lead to analyte degradation or conversion, etc.) [3], [4], [19]–[22]. Establishing the most
166 suitable sampling procedure is hence intricate: the sampling device must be operable in the field, the com-
167 position of collected samples must be representative of that of the studied gas and must remain as unchanged
168 as possible until effective analysis is performed; the sample must be easily transportable to the laboratory;
169 the recovery of targeted analytes from the sampling vessel must be maximal; and finally, the whole sam-
170 pling procedure must be economically affordable [3], [4], [22].

171 There are currently two gas sampling approaches: whole gas sampling and gas sampling with enrichment
172 (preconcentration) of targeted analytes [4], [23], [24]. In the first approach, a whole bulk gas volume is
173 sampled in a dedicated container (gas bags, canisters or cylinders) without enriching the targeted trace
174 analytes. The container is subsequently transported to the laboratory, where an analyte enrichment step
175 must be performed to isolate the targeted trace compounds from the sampled gas matrix via a precon-
176 centration technique. Whole gas sampling and subsequent transport to the laboratory thus imply the precon-
177 centration step is delayed, which causes a risk of analyte loss or changes in composition due to chemical

178 reactions inside the sampling container during the transport and storage phases [3], [4], [20], [21]. The
179 second sampling approach involves sampling with direct enrichment (preconcentration, trapping) of trace
180 compounds on a dedicated support, which can be solid (sorbent tubes for physisorption or chemisorption,
181 amalgamation tubes, solid phase microextraction fibers), liquid (absorption in impingers) or cryogenic. In
182 contrast to whole gas sampling, the gas matrix (e.g., CH₄, CO₂) is not sampled because it is not retained
183 and passes through the preconcentration unit, which retains only trace compounds for which it has affinity.
184 To avoid disadvantages related to utilizing whole gas sampling containers, the development of direct *in situ*
185 preconcentration techniques for trace analytes is being increasingly considered and recommended [3], [4],
186 [17], [25], [26].

187 In this paper, all currently known whole gas sampling and preconcentration techniques for the determina-
188 tion of trace compounds in methane-like gas samples are critically reviewed for nonmetal(loid) volatile
189 organic trace compounds (aliphatic, aromatic, halogenated and oxygenated species; organic silicon com-
190 pounds (siloxanes, silanes), and (in)organic sulfur compounds) as well as for volatile (in)organic metal(loid)
191 compounds. To the authors' knowledge, this review is the first to comprehensively discuss all preconcen-
192 tration techniques that are available for both nonmetal(loid) and metal(loid) trace compounds in methane-
193 like field gas samples, bringing new insights into the possibility of using similar sampling and preconcen-
194 tration techniques for both types of trace compounds. Additionally, for each preconcentration technique
195 discussed, scientific studies that specifically use the technique to determine trace compounds in landfill gas,
196 biogas and biomethane have been critically tabulated.

197 As biogas and biomethane sampling and analysis is a relatively recent endeavor and has not yet benefitted
198 from standardized methods, natural gas sampling methods, being already well standardized (EN ISO
199 10715:2000 [27]; ISO 6974 [28]; ISO 6978 [29], [30]), are referred to in this review as suitable for biogas
200 and biomethane considering the similarity of the matrices (CH₄) and of some trace compounds in those
201 gases. Standardized methods for ambient air sampling (EN ISO 16017-1:2000 [31]; EPA Compendium of
202 Methods for the Determination of Toxic Organic Compounds in Ambient Air [32], [33]) are also noted as
203 suitable for biogas and biomethane. Whereas the matrices of air and biogas or biomethane differ, common
204 families of trace compounds are targeted both in air and biogas or biomethane (volatile organic compounds,
205 siloxanes, volatile metal(loid) compounds, etc.). Therefore, efficient sampling techniques applied for those
206 compounds in air are also expected to be suitable and efficient for biogas and biomethane. In the discus-
207 sions, 'semivolatile', 'volatile' and 'very volatile' organic compounds will be addressed. According to the
208 U.S. Environmental Protection Agency (EPA), semivolatile compounds have boiling points that range from
209 240-260 °C to 380-400 °C. Volatile compounds have boiling points that range from 50-100 °C to 240-260
210 °C. Very volatile compounds have boiling points < 50-100 °C.

211 **2. Whole gas sampling**

212 Sampling in which targeted analytes are not enriched involves whole gas sampling in gas bags, canisters or
213 cylinders, without discrimination between sampled compounds [3], [4], [23]. Such sampling methods are
214 attractive considering the ease of sampling: the whole gas matrix is collected together with all contained
215 compounds in their original concentration [22], [34]–[36]. Additionally, gas moisture has little effect on
216 sample integrity and stability [22], [35], [37], [38], and a last benefit is that repeated analyses of the same
217 sample can be achieved by performing multiple withdrawals from the sample vessel [14], [22], [34]. Gas
218 bags, cylinders and canisters nevertheless only allow to sample a defined gas volume, so the effective col-
219 lected quantities of trace compounds may be insufficient to be reliably detected [21]. Whole gas sampling
220 is therefore only to consider either if available analytical devices offer detection limits sufficiently low to
221 detect analytes in the raw sample (direct sample analysis) or if the sample is subsequently preconcentrated
222 in the laboratory [39]. However, as sample transport to the laboratory may take days to weeks, the delayed
223 direct analysis or preconcentration of trace compounds from the gas matrix may result in losses of trace
224 analytes during the storage period, owing to sorption on or permeation through the sample container walls,
225 leaks in the container and chemical reactions in the container that induce analyte degradation or conversion
226 [3], [4], [20]–[22]. Another disadvantage to biogas- or biomethane-filled bags, cylinders and canisters is
227 that the flammable methane matrix of biogas or biomethane is contained in the vessel, which is accordingly
228 considered as a dangerous good with corresponding restrictive implications for transport to comply with
229 the regulations in place [21].

230 **2.1. Gas sampling bags**

231 Gas sampling bags (Fig. 1 a) are gas-tight bags equipped with a valve fitting. Bag materials include poly-
232 vinyl fluoride (PVF, tradename: Tedlar), polyethyleneterephthalate (PET, tradename: Nalophan), polytet-
233 rafluoroethylene and fluorinated ethylene propylene copolymer (PTFE and FEP, tradename: Teflon), pol-
234 yester aluminum (PEA), polyethyleneterephthalate-nylon-aluminum, and polyvinylidene difluoride (PVDF,
235 tradenames: Altef, Kynar, Supel Inert Film) [3], [4], [20], [40]–[42]. Table 1 lists some useful features of
236 sampling bags based on the manufacturer’s information. Gas bags are relatively inexpensive, simple to use
237 and do not require trained personnel [21], [22], [35], [36], [40]: a piping is plugged onto the bag valve hose
238 to inflate the bag until a sufficient volume is sampled. Bags exist in volumes from 0.5 to 100 L and even
239 1000 L depending on the material and manufacturer, and some companies also offer custom-sized bags or
240 polymer film rolls [43]–[45]. Bags must not be filled to more than 80-90% of their volume during sampling,
241 and the inflation pressure must not exceed ~0.14 bar above the atmospheric pressure [43]. Gas sampling
242 bags are hence typically designed for sampling at atmospheric pressure, forbidding a high-pressure-based
243 preconcentration of low-concentrated analytes [46]. It is also recommended to transport filled gas bags in
244 rigid opaque containers to avoid perforating or damaging the bags, to transport and store them above 0 °C
245 to prevent sample condensation, to avoid air-shipping unless the bags are in a pressurized zone, to protect
246 the bags from sunlight and to analyze the sample as soon as possible [43].

247 Each bag material may be specifically recommended for the sampling of given targeted compounds [3],
248 [4], [40], [47], [48] since the polymer bag material and its inherent impurities may be incompatible with
249 the successful sampling of certain compounds: compound-specific permeation and -adsorption effects can
250 occur through and on the bag film [3], [35], [40], [47]–[53]. For instance, Tedlar bags are known to contain
251 traces of dimethylacetamide and phenol, while Altef bags do not, but Altef bags are not recommended for

252 sampling of ketones, esters, acetates, H₂S and permanent gases [43], [54], [55]. The suitability of PEA
253 versus Tedlar bags for the short-term storage of VOCs in a N₂ matrix has been investigated by Kim et al.
254 [48]. After 3 days of storage in both bag types, their results showed that the recoveries of compounds from
255 PEA bags were significantly higher than the recoveries from Tedlar bags. Kim [56] found the opposite
256 trend for reduced sulfur compounds for which the recoveries from Tedlar bags (87%) were higher than
257 those from PEA bags (77%). PEA bags were also studied by Ahn et al. [52] to examine sorption losses of
258 VOCs as a function of storage time. Notably, it is not possible to assess a universal suitability of a given
259 bag material for a given (family of) compound(s). Indeed, Jo et al. [47] compared the storability of several
260 sulfur compounds in a N₂ matrix in PEA and Tedlar bags. They concluded that the most decisive factor for
261 the storage stability of S-compounds in both bags was the initial concentration and not the bag material.
262 Other factors that influence the stability of S-compounds included the nature and molecular weight of the
263 compound, the storage time and the bag material. Brown et al. [40] also noticed a concentration-dependent
264 adsorption loss pattern for H₂S in CH₄ in FlexFoil and FlexFilm bags. The relative H₂S loss of their 4.99
265 $\mu\text{mol H}_2\text{S}\cdot\text{mol}^{-1}\text{ CH}_4$ mixture was greater than that of the 9.95 $\mu\text{mol}\cdot\text{mol}^{-1}$ mixture. As both tested bags had
266 similar internal surface areas, this result is the consequence of a fixed number of potential sorption sites per
267 m² bag film, which must be occupied by a fixed amount of (H₂S) molecules to reach saturation [40]. A
268 lower concentrated mixture henceforth loses relatively more molecules than a higher concentrated mixture
269 before sorption losses stop. Next, Nalophan bags are especially used in odor sampling studies because of
270 their neutral odor background contaminants [41], [49], [50], but have also been used for biogas sampling
271 and trace compound analysis [57]–[61]. Papurello et al. [61] preferred Nalophan bags to Tedlar bags for
272 sampling trace compounds such as VOCs, thiols and siloxanes, as it was shown that Nalophan bags gave
273 cleaner backgrounds than Tedlar bags, which released degradation compounds that interfered with the de-
274 tection of the low amounts of targeted compounds [41]. However, the permeability of Nalophan films may
275 be high for some compounds, such as S-species (H₂S, CH₃SH, CS₂) in particular, due to their small mo-
276 lecular dimensions [49], [50], [53]; hence, those bags may be unsuitable for sample storage when such
277 compounds are targeted. Teflon bags were used by Badjagbo et al. [62] for biogas sampling. Finally, Mo-
278 chalski et al. [53] compared the suitability of Nalophan, transparent Tedlar, black layered Tedlar, Teflon
279 and FlexFoil bags for the sampling and storage of volatile sulfur compounds (VSC) in a N₂ (air) matrix.
280 They first measured the background emissions of potential contaminants from new, unused bags and found
281 that the Nalophan, Teflon and Flexfoil did not emit contaminants that could interfere with their target S-
282 analytes, while the Tedlar bags did (emission of COS and CS₂). Subsequently, they studied the stability of
283 VSC in each of those bags. Considerable (permeation) losses in VSC were observed within 6 h of storage
284 in the Teflon and Nalophan bags; hence, they were not recommended for VSC sampling and storage. Trans-
285 parent and black Tedlar bags provided good VSC stabilities during the first 6 h of storage with recoveries
286 > 90%. After 24 h of storage, H₂S and COS losses occurred, and longer storage times resulted in losses of
287 all VSC. They did not record any significant influence of daylight on the stability of the VSC in transparent
288 Tedlar bags. In the Flexfoil bags, H₂S was the only species that decreased during the first 6 h of storage,
289 and after 24 h, the concentration of other VSC also decreased. Despite the above results, Tedlar bags are
290 the most widely used bags [4], [35], [48]. Tedlar bags are generally appropriate for sampling and short-
291 term storage of VSC and are used in industrial routine analyses for this purpose [40], [56], [63], [64], but
292 they have also often successfully been used for biogas and biomethane sampling [3], [16], [20], [21], [35],
293 [36], [65]–[69]. Black-layered Tedlar bags have also been developed to sample photosensitive compounds.
294 Walls of these bags consist of an inner polyvinyl fluoride layer and an outer light-blocking layer of carbon

295 black. The inner PVF layer theoretically prevents sampled compounds from adsorbing into the carbon black
296 material. Nonetheless, permeation of analytes through the first PVF layer can lead to adsorptive losses into
297 the carbon black layer [63]. Sulyok et al. [63] compared standard with black-layered Tedlar bags for the
298 storage of VSC and found better VSC recoveries in the standard Tedlar bags even after 300 h storage, while
299 significant losses were observed in the black-layered Tedlar bags after only 1 h. The authors proposed that
300 these losses were due to VSC permeation through the inner Tedlar layer and adsorption in the outer carbon
301 black layer.

302 Analyte loss in gas bags during the storage phase between sampling and analysis has been proven to be
303 especially caused by adsorption effects on bag walls [3], [20], [35], [47], [48], [51], [70] and on valve fitting
304 materials [35]. Additionally, several other factors contribute to analyte loss during storage, including per-
305 meation through the walls [3], [20], [35], [47]–[50], [53], leaks through the septum of the valve [20], [48],
306 especially once it has been pierced with a needle or syringe for analysis [63], photochemical degradation
307 (photolysis) when bags are not protected from sunlight [16], [22], [37], [47], [65], [71], and chemical con-
308 version reactions between sampled compounds [22]. Gas permeation and diffusivity through polymeric bag
309 films are governed by the polymer type, its crystalline structure, porosity, hydrogen bonding capacity and
310 polarity [50]; by the film thickness and bag dimensions (surface); by the molecular size, volatility and
311 molecular diffusion coefficient of the diffusant in the film; and by the concentration gradient of the dif-
312 fusants across the inner and outer bag sides [49]. Additionally, the relative humidity and temperature of the
313 sample inside the bag and of the atmosphere around the bag also impact the permeation rates [50]. Ambient
314 air from the bag surroundings as well as the bulk gas matrix of the sample inside the bag can also permeate
315 into and out of the bag, respectively, affecting the concentrations of stored analytes [35].

316 The stability of sampled species in gas bags is also influenced by the initial sampled concentration, as was
317 indicated by Jo et al. [47] for reactive sulfur compounds in a N₂ matrix in PEA and Tedlar bags: compounds
318 sampled in high concentrations (1 ppm and 10 ppm) disappeared faster than the same compounds sampled
319 in lower concentrations (1, 10 and 100 ppb), due to adsorption and diffusion effects being enhanced for the
320 compounds present in high concentrations [47]. However, the opposite trend is also often observed: adsorp-
321 tion losses are relatively higher when low analyte concentrations are stored in bags since sorption on inner
322 bag surfaces occurs until all sorption sites are occupied [3]. If the analyte concentration is lower than or
323 equal to the corresponding sorption site capacity, all analyte molecules can potentially be lost to adsorption.
324 Another concentration effect was observed by Arrhenius et al. [3] in a study on the stability of HVOCs in
325 Altef bags. All compounds showed a decrease in concentration over time, but after 4 days, a slight increase
326 in concentration was recorded for 1,1,2-trichlorotrifluoroethane and tetrachloroethylene. The authors sug-
327 gested that this concentration increase was due to outgassing of those compounds from bag walls where
328 they initially adsorbed during the first storage days, owing to the drop in gas volume in the bag as a result
329 of daily gas withdrawal from the bag for analysis [3]. Why only two out of the four tested HVOCs displayed
330 this pattern was not clarified. In addition to concentration effects, adsorption effects on bag walls and cor-
331 responding analyte losses are also promoted for high molecular weight, less volatile analytes [3], [4]. Kim
332 et al. [48] tested the stability of VOCs in PEA and Tedlar bags: lighter compounds, such as benzene and
333 toluene, were relatively stable after 3 days in both bag types (>86% recovery) while the heavier p-xylene
334 and styrene were less stable after 3 days in both bag types (<81% recovery). Similarly, Mariné et al. [20]
335 found that high-molecular-weight alkanes in biogas were lost by adsorption on bag walls immediately after
336 sampling in Tedlar bags. Arnold et al. [67] found that the concentration of the relatively heavy siloxane D5

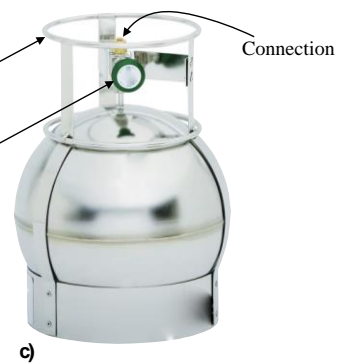
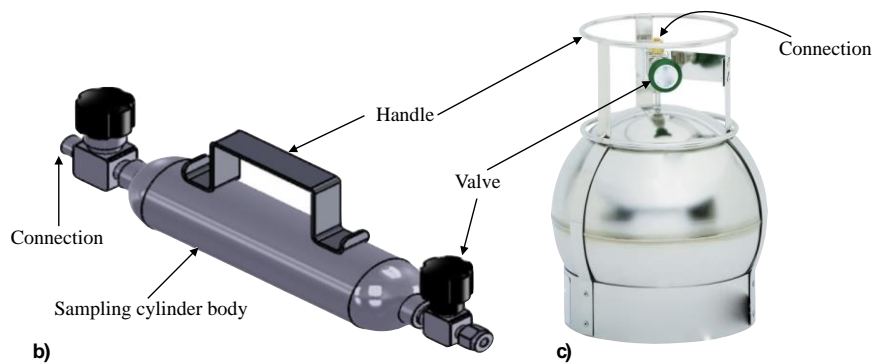
337 in a real biogas sample was only 65% of the initial concentration after 1 day of storage in a Tedlar bag, while
338 the concentrations of lighter siloxanes (D4 and L4) were respectively 87 and 88% of the initial concentra-
339 tions after 1 day in the Tedlar bag. Ajhar et al. [35] also found that D5 siloxane, the heaviest siloxane they
340 studied, was adsorbed the fastest in Tedlar bags. Arrhenius et al. [3] performed 12-day stability tests with
341 L2, L3, D4 and D5 siloxanes in CH₄ in Altec and Tedlar bags. Light L2 and L3 siloxanes were stable over
342 the whole storage period in both bag types, while the response of heavier D4 and D5 markedly decreased
343 during the first storage days in both bags. To limit adsorption losses in bags, on bag valves and in sampling
344 connection tubing, Ajhar et al. [35] suggest flushing the entire bag sampling setup for 5 min with the gas
345 to sample prior to effective sampling so that the potential sorption sites would become occupied. These
346 authors also found that a high relative humidity (90% RH) in a standard siloxane mixture in a synthetic
347 biogas matrix stored at 37 °C in Tedlar bag led to less sorption losses of siloxanes because water molecules
348 tended to first sorb onto the bag surface sorption sites. However, under the same 90% RH condition but at
349 lower temperature (20 °C), no effect was observed on the siloxane recoveries from the bag [35]. Tedlar
350 bags may hence be favorable sampling vessels for humid biogases, yet the bags should be stored and ana-
351 lyzed at relatively high temperatures to avoid condensation (50 °C was used by Ajhar et al. [35]).

352 The stability of volatile metal(loid) compounds in Tedlar bags has also been studied. Haas and Feldmann
353 [22] generated standard gases of trace amounts (0.3 to 18 ng·L⁻¹) of various volatile arsenic, tin and anti-
354 mony species in moisturized air in Tedlar bags and also sampled sewage sludge digester gas in Tedlar bags.
355 All bags were stored in the dark. The stability of volatile metal(loid)s in standard Tedlar bags was investi-
356 gated under different conditions: storage of the bags at 20 °C for 8 weeks and storage at 50°C for 5 weeks.
357 Tedlar bags containing real gas were stored at 20 °C for 48 h. Surprisingly high recoveries were obtained
358 for the standard gas: after 8 h both under 20 °C and 50 °C storage, >95% of all metal(loid) analytes were
359 recovered. After 24 h at 20 and 50 °C, all analytes were still recovered at 81-99%, except (CH₃)₃Sb and
360 (CH₃)₃As which showed considerable losses especially at the higher temperature [22]. In the real gas after
361 24 h of storage, losses of (CH₃)₃Bi and (CH₃)₂Te amounted to ~10%, while losses of (CH₃)₃Sb amounted
362 to 44%. The long-term (5-8 weeks) stability study of the standard gases revealed that the central metal atom
363 of each analyte strongly determined its stability in the bag. All stibines were less stable than As and Sn
364 counterpart species, the most stable species being AsH₃ (75% recovery after 8 weeks at 20 °C), and the
365 least stable being (CH₃)₃Sb (3% recovery after 4 days at 50 °C) [22]. Determining the loss mechanisms of
366 volatile metal(loid) compounds in Tedlar bags is intricate since these compounds are thermodynamically
367 unstable and susceptible to several loss or degradation pathways such as diffusion, oxidation, hydrolysis,
368 photodecomposition, adsorption, absorption, and heterogeneous surface-catalyzed breakdown [22]. Never-
369 theless, the results of Haas and Feldmann demonstrated that adsorption to bag walls was not the main un-
370 derlying loss mechanism for the standard in the air matrix [22]. Instead, chemical reactions, such as oxida-
371 tive breakdown in the aerobic atmosphere, oxidation and demethylation were probably responsible for the
372 immobilization and instability of the volatile metal(loid) compounds in the Tedlar bags [22]. In accordance
373 with these thermodynamic considerations, all compounds showed poorer stabilities at higher temperatures
374 (50 °C), particularly in the long-term storage experiments. Especially fully methylated As and Sb species
375 were less stable at this temperature. The authors concluded that Tedlar bags are convenient for sampling
376 volatile metal(loid) compounds in air if the samples are analyzed within 24 h and stored at low temperatures
377 (20 °C) [22]. Accordingly, Feldmann et al. [15] successfully used Tedlar bags to sample biogases with a
378 particular focus on volatile Sb, Sn and Bi compounds speciation. Another study by Arndt et al. [72] evalu-
379 ated the storage stability of volatile arsenicals generated in a standard gas mix in Tedlar bags in the presence

380 of (reactive) test-gases such as O₂, CO₂, SO₂ and H₂S in a N₂ matrix. Tedlar bags were stored in the dark at
381 5 °C for 21 days. In the absence of test-gases, no sorption losses or losses by precipitation of the As species
382 occurred on the Tedlar bag walls [72], agreeing with the results of Haas and Feldmann [22]. Arndt et al.
383 obtained recoveries of AsH₃, (CH₃)AsH₂, and (CH₃)₂AsH from the bags of 106 ± 3%, 103 ± 1%, and 101
384 ± 4%, respectively, after 19 days. (CH₃)₃As had a mean recovery of 85 ± 3%. This compound probably
385 partly converted into less methylated arsines during the storage period [72], simultaneously explaining its
386 loss and the recoveries >100% for the other arsines. The stability results of As species in 3800 ppm_v CO₂
387 in N₂ and in 20% O₂ in N₂ after 21 days were very similar to those of As species in the N₂ reference case
388 since CO₂ is not a reactive gas and O₂ apparently has no effect on the stability of the four target As species.
389 With 20% O₂ in a N₂ matrix, Arndt et al. [72] obtained higher recoveries than those of Haas and Feldmann
390 [22] who investigated the stability of the same As species in air in Tedlar bags, thanks to the lower storage
391 temperature (5 °C) than that used by Haas and Feldmann (20 or 50 °C). SO₂, however, had a detrimental
392 effect on the stability of the As species [72]. In the SO₂-doped matrix, the recoveries of AsH₃, (CH₃)AsH₂,
393 (CH₃)₂AsH, and (CH₃)₃As dropped to 72, 72, 41 and 11%, respectively, after 21 days. It is unclear whether
394 SO₂ induces these losses by bag wall sorption or by precipitation of arsines into As₂O₃ or As-S compounds.
395 The effect of H₂S was especially pronounced for (CH₃)₃As, which was only recovered at 67% after 17 days
396 in the H₂S-doped matrix. (CH₃)₂AsH, (CH₃)AsH₂ and AsH₃ were recovered at respectively 89, 105 and
397 123% after 17 days, suggesting that H₂S induces the conversion of methylated species to nonmethylated
398 species [72]. Regardless of the matrix of the standard As-mix, the results of Arndt et al. [72] agree with
399 those of Haas and Feldmann [22] concerning the lower stability of increasingly methylated arsines stored
400 in Tedlar bags, which is due to either precipitation or conversion to more stable nonmethylated species.

401 Next to bag walls, the valve fitting material of sampling bags may also influence the stability of sampled
402 compounds, as demonstrated by Ajhar et al. [35] in a stability study of landfill biogas siloxanes in Tedlar
403 bags equipped either with a polypropylene fitting with integrated PTFE-septum or a dual port stainless-
404 steel fitting with o-ring. The results showed that polypropylene fittings led to much better siloxane stabili-
405 ties than stainless-steel fittings. Nevertheless, Mochalski et al. [53] compared the stability of VSC in black
406 layered Tedlar bags equipped either with stainless-steel or PTFE valve fittings and found comparable sta-
407 bility results. They concluded that losses in VSC due to contact with stainless-steel were insignificant.

408 Finally, reusing gas sampling bags is not recommended [20], [43], [45], [51], [73]. McGarvey et al. [51]
409 investigated the reusability of Tedlar bags used for sampling of VOCs in air. After storage stability tests,
410 the bags were cleaned via N₂-flushing and gentle heating in an attempt to desorb the VOCs that had ad-
411 sorbed on the bag walls during the storage phase. These cleaning operations were not sufficient to remove
412 all compounds, in particular styrene, ethylbenzene and methanol were not quantitatively recovered. The
413 authors concluded that reusing Tedlar bags led to substantial contamination of subsequent samples via off-
414 gassing of compounds formerly adsorbed on bag walls. Reusing Tedlar bags would only be acceptable if
415 the content of the bag was immediately analyzed after sampling and the bag was immediately cleaned by
416 N₂-flushing and heating. Notwithstanding, Mochalski et al. [53] tested the efficiency of several bag cleaning
417 procedures with a focus on bag reuse and concluded that the bags could be reused if the following cleaning
418 steps were executed : N₂ flush, heating at 45 °C for 6 h, N₂ flush, heating at 45 °C for 6 h, and N₂ flush.



419

420 *Figure 1: Whole gas sampling vessels: a) Polymer bag. b) Cylinder. c) Canister.*

421 *Table 1: Physico-chemical features of common gas sampling bags according to the manufacturer's information. Bags with stain-*
 422 *less-steel valves usually have a higher maximal working temperature due to the higher thermal resistance of the o-ring in those*
 423 *valves compared to that of the polypropylene valves with integrated septum.*

Commercial bag name	Tedlar	Altef	Kynar	Nalophan	Teflon	Teflon
Film composition	polyvinyl fluoride	polyvinylidene difluoride	polyvinylidene difluoride	polyethylene-terephthalate	fluorinated ethylene propylene (FEP)	polytetrafluoroethylene (PTFE)
Available valve materials	PP; SS	PP	PP; SS; PTFE	PP; PTFE; PTFE-coated nylon	PP; PTFE	PP; PTFE, PTFE-coated nylon
Pressure (P) and temperature (T) working range	Max operating T: PP valve 82 °C; SS valve 202 °C Max filling P relative to atmospheric P: ~ 0.14 bar or ≤80% filled	Max operating T: 82 °C Max filling P relative to atmospheric P: ~ 0.14 bar or ≤80% filled	Max operating T: PP valve 93.3°C ; SS and PTFE valves 107.2°C	Not found	PTFE valve working T range: -60°C to +150°C Max filling P relative to atmospheric P: 0.06 bar or ≤90% filled	Not found
Available bag volumes	0.5 – 100 L	0.5 – 100 L	0.5 - 1000 L	1 – 60 L and film rolls	0.5 – 100 L	Not found
Measured permeability to permanent gases at 1 bar filling	O₂: 50 cc/m ² /day H₂O vapor: 9–57 g/m ² /day CO₂: 172 cc/m ² /day	O₂: 58 cc/m ² /day H₂O vapor: 12-15 g/m ² /day CO₂: 172 cc/m ² /day	Not found	Not found	O₂ : 2400cc/m ² /day H₂O vapor: 1.3g/m ² /day	Not found
Remarks	Background levels of dimethyl-acetamide and phenol	Lower VOC and sulfur background contamination than Tedlar (no dimethyl-acetamide or phenol background) Not recommended for ketones, esters, acetates, hydrogen sulfide, permanent gases	Low VOC and sulfur background Resistant to corrosion Good stability for VOC, CO, CO ₂ , CH ₄ Good 24-h storage stability for some S-compounds	Especially used and recommended for odors sampling for gases with moderate H ₂ S and VOC contents being analyzed within less than 6 h after sampling Not recommended for samples being processed more than 6 h after sampling, nor for samples with high humidity, high H ₂ S, high VOC because of poor stability of those compounds due to high permeability rates and adsorption effects	Suitable for corrosive and reactive compounds Suitable for VOC samples Low adsorbability of compounds on bag walls	Suitable for VOC and S-compounds including H ₂ S Excellent stability for CO, CO ₂ , CH ₄ , SF ₆ Resistant to contamination, low adsorbability of compounds on bag walls, hence possible cleaning and reuseability Not recommended for samples processed more than 30 h after sampling
References	[43]	[43]	[45]	[41], [44], [45], [49], [50], [71]	[45]	[44]

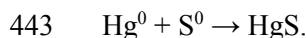
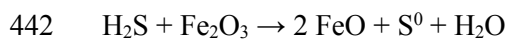
424 **PP:** polypropylene. **SS:** stainless-steel. **PTFE:** polytetrafluoroethylene.

425

426 2.2. Gas cylinders

427 Gas sampling cylinders (Fig.1 b) allow to collect gas under high pressure [4] (up to 5000 psi = 344 bar) and
428 exist both in aluminum or stainless-steel in volumes from 40 to 3785 cm³ [40], [74]–[78]. Stainless-steel
429 cylinders have long been used to sample natural gas [4], [17], [25], [79]. As biogas and biomethane are
430 predominantly produced at near-atmospheric pressures, cylinders have seldom been relevant for biogas or
431 biomethane sampling [4]. However, cylinder-sampling of compressed biomethane at natural gas grid injec-
432 tion stations may be relevant.

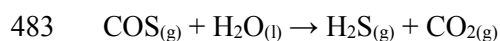
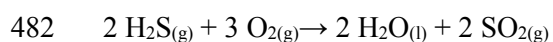
433 A well-known concern with stainless steel cylinders is the loss of trace compounds by sorption on the
434 surface-iron atoms of inner cylinder walls that act as active sites for sorption and catalysis phenomena [3],
435 [25], [40], [66], [75], [78], [80]. Reactive VSC [40], [63], [78], [80] as well as volatile arsenicals [25]
436 sampled in cylinders have especially been found to be lost by adsorption on cylinder walls. Larsson et al.
437 [81] found low recoveries of gaseous mercury (Hg⁰) when the gas was collected over stainless-steel sur-
438 faces. In natural gas containing H₂S, the authors proposed that stainless-steel may act as a sink for Hg⁰
439 through the following reactions, which involve first a reaction of H₂S with stainless-steel iron, and then a
440 reaction between the resulting gaseous sulfur and the gaseous mercury, causing the formation of solid mer-
441 curic sulfide (HgS):



444 Surface treatment and passivation technologies have therefore gradually been developed to render the inner
445 cylinder walls more inert to targeted analytes. An example of treatment technology is polishing the walls
446 to reduce the internal surface area and as such reduce the number of sorption sites [40]. Surface passivation
447 technologies involve coating or chemically treating the inner cylinder walls [3], [40] to occupy and obstruct
448 active sorption areas (creation of a smooth surface) and minimize the adsorption of targeted compounds
449 [3]. Several commercial passivation processes exist such as Spectraseal (BOC) [82], Experis (Air Products)
450 [83], Aculife (Scott Speciality Gases) [84], AlphaTec (Air Liquide), SilcoNert (SilcoTek® Corporation)
451 [85] and Silonite (Entech Instruments Inc.) [86], and each is recommended for the safe sampling of specific
452 targeted compounds [3], [25], [40]. Other gas sampling cylinder suppliers propose PTFE coatings offering
453 smooth nonsticking surfaces [77]. Currently, SilcoNert®1000 (formerly known as SilcoSteel®) and Sil-
454 coNert®2000 (formerly known as Siltek® and Sulfinert™), made of amorphous silicon, offer among the
455 most inert coatings. SilcoNert®2000 is especially recommended when dealing with trace levels of active
456 species, such as H₂S, mercaptans, NH₃, NO_x, SO_x, mercury [78], [85], and siloxanes, CS₂, (CH₃)₂S,
457 (CH₃)₂S₂ and tetrahydrothiophene [3], [87]. However, during short-term stability tests, Arrhenius et al. [3]
458 found that BTEX sampled in Sulfinert (SilcoNert®2000) -coated gas cylinders were not stable: the concen-
459 trations of all BTEX decreased, especially during the first day. After one storage day, the BTEX levels
460 decreased by 15% (benzene), 25% (toluene), 40% (ethylbenzene) and 45% (o-xylene) compared to the
461 initial concentrations. The authors concluded that the Sulfinert coating is not suitable for gas sampling and
462 storage when BTEX are targeted. Note that the order of decrease percentages of BTEX follows the molec-
463 ular weights of BTEX, in which the heavier compounds are more prone to sorption effects than lighter
464 compounds. Next, the Silonite coating was found to be suitable for the same compounds as SilcoN-
465 ert®2000, i.e., compounds with reactive functional groups such as oxygen, nitrogen, siloxanes, H₂S, CS₂,

466 CH₃SH, (CH₃)₂S, (CH₃)₂S₂ and tetrahydrothiophene, but this coating is not suitable for BTEX [3], [87]. A
467 more convenient coating for storing BTEX is the Experis passivation [3]. Compounds with polar functional
468 groups are, however, unstable in Experis-passivated cylinders [3]. Next, Sulyok et al. [63] investigated the
469 stability of several VSC in SilcoSteel® cylinders. The recoveries measured after a few hours were signifi-
470 cantly >100% for all compounds except methanethiol (~100%), and after 200 h, all compounds were still
471 recovered at ~100% or more except for 1-butylmercaptan which was recovered at <95%. As the authors
472 flushed the cylinders with their multicomponent gas prior to effectively filling the cylinder for storage as-
473 sessments, they proposed that the overestimation of initial recoveries was due to an enrichment of analytes
474 from the gas on the cylinder walls during the pre-flush operation, and to the subsequent outgassing of these
475 analytes due to a pressure drop in the cylinder during the analysis period (sample withdrawal) [63]. None-
476 theless, they concluded that SilcoSteel® cylinders were appropriate for sampling VSC.

477 Suitably passivated cylinders do however not guarantee the stability for all compounds, as chemical con-
478 version or degradation reactions can occur in the cylinder between unstable sampled compounds. For in-
479 stance, if biogas is sampled in a cylinder that is suitably passivated against sulfur compounds, the latter
480 compounds could still react with the water and oxygen present in the biogas, for instance through the fol-
481 lowing equations [40]:



484 Furthermore, considering the diversity of trace components in biogas and biomethane and of the diversity
485 in their boiling points, polarities, water solubilities, and reactivities [4], determining one optimal cylinder
486 passivation treatment that results in reliable sampling is challenging [3]. Instead, several cylinders with
487 different passivation treatments should be used to obtain a sufficient storage stability for the different tar-
488 geted analyte families [3]. Another example of chemical reactions impacting the stability of samples in
489 cylinders was provided by Enrico et al. [80]. The authors found that an oxidized Hg species was formed
490 during the storage of Hg⁰-doped argon gas in silicon- and PTFE-passivated cylinders that were already used
491 for natural gas sampling. The underlying reaction mechanism they propose is as follows: reduced sulfur
492 compounds from previous natural gas samples (H₂S, natural thiophenes, added tetrahydrothiophene, etc.)
493 remain adsorbed onto the cylinder walls despite passivation, and act as suitable sorption sites for subse-
494 quently added gaseous Hg⁰. This physically adsorbed Hg⁰ is then oxidized and undergoes further complex-
495 ation with the reduced sulfur compounds on the cylinder walls. The authors proved that silicon- and PTFE-
496 passivated cylinders, presumably inert toward Hg, are not inert and do not allow reliable sampling and
497 storage of real gases when targeting Hg species. Additionally, Enrico et al. [80] demonstrated that the out-
498 gassing (desorption) of previously adsorbed Hg species from used cylinders could falsify the analytical
499 speciation and quantification results of future samplings.

500 The relative extent of analyte losses due to adsorption effects on (passivated) cylinders has furthermore
501 been proven to be linked to the initial sample concentration, analogously to gas sampling bags. The recovery
502 of compounds initially present in low concentrations in the cylinder, or sampled at low pressures, is typi-
503 cally lower than the recovery of the same compounds initially present in higher concentrations or sampled
504 at higher pressures [3], [40]. This effect seems to be due to the presence of a fixed number of active sorption
505 sites on the cylinder walls [3], and losses of a given species occur by adsorption on each of those individual

506 sites until all sites are saturated. Therefore, when low initial concentrations are sampled, the proportion of
507 analytes that adsorb on the sorption sites until saturation may be great compared to the total analyte quantity
508 present. Following this theory, Barone et al. [88] found that an 11 ppb_v mixture of H₂S and CH₃SH was
509 stable for a longer period (14 days) in a SulfinerTM cylinder than the same mixture at 1.5 ppb_v (6 days).
510 Arrhenius et al. [3] also observed much better stabilities for siloxanes and sulfur compounds when sampled
511 and stored at higher pressures (> 6 MPa) in passivated cylinders than at lower pressures (0.8 MPa). In the
512 case of biogas and biomethane cylinder sampling, the authors accordingly recommend sampling at > 5-6
513 MPa to ensure reliable storage.

514 A method to improve undesired sorption effects is to condition the cylinders prior to sample collection to
515 prevent both underestimating compounds (due to adsorption) and overestimating other compounds (due to
516 outgassing of previously adsorbed compounds) [3]. Heating the cylinder (within the material and pas-
517 sivation coating working temperature range) and flushing with a pure N₂-stream greatly contributes to
518 cleaning the cylinder walls by triggering the desorption of previously sorbed compounds. It is additionally
519 advised to flush the cylinder with the gas to be sampled just before sample collection [63], so that the
520 potential sorption sites on the cylinder walls become occupied, which prevents analyte losses in the effec-
521 tive sample. This can nevertheless lead to an overestimation of analyte recoveries inasmuch as the com-
522 pounds adsorbed during this pre-operation, can in turn desorb and outgas from the walls upon pressure drop
523 in the cylinder during sample withdrawal for analysis [63].

524 **2.3. Canisters**

525 Canisters (Fig. 1 c) are stainless-steel whole gas sampling containers with specifically passivated internal
526 surfaces and are commercially available in volumes from of 0.4 to 15 L [4], [34], [43], [89] or up to 100 L
527 [18]. Canisters do not allow pressurized gas sampling. Small canisters are used for concentrated gas sam-
528 ples, larger canisters are used for lower concentrated samples [89]. Canister sampling has especially been
529 used for air sampling and monitoring [22], [34], [37], [38], [73], [90], [91].

530 Analogously to cylinders, the surface-iron atoms of stainless-steel inner canister walls act as active sorption
531 sites. Polishing and passivation of the inner surfaces has hence been found necessary to prevent analyte
532 losses by sorption or by conversion due to reactions catalyzed by iron sites and to prevent corrosion of the
533 steel by corrosive or acidic sampled compounds. The first canister passivation treatment was SUMMA®
534 (also TO-Can®) [89], [92]: in this treatment, stainless-steel is electropolished and coated with a 500-1000
535 Å thick nickel chromium oxide (NiCrOx) layer to become inert toward (H)VOCs [92]. The NiCrOx layer
536 itself can however also act as a catalyzer or adsorb polar and aromatic VOCs as well as reactive sulfur and
537 amine compounds, which are not stable in SUMMA® canisters unless the sampled gas contains enough
538 water vapor to saturate the sorption sites on the NiCrOx layer [93]. SUMMA® are general-purpose canis-
539 ters recommended in air sampling and VOC-analysis methods such as US EPA methods TO-14A [94] and
540 TO-15 [95]. A canister passivation treatment that was developed more recently is SiloniteTM (Entech In-
541 struments), which is a chemical vapor deposited silica layer offering even more inert surfaces than the
542 SUMMA® process and enabling reliable sampling, storage and recovery of a broader range of reactive
543 analytes [92], [93]. A canister passivation similar to Silonite is Siltek® (SilcoCan® canister, by Restek
544 Corporation), which is an inert fused silica layer chemically bound to the inner stainless-steel walls. The
545 excellent inertness of this Siltek coating, compared to SUMMA®, enables to sample, store and reliably

546 recover low concentration levels of compounds that are usually reactive with metal surfaces, such as polar-
547 , halogenated- and sulfur compounds [37], [89].

548 Two sampling approaches are possible with canisters: either active or passive sampling [89]. In both cases,
549 prior to sampling, the canister is vacuumed and equipped with a pressure gauge [4], [89], [96]. In active
550 sampling, the gas sample is pumped into the canister, enabling to slightly sur-pressurize the sample (up to
551 2.75 bar) and to double the sampled volume [34], [89]. Passive sampling requires no pump: the pressure
552 gradient between the vacuumed canister and the gas to sample causes the sample to flow into the canister.
553 In passive ‘grab’ sampling, the gas is collected at an uncontrolled rate over 10 – 30 s until pressure equilib-
554 rium is reached between the canister and the atmosphere of the gas. This easy sampling method is advan-
555 tageous as it does not require additional equipment such as flowmeters. In ‘time-integrated’ passive sam-
556 pling, a flow restrictor is used to guarantee a constant flow rate of gas into the canister during the entire
557 sampling time interval (minutes to days) to ensure that a representative, time-weighted average gas com-
558 position is sampled despite the progressive pressure increase in the canister and environmental parameters
559 variations (temperature, humidity, etc.) [4], [89], [96]. Canisters are reusable provided proper canister
560 cleaning prior and between sampling campaigns to ascertain that actual samples are not contaminated with
561 residues from previous samplings or laboratory air contaminants. Cleaning procedures are for instance de-
562 scribed in US EPA method TO-14A [94], in a technical guide of Restek [89] and in scientific publications
563 [14] and mainly involve purging the whole sampling train and canister with humidified pure N₂ or air with
564 simultaneous heating, sonicating the disassembled pieces in a solvent, such as methanol, to remove possibly
565 condensed high boiling compounds and oven baking pieces to discard residual organic vapors. Once
566 cleaned, filling the canister with humidified air, passing the air through an adsorbent trap and analyzing the
567 air toward targeted compounds should give the spectrum of eventual residual contaminants. Schweigkofler
568 and Niessner [14], however, found that a simpler cleaning procedure was sufficient for canisters in which
569 landfill and sewage biogases had been collected: six cycles of canister evacuation and flushing with dry
570 pure N₂ were performed without heating and yielded very low blanks.

571 Similarly to gas sampling bags and cylinders, disadvantages to canisters are related to the poor stability and
572 recovery of high boiling, high polarity or water soluble compounds due to sorption effects on inner canister
573 walls, dissolution in condensed water, compound instability and to chemical conversion reactions between
574 sampled compounds [4], [14], [37], [38], [90], [97], [98]. Coutant [98] found that the losses of (polar) VOCs
575 due to physical adsorption in canisters were strongly related to a complex interaction of compound-specific
576 physicochemical properties such as polarizability, equilibrium vapor pressure, temperature and sample va-
577 por concentration. Adsorption losses seem to decrease when a relatively high water vapor level is present
578 in the sample, as water then occupies the sorption sites on inner canister walls [37], [38]. The characteristics
579 of the canister surface (e.g., passivation treatment), usage history of the canister, canister pressure and tem-
580 perature during sampling and storage also influence the storage stability of VOCs [37], [38], [98]. Com-
581 pounds unlikely to be stable in canisters are those with relatively high polarity, water solubility, Henry
582 constant, reactivity (with water or other compounds) and boiling point. Considering all factors that influ-
583 ence the stability of trace compounds in canisters, the stability of targeted compounds should always be
584 tested prior to sampling, under the same conditions as the future sample. Hsieh et al. [37] compared Summa
585 and SilcoCan canisters for the storage of 56 VOCs (alkanes, alkenes, aromatics and biogenics) at 25 °C or
586 35 °C and at relative humidities (RH) of 30%_{RH} or 90%_{RH}. According to a first-order decay model, the
587 authors found that the fastest compound losses occurred at the higher temperature and lower RH (35 °C

588 and 30%) for all VOCs tested in both canisters. Hence, low temperatures and high relative humidity storage
589 conditions are advised to enhance the stability of VOCs. The favorable effect of low temperatures was
590 explained by associated lower degradation rate constants; the favorable effect of high relative humidities
591 was explained by the fewer adsorption losses that occurred as more water molecules occupied sorption sites
592 on inner canister walls [37].

593 Biogas and biomethane have seldom been sampled in canisters, and studies found that used canisters all
594 targeted siloxanes [14], [70], [97], [99], [100]. Hayes et al. [97] and Saeed et al. [100] compared the per-
595 formance of Summa canister sampling with other preconcentration techniques (methanol impingers and
596 charcoal adsorbent cartridges) in terms of ease of sampling, representative sample collection and siloxane
597 recovery. According to these authors, the greatest advantages of canisters are the ease of sampling and short
598 sampling time when performing grab sampling, as well as the ability to directly transport samples to the
599 laboratory. The siloxane recovery efficiency of canisters was better for light, volatile siloxanes than for
600 heavier, less volatile ones [14], [97], [100] due to the previously discussed wall adsorption effects increas-
601 ing for compounds with relatively high boiling points and polarities. Hayes et al. [97] and Saeed et al. [100]
602 found that methanol impingers were better than canisters for sampling heavier siloxanes such as D4, D5
603 and D6, while Summa canisters were better suited for light siloxanes such as D3 and pentamethyldisiloxane.
604 Consequently, as D4 and D5 siloxanes have been found to be abundant in biogases [14], [35], [59], [101],
605 [102], Saeed et al. [100] concluded that canisters were not convenient for reliable and representative silox-
606 ane sampling from biogases. Analogously, Eichler et al. [70] compared the performance of Summa canis-
607 ters, Tedlar bags, methanol impingers and sorbent tubes to sample and store a standard gas of D5 siloxane
608 in N₂. They quantified the adsorption process of the semivolatile D5 onto the inner Summa canister surfaces
609 by first flushing the canister with the D5 gas while analyzing the outlet gas to quantify the exiting D5 level
610 as a function of time. During the first 60 min of this operation, the canister walls acted as a sorption sink
611 for D5, and after this time, all sorption sites seemed to be saturated as the D5 level exiting the canister
612 reached a steady state with a ~95% recovery of the incoming reference concentration. The canister was then
613 flushed with pure N₂ to trigger the desorption of adsorbed D5. After 60 min, the D5 level exiting the canister
614 in the N₂ stream reached ~2% of the initial concentration. Finally, the canister was washed with methanol
615 to extract the remaining D5. Approximately 4% of the initial D5 concentration was recovered in this way.
616 Eichler et al. [70] concluded that Summa canisters were not suited for D5 sampling and storage, as quanti-
617 tative desorption is unlikely. However, a drawback of their study is that pure D5 in a pure N₂ matrix was
618 used as the sole test gas, which is not representative of real biogas samples containing a broad range of
619 other species that may compete or interfere with the described sorption process of D5.

620 Finally, a study by Khan et al. [103] provides some insight into the relevance of reusing old canisters. They
621 investigated the storage losses of a mixture of 10 nL·L⁻¹ reduced sulfur compounds in air in 6-year-old
622 versus 1-year-old (new) commercial SilcoCan canisters. Both canister generations were electropolished and
623 coated with amorphous silicon, but the newest canisters had a thicker silica layer purported to improve the
624 inertness of the inner canister walls [103]. In the old canister, >50% of H₂S and CH₃SH were lost after 1
625 storage day while other compounds remained stable in this vessel for 10 more days. Furthermore, the au-
626 thors observed the formation of DMDS concurrently to the disappearance of H₂S and CH₃SH. They sug-
627 gested that these two compounds were quantitatively converted to the more stable DMDS. Past usage his-
628 tory of the old canister may also have induced cracks in the old coating, possibly contributing to analyte
629 losses. In contrast, >96% of COS, DMS and CS₂ and > 85% of H₂S and CH₃SH were recovered in the new

630 canister after 7 storage days, confirming that recently coated SilcoCan canisters were more inert toward
631 trace levels of reduced sulfur compounds [103].

632 **3. Gas sampling with enrichment (preconcentration)**

633 In contrast to whole gas sampling vessels, which are limited in sampleable volumes and induce analyte
634 losses during storage periods due to wall-effects and reactions between unstable sampled compounds, sam-
635 pling with direct on-site enrichment not only allows considerable gas volumes to be sampled [22] but also
636 enables the preconcentration of low-concentrated analytes by selective isolation from the gas matrix in or
637 onto a small dedicated support. This purposeful enrichment aims at reaching analyte concentrations superior
638 to the available analytical detection limits [39]. Sampling with preconcentration is based on three main
639 methods: trapping on solid media (physical or chemical adsorption, amalgamation), trapping in liquid me-
640 dia (absorption, bubbling) and cryogenic trapping (condensation) [4], [39]. In each of those approaches, the
641 gas matrix actively flows through, but is not retained in, the trapping system as long as necessary to trap
642 sufficient amounts of targeted compounds [21]. The more dilute the compounds are, the larger the gas
643 volume needed. Once sampled, the trap is generally transported to the laboratory for analysis. For biogas
644 and biomethane, as the flammable methane matrix is not retained in the traps, the latter samples are not
645 considered as dangerous goods and do not require specific transport consignments, which is the case for
646 whole gas sampling vessels [21]. The storage period of trapped analytes should be kept as short as possible
647 even though analyte stability should be better on selective traps than in bags, cylinders or canisters [20].
648 Importantly, appropriate conditions (temperature, humidity, etc.) governing the stability of analytes in their
649 trapping media have to be respected during transport and storage.

650 Drawbacks to almost all preconcentration techniques include:

- 651 • *Saturation of the trapping medium*: solid adsorbents and liquid absorbents have limited sorption capac-
652 ities toward targeted molecules. A sorption medium becomes saturated with respect to an analyte (sat-
653 uration point) when all molecular sorption/binding sites of the medium are occupied by analytes so that
654 no additional analyte can be sorbed. At a given analyte concentration in the gas, the saturation point
655 can be expressed in L gas · g⁻¹ adsorbent or L gas · mL⁻¹ absorbent. Saturation is ruled, among others,
656 by the analyte concentration in the gas, its affinity for the medium binding sites and by the gas volume
657 sampled.
- 658 • *Analyte breakthrough* [18], [22], [23], [34], [39]: the breakthrough volume (L gas · g⁻¹ adsorbent or L
659 gas · mL⁻¹ absorbent) is the volume of a gas with a constant concentration that, when passed through
660 the preconcentration trap, results in a detectable level of analyte (typically 5% of the initial concentra-
661 tion) at the outlet of the trap [23], [91], [104], [105]. When an analyte breaks through the trap, it does
662 not mean that the sorption medium is saturated with respect to that analyte, but that the analyte may
663 begin to be displaced by another compound exhibiting a stronger binding affinity for the medium [23].
664 If a gas volume larger than the breakthrough volume is sampled, the analyte concentration in the trap
665 may be underestimated and the saturation point of the sorption medium relative to the targeted analyte
666 may eventually be reached, in which case further analyte molecules will not be trapped. For gases of
667 unknown composition, breakthrough is usually avoided by placing several preconcentration traps in
668 series to recover analytes breaking through the previous trap.

- 669 • *Negative effect of moisture* [21]–[23], [35]: a high humidity percentage in the gas may be harmful, as
670 water may compete with targeted analytes for the sorption sites on solid adsorbents or for the solubility
671 capacity in liquid absorbents. In cryogenic traps, ice blocks can form when sampling humid gases. This
672 can nevertheless be prevented by using hydrophobic adsorbents or by a preliminary gas drying.
- 673 • *Impossibility of repeated sample analysis* [22], [23]: in contrast to a single whole gas sample from
674 which several batches of gas can be analyzed, each preconcentration support is individualized and can
675 generally only be analyzed once, implying that numerous replicates must be sampled.

676

677 **3.1. Trapping on solid media**

678 **3.1.1. Adsorbent tubes**

679 Adsorbent tubes are borosilicate glass or surface-passivated stainless-steel tubes packed with one or several
680 solid (powdered) adsorbent materials (Fig.2). Typical commercial tube dimensions are 6.35 mm OD, 4 mm
681 ID (for glass tubes) or 5 mm ID (for stainless-steel tubes), and 89 mm length. During sampling, gas actively
682 flows through the tubes while targeted analytes are selectively sorbed onto the surface of adsorbent parti-
683 cles. Solvent or thermal desorption of the tubes subsequently enables recovering sorbed analytes from the
684 adsorbents to analyze them [106]. While solvent desorption irretrievably damages the adsorbents, thermal
685 desorption is nondestructive. Most thermal desorption units only allow to desorb and analyze each tube
686 once (one-shot analysis). However, when coupled to a gas chromatograph with an injection in split mode,
687 some modern thermal desorption units allow to recollect the split-fraction desorbed from the primary tubes
688 onto a second identical fresh tube, enabling repeated analyses of a given sampled tube [106].

689 Adsorbents are especially suited to trap intermediate-, semi- or very-volatile (halogenated) organic com-
690 pounds [4], [18], [20], [21], [40], [107]–[112], volatile sulfur compounds [18], [20], [40], [112]–[118] and
691 volatile silicon compounds such as siloxanes [4], [18], [20], [35], [59], [105], [112], [119], [120], with
692 various polarities and volatilities. The preconcentration of volatile metal(loid) compounds on adsorbents is
693 nevertheless less advised as the physico-chemical interactions between such unstable analytes and the ad-
694 sorbent are too strong and would lead to irreversible adsorption or analyte degradation during desorption,
695 alteration of the chemical speciation of the analytes or artifact build-up [22].

696 Multibed adsorbent tubes (up to 4 beds in 89 mm long tubes) are attractive preconcentration units for biogas
697 and biomethane which contain a large diversity of trace compound families over large boiling point- and
698 polarity-ranges [3]–[5], [21], [36], [42], [58]. While no adsorbent is universal enough to retain all trace
699 compounds [4], [121], multibeds precisely enable the preconcentration of a large range of compounds in a
700 wide volatility range in a single sampling run by arranging different adsorbent materials in order of increas-
701 ing sorption strength (increasing surface area and polarity, decreasing pore size, Table 2) in the gas sam-
702 pling direction (Fig. 2) [23], [104]. When sampling a multicomponent gas, high molecular weight com-
703 pounds with low volatilities are easily trapped onto the weakest front adsorbent bed. Volatile compounds,
704 however, are not trapped yet as the sorption strength of front adsorbents is insufficient. These compounds
705 therefore further flow in the tube and gradually reach stronger adsorbents whereon they are trapped. In this
706 way, heavy compounds never meet strong adsorbents that they would saturate and whereon they would be

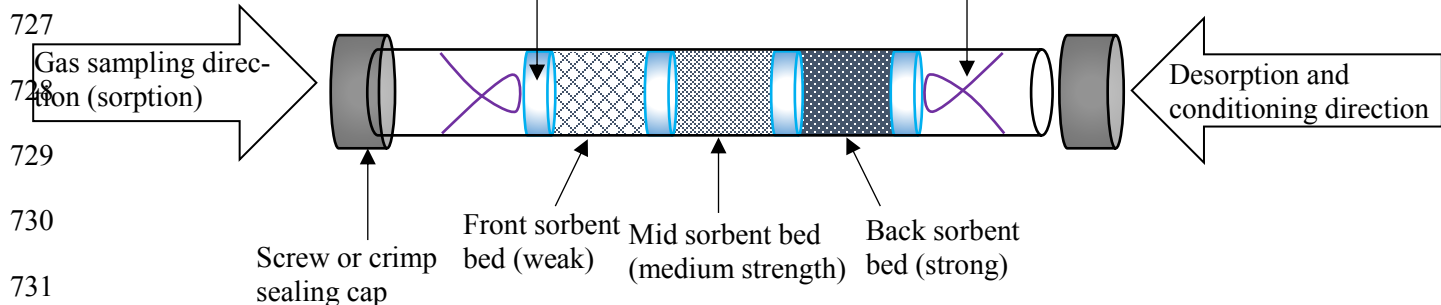
707 irreversibly or too strongly adsorbed to be further quantitatively desorbed. Back strong adsorbents are hence
708 dedicated to the sorption of (very) volatile species [23], [39], [104], [109], [121].

709 A multitude of commercial solid adsorbents exist (Table 2): quartz or glass beads (very
710 weak, hydrophobic), porous polymers (weak or medium strength, hydrophobic), graphitized carbon blacks
711 (GCB) (weak to medium strength, hydrophobic) and carbon molecular sieves (CMS) (strong, relatively
712 hydrophilic). All differ in their density, temperature stability, surface area, surface functionalities and po-
713 larity, pore dimensions, etc., and the resulting differences in kinetic and thermodynamic behaviors (break-
714 through volumes, adsorption isotherms, adsorbent-adsorbate interactions, etc.) greatly influence their pre-
715 concentration and desorption efficiencies and hence the adsorbent choice for a given application [23], [24],
716 [105], [109], [122], [123]. Numerous ready-to-use sorbent tube configurations are commercially available.
717 However, it has been shown that the background contamination of commercial sorbent tubes is higher than
718 that of self-assembled tubes, leading to higher detection limits [18]. Therefore, sorbent tube self-assembly
719 is reviewed here to provide insight into preparation steps critically influencing the final background con-
720 tamination level of sorbent tubes. Fig. 2 depicts the sorbent tube constituents. Both tube extremities should
721 be equipped with detachable sealing connectors: stainless-steel, brass or PTFE gas-tight screw-fittings
722 (ferrules and nuts) are often used [18], [20], [23], [91], [107]. Alternatively, especially glass sorbent tubes
723 can be fitted with crimp caps with central septa.

724

725

726



732 *Figure 2: Schematic of a multibed sorbent tube. 100 mesh stainless-steel gauzes and tension springs are typically used together in*
733 *stainless-steel tubes whereas unsilanized glass or quartz wool plugs are used in glass tubes to secure adsorbent beds [104]. Con-*
734 *striction of the tube internal diameter at the tube extremities can additionally help secure the sorbent beds. The desorption direction*
735 *is always the reverse of the sampling direction even for single bed tubes [109].*

736 As any part constituting a sorbent tube may be a source of contamination, it is advised to clean all of the
737 parts prior to assembling the tube and to always handle the parts with disposable gloves in order to obtain
738 the lowest blanks [18], [104], [107]. Note that the tube material itself may also act as a sorption and catalysis
739 surface, as studied by Arnts for untreated stainless-steel versus Sulfinert™ or SilcoSteel® passivated stain-
740 less-steel tubes [124]. When using stainless-steel sorbent tubes, it is advised to opt for surface-passivated
741 stainless steel [20], [124]. Helmig [107] sonicated all metal (stainless-steel tube, tension springs, gauzes
742 and sealing ferrules and nuts) and PTFE (alternative sealing caps) parts in methanol before use, and stain-

743 less-steel parts were additionally baked at 150 °C for 4 h. Glass or quartz wool plugs used to secure adsorbent
744 beds in glass tubes should also be precleaned by thermal conditioning to remove any impurity trapped
745 in the wool [104]. Sheu et al. [18] thermally cleaned all loose parts and empty tubes in dedicated ovens with
746 simultaneous high-purity N₂ flow. Before packing adsorbents in tubes, Sheu et al. [18] also thermally
747 cleaned all adsorbents by placing them in a tube furnace at their material-specific temperatures (Table 2)
748 with simultaneous high-purity N₂ flow for several hours to induce the desorption of contaminants from the
749 adsorbents.

750 The adsorbent mass or volume to be loaded in a sorbent tube is determined by the tube geometry, the
751 number of sorbent beds placed in series in the tube (Fig. 2), the adsorbent sorption capacity properties and
752 the concentration of analytes targeted in the gas to be sampled [73]. When tubes are aimed to be analyzed
753 by thermal desorption, the total length of (successive) sorbent bed(s) must be within the central zone of the
754 tube that will later be heated by the thermal desorption device [104], [121], [125]. It is therefore suggested
755 to pack the tubes with a fixed volume V of each adsorbent [121] so that all beds occupy the same length,
756 with $V = m / \rho$, where m is the adsorbent mass and ρ is the packing density of the adsorbent (Table 2). Each
757 adsorbent should be kept in a discrete bed separated from the others by glass or quartz wool plugs (3 mm
758 length) [104], [126], glass-fiber filter discs [107] or any other suitable fritted disks or gauze (Fig.2). Note
759 that quartz and glass wool may act as sorbents for semi-VOCs. Moreover, glass wool tends to physically
760 degrade at elevated temperatures during thermal desorption [18], [124], and silanized glass wool releases
761 siloxanes upon heating. Using high purity unsilanized quartz wool is henceforth preferable [18], [104],
762 [121]. If metallic gauzes are used, sorption and desorption interferences are expected since high boiling
763 compounds are prone to sorption on metallic surfaces, as was discussed for nonpassivated stainless-steel
764 cylinders and canisters. Additionally, the inertness of such gauzes upon heating is poorly documented, and
765 metallic compounds could be released in the sample.

766 The step following sorbent tube packing is tube conditioning. Adsorbent tubes are mounted on a manifold
767 and heated at the adsorbent material-specific conditioning temperature (Table 2) under a continuous clean
768 gas (N₂ or He) stream for several hours to induce the desorption of contaminants passively adsorbed onto
769 the adsorbents during tube assembly. Freshly conditioned and sealed sorbent tubes must be properly stored
770 if not immediately used for sampling. Sorbent tubes are generally stored in dedicated refrigerators at ≤ 4
771 °C or in freezers at ≤ -30 °C in clean airtight recipients with desiccant material [18], [20], [42], [104], [107]
772 since it has been proven that cold temperature storage reduces the formation of adsorbent artifacts contrib-
773 uting to background contamination [18], [107]. Helmig [107] also placed commercial activated charcoal
774 adsorption cartridges (opened) in the storage jars to keep the headspace above the tubes hydrocarbon-free,
775 as also suggested by others [23], [91]. The shelf life of rightly assembled, preconditioned and stored tubes
776 may last several months [23], [91], although after 30 days of storage, reconditioning may be recommended
777 right before using the tube [23]. Finally, it is analogously advised to store and transport *sampled* sorbent
778 tubes at cold temperatures (≤ 4 °C [20], [104], [110], [127]; -18 °C [57], [59]; -20 °C [106] or -30 °C [18],
779 [107]) in hermetic vessels with desiccants if desorption and analysis of sampled analytes cannot be executed
780 immediately after sampling, as cold temperatures inhibit desorption, chemical reactions and analyte diffu-
781 sion processes in the tubes [18]. The storage stability of trace compounds on adsorbent tubes has been
782 widely studied, e.g., [4], [20], [108], [110], [117], [126], [128], but no universal storage recommendation

783 can be provided since stability depends on the targeted analytes, the adsorbent tube configuration, the sam-
784 pling conditions and the contaminations during sampling, transport or storage. The only valid rule is to
785 analyze sampled sorbent tubes as soon as possible (e.g., within 3 days [110]).

786
787
788

789 *Table 2: Properties of common commercial adsorbents used in thermodesorption applications.*
790 *Adsorbents are listed in order of increasing sorption strength. Data are compiled from [24], [104], [109], [121], [123], [129]–*
791 *[133]. The sole difference between Carbotraps and Carbopacks is the mesh size: Carbotraps are 20/40 mesh size ($420\ \mu\text{m} <$*
792 *particle diameter $< 841\ \mu\text{m}$) and Carbopacks are 40/60 mesh ($250\ \mu\text{m} <$ particle diameter $< 420\ \mu\text{m}$) or smaller [121], [129].*
793 *Note that sorption strength categories are not strictly defined. In particular, Carbopack X, Carbotrap X, Carbograph 5 and Car-*
794 *boxen 569 are often considered as “strong” adsorbents. However, in this table, the sorbent strength criteria proposed in the US*
795 *EPA method TO-17 [104] are chosen to distinguish weak, medium and strong adsorbents based on their surface areas: adsorbents*
796 *with surface area $< 50\ \text{m}^2\cdot\text{g}^{-1}$: weak; surface area between 100 and $500\ \text{m}^2\cdot\text{g}^{-1}$: medium; surface area $> 1000\ \text{m}^2\cdot\text{g}^{-1}$: strong. Note*
797 *that adsorbents with pore diameters $> \sim 1000\ \text{Å}$ are considered as nonporous. Trademarks: Carbopack, Carbotrap, Carboxen,*
798 *Carbosieve: Sigma–Aldrich Co.; Carbograph: LARA s.r.l, Italy; Anasorb: SKC, Inc.; Spherocarb: Analabs Inc.; Tenax: Enka*
799 *Research Institute, The Netherlands; Porapak: Waters Corporation; Chromosorb: Celite Corporation, USA; HayeSep: Hayes Sep-*
800 *aration Inc.; Amberlite: Rohm and Haas; UniCarb: Markes International.*

801

Adsorbent name	Adsorbent class \diamond	Packing density $\text{g}\cdot\text{cm}^{-3}$	Conditioning T ($^{\circ}\text{C}$)	Desorption T ($^{\circ}\text{C}$)	Approximate surface area ($\text{m}^2\cdot\text{g}^{-1}$)	Mean pore diameter (\AA)	Sorbent strength	Hydrophobic / Hydrophilic
Glass Beads	SiO ₂	1.68	350	330	<5	>3000		
Quartz Wool	SiO ₂				<5	-		
Carbopack F	GCB	0.81	350	330	5	1000-3000	Very weak	
Carbograph 3	GCB				5	1000-3000		
Carbopack C	GCB	0.85	350	330	10	2000		
Carbograph 2	GCB		350	330	10	2000		
Anasorb GCB2	GCB		350	325	12	2000		
Tenax GR	PP	0.41	320	300	24	200-1000	Weak	
Carbopack Y	GCB	0.51	350	330	24	1000-3000		
Tenax TA	PP	0.28	320	300	35	720		
Carboxen-1016	CMS	0.48	350	330	75	-		
Carbopack B	GCB	0.43	350	330	100	3000	Weak / Medium	
Carbograph 1	GCB		350	330	100	3000		
Anasorb GCBI	GCB		350	325	100	3000		
Carbopack X	GCB	0.58	350	330	240	100		hydrophobic
Carbograph 5	GCB		350	330	240			
PoraPak N	PP	0.37	190	180	300	75		
Amberlite XAD 2	PP		190	180	300	10-20		
Chromosorb 102	PP		250	225	350	90	Medium	
Carboxen-564	CMS	0.59	350	330	400	6-9		
Carboxen-569	CMS	0.61	350	330	485	5-8		
Carboxen 1001	CMS	0.58	350	330	500	5-8		
Carboxen-563	CMS	0.55	350	330	510	7-10		
PoraPak Q	PP		250	225	550	75		
Carboxen-1018	CMS	0.80	350	330	700	6-8	Medium / Strong	
Chromosorb 106	PP	0.30	190	180	750	50		
Amberlite XAD 4 *	PP		140	130	750	50		
Hayesep D	PP	0.35	190	180	795			
Anasorb CMS	CMS		350	325	800			
Carbosieve S-III	CMS	0.76	350	330	820	4-11		
Carboxen-1003	CMS	0.45	350	330	1000	5-8		
Petroleum A.C. *	Charcoal	0.50	190	180	1050	4-20		
Coconut A.C. *	Charcoal	0.57	190	180	1070	4-20	Strong	relatively hydrophilic
Carboxen-1002	CMS	0.46	350	330	1100	10-12		
SpheroCarb	CMS		400	390	1200	13-15		
Carboxen-1000	CMS	0.52	350	330	1200	10-12		
UniCarb (SulfiCarb)	CMS		350	330	1200			

803 \diamond GCB: graphitized carbon black. PP: porous polymer. CMS: carbon molecular sieve.

804 * Not compatible with thermal desorption (charcoals and Amberlite resins) yet still given as indication.

805

806 Several important parameters have to be considered when designing adsorbent tubes and using them to
807 sample biogas and biomethane. First, the breakthrough volume of an analyte on an adsorbent tube is influ-
808 enced by several factors as follows:

- 809 • The adsorbent material: its porosity, surface area, chemical composition, polarity, particle mesh size,
810 etc., influence its capacity and affinity for given analytes [23], [91], [122], [130], [134].
- 811 • The mass of adsorbent packed in the tube and the tube geometry [130], [134]. The higher the mass of
812 adsorbent is, the higher the breakthrough volume.
- 813 • The configuration (single- or multibed) of the adsorbent tube. Multibeds have higher breakthrough
814 volumes than single beds, as demonstrated by Gallego et al. [135] in a comparison of single Tenax TA
815 beds (200 mg) versus multibeds composed of Carbotrap B (70 mg), Carbopack X (100 mg) and Car-
816 boxen 569 (90 mg) for the trapping of VOCs in air. Multibeds normally always have a higher total
817 surface area than single beds (e.g., $\sim 70 \text{ m}^2$ for the multibed versus $\sim 7 \text{ m}^2$ for the Tenax bed [135]) and
818 therefore have higher adsorption capacities.
- 819 • The temperature during sampling [105], [122]. When sampling above $20 \text{ }^\circ\text{C}$, the breakthrough volume
820 is reduced by a factor of 2 for each $10 \text{ }^\circ\text{C}$ rise in temperature [125] (very approximate rule [109]) since
821 adsorption is an exothermic process.
- 822 • The gas flow rate. Over the range of 5 to $500 \text{ mL}\cdot\text{min}^{-1}$, the breakthrough volume for tubes of typical
823 commercial dimensions (89 mm length, 4 or 5 mm ID) is independent of the flow rate and only de-
824 pendent on the total volume passed. However, at sampling flow rates < 5 or $> 500 \text{ mL}\cdot\text{min}^{-1}$, the break-
825 through volume is substantially reduced [23], [125]. An optimal sampling flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$ is
826 often mentioned (for air samples) for tubes of typical commercial dimensions [21], [73], [91], [125].
- 827 • The nature, volatility and concentration of the analyte. On a given adsorbent, more volatile species have
828 lower breakthrough volumes than less volatile ones [135]. The more concentrated an analyte is, the
829 lower its breakthrough volume [125], [134].
- 830 • The composition of the gas. The presence of competing analytes and especially water vapor in the gas
831 can affect the breakthrough volume of hydrophilic adsorbents [23], [91], [109] such as carbon molec-
832 ular sieves: water vapor will tend to occupy sorption sites, impeding the sorption of targeted analytes
833 and accordingly reducing their breakthrough volume. At high relative humidity (95%), the break-
834 through volume of such strong adsorbents can be reduced by a factor of 10 as compared to a low hu-
835 midity scenario, while the breakthrough volume of more hydrophobic porous polymer adsorbents is
836 only reduced by a factor of 2 [125]. Other sources report that the breakthrough volume of hydrophobic
837 adsorbent materials (graphitized carbons, porous polymers) is not affected by relative humidities even
838 up to 90% [109].

839 Breakthrough volume data for the sorption of a wide list of (H)VOCs on different adsorbents at $20 \text{ }^\circ\text{C}$ and
840 how to determine them is available in the literature (e.g., [31], [91], [105], [125]).

841 Second, when sampling humid gases such as biogas, sorbent tubes and all parts of the sampling train must
842 be maintained at a temperature slightly higher than the sampled gas to prevent any condensation of water
843 or semivolatile compounds to occur on cold parts [104], [109]. It is not advised to place a water-retaining
844 tube or membrane upstream of the sorbent tube insofar as water retaining materials (Nafion membranes,
845 ascarite (NaOH coated silica), charcoal, drierite (CaSO_4), sodium carbonate, sodium sulfate, magnesium
846 perchlorate, calcium chloride, calcium sulfate...) will also trap targeted analytes and prevent them from

847 being sampled [18], [126], [136]–[139], even though some authors have advised the use of anhydrous cal-
848 cium chloride before sampling siloxanes from wet synthetic biogas on silica gel adsorbent tubes [128].
849 When dry gases are sampled, however, such as biomethane, it may be advantageous to electrically cool
850 sorbent tubes to 5 – 15 °C during sampling since adsorption is an exothermic process [18]. Another precau-
851 tion is to place a particle filter upstream of the sorbent tube to prevent fine particles in the gas from entering
852 the adsorbent beds in which they could also act as adsorbing surfaces for targeted analytes, although the
853 particle filter itself (e.g., a 2 µm Teflon mesh; a glass wool plug) can also adsorb targeted analytes and
854 hence prevent their sampling [104].

855 Studies using adsorbent tubes to preconcentrate trace compounds in biogas, landfill gas and biomethane are
856 reviewed in Table 3. Pioneering work in this regard aimed to identify and quantify trace compounds in
857 landfill gas emissions responsible for odoriferous and toxicological nuisances and associated health and
858 environmental hazards [140]–[143]. Brookes and Young [141] and Assmuth et al. [143] established a
859 method to preconcentrate landfill gas trace compounds from landfills where no gas collection systems had
860 yet been installed. Tenax GC, intended to retain a large spectrum of (nonpolar) compounds, and Porapak
861 Q, intended to retain acid, neutral and low molecular weight (volatile) compounds were used by Brookes
862 and Young [141]. The Tenax GC tubes were sampled with landfill gas at ambient temperature and the
863 Porapak Q tubes were sampled at -80 °C. The sampling and analytical method in [141] was applied in the
864 field by Young and Parker [140] to identify and quantify trace compounds in landfill gas from 6 sites bur-
865 ying various types of domestic or industrial wastes. Approximately one hundred different trace compounds
866 were characterized and were dependent on the type and age of wastes in the landfill [140]. Assmuth et al.
867 [143] collected landfill gas on baked steel Tenax GC tubes. Before effective sampling, the sampling train,
868 without the Tenax GC tubes, was flushed with landfill gas to avoid cross-contamination between study
869 sites. Two sorbent tube storage temperatures were tested for the sampled tubes: 4 °C and -20 °C and the
870 authors found that 4 °C was sufficient to guarantee sample integrity [143]. They also found that the con-
871 centrations determined for chlorofluorohydrocarbons were potentially underestimated since those com-
872 pounds were not effectively retained on Tenax GC [143]. Allen et al. [127], [144] also characterized trace
873 (H)VOCs in landfill gases using multibed adsorbent tubes composed of Tenax TA, Chromosorb 102 and
874 Carbosieve SIII in a 1:1:1 volume ratio. The sampled tubes were stored at 4 °C and analyzed within 24 h.
875 The tube configuration yielded no breakthrough during sampling, and all analytes could be recovered with
876 ~100% from the adsorbents. Landfill gas was sampled at seven sites, and over 140 VOCs were identified
877 and quantified. Next, Narros et al. [69] compared three different *in situ* sampling methods for VOCs and
878 siloxanes in landfill gas. These methods included whole gas sampling in 10 L Tedlar bags; adsorbent tube
879 sampling on two single bed tubes assembled in series (Tenax TA and Carbosieve III); and sampling via
880 absorption in methanol impingers. Once in the laboratory, landfill gas sampled in Tedlar bags was intended
881 to be transferred either to the impingers or to the adsorbent tubes to study the difference between direct
882 absorption or adsorption on site or first whole gas sampling and then preconcentration. The authors con-
883 cluded that direct *in situ* sampling with adsorbent tubes was the best option [69]. Tenax TA and Carbosieve
884 III enabled the simultaneous sampling of VOCs, siloxanes and trimethylsilanol (TMS) (trapped on Tenax
885 TA) while methanol impingers could not trap TMS. Adsorption tubes also provided higher quantitative
886 results than those of the impingers for the most volatile siloxanes L2 and D3, but lower results for the less
887 volatile siloxanes D4 and D5, probably due to difficulties in quantitatively desorbing those more heavy
888 species from the adsorbents [69]. A similar study was led by Raich-Montiu et al. [102] to preconcentrate
889 siloxanes and TMS in biogas generated from sludge digestion. The authors compared *in situ* direct biogas

890 sampling and preconcentration on commercial ORBO 32 adsorbent tubes and in impingers with whole gas
891 sampling in a 200 L Tedlar bag followed by laboratory preconcentration of the bag content on the same
892 adsorbent tubes and impingers. Statistical analysis showed that there was no significant difference between
893 the results from direct biogas sampling on adsorbent tubes (or impingers) and the results from biogas sam-
894 pling in Tedlar bags and subsequent transfer to adsorbent tubes (or impingers), contrasting with the conclu-
895 sions of Narros et al. [69]. However, for the samples taken directly at the biogas source, adsorbent tubes
896 yielded higher concentrations than those of the impingers for D4 and D5 siloxanes; hence, adsorbent tubes
897 prevented the siloxanes from being underestimated and were thus preferred [102]. Kim et al. [119] also
898 compared the conventional methanol impinger technique with adsorption on solid adsorbents for the deter-
899 mination of siloxanes in landfill gas. They evaluated three adsorbents: coconut-activated carbon, coal-acti-
900 vated carbon and silica gel, all intended for solvent (methanol) desorption. Using a standard gas of siloxane
901 D4 in N₂, the results indicated that coconut-activated carbon yielded the highest reproducibility, accuracy,
902 precision and recovery compared to the other adsorbents tested and the closest results to the conventional
903 impinger method. The worst reproducibility was obtained for silica gel [119]. In real landfill gas, the silox-
904 ane concentrations obtained with coconut- and coal-activated carbon sorbent tubes were not significantly
905 different from those obtained with the impinger method, while those obtained with silica gel were signifi-
906 cantly different (lower) [119]. Since adsorbent tube sampling is less labor intensive and is faster than im-
907 pinger sampling, the authors suggested that coconut-activated carbon adsorbent tube sampling was a reli-
908 able and suitable alternative for the accurate quantification of siloxanes in biogas. Activated carbon adsor-
909 bent tubes were also considered in series by Tansel et al. [120] for the preconcentration of siloxanes in
910 landfill gas and biogas, with an investigation of breakthrough volumes. The results highlighted that a single
911 activated carbon tube of ~700 mg could quantitatively retain the light compounds TMS and hexamethyl-
912 disiloxane (L2) but could not quantitatively trap heavier targeted siloxanes (L3, D3, D4, D5 and D6), which
913 were found in various percentages on the second, third or even fourth tubes of the breakthrough series. The
914 inability of activated carbon tubes to quantitatively retain heavy siloxanes was not especially related to the
915 high concentrations in the gas or to too high of a sampled volume, but, according to the authors, rather to a
916 lower affinity of activated carbon for high molecular weight siloxanes owing to competitive sorption ef-
917 fects: in the landfill gas and digester biogas studied, a high concentration of relatively light compounds
918 ($3800 \mu\text{g}\cdot\text{m}^{-3}$ TMS in landfill gas; $2725 \mu\text{g}\cdot\text{m}^{-3}$ D4 in digester biogas) was quantitatively adsorbed in the
919 first or second tube. These light compounds may limit the number of available sorption sites for heavier
920 compounds [120]. Several other studies have combined gas sampling bags for *in situ* sampling with subse-
921 quent transfer to adsorbent tubes (Table 3). Arrhenius et al. [21], [145] sampled biogas and biomethane in
922 Altef gas bags with immediate transfer to Tenax TA adsorbent tubes for VOC and terpene analysis. The
923 authors argue that this two-step sampling and preconcentration procedure combines the advantages of sam-
924 pling bags and sorbent tubes while eliminating their disadvantages. Gas bags can be filled at any flow rate,
925 even at unstable rates, but the main disadvantage of gas bags is the poor short-term storage stability of trace
926 compounds. On the other hand, the short-term storage stability of analytes trapped on an adsorbent material
927 is very good [20], but the main disadvantage of adsorbent tubes is the necessity of a constant gas flow rate
928 through the tubes during sampling [21]. In [21], gas transfer from the Altef bags to the Tenax TA tubes was
929 executed via three methods, each time transferring the gas to a single Tenax TA tube at a controlled flow
930 rate. A gas-tight syringe was used in method 1; a commercial special syringe (“easy VOC” grab sampler)
931 regulating the gas flow rate through the sorbent tube independently of the force used to pull the gas was
932 used in method 2; and a pump was used in method 3. Similar compound recoveries were obtained from the

933 Tenax tubes when using the two syringe transfer methods. With the pump method, however, identical re-
934 sults to those of the syringe methods were observed only if the sampled gas had a high humidity content.
935 In gas samples with low humidity, low boiling analytes (up to 120 °C boiling point) were quantified simi-
936 larly to the two other methods, but heavier, higher boiling analytes were underestimated. These results were
937 explained by the lower flow rate used in the sampling pump method and by water adsorption effects in the
938 Altec gas collection bags [21]. At a low humidity, sorption sites on inner bag wall surfaces are not saturated
939 with water and remain available for especially less volatile analyte sorption, causing their loss for analysis.
940 Low sampling flow rates from the bags probably do not trigger the desorption of the compounds retained
941 on bag walls, while this occurs with higher flow rates. The authors hence advised sampling gas from the
942 bags through the sorbent tubes using a high flow rate ($>300 \text{ mL}\cdot\text{min}^{-1}$), especially for gases with low mois-
943 ture content [21]. Regarding the Tenax TA trapping efficiency for the targeted VOCs and terpenes, the
944 results in [145] showed that terpenes in a standard mix were quantitatively recovered ($>85\%$) from the
945 Tenax TA tubes. *p*-Cymene and d-limonene displayed slightly lower recoveries, likely due to sorption ef-
946 fects on bag walls since those compounds were present in higher concentrations in the standard [145]. Rey
947 et al. [112] investigated trace compounds in MSW landfill gas and targeted (H)VOCs and siloxanes. Gas
948 was sampled into Tedlar bags and subsequently transferred to a preconcentration system as either a com-
949 mercial adsorbent tube (Tenax TA or Carbotrap 349, the latter is a multibed packed with Carbopack Y,
950 Carbopack B, Carboxen 1003), a carboxen-polydimethylsiloxane (CAR-PDMS) SPME fiber, or an acti-
951 vated carbon column inserted in a special device intended to analyze halogenated components (Total Or-
952 ganic Halogen Analyzer). The results indicated that the SPME method was the easiest to perform. However,
953 more compounds were resolved and quantified via the adsorbent tubes. A total of 119 VOCs were charac-
954 terized via only the Tenax TA tubes. The multibed Carbotrap 349 adsorbed more compounds than Tenax
955 TA due to the different adsorbent strengths of its constituent materials, but desorption from Carbotrap 349
956 was not always evident [112]. The use of another SPME fiber (Divinylbenzene–Carboxen–Polydime-
957 thylsiloxane) was also compared to multibed adsorbent tubes composed of Carbosieve 111 – Carboxen B
958 – Carboxen C for the preconcentration of VOCs in landfill gas [146]. These SPME fiber and multibed
959 adsorbent tubes were found to be both efficient and provided comparable VOC compositions in the ana-
960 lyzed gases [146]. Next, PET gas sampling bags (Nalophan), supposedly inert to siloxanes [147], have also
961 been used to sample biogas and biomethane for subsequent transfer to adsorbent tubes packed with amber-
962 lite XAD-2 or XAD-4 resins, activated carbon type F-400 or polyurethane foam [147] or with Tenax GR
963 [57], [59] for the analysis of VOCs, siloxanes and TMS. VOCs, siloxanes and TMS in a landfill biogas
964 have also been determined by first sampling the gas in PVDF gas sampling bags and then immediately
965 transferring the gas to a multibed adsorbent tube composed of Carbotrap B, Carbopack X and Carboxen
966 569 [42]. In particular, very volatile compounds such as acetaldehyde, carbon disulfide, ethanol and 1,3-
967 butadiene had high breakthrough percentages through the multibeds [42]. Lastly, Schweigkofler and
968 Niessner [99] sampled biogas from a sewage treatment plant directly into evacuated stainless-steel canis-
969 ters. Biogas samples were then drawn through an adsorbent tube packed with silica gel. The study shows
970 that silica gel can be a suitable adsorbent for the screening analysis of siloxanes over a broad range of
971 volatilities and polarities. The study also shows that silica gel adsorbent tubes can be thermally desorbed.
972 However, in a similar study by Sigot et al. [148], it was stressed that silica gel thermal regeneration can be
973 ineffective due to siloxane polymerization to silicone on the surfaces of the adsorbent. They proposed that
974 it is easy to desorb hydrogen bonds that form between siloxanes and silica gel at low siloxane uptake, while
975 stronger bonds are created by surface polymerization at higher siloxane loads, hampering their desorption

976 [148]. Despite the ease of gas sampling bags as *in situ* sampling media, directly sampling biogas and bio-
977 methane on adsorbent tubes may still be preferred, as the storage stability of trace compounds has been
978 demonstrated to be higher in adsorbent tubes than in gas bags by Mariné et al. [20]. These authors compared
979 the 4-day storage stability of biogas trace compounds in Tedlar bags (stored at room temperature) and in
980 multibed adsorbent tubes (Tenax TA – Unicarb) (stored at 4 °C) by means of a standard containing silox-
981 anes, alkanes, mercaptans and VOCs. The storage stability was better on adsorbent tubes (insignificant
982 analyte loss after 3 days) than in Tedlar bags (significant analyte loss after 1 day). Only after 4 days of
983 storage on adsorbent tubes did some compounds have a lower recovery [20]. Biogas and biomethane have
984 directly been sampled on Tenax TA adsorbent tubes for the analysis of VOCs, silicon- and sulfur organic
985 compounds [67], [149], [150], yet small alcohols, aldehydes and some thiols could not be quantified on the
986 Tenax TA tubes [150]. Various other adsorbent tubes packed with adsorbents, such as graphitized and ac-
987 tivated carbon [151] and amberlite XAD-2 [5], [152] and charcoal [5], have also been directly used for the
988 preconcentration of VOCs and siloxanes in biogas and biomethane. Hilaire et al. [5] used commercial
989 ORBO 609 Amberlite XAD-2 and ORBO Charcoal tubes and found that blank XAD-2 tubes contained 33
990 background contaminants, while charcoal contained 47. ORBO 609 Amberlite XAD-2 tubes were found to
991 be more efficient in trapping and recovering biogas trace compounds: for a biogas sample, 216 chromato-
992 graphic peaks were detected with the XAD-2 tube against 98 peaks with the charcoal tubes [5].

993 Finally, dimethylmercury is the sole metallic trace compound that has successfully been sampled on adsor-
994 bent tubes from MSW landfill gas. In landfill gas, gaseous Hg^0 is the most abundant mercury species.
995 Lindberg et al. [153], [154] preconcentrated dimethylmercury in landfill gas on Carbotrap™ adsorbent
996 tubes which have high adsorption affinity and capacity for dimethylmercury while not retaining the most
997 abundant Hg^0 . During sampling operations, as landfill gas is humid, Carbotrap™ tubes were placed down-
998 stream of condensate traps and were purged with dry nitrogen immediately after sampling to expel residual
999 water. In [154], Carbotrap™ tubes were also maintained at a few degrees above ambient temperature to
1000 prevent water condensation on the adsorbent. Additionally, a 5 µm Teflon filter and a guard column were
1001 placed upstream of each Carbotrap™ tube to respectively retain particulate matter and other semivolatiles
1002 organic trace compounds and prevent their sorption on the Carbotrap™. After sampling, the Carbotrap™
1003 tubes were protected from light and refrigerated for storage until analysis. Together with purging the sam-
1004 pled tubes with an inert dry gas immediately after sampling, those precautions proved to safeguard high
1005 dimethylmercury stability on the Carbotrap™ tubes for >28 days [155]. In [154], the authors pointed out
1006 that the recovery of dimethylmercury from Carbotrap™ was higher at smaller sampled gas volumes, prob-
1007 ably due to the displacement (when large gas volumes are sampled) of the relatively weakly bound dime-
1008 thylmercury by other trace compounds (despite the guard column) having stronger binding affinities with
1009 Carbotrap™ [155]. In [155], the authors investigated the influence of sampling flow rate and volume, tem-
1010 perature and humidity on the breakthrough of dimethylmercury through the Carbotrap™ tubes. The total
1011 volume sampled was more critical than the flow rate for the breakthrough determination. The breakthrough
1012 volume sharply decreased at high humidities (>70%RH) and temperatures (>35 °C). Finally, other adsorbent
1013 matrices were considered in [155] for the preconcentration of dimethylmercury: Tenax™, Carbosieve™ S-
1014 III, Carboxen™-563, Carboxen™-564 and Carboxen™-569. None of these matrices were suitable: Tenax™
1015 did not adsorb dimethylmercury, while this latter was too strongly adsorbed on all carbon molecular sieves
1016 tested with nonquantitative recovery as a result.

1017 Importantly, all studies presented in Table 3 sampled the gases at near atmospheric pressure. No single
1018 pressurized sample was collected. The absence of standardized methods is also striking: every study was
1019 conducted under unique conditions, targeting distinct analytes with a unique set of adsorbent material and
1020 tube configuration, sampling conditions and analytical methods.

Table 3: Review of studies that used adsorbent tubes to sample and preconcentrate trace compounds in landfill gas, biogas and biomethane. All gas samples were taken at near atmospheric pressure.

MSW = municipal solid waste. AD: anaerobic digestion. WWTP = wastewater treatment plant (anaerobic digestion of WWTP sludge). TD-GC-MS = thermal desorption – gas chromatography – mass spectrometry. FID = flame ionization detector. ATD = automated thermal desorption system. TDS = thermal desorption system. ToF-MS: time-of-flight mass spectrometry. TMS = trimethylsilanol. VMS = volatile methyl siloxane. RH = relative humidity.

Adsorbent tube composition	Sampled gas	Sampling conditions	Characterized compounds	Concentration range observed	Analytical method	References
Single beds: Tenax GC (0.13 g, 60/80 mesh) or Porapak Q (1 g, 60/80 mesh)	Landfill gas	Tenax GC tubes: 25 mL gas drawn through the tube at ambient temperature, via a syringe; Porapak Q tubes: 100 mL gas drawn through the tube at -80°C, via a syringe	alkanes, cycloalkanes, alkenes, aromatic hydrocarbons, terpenes, halogenated hydrocarbons, alcohols, ketones, esters, ethers, organosulfur compounds	2.6 to 650 mg·m ⁻³	TD – GC – MS (GC with 80/100 mesh Chromosorb 101 packed column (1 m x 2 mm ID) for analysis of the Porapak Q tubes, and SE30 capillary column (50 m x 0.3 mm ID) for the analysis of the Tenax GC tubes – VG Micro-mass MM16F MS)	[140], [141]
Tenax GC	Landfill gas	Sampling at 10 - 15 mL·min ⁻¹ during 72 h by means of electric suction pump	12 halogenated aliphatic hydrocarbons; 10 aromatic hydrocarbons and phenolic compounds; 9 halogenated benzenes	< 0.01 – 143 mg·m ⁻³	TD – GC – FID	[143]
Multibed (1:1:1 volume ratio): Tenax TA (80/100 mesh) + Chromosorb 102 (80/100 mesh) + Carbosieve SIII (60/80 mesh)	Landfill gas	500 mL landfill gas passed through the sorbent tube at 50 mL·min ⁻¹ Tubes stored at 4°C and analyzed within 24 h	Over 140 VOCs, belonging to several chemical groups: alkanes, aromatic compounds, cycloalkanes, terpenes, alcohols and ketones, halogenated compounds	(mg·m ⁻³) alkanes (302-1543); aromatic compounds (94-1906); cycloalkanes (80-487); terpenes (35-652); alcohols and ketones (2-2069); halogenated compounds (327-1239)	TD-GC-MS (Perkin Elmer ATD 50 with second refocusing trap Tenax TA – HP 5890 GC with Restek RTX-1 column (60 m x 0.32 mm x 1.5 µm) – HP 5970 MS) LOD between 0.02 (decane) and 0.1 mg·m ⁻³ (dichloromethane)	[127], [144]
Two different single bed tubes in series: Tenax TA (60/80 mesh) and Carbosieve III (60/80 mesh)	Landfill gas	100 mL gas drawn through the tubes via a manual sampling Gastec pump	Alkanes, aromatic hydrocarbons, organosulfur compounds, halogenated compounds, ketones, alcohols, esters, terpenes, siloxanes, trimethylsilanol	< 0 to 320 mg·Nm ⁻³	TD-GC-MS (Perkin Elmer TurboMatrix 650 ATD – Perkin Elmer Clarus 600 GC with Supelco Equity-1 column 60 m x 0,25 mm x 1,0 µm – Perkin Elmer Clarus 600T MS)	[69]
Commercial ORBO 32 tubes (activated coconut charcoal matrix (24–40 mesh) divided into beds A (400 mg) and B (200 mg) (Sigma–Aldrich)	WWTP biogas	10 L sampled at 1 L·min ⁻¹	Siloxanes (L2, L3, L4, L5, D3, D4, D5, D6) and TMS	(mg·Nm ⁻³) TMS: <0.02 – 0.9; L2: <0.01; L3: 0.05 – 0.28; L4: <0.01 – 0.31; L5: <0.0 – 0.8; D3: <0.01 – 0.2; D4: 1.5 – 10.1; D5: 12.5 – 124; D6: 0.4 – 0.5.	Solvent desorption – GC – MS (n-hexane as solvent – Agilent 6890N GC with DB-624 column (6%-cyanopropylphenyl–94%-dimethylpolysiloxane 30 m x 0.25 mm x 1.4 µm) – Agilent 5975B MS). LOQ : 0.02 mg·m ⁻³ for TMS and 0.01 mg·m ⁻³ for the siloxanes	[102]

Table 3: continued

Adsorbent tube composition	Sampled gas	Sampling conditions	Characterized compounds	Concentration range observed	Analytical method	References
Three tubes of one and the same adsorbent in series. Three adsorbents evaluated: coconut-activated carbon (10-25 mesh), coal-activated carbon (10-25 mesh), silica gel (5-10 mesh)	Landfill gas	Sampling 18 L of gas for 30 min (600 mL·min ⁻¹)	Siloxanes (total)	Average concentrations total siloxanes (mg·Nm ⁻³) * Coconut- activated carbon: 7.91±1.86 * Coal-activated carbon: 7.67±2.12 * Silica gel: 5.54±2.53	Solvent desorption – GC – MS (HPLC-grade methanol as solvent – Agilent 6890 GC with Agilent HP-1MS column (300 m × 0.25 mm × 0.25 µm) – Agilent 5973N MS) LOD of the targeted siloxanes range from 0.88 to 2.46 µg·mL ⁻¹	[119]
Four activated carbon tubes in series (~700 mg activated carbon per tube)	Landfill gas and AD biogas	Sampling at 0.2 L·min ⁻¹ flow rate. 6 L gas sampled on one set of 4 tubes in series; 12 L gas sampled on another set of 4 tubes in series	Siloxanes (trimethylsilanol, L2, D3, L3, D4, D5, D6)	(µg·m ⁻³) TMS : 195 – 3800 L2 : 16 – 313 D3 : 190 - 203 L3 : 111 D4 : 550 – 2725 D5 : 609 – 724 D6 : 60 - 253	TD – GC – MS (Tekmar Autocan TDS – HP5890 II GC – HP5972 MS)	[120]
Tenax TA	Biogas and bio-methane	Altef bag sampling and subsequent transfer to sorbent tubes via 3 methods, each one transferring 100 mL gas from the bag to the sorbent tube: 1) gas-tight syringe, flow rate 200 mL·min ⁻¹ 2) “easy VOC™ grab sampler”, flow rate 500-600 mL·min ⁻¹ 3) laminar flowmeter + sampling pump, flow rate 50 mL·min ⁻¹	130 VOCs from different families: alkanes (heptane, octane, decane, undecane, dodecane, tridecane, tetradecane, decahydronaphthalene and methyldecahydronaphthalene), aromatic hydrocarbons (toluene, o-xylene), terpenes (α -pinene, β -pinene, camphene, 3-carene, d-limonene, <i>p</i> -cymene), alcohols (1-propanol, 2-butanol), ketones (2-butanone, 3-pentanone, 2-pentanone), esters (ethyl propanoate, ethyl butanoate, ethyl pentanoate), furans (2-methylfuran, ethyl-furan) and sulfur compounds (dimethylsulfide, dimethyl disulfide, thiophene, 2-methylthiophene, tetrahydrothiophene, 1-propanethiol)	30 µg·m ⁻³ to 35 mg·m ⁻³	TD – GC – MS/FID (Markes TD100) – Agilent 6890N GC with column BPX5 (5% phenyl polysilphenylene-siloxane, polysilphenylene-siloxane, 50 m x 0.32 mm x 1 µm) – Agilent 5975C MS or FID)	[21]

Table 3: continued

Adsorbent tube composition	Sampled gas	Sampling conditions	Characterized compounds	Concentration range observed	Analytical method	References
Tenax TA	AD biogas and biomethane (food wastes)	Altef bag sampling and subsequent transfer to sorbent tube at a controlled flow over 1-2 min	Terpenes (dominant species were d-limonene, <i>p</i> -cymene, α -pinene, β -pinene)	Total terpene concentration ($\text{mg}\cdot\text{m}^{-3}$): In biogas: 360 – 1650 In biomethane: 5 – 240	TD – GC – MS/FID (Markes TD100 – Agilent 6890N GC with 5% phenyl polysilphenylene-siloxane, BPX5, 50 m x 0.32 mm x 1 μm column – Agilent 5975C MS or FID)	[145]
Single bed: Tenax TA or Carbotrap 349 (multibed packed with Carboxen Y, Carboxen B, Carboxen 1003)	Landfill gas	1-2 L Tedlar bag and subsequent transfer to sorbent tube (8260 US EPA method)	119 VOCs including aliphatic and aromatic compounds, alcohols, ketones, esters, ethers, carbamates, terpenes, siloxanes, (in)organic sulfur compounds and halogenated compounds.	1.85·10 ⁻² to 72.6 $\text{mg}\cdot\text{Nm}^{-3}$ Total halogen content in all the samples was < 22 $\text{mg Cl}\cdot\text{Nm}^{-3}$	TD-GC-MS (horizontal Gerstel TDS-2 – Agilent 6890N GC with Agilent DB-624 column (30 m x 0.25 mm x 1.4 μm) – Agilent 5973N MS)	[112]
Multibed: Carbosieve 111 + Carboxen B + Carboxen C	MSW landfill gas	Pre-evacuated glass vial sampling with subsequent pumped transfer to the tubes (2 L at 200 $\text{mL}\cdot\text{min}^{-1}$)	VOCs (linear and cyclo- alkanes, alkenes, aromatics, poly aromatics, furans, halogenated, aldehyde, alcohols, organosulfur compounds)	0.6 – 102000 ppb	TD-GC-MS (DANI Master TD including a 3-phase quartz refocusing trap (-5°C) – GC column TR-V1 30 m x 0.25 mm ID x 1.4 μm film thickness (Thermo))	[146]
Different adsorbents evaluated: Amberlite XAD-2 or XAD-4, activated carbon type F-400, polyurethane foam	WWTP biogas	Polyethyleneterephthalate bag sampling with subsequent transfer through adsorbent tube at 500 $\text{mL}\cdot\text{min}^{-1}$	Siloxanes (D3, D4, D5, D6)	Not mentioned	Solvent desorption – GC – FID/MS (hexane, cyclohexane or hexamethyldisiloxane as solvent – Varian 3700 GC with SE 54 fused-silica capillary column 50 m, 0.32 mm, 0.25 μm (CS Chromatographie Service Germany) – FID or TSQ 70 MSD)	[147]
Tenax GR	Biogases from different sources (landfill, WWTP and farm AD)	Nalophan bag sampling and subsequent transfer to adsorbent tubes at 90 $\text{mL}\cdot\text{min}^{-1}$	VOCs including organic silicon compounds	Total VOC concentration: 5 – 268 $\text{mg}\cdot\text{m}^{-3}$; Benzene: 0.1 – 2.3 $\text{mg}\cdot\text{m}^{-3}$; Toluene: 0.2 – 11.8 $\text{mg}\cdot\text{m}^{-3}$; Halogenated compounds: <0.1 – 1.3 $\text{mg}\cdot\text{m}^{-3}$; Organosilicon compounds: <0.4 – 10.6 $\text{mg}\cdot\text{m}^{-3}$	TD – GC – MS (Tekmar Purge & Trap Concentrator 3000 TDS – Agilent 6890+ GC – Agilent 5973 N MS)	[57]
Two Tenax GR (200 mg/tube) tubes in series	Biogases from different sources (WWTP, landfills, co-digestion plants)	Nalophan bag sampling and subsequent transfer to 2 sorbent tubes in series at 90 $\text{mL}\cdot\text{min}^{-1}$	Siloxanes (L2, D3, L3, D4, L4, D5, L5) and TMS	Concentration total organic silicon compounds varied from 24 to 2460 $\mu\text{g}\cdot\text{m}^{-3}$. Concentration individual organic silicon compounds ranged from 1 $\mu\text{g}\cdot\text{m}^{-3}$ (L2) – 1.27 $\text{mg}\cdot\text{m}^{-3}$ (D5)	TD-GC-MS (Tekmar Purge & Trap Concentrator 3000 – Agilent 6890+ GC with Agilent HP5 column (30 m x 0.25 mm x 1 μm) – Agilent 5973N MS)	[59]

Table 3: continued

Adsorbent tube composition	Sampled gas	Sampling conditions	Characterized compounds	Concentration range observed	Analytical method	References
Multibed: Carbotrap B (20/40 mesh, 70 mg) + Carbopack X (40/60 mesh, 100 mg) + Carboxen 569 (20/45 mesh, 90 mg)	Landfill gas	Supel™ Inert Film bag sampling and immediate transfer to sorbent tubes via a pump, at 100 mL·min ⁻¹ . Drawing 100 and 250 mL gas through the sorbent tubes was evaluated	VOCs (alkanes, aromatic hydrocarbons, alcohols, ketones, furans, halocarbons, aldehydes, esters, terpenes, chlorinated compounds); sulfur and nitrogen compounds; VMS (TMS, linear and cyclic siloxanes). Total amount identified compounds: 117	100 mL drawn through tube: 1.3 µg·m ⁻³ (1-methylnaphthalene) to 458 000 µg·m ⁻³ (<i>p</i> -cy-mene); 250 mL drawn through tube: 1 µg·m ⁻³ (1-methylnaphthalene and 2-methylnaphthalene) to 340 000 µg·m ⁻³ (<i>p</i> -cy-mene).	TD – GC – MS (Perkin Elmer ATD 400 – Thermo Quest Trace 2000 GC with column DB-624, 60 m x 0.25 mm x 1.4 µm – Thermo Quest Trace Finnigan MSD)	[42]
Silica gel (particle size 1–3 mm) (2 g)	WWTP biogas. Raw biogas (RH _{20°C} >85%) and biogas dried by refrigeration (RH _{20°C} =38%) were sampled	Sampling into evacuated 15 L stainless-steel Tekmar canisters with subsequent transfer through adsorbent tube at 1 L·min ⁻¹	Siloxanes (L2, D3, D4, D5)	Total siloxane concentrations (mg·m ⁻³): raw biogas: 16.2 dried biogas: 14.8	TD – GC – MS/AES (Tekmar 6000 TD unit with Tekmar cryofocusing module – HP 5890 II GC with DB-5 column 30 m x 0.32 mm x 0.25 µm – HP 5971 A MS operated in parallel with a HP 5921 A AES)	[99]
Multibed bed: Tenax TA and Unicarb (400 mg total)	WWTP biogas	500 mL biogas sampled through the tube via a sampling pump at 50 mL·min ⁻¹	Volatile organic and inorganic sulfur compounds; (H)VOCs; terpenes; alkanes	0.005 – 95 mg·m ⁻³	TD – GC – MS (Unity TDS + Ultra A automatic sampler from Markes International – Agilent 7890A GC – Agilent 5975C MS)	[20]
Tenax TA (60/80 mesh)	AD biogas and MSW landfill gas	100 mL, sampled at ~100 mL·min ⁻¹	Siloxanes (L2, L3 L4, D3, D4, D5), trimethylsilanol and halogenated compounds	Siloxanes: 0.04 – 27.05 mg·m ⁻³ ; Trimethylsilanol: <0.01 – 2 mg·m ⁻³ ; Halogens: <0.1 – 7 mg·m ⁻³	TD–GC–MS (Perkin Elmer ATD 400 – HP 5890 GC – HP 5972 MS) LOD for siloxanes: 30 µg·m ⁻³ ; for halogenated compounds: 100 µg·m ⁻³	[67]
Tenax TA	Biogas and biomethane from different sources (landfills, WWTP, AD of energy crops, by-products from food industry and manure)	Controlled flow of the gas passed through the adsorbent over a short time (1-4 min)	VOCs with boiling point in the range 70-320°C : Alkanes (nonane, decane, undecane, dodecane, tridecane); linear, branched or cyclical hydrocarbons (C5 to C13, decahydronaphthalene, methyl decahydronaphthalene, etc.); aromatic hydrocarbons (benzene, toluene, xylenes, trimethylbenzenes, tetramethylbenzenes, etc.); terpenes (<i>p</i> -cymene, d-limonene, α-pinene, β-pinene, 3-carene, santolina triene); chlorinated and fluorinated hydrocarbon; esters; ketones (2-butanone, pentanones, hexanones and heptanones, furans); sulfur compounds (methylmercaptan, DMS, DMDS); dioxolanes; siloxanes (decamethylcyclopentasiloxane (D5)); nitrogen compound ethylmethylpyridine	Concentration individual compounds in biogases: <0 – 190 g·m ⁻³ . Typical total VOC concentrations in biogases: 20 – 700 mg·m ⁻³ Typical total VOC concentrations in biomethanes: <10 mg·m ⁻³	TD – GC – MS/FID (Perkin Elmer TurboMatrix 650 TDS – Agilent 6890N GC with column 5% phenyl polysilphenylene-siloxane, BPX5, 50 m x 0.32 mm x 1 µm) -Agilent 5975C MS of FID)	[149]

Table 3: continued

Adsorbent tube	Sampled gas	Sampling	Characterized	Concentration range	Analytical method	References
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composition		conditions	compounds	observed	
Tenax TA (30/60 mesh, 200 mg) in inert coated stainless-steel tubes (8.89 mm length, 6.35 mm ID)	AD biogas (from 3 different AD plants)	100 mL·min ⁻¹ during 30 s or 1 min	51 VOCs (organic silicon compounds, terpenes, BTEX, furanes, ketones, alcohols, alkanes, esters and sulfur-organic compounds)	0.01 mg·Nm ⁻³ (decamethyltetrasiloxane) to 359.84 mg·Nm ⁻³ (<i>p</i> -cy-mene)	TD-GC-MS (Shimadzu TD20 – Shimadzu QP2010Plus with column Restek Rxi-5MS 60 m x 0.25 mm x 1 µm) [150]
Carbon cartridges filled with graphitized and activated carbon	WWTP biogas and biomethane	Different volumes sampled in the range 40 mL – 2 L	Siloxanes, VOCs (aromatics, terpenes, alkanes, halogenated compounds, organosulfur compounds)	total volatile silicon in biogas: >2 mg·m ⁻³ ; in biomethane: > 0.03 mg·m ⁻³ Aromatics in biogas: 225 µg·m ⁻³ ; in biomethane: 0.8 µg·m ⁻³ Terpenes in biogas: 65.9 µg·m ⁻³ ; in biomethane: <0.5 µg·m ⁻³ Alkanes in biogas: 1540 µg·m ⁻³ ; in biomethane: <1 µg·m ⁻³ Halogenated in biogas: 184 µg·m ⁻³ ; in biomethane: <3 µg·m ⁻³ Organosulfur in biogas: 114 µg·m ⁻³ ; in biomethane: <0.5 µg·m ⁻³	TD-GC-MS (Chrompack CP 4020 TD unit – Trace Ultra GC with DB1-MS column (50 m length, 0.25 mm inner diameter, 0.25 mm film thickness) – SQ MS (Thermo Fisher Scientific, 168 3rd Ave, Waltham, MA 02451 USA). [151]
XAD-2	WWTP, landfill and AD biogas and biomethane	1 L·min ⁻¹ during 1 h	Semi-VOCs	0.10–647.9 ppb _v	Solvent desorption (ethyl acetate) – GC – ToF-MS (Agilent 7890 gas chromatograph and Agilent 7200 quadrupole time-of-flight mass spectrometer) [152]
Two commercial (Supelco) tube compositions tested, each containing two beds of the sorbent: ORBO 609 Amberlite XAD-2 tube or ORBO Charcoal tube	MSW landfill gas (raw and treated), WWTP and AD biogas and biomethane	Raw biogas: 100 mL·min ⁻¹ through each individual tube. 1 – 5 L collected Treated biogas and biomethane: 500 mL·min ⁻¹ through each individual tube. 20 L collected	Oxygenated-organic compounds, halogenated compounds, mono- and poly-aromatic hydrocarbons, alkanes, cycloalkanes, alkenes, terpenes, siloxanes, sulfur compounds	Raw biogases: total concentration ranges (ng·mL ⁻¹): oxygenated compounds: <0 – 300; halogenated compounds: <0 – 300; monoaromatic hydrocarbons: 0 – 16000; alkanes: <0 – 1400; terpenes: 0 – 4200; siloxanes: 0 – 1300	Solvent desorption – GCxGC – MS (Pressurized Liquid Extraction, Dionex™ ASE 200 system with acetone/dichloromethane in 1:1 volume ratio – TRACE GC × GC™ Thermo-Fischer Scientific. First dimension column: Agilent nonpolar DB-5MS (30 m × 0.25 µm; 0.25 µm); second dimension column: Agilent semi-polar DB-17 (1.35 m × 0.1 µm; 0.1 µm)) – ISQ™ quadrupole MS) [5] LOD: 1 ng·Nm ⁻³ for octamethylcyclotetrasiloxane, and 9 ng·Nm ⁻³ for toluene LOQ: 1.5 ng·Nm ⁻³ for octamethylcyclotetrasiloxane and 14 ng·Nm ⁻³ for toluene
Carbotrap™ (40-60 mesh, 10 cm × 4 mm ID adsorbent bed, packed between silanized glass wool plugs in a silanized glass tube)	MSW landfill gas	Upstream the adsorbent tube: condensate trap + 5 µm Teflon particle filter + guard column (OV-3 on Chromasorb WAW-DMCS 80/100 mesh). 5 L landfill gas sampled at 300 mL·min ⁻¹ and subsequently purged with dry N ₂ + protected from light and refrigerated until analysis	Dimethylmercury	~30 ng·m ⁻³	TD – GC – CVAFS (isothermal GC 80 ± 2°C; 1 m × 4 mm ID column of 15% OV-3 on Chromasorb WAW-DMCS 80/100 mesh) + GC output to pyrolytic cracking column (700°C) [153]–[155]

1387 Table 3 also indicates that adsorbent tubes have seldom been used for the trapping of volatile metal(loid)
1388 compounds in biogas, landfill gas or biomethane. Some publications [156]–[159] did, however, address this
1389 topic for volatile mercury (Hg), lead (Pb) and arsenic (As) traces in air. Although these publications are
1390 slightly dated (no recent studies were found on that topic), they still provide methods that could be applied
1391 in the modern context of biogas, landfill gas and biomethane. Ballantine and Zoller [156] evaluated the
1392 trapping efficiency of several adsorbent phases for methylmercury chloride (MMC) and dimethyl-mercury
1393 (DMM) in atmospheric air as follows: 5% FFAP on Gas Chrom Q; 20% Carbowax 20M on Supelcoport;
1394 3% OV-1 on Gas Chrom Q; 3% Hi-eff 8BP on Gas Chrom Q; Chromosorb 101, Chromosorb NAW;
1395 Porapak P; Amberlite XAD-2; and Tenax GC. Chromosorb 101 was the sole material able to significantly
1396 retain MMC and DMM. The collection efficiency of Chromosorb 101 for MMC at 25 °C was $95 \pm 3\%$ and
1397 was found to be independent of the relative humidity of the sampled air [156]. The trapping of DMM (more
1398 volatile than MMC) on Chromosorb 101 was not efficient at ambient temperature (25 °C) (low break-
1399 through volume). Therefore, when targeting this compound, the Chromosorb 101 tubes were cryogenically
1400 maintained at -60 °C and a drying tube containing drierite was placed upstream of the adsorbent tube to
1401 trap humidity and prevent ice clogging or condensation in the adsorbent tube. The drying tube did not retain
1402 DMM. In this way, the collection efficiency of Chromosorb 101 for DMM was $96 \pm 2\%$ [156]. Regarding
1403 lead, the suitability of several adsorbents to trap tetraalkyllead compounds from air has been investigated
1404 [157]–[159]. Porapak, Amberlite XAD-2, XAD-4 and XAD-7, Tenax, Chromosorb, active charcoal and
1405 polyurethane foam (PUF) were evaluated for the preconcentration of synthetic air doped with tetraethyllead
1406 (Et_4Pb). Porapak and Tenax were found to be the only suitable adsorbents, yielding Et_4Pb recoveries of ~92
1407 and ~96%, respectively. The recoveries from PUF, XAD-4, XAD-2, XAD-7, activated charcoal and Chro-
1408 mosorb were <10, <20, <5, <5, <30 and <60%, respectively [157]. Synthetic gases doped with gasoline and
1409 other tetraalkyllead compounds (tetramethyllead (TML), trimethylethyllead (TMEL), dimethyldiethyllead
1410 (DMDEL), methyltriethyllead (MTEL), and tetraethyllead (TEL or Et_4Pb)) were then loaded on separate
1411 Porapak and Tenax tubes, which were found to complement each other as follows: Tenax did not trap the
1412 more volatile TML and TMEL as efficiently as Porapak did. Tenax was, however, more efficient than
1413 Porapak in trapping and desorbing the less volatile DMDEL, MTEL and TEL. A multibed tube with Tenax
1414 as the front bed and Porapak as the back bed was accordingly found to be suitable to trap tetraalkyllead
1415 compounds in real air matrices since it yielded higher recoveries than the separate Tenax and Porapak beds
1416 for the 5 tetraalkyllead compounds [157]. Single Porapak Q adsorbent tubes were, however, found to effi-
1417 ciently (>90%) recover all 5 tetraalkyllead compounds and to keep those analytes stable for 14 days when
1418 tubes were stored at -10 °C [158]. Porapak N and Porapak QS were also specifically considered to trap
1419 TML and TEL [159]. Porapak QS was more suitable for the trapping of TML: the breakthrough volume of
1420 TML at 30 °C was $170 \text{ L}\cdot\text{g}^{-1}$ Porapak QS against $64 \text{ L}\cdot\text{g}^{-1}$ Porapak N, and recoveries from Porapak QS were
1421 > 100% against ~90% on Porapak N. Porapak N was more efficient for the recovery of TEL (~70% against
1422 ~50% recovery from Porapak QS) [159]. Finally, the NIOSH method 6001 for trapping gaseous arsine
1423 (AsH_3) in air [160] recommends the use of solid sorbent tubes filled with two beds of activated coconut
1424 shell charcoal. With a sampling flow rate between 0.01 and $0.2 \text{ L}\cdot\text{min}^{-1}$ and a sampled volume of $0.1 - 10$
1425 L for a concentration range $0.001 - 0.2 \text{ mg}\cdot\text{m}^{-3}$, the sample stability on the tubes is guaranteed by the method
1426 to be at least 6 days at 25 °C. Charcoal beds are solvent desorbed in 0.01 M HNO_3 with sonication. Note
1427 that other As species can adsorb onto the charcoal beds and that the analysis technique is not species spe-
1428 cific, so only the total As content is reported [160].

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1433 **3.1.2. Chemisorption (chemotrapping) and on-tube derivatization**

1434 In contrast to physical sorption, chemical sorption (chemisorption) involves a chemical reaction, with as-
1435 sociated bond breaking and creation, between the target analyte and a specific chemical (derivatizing agent)
1436 immobilized on a solid sorbent material placed in a tube (“chemotrap”). The purpose is to produce a target
1437 analyte derivative whose stability is enhanced (e.g., lower vapor pressure) or whose analysis is facilitated
1438 compared to the parent analyte. This approach is appropriate in cases that an analyte is not retained by
1439 physisorption on solid adsorbents due to lack of affinity for the adsorbent material or due to a very high
1440 volatility [23], [39], [73]. Ideally, parent target analytes are quantitatively stripped off the sampled gas, and
1441 the generated derivative preserves the identity characteristics of the parent analyte so that post-trapping
1442 speciation is secured [161]. In air monitoring, a derivatizing agent commonly used is 2,4-dinitrophenylhy-
1443 drazone (DNPH), which derivatizes carbonyl compounds (e.g., aldehydes) into hydrazones [23], [39], [73].
1444 Sorbents with large, open pores, such as silica gel and Chromosorb W, are often used as support for the
1445 derivatizing agent: the wider pore space facilitates reactions, enables loading more derivatizing agent and
1446 provides more potential sorption sites for the reaction product. Note that the occurrence of chemical reac-
1447 tions in chemisorption potentially results in slower kinetics than in physisorption; therefore, lower sampling
1448 flow rates or larger sorbent beds are advised to reach sufficient contact times between analytes and derivat-
1449 izing agents and as such to complete the reactions. Solvent desorption of the chemotraps is the state-of-the
1450 art technique since the excess derivatizing agent would cause analytical problems upon thermal desorption
1451 [17], [23], [25]. Chin et al. [152] applied this approach and sampled 23 biogas and biomethane samples
1452 from various production sites (landfills, wastewater treatment plants and anaerobic digestion plants treating
1453 diverse feedstocks) through DNPH-loaded silica sorbent tubes at 1 L·min⁻¹ for 1 min for the targeted pre-
1454 concentration of carbonyls. Acetonitrile was used as the solvent to extract carbonyls from the DNPH-silica
1455 tubes.

1456 In the field of biogas and biomethane, one element for which preconcentration by chemotrapping with on-
1457 tube derivatization is particularly interesting is arsenic (As) and its different volatile species. Several liquid
1458 or solid agents, such as H₂O₂, NaOCl, Hg(NO₃)₂, activated charcoal, KI, HNO₃ and AgNO₃, react with and
1459 have been used to chemotrap volatile As species [161], [162]. Mestrot et al. [161] and Uroic et al. [25] used
1460 the same AgNO₃-impregnated silica gel tube method to quantitatively trap volatile arsenic from paddy soil
1461 emissions and natural gas, respectively. While Uroic et al. [25] only examined total As from spiked trime-
1462 thylarsine, the chemotrapping mechanism used by Mestrot et al. relied on oxidation of the volatile arsenicals
1463 to their pentavalent oxy-species (arsine to arsenate, methylarsine to monomethylarsonic acid, dimethylar-
1464 sine to dimethylarsinic acid, and trimethylarsine to trimethylarsine oxide) which preserve the As-C bond
1465 and thus the speciation of the parent analytes [161]. Silver nitrate-impregnated silica gel absorption tubes
1466 were prepared on commercial silica gel tubes (glass tubes, 225 mg silica gel split into 2 compartments and
1467 plugged with active charcoal foam and glass wool) where on different concentrations of silver nitrate solu-
1468 tions (0%, 0.001%, 0.01%, 0.1% and 1% (m/v)) were impregnated for the natural gas study [25]. Natural
1469 gas samples were collected on gas fields in SulfinertTM surface-treated gas cylinders and subsequently trans-
1470 ferred to the AgNO₃-silica gel tubes, which were themselves field-deployable, for preconcentration of the

1471 arsenicals. Liquid desorption with boiling hot nitric acid was used to extract the trapped arsenicals from the
1472 tubes. Extraction efficiencies of > 90% were reached this way [25]. Krupp et al. [17], who introduced this
1473 method, pointed out that the non-100% extraction efficiency of alkylated arsenicals from the chemotraps
1474 may be due to incomplete sorption on the tubes owing to their nonpolarity and low boiling point, or to
1475 irreversible sorption. The absorption efficiency of TMA on the chemotraps as a function of the impregnated
1476 AgNO₃ concentration was then studied. An absorption of 10.3% TMA was already recorded for nonim-
1477 pregnated silica gel, but 98% absorption was reached in silica gel tubes impregnated with 0.01% AgNO₃.
1478 However, to keep the breakthrough <1% of the loaded TMA amount and hence guarantee an absorption
1479 efficiency of >99.5% TMA, the impregnated AgNO₃ concentration had to be at least 0.1%_{m/v}. Silica gel
1480 tubes impregnated with 1%_{m/v} AgNO₃ could quantitatively accumulate up to 4.8 µg As without break-
1481 through (>99.8% absorption efficiency), which is a sufficient achievement since the authors found that real
1482 natural gas samples did not contain more than 2.8 µg As per chemotrap for 20 L gas samples [25]. The
1483 authors also found that hydrocarbons and volatile sulfur compounds present in real natural gas had no effect
1484 on the absorption efficiency of TMA in the AgNO₃-silica gel chemotraps. The limits of detection of 1 mg
1485 TMA·m⁻³ in a 20 L gas sample were found for the blank chemotrap tubes [25]. Yet this LOD is satisfactory
1486 for gas industry requirements [25], it is relatively high and Mestrot et al. [161] found that the glass wool of
1487 the tubes was the main As contamination source (146 ng As per tube); the foam contained 6.6 ng As per
1488 tube, and the AgNO₃-impregnated silica gel contained 4.2 ng As per tube. Mestrot et al. [163] further em-
1489 ployed their AgNO₃-impregnated silica gel chemotraps to study the arsenic volatilization in the biogas of
1490 model anaerobic digesters as a function of the initial As species (Roxarsone, monomethylarsonic acid
1491 (MMA(V)), As(V) or no initial As) amended in the organic matter feedstock. The chemotraps were placed
1492 on the outlet of the model reactors. Total As and speciation analysis were performed every 2 weeks from
1493 the harvested traps. Over a 42-day period, the authors found that model digesters volatilized 25 ± 4 ng of
1494 As (non-As-amended), 51 ± 23 ng of As (Roxarsone-amended), 177 ± 28 ng of As (As(V)-amended) and
1495 413 ± 148 ng of As (MMA(V)-amended), with trimethylarsine being the dominant species in all cases
1496 [163].

1497 Further, gaseous mercury can also be trapped via chemisorption on iodine (I₂)-impregnated silica gel, where
1498 it is retained as HgI₂, as explained in the ISO 6978-1:2003 standard method for the determination of mer-
1499 cury in natural gas [29], [164]. No speciation can be performed with this method, as all Hg species are
1500 reduced to Hg⁰. The sampling pressures on the chemotraps can reach up to 400 bar, and the method is
1501 convenient for Hg concentrations in the range of 0.1 – 5000 µg·m⁻³. The total Hg content is quantified by
1502 measuring the absorbance or fluorescence of Hg⁰ vapor at 253.7 nm. Similarly, Lindberg et al. [153], [154]
1503 collected total gaseous mercury (Hg⁰, Hg(II) and organic Hg species) in landfill gas through activated io-
1504 dated charcoal traps that were heated slightly above landfill gas temperatures (~50 °C) to avoid condensa-
1505 tion of compounds onto the sorption sites. Mercury species were recovered from the iodated charcoal traps
1506 by acid leaching the traps in a hot-refluxing HNO₃/H₂SO₄ system. The acid leachate from that system was
1507 further oxidized by a 0.01 N BrCl solution. Both acid and oxidized leachates were then analyzed by cold
1508 vapor-atomic fluorescence spectrometry (CV-AFS) at 253.7 nm.

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1511 **3.1.3. Amalgamation: trapping of volatile mercury species**

1512 Mercury species, including both elemental (Hg^0) and organic or inorganic forms such as CH_3HgCl or HgCl_2 ,
1513 occur at $\text{ng}\cdot\text{m}^{-3}$ to $\text{mg}\cdot\text{m}^{-3}$ levels in natural gas [81], [165], [166] and in landfill gas [153], [154], [167]–
1514 [170]. These species can specifically be preconcentrated from those gases by the chemical amalgamation
1515 reaction between mercury and other noble metals, such as gold (Au), platinum (Pt), silver (Ag), palladium
1516 (Pd), and copper (Cu) [165], [169]–[172]. Quartz gas sampling tubes (e.g. ID 5 mm, L 160 mm) packed
1517 with noble metal-coated sand beds or containing noble metal gauzes have especially been used for that
1518 purpose [165]. For an amalgam to be formed, both mercury and the noble metal must be in their elemental
1519 state [171], although noble metals such as Au and Au/Pt alloys also react with inorganic and organic Hg
1520 species [164], [165]. Frech et al. [165] evaluated the efficiency of several noble metals (Au, Ag, Au/Pt
1521 alloy) for the amalgamation of gaseous elemental mercury (Hg^0) and dimethylmercury ($(\text{CH}_3)_2\text{Hg}$) in nat-
1522 ural gas as follows: crumpled Au wire, Ag wire, Au/Pt wire or coiled Au/Pt gauzes were packed in quartz
1523 test tubes. For Hg^0 , silver was found to yield poorer amalgamation efficiencies than gold and gold/platinum
1524 alloy. The Au/Pt test tubes quantitatively trapped Hg^0 at flow rates up to $9.3 \text{ L}\cdot\text{min}^{-1}$, compared with 8.0
1525 and $2.0 \text{ L}\cdot\text{min}^{-1}$ for Au and Ag test tubes, respectively. Inasmuch as silver is also known to inefficiently
1526 amalgamate organic Hg species, the authors concluded that silver was an unsuitable material for both spe-
1527 cies-specific and total Hg characterization. Au/Pt tubes proved to collect metallic Hg^0 with a greater effi-
1528 ciency than that of Au tubes in real natural gas, and the organic $(\text{CH}_3)_2\text{Hg}$ species in natural gas was also
1529 quantitatively amalgamated onto Au/Pt tubes [165], although with an efficiency lower than that of metallic
1530 Hg^0 [164]. The noble metal alloy Au/Pt hence seems to deliver the highest quantitative amalgamation effi-
1531 ciencies for both metallic and organic Hg species [165]. Nevertheless, simple Au tubes have been most
1532 often used for both natural gas and landfill gas mercury investigations [46], [80], [153], [169], [170].

1533 Preconditioning and properly storing newly assembled amalgamation tubes is as important as it is for ad-
1534 sorbent tubes. New amalgamation tubes are typically blanked at $500 \text{ }^\circ\text{C}$ [81], [170], [173], [174] or $800 \text{ }^\circ\text{C}$
1535 [165] under a continuous Hg-free gas flow (e.g. Ar, N_2 , air) for several hours. Sealing blanked amalgama-
1536 tion tubes to avoid passive uptake of Hg traces from the ambient atmosphere is most efficient with gas-tight
1537 Teflon plugs [170], [173], [174] and refrigerating the tubes during the storage period until utilization was
1538 found to guarantee blank levels up to 600 h [173].

1539 To recover amalgamated Hg species from the tubes and regenerate them for reuse, the amalgam must be
1540 decomposed, which occurs by heating the tubes. During this thermal desorption, inorganic and organic Hg
1541 species are reduced and released as gaseous Hg^0 [164]. A two-stage amalgamation-thermal desorption pro-
1542 cedure is often appropriate: the sampled noble metal packed tubes are first thermally desorbed at $400 - 800$
1543 $^\circ\text{C}$ for 50-100 s while a Hg-free carrier gas (e.g., Ar) blows the released mercury into a second calibrated
1544 amalgamation trap, typically packed with Au or Au/Pt and permanently installed in the analytical device
1545 [80], [165], [171], [173]. This tube is itself subsequently quickly thermally desorbed (e.g., $500 \text{ }^\circ\text{C}$ for 15 s
1546 [80]), and the as such recovered total Hg^0 vapor is carried to the detector, typically either a cold vapor
1547 atomic absorption spectrometer (CVAAS) or a cold vapor atomic fluorescence spectrometer (CVAFS) op-
1548 erated at 253.7 nm , to be quantified. This method has been validated and standardized for field measure-
1549 ments of Hg in natural gas in the norm ISO 6978-2:2003 [30]. The speciation of distinct Hg species is more
1550 complex and was reviewed [164].

1551 Important practical considerations for the optimal use of noble metal (Au/Pt) tubes for the amalgamation
1552 of Hg^0 and $(\text{CH}_3)_2\text{Hg}$ in natural gas were highlighted by Frech et al. [165]. First, the highest quantitative

1553 trapping efficiencies are obtained for both Hg species when the Au/Pt tubes are heated to 80 °C during
1554 sampling, since such temperatures inhibit the condensation of other organic natural gas constituents on the
1555 noble metal surfaces, which would otherwise passivate the amalgamation sites. After sampling, the tubes
1556 can be washed with a few milliliters isooctane and methanol to eliminate potential condensates, and surplus
1557 washing solvent can then be removed by flushing the tubes with Hg-free air. Second, as noble metal surfaces
1558 are gradually covered and inactivated by natural gas constituents other than Hg during sampling, the sam-
1559 pled volumes should be limited to ~10 L (for tubes packed with 1.5 – 4.5 g Au/Pt wire) to guarantee a
1560 quantitative Hg-trapping efficiency and minimize the breakthrough of Hg species. Additionally, sampling
1561 flow rates should be kept low (2 or 3 L·min⁻¹ for tubes packed with 1.5 – 4.5 g Au/Pt wire) to increase the
1562 residence time of Hg species in the tube and thus increase the contact opportunities with amalgamation
1563 sites. Finally, as amalgamated Hg tends to migrate into the inner layers of the noble metal surfaces, espe-
1564 cially when thermal desorption of the tubes is not performed within hours after sampling, and to only slowly
1565 get released from these inner layers during thermal desorption, memory effects can build up across repeated
1566 use of amalgamation tubes. These undesirable effects can be mitigated by coating support materials, such
1567 as sand, silica or glass beads, with highly dispersed thin noble metal layers, e.g., via vapor deposition of
1568 noble metal wire [165], [173], concomitantly increasing the available amalgamation surface area. Too
1569 tightly packed noble metal-coated sand beds can nevertheless lead to adverse pressure drops upon gas sam-
1570 pling, leading to the condensation of, e.g., hydrocarbons of natural gas on the noble metal surfaces [165].
1571 In that respect, Larsson et al. [81] investigated three Au/Pt amalgamation tube designs: ‘Standard tubes’
1572 were packed with 2 m crumpled Au/Pt alloy wire (0.1 mm diameter) eventually occupying a length of 50
1573 mm in the tube. ‘Compact tubes’ were obtained by further compressing this crumpled Au/Pt wire to 10 mm
1574 length in the tube. Finally, to simulate a poorly packed or a collapsed noble metal structure, ‘tubes with
1575 orifice’ were prepared as the ‘compact tubes’ but with an additional piercing of a 2 mm wide orifice through
1576 the Au/Pt wire filling. ‘Standard tubes’ gave a quantitative collection (amalgamation plus recovery) when
1577 either air or CH₄ containing 1% H₂S, both enriched with Hg⁰, were sampled at 1 L·min⁻¹, but at 10 L·min⁻¹
1578 the collection efficiency was ~90%. Thus, the collection efficiency was independent of the nature of the
1579 gas tested, even in the presence of H₂S. At 10 L·min⁻¹, the ‘compact tubes’ exhibited a better performance
1580 than that of the ‘standard tubes’ with collection efficiencies ~95%. These results contrast with those of
1581 Frech et al. [165] who observed reduced efficiencies when using more densely packed tubes due to pressure
1582 drops and associated condensation of non-Hg species, which passivated the amalgamation sites. However,
1583 comparing collection efficiencies of various tube configurations is only relevant if the studied gas is the
1584 same, which is not the case between the study of Larsson et al. [81] and that of Frech et al. [165], as the
1585 chemical composition of each (natural) gas might vary and influence the collection efficiencies of Hg⁰. In
1586 that respect, Fernández-Miranda et al. [171] found higher mercury retention percentages on noble metal-
1587 coated materials when acid gases, such as SO₂ and HCl, were present in the sampled gas, indicating that
1588 those gases could contribute to another mercury capture mechanism than the sole amalgamation mecha-
1589 nism. For the ‘tubes with orifice’, Hg⁰ collection efficiencies rose from 29 to 44% when the gas sampling
1590 flow rate increased from 1 to 10 L·min⁻¹. A transition from laminar to turbulent gas flow regime within the
1591 orifice in the Au/Pt filling could explain the higher collection efficiencies at higher flow rates, with a larger
1592 fraction of the gas penetrating the compacted Au/Pt material surrounding the orifice owing to the higher
1593 pressure under turbulent flow conditions [81]. This highlights the importance of homogeneously packing
1594 amalgamation tubes.

1595 Lastly, Hg species have also been preconcentrated by amalgamation using the solid-phase microextraction
1596 (SPME) approach by coating fibers with noble metals. Romero et al. [172] compared three palladium (Pd)
1597 supports for the SPME of Hg⁰ vapors: a pure Pd-wire, a Pd-coated stainless-steel wire and a Pd-coated
1598 silica fiber, all three implemented as the ‘fiber’ in the needle of a typical SPME device. After 30 min of
1599 contact with Hg-loaded gases during which Hg⁰ amalgamated on the Pd support, those modified SPME
1600 fibers were thermally desorbed, and released Hg species were analyzed by atomic absorption spectrometry.
1601 Hg⁰ amalgamation onto the Pd-wire yielded the highest performance regarding the limit of detection, sen-
1602 sitivity and fiber lifetime; nonetheless, the mechanical resistance of such noble metal wires was too weak
1603 for a routine assembly in a SPME device. Since Pd-coated stainless-steel wires had short lifetimes and gave
1604 low Hg-collection efficiencies, Pd-coated silica fibers, yielding high Hg-collection performances and easy
1605 assembly in a SPME needle, were the best compromise.

1606

1607 **3.1.4. Solid phase microextraction**

1608 Solid phase microextraction (SPME) is a preconcentration technique based on the passive absorption or
1609 adsorption of analytes in the gas phase onto a fused silica or metal alloy fiber (~ < 5 cm long) coated with
1610 a thin stationary phase layer (1 or 2 cm long on the fiber). The stationary phase coating (thickness ranging
1611 from 7 – 100 μm) is either a polymeric film for the *absorption* of analytes or a polymeric film embedding
1612 adsorbent particles for the *adsorption* of analytes. Commercially available absorption coatings are based
1613 on polydimethylsiloxane (PDMS), polyacrylate (PA), and polyethylene glycol (PEG), while commercially
1614 available adsorption coatings embed porous adsorbent particles of divinylbenzene (DVB), Carboxen®
1615 (CAR) or a combination of both, usually bound in a PDMS film. Selecting the most appropriate SPME
1616 fiber coating is a crucial yet delicate step [175]. In addition to the literature [176], manufacturers such as
1617 Supelco (Bellefonte, PA, USA) provide SPME fiber selection guides depending on the nature and polarity
1618 of the targeted analytes. The fiber is anchored in a hollow protective needle device (outer diameter < 1
1619 mm): when not in use, the fiber is retrieved inside the protective needle to keep the stationary phase coating
1620 under safe storage conditions. As the fiber is mechanically extremely weak, the needle is used to pierce,
1621 e.g., the septum of a glass vial or of a gas bag containing a gas to analyze. Then, the fiber is exposed to the
1622 gas (atmospheric pressure), allowing analytes to sorb onto the stationary phase coating. A partition equilib-
1623 rium must be reached between analytes present in the bulk gas phase in the sample, and analytes sorbed on
1624 the fiber. Determining this equilibrium and the appropriate exposure time period (from seconds to ~30 min)
1625 is complex as these factors depend on the distribution constant or partition coefficient of each analyte, their
1626 concentration, the thickness of the stationary phase, the temperature, humidity and volume of the gas sur-
1627 rounding the fiber, as reviewed in [176]–[178]. At the end of the fiber exposure time, the fiber is retrieved
1628 in the needle, the SPME needle device is withdrawn from the sample and then generally placed in the heated
1629 injection port of a GC for thermal desorption of the fiber coating. The main shortcomings of SPME are the
1630 limited variety of commercially available coatings and the poor mechanical strength of the fibers (breakage,
1631 stripping of coatings) and of the needle (bending) [172]. Nonetheless, SPME is promoted as an easy and
1632 rapid sampling and preconcentration system with a longer lifetime (numerous sorption-desorption cycles)
1633 than adsorbent tubes and no clogging issues [19]. Critical comparisons between SPME and adsorbent tubes
1634 are available in [36], [112], [146].

1635 The application of SPME has been extensively evaluated and reviewed for the determination of volatile
1636 organic trace compounds in gaseous matrices, especially atmospheric, indoor or workplace air [19], [23],
1637 [176], [179]–[182]. A broad range of other compound classes can be determined via SPME, including the
1638 following: polyaromatic hydrocarbons, halogenated volatile organic compounds, oxygenated organic com-
1639 pounds, pesticides and drugs [19], [176], sulfur compounds [40], [183], siloxanes [36], organic or inorganic
1640 metals and metalloids (Sn, Hg, Se, As, Pb, Mn, etc.) [172], [176].

1641 Table 4 reviews publications on the use of SPME for the determination of trace compounds in biogas,
1642 biomethane and landfill gas. The gas is often first sampled in a gas bag prior to piercing the bag septum
1643 with the SPME needle. The PDMS/DVB, PDMS/CAR and DVB/CAR/PDMS fibers are the most fre-
1644 quently used fiber coatings for the preconcentration of VOCs, siloxanes and volatile organic sulfur com-
1645 pounds. Metal(loid) compounds have not been studied by SPME in biogases.

SPME fiber coating	Sampled gas	Sampling conditions	Targeted and characterized compounds	LOD	Analysis	Reference
65 µm PDMS/DVB	AD and WWTP biogas and biomethane	Tedlar bag sampling with subsequent SPME within a day (various exposure times: 1, 5, 10, 20 and 50 min)	Linear (L2 – L5) and cyclic (D3 – D5) volatile methyl siloxanes. Additional compounds identified: D-limonene, α- and β-pinene, camphene, terpinenes, β-caryophyllene	mg·m ⁻³ L2 0.0036 L3 0.0075 L4 0.0031 L5 0.0050 D3 0.0084 D4 0.0091 D5 0.0150	GC-MS	[36]
3 fibers tested in the laboratory: 100 µm PDMS; 85 µm PDMS/CAR; 50-30 µm DVB/CAR/PDMS; 50-30 µm DVB/CAR/PDMS used for real landfill samples	Odorant emissions from landfills	Nalophan bag sampling with subsequent SPME within 30 h (exposure 30 min)	Over 100 VOCs (alkanes, alkenes, terpenes, halogenated, oxygenated, aromatics) and dimethyl disulfide	<0.1 ppb for VOC; 50 ppb for dimethyl disulfide	GC-MS	[71]
CAR/PDMS	Landfill gas	Tedlar bag sampling with subsequent SPME (exposure time 2 h)	VOCs (amines, sulfur compounds, alkanes, alkenes, terpenes, halogenated, oxygenated, aromatics, siloxanes)	Not available	GC-MS	[112]
Not available	AD and WWTP biogas and biomethane	Not available	Volatile sulfur compounds (H ₂ S, COS, methanethiol, dimethyl sulfide, dimethyl disulfide) and oxygenated organic compounds (ketones, alcohols, and esters)	Not available	GC-MS	[183]
50-30 µm DVB/CAR/PDMS	Landfill gas	250 mL pre-evacuated glass vial sampling with subsequent SPME (exposure time 30 min at 20°C)	VOCs (linear and cyclo-alkanes, alkenes, aromatics, poly aromatics, furans, halogenated, aldehyde, alcohols, sulfur compounds)	Not available	GC-MS	[146]

1647 **LOD:** limit of detection. **PDMS:** polydimethylsiloxane. **DVB:** divinylbenzene. **CAR:** Carboxen®. **WWTP:** wastewater treatment
 1648 plant (anaerobic digestion of WWTP sludge). **AD:** anaerobic digestion. **GC-MS:** gas chromatography-mass spectrometry.

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1650

1651 **3.2. Trapping in liquid media: absorption in bubbling traps/impingers**

1652 Another technique to preconcentrate trace compounds from gaseous samples involves bubbling the gas
1653 through one or a series of purpose-built bubbling traps ('impingers'), which are generally made of glass,
1654 containing a solvent solution and a built-in fritted bubbler nozzle to generate gas bubbles as small as pos-
1655 sible to maximize the gas-liquid exchange surface area and stimulate the dissolution and absorption of
1656 targeted trace compounds in the solvent. To avoid solvent losses by evaporation or transfer to the gas phase,
1657 a high-boiling solvent can be chosen [24], but since low boiling solvents, such as methanol, are predomi-
1658 nantly used, the solvents must be chilled [70], [97], [119]. The solvent nature, volume and temperature, gas
1659 bubbling flow rate and total gas sampling volume must be optimally determined depending on the gas
1660 composition, concentrations, targeted compounds, etc. This preconcentration technique can be directly im-
1661 plemented in the field, although it is not very practical as the sampling connection train can be complex,
1662 installation is time-consuming [70], [119] and potentially dangerous solvents must be handled (e.g., acids,
1663 AgNO₃) [17], [46], [87], and since additionally a cooling bath is often necessary to chill the solvent [97].
1664 The trace compound-enriched solvent is subsequently analyzed via appropriate analytical methods (Table
1665 5). Critical comparisons between impinger-, adsorbent tube-, gas sampling bag- or canister-gas sampling
1666 are available in several sources [17], [69], [70], [97], [100], [102], [119], [128]. Publications on the use of
1667 impingers for the determination of trace compounds in biogas, biomethane, landfill gas or natural gas are
1668 reviewed in Table 5.

1669 The suitability of the impinger method has been extensively evaluated for volatile methyl-siloxanes in bi-
1670 ogas matrices, and methanol, acetone and n-hexane were found to be the best and most often used solvents
1671 (Table 5). Methanol has successfully been used as an absorption medium for siloxanes (L2, L3, L4, L5, D3,
1672 D4, D5, D6) in biogas, landfill gas and synthetic test gases, with recoveries >80% upon analysis [69], [70],
1673 [97], [100], [119], [184]. Whereas Saeed et al. [97], [100] highlighted that methanol could not stabilize or
1674 quantitatively recover pentamethyldisiloxane and hexamethylcyclotrisiloxane (D3), Wang et al. [184] were
1675 able to quantitatively trap and recover D3 from methanol impingers using the more sensitive Purge and
1676 Trap-GC-MS analytical system. Narros et al. [69] and Kim et al. [119] also identified D3 from methanol
1677 impingers using GC-MS. Narros et al. [69] nevertheless pointed out that methanol impingers were not able
1678 to recover trimethylsilanol (TMS). Despite the solubility differences between TMS and other siloxanes
1679 [105], TMS could be recovered, together with other siloxanes, in acetone [185] and in n-hexane [102].
1680 Piechota et al. [185]–[188] investigated the use of various impinger solvents, namely, acetone, methanol,
1681 n-hexane and dodecane, for the preconcentration of siloxanes in landfill gas and biogases. Their work sys-
1682 tematically revealed that acetone solvates the best siloxanes from the gas samples (L2, L3, L4, D3, D4, D5,
1683 D6 and TMS) while yielding the highest recoveries upon GC-MS analysis. In [186], they demonstrated that
1684 acetone was able to absorb and recover all siloxanes, while methanol and n-hexane did not enable the de-
1685 tection of L3 and L4, and L4 and D6, respectively. In another study [188], the concentration of siloxanes
1686 recovered from acetone was globally 81% higher than that quantified in methanol, and dodecane was unable
1687 to detect most siloxanes at concentrations below ~1 mg·m⁻³, highlighting the importance of using relatively
1688 polar solvents such as acetone for the solvation of siloxanes. However, in a study using a synthetic gas (N₂
1689 containing L2, D3, D4, D5 siloxanes), Wang et al. [128] also used acetone and found relatively low recov-
1690 eries for D3 (45%) and L2 (64%) while fair recoveries for D4 (86%) and D5 (92%). They also evaluated
1691 the efficiency of the acetone impingers for preconcentrating the siloxanes from the wetted synthetic gas and
1692 found lower siloxane recoveries than from the dry gas, especially for L2, which could be a consequence of

1693 the competitive adsorption between L2 and water in acetone. Raich-Montiu et al. [102] used n-hexane for
1694 the absorption of siloxanes in biogas, and they detected all siloxanes (L2, L3, L4, L5, D3, D4, D5, D6) and
1695 TMS using n-hexane, in contrast to Piechota et al. [186] where n-hexane did not enable the detection of L4
1696 and D6. Oshita et al. [189] also successfully used n-hexane to study siloxanes in an experimental biogas
1697 generated from the anaerobic digestion of a sludge in which the siloxane levels were reduced via a prelim-
1698 inary treatment. Lastly, impinger preconcentration with subsequent derivatization of absorbed analytes has
1699 been proposed for the determination of total silicon content in biogas or biomethane [87]. The gas is first
1700 bubbled at 10 mL·min⁻¹ through a heated HNO₃-filled impinger whereafter an 8 M NaOH and an HF solu-
1701 tion are added to trigger derivatization, leading to total Si recoveries of 65 – 88 %. ICP-AES or GC-ICP-
1702 MS is then used for total Si quantification or for the identification and quantification of individual silicon
1703 compounds, respectively.

1704 Next to siloxanes, bubbling traps have been used for the preconcentration of metals and metalloids (Table
1705 5). Whereas gases are generally bubbled through the impingers by means of a pump when the feed line is
1706 not pressurized enough, for instance at biogas or landfill gas plants [97], [102], [154], [184], Cachia et al.
1707 [46] developed a high-pressure bubbling sampling train to preconcentrate metals and mercury from pres-
1708 surized gases such as natural gas or compressed biomethane by directly connecting the impinger train to
1709 the field gas pipeline for pressures up to 100 bar_a. Acidic solutions specific for metals or mercury (Table 5)
1710 were used in three impingers in series. Impingers were made of an inner Teflon cylinder avoiding metal
1711 sorption on impinger walls. For a Hg⁰-spiked argon gas, laboratory validation experiments indicated that
1712 >96% of Hg⁰ was trapped in the acid solution at various sampling pressures (6 and 50 bar_a), with >90% of
1713 the Hg⁰ trapped in the first impinger. The 3 high-pressure impingers were then used in the field to sample
1714 a natural gas at 60 bar_a at 20 L·min⁻¹ for 1 day for mercury and for 5 days for other metals. These long
1715 sampling times were operated to preconcentrate sufficient metals and have a time-weighted average repre-
1716 sentation of the gas composition. The efficiency of the high-pressure impinger train was found to be metal
1717 dependent, as all metals and mercury were predominantly trapped in the first impinger, going from 51%
1718 total Se to 93% total As trapped in the first impinger [46]. This high-pressure impinger sampling train was
1719 then used to sample biomethane and landfill gas [26]. Using similar acidic impinger solutions (Table 5),
1720 Chin et al. [152] also determined metals and metalloids in 23 biogas and biomethane samples from various
1721 production sites. Gaseous monomethyl mercury has also been preconcentrated from landfill gas using aque-
1722 ous 0.001 M HCl solution in impingers [154]. In the field, the entire sampling train (tubing, impingers, etc.)
1723 was shielded from light to avoid the photolytic degradation of monomethyl mercury and the photoinduced
1724 conversion of other Hg compounds (e.g., dimethylmercury) into monomethyl mercury. These authors also
1725 used methanol impingers to trap dimethylmercury from landfill gas, as they argued that this compound is
1726 highly soluble and stable in methanol. Methanol impinger solutions were then analyzed by spiking Car-
1727 botrap™ tubes with small aliquots of the methanol solution followed by thermal desorption of the tubes
1728 [154]. Next, Krupp et al. [17] developed a field method specific to volatile arsenic species by preconcen-
1729 tration in 200 mL 2%_{vol} silver nitrate impingers. After gas bubbling through the impingers, 7 mL of the
1730 AgNO₃ solution was mixed with 1.5 mL HNO₃ and 1.5 mL H₂O₂ and this mixture was then digested in a
1731 microwave. The total arsenic content in the digested solution was determined by furnace atomic absorption
1732 spectroscopy (FAAS). The authors indicated that this analytical technique produced quantification results
1733 ~30% lower than those determined with GC-ICP-MS, which was probably due to the incomplete absorption
1734 of the nonpolar As species (trimethylarsine) in the impinger solution and to sorption losses on impinger

1735 container walls [17]. Xu et al. [190] further explored this arsenic bubbling method and compared the effi-
1736 ciency of aqueous solutions of AgNO_3 versus HNO_3 as absorbing media. Concentrations of 2% AgNO_3 and
1737 50% HNO_3 yielded the highest trapping efficiencies for trimethylarsine. The AgNO_3 solution systematically
1738 provided higher arsenic trapping efficiencies than the HNO_3 solution, except when high H_2S levels were
1739 present in the sampled gas insofar as the reaction between AgNO_3 and H_2S generates black silver sulfide
1740 (Ag_2S) solid particles interfering with any further analytical step [190].

1741 Recoveries of trace analytes from impingers depend not only on the affinity with the solvent but also on the
1742 impinger storage conditions (duration, temperature, exposure to light, etc.) between sampling and analysis.
1743 For siloxanes, Saeed et al. [100] found that siloxane-sampled methanol impingers kept the siloxanes stable
1744 for 21 days. Ajhar et al. [35] nonetheless discouraged the storage of siloxanes in methanol, as they observed
1745 low recoveries for D3 (16%), L2 (57%) and L3 (76%) after 23 days of storage at 4 °C. Generally, sampled
1746 impinger solutions should be analyzed as soon as possible while stored at 0 – 4 °C for siloxanes [184],
1747 [185] as well as for metal(loid)s [26], and in the dark to avoid photolytic degradation reactions of targeted
1748 analytes [154]. For metal(loid)s, it is advised to transfer the solutions into trace-metal cleaned amber glass
1749 bottles for transport and storage [17], [154]. Besides, to avoid a loss in analytes by saturation of the solvent
1750 and breakthrough upon sampling, several impingers are often placed in series using appropriate solvent
1751 volumes and gas flow rates and volumes (Table 5).

1752 A general observation from Table 5 reveals that impinger sampling times are generally long, lasting from
1753 10 min to 5 days (but most often several hours), since large gas volumes (from 10 L to 140 000 L) must be
1754 bubbled at low and constant flow rates to guarantee sufficient contact between gas and absorbing solvent
1755 and to guarantee that preconcentrated analyte levels are sufficient to be detectable. This is a major drawback
1756 to the impinger method, especially when replicates have to be taken in the field and when several field
1757 locations have to be sampled. Additionally, due to the relatively large solvent volumes used (up to 200 mL),
1758 the detection limits are high. For instance, for an impinger containing 20 mL n-hexane for the preconcen-
1759 tration of siloxanes, Raich-Montiu et al. [102] diluted the siloxane-loaded 20 mL n-hexane to 25 mL with
1760 clean n-hexane, and 2 μL of that resulting solution was eventually analyzed.

Table 5: Review of the applications of impingers for the determination of trace compounds in biogas, biomethane and landfill gas.

LOD: limit of detection. WWTP: wastewater treatment plant (anaerobic digestion of WWTP sludge). AD: anaerobic digestion. GC: gas chromatography. MS: mass spectrometry. FID: flame ionization detector. ICP: inductively coupled plasma. AES: atomic emission spectrometry. FAAS: furnace atomic absorption spectroscopy. TD-GC-CVAFS: thermal desorption – GC – cold vapor atomic fluorescence spectrometry

Solvent *	Sampled gas	Sampling conditions	Targeted compounds	Compounds identified \diamond	LOD (unless otherwise stated)	Analysis	Reference
6 mL methanol (chilled at 4±2°C)	WWTP biogas	2 impingers in series. 20 L gas bubbled (3 h at 112 mL·min ⁻¹)	Volatile methyl-siloxanes	L2 L3 D4 D5 D6	1 µg per mL solvent (~50 ppbv)	GC-MS	[97], [100]
30 g acetone (chilled at 0°C)	Landfill gas; WWTP and AD biogas	2 impingers in series. 20 L gas bubbled (40 min at 0.5 L·min ⁻¹)	Volatile methylsiloxanes, trimethylsilanol	L2 L3 L4 D3 D4 D5 D6 Trimethylsilanol	0.01 µg per g acetone Siloxanes: 0.04 - 0.11 mg·Nm ⁻³ gas Trimethylsilanol 0.08 - 0.12 mg·Nm ⁻³ gas	GC-MS	[185], [187]
acetone; n-hexane; or methanol (chilled at 0°C)	WWTP biogas	3 impingers in series	Volatile methyl-siloxanes	L2 L3 L4 D3 D4 D5 D6	GC-MS : 0.01–0.03 µg·g ⁻¹ GC-FID : 0.05–0.09 µg·g ⁻¹	GC-MS GC-FID	[186]
Acetone; methanol; or do- decane (chilled at 0°C)	Landfill gas; WWTP and AD biogas	2 impingers in series. 20 L gas bubbled (40 min at 0.5 L·min ⁻¹)	Volatile methylsiloxanes	L2 L3 L4 D3 D4 D5 D6	0.01 – 0.03 mg·m ⁻³	GC-MS	[188]
Front impinger: 30 g sol- vent; back impinger: 10 g solvent		Micro-impingers also evaluated (scaled at the ra- tio 1:2, v/v, including solvent mass and gas flow)					
6 mL methanol (chilled in ice bath)	Landfill gas	3 impingers in series. 18 L gas bubbled (2 h at 150 mL·min ⁻¹)	Volatile methyl-siloxanes	L2 L3 L4 L5 D3 D4 D5	Method detection limit: 0.88-2.46 µg per mL methanol	GC-MS	[119]

Table 5: continued

Solvent *	Sampled gas	Sampling conditions	Targeted compounds	Compounds identified \diamond	LOD (unless otherwise stated)	Analysis	Reference
Methanol (chilled in ice-water bath)	Landfill gas	2 impingers in series	33 VOCs (alkanes, aromatics, terpenes, halogenated, ketones, alcohols, esters, dimethyl sulfide) and 6 siloxanes (L2, L3, L4, D3, D4, D5, trimethylsilanol)	L2 L3 L4 D3 D4 D5		GC-MS	[69]
20 ml n-hexane (chilled in ice-water bath)	WWTP biogas; landfill gas	2 impingers in series. 10 L gas bubbled (10 min at 1 L·min ⁻¹)	Volatile methylsiloxanes, trimethylsilanol	L2 L3 L4 L5 D3 D4 D5 D6 trimethylsilanol	Trimethylsilanol: 0.04 ng per L n-hexane Siloxanes: 0.02 ng per L n-hexane	GC-MS	[102]
10 mL methanol (chilled in ice bath)	Landfill gas	2 impingers in series. 12 L gas bubbled (1 h at 0.2 L·min ⁻¹)	Volatile methyl-siloxanes	L2 L3 L4 L5 D3 D4 D5 D6	6.9 – 73.2 ng per L methanol	Purge and trap – GC-MS	[184]
100 mL n-hexane	Experimentally generated AD biogas	Aluminum gas bag sampling (2 L) and subsequent transfer to 2 impingers in series	Volatile methyl-siloxanes	L2 L3 L4 L5 D3 D4 D5 D6	Not available	GC-MS	[189]
Concentrated HNO ₃ at +60°C	Biogas or bio-methane	Impinger, gas bubbling rate: 10 mL·min ⁻¹	Total silicon	Not available	Not available	ICP-AES or GC-ICP-MS	[87]

Table 5: continued

Solvent *	Sampled gas	Sampling conditions	Targeted compounds	Compounds identified \diamond	LOD (unless otherwise stated)	Analysis	Reference
50 mL HNO ₃ 10% _w + H ₂ O ₂ 5% _w in Milli-Q water	Natural gas	3 high-pressure impingers in series. Gas bubbled at 60 bar _a during 5 days at 20 L·min ⁻¹ (~140 Nm ³ collected)	Metals and metalloids	Ba Sn As Cu Al Se Zn	Limit of quantification (μg per liter solvent): 10 ⁻¹ for Al and Mn; 10 ⁻² for Se, Ba, Zn, Cu, Ni, Cr 10 ⁻³ for Mo, Ag, Cd, Sn, Pb, V, As	ICP-MS	[46]
50 mL KMnO ₄ 1% _w + H ₂ SO ₄ 5% _w in Milli-Q water	Natural gas	3 high-pressure impingers in series. Gas bubbled at 60 bar _a during 1 day at 20 L·min ⁻¹ (~40 Nm ³ collected)	Mercury	Hg	Limit of quantification: 0.6 μg per liter solvent	ICP-MS	[46]
50 mL HNO ₃ 10% _w + H ₂ O ₂ 5% _w in Milli-Q water	AD biomethane and raw and pre- treated landfill gas	3 high-pressure impingers in series. ~140 Nm ³ gas bubbled at 1-4 bar _a (landfill gas) or 40 bar _a (biomethane) during 5 days at 20 L·min ⁻¹	Metals and metalloids	Se Cd Ni Sb As Zn Pb Sn Cr Ba Al V Mo Cu Ag	Limit of quantification (μg per li- ter solvent): 10 ⁻¹ for Se, Al, Zn, Cu 10 ⁻² for As, Sb, Sn, Mo, Cd, Ba, Ni, Cr 10 ⁻³ for Ag, Pb, V	ICP-MS	[26]
20 mL HNO ₃ 5% + H ₂ O ₂ 10% in double deionized water	WWTP, landfill and AD biogas and biomethane	3 impingers in series. 30 L gas bubbled (1 h at 0.5 L·min ⁻¹)	Metals and metalloids	Be Cr Mn Co Ni Cu Zn As Se Sr Mo Cd Sb Ba Hg, Tl, Pb	Limit of quantification: 0.005 – 0.1 $\mu\text{g}\cdot\text{m}^{-3}$	ICP-MS	[152]

Table 5: continued

Solvent *	Sampled gas	Sampling conditions	Targeted compounds	Compounds identified \diamond	LOD (unless otherwise stated)	Analysis	Reference
0.001 M HCl in double deionized water	Landfill gas	3 impingers in series, followed by a water condensation trap. 16 L gas bubbled (20 min at 0.8 L·min ⁻¹)	Monomethylmercury	Monomethylmercury (Hg(CH ₃))	Not available	Distillation, ethylation, Cabotrap™ preconcentration, TD-GC, thermal conversion and CVAFS detection	[154]
Methanol	Landfill gas	Impinger. 11 L gas bubbled.	Dimethylmercury	Dimethylmercury (Hg(CH ₃) ₂)	Not available	Preconcentration on Carbotrap™ + TD-GC-CVAFS	[154]
200 mL 2% _{vol} AgNO ₃ in doubled distilled water	Natural gas	2 impingers in series. 40 L gas bubbled (20 min at 2 L·min ⁻¹)	Volatile arsenic species (trialkylated As species)	Mainly trimethylarsine (As(CH ₃) ₃)	Total As content: 5.0 µg per L solvent	FAAS	[17]
50% HNO ₃ or 2% AgNO ₃ (aqueous solutions)	Natural gas (site A and site B)	Site A: 2 impingers in series. 150 L gas bubbled (~ 1 h at ~ 2 L·min ⁻¹) Site B: 2 impingers in series. 450 L gas bubbled (5 h at 1.5 L·min ⁻¹)	Trimethylarsine	Total arsenic	Total As content: 9.0 µg per L solvent	ICP-MS	[190]

* Solvent volumes mentioned are volumes brought in each impinger of the series when several impingers are placed in series, unless otherwise stated

\diamond **Siloxane abbreviations:** L2: hexamethyldisiloxane; L3: octamethyltrisiloxane; L4: decamethyltetrasiloxane; L5: dodecamethylpentasiloxane; D3: hexamethylcyclotrisiloxane; D4: octamethylcyclotetrasiloxane; D5: decamethylcyclopentasiloxane; D6: dodecamethylcyclohexasiloxane

1859 **3.3. Cryogenic preconcentration (cryotrapping)**

1860 A last preconcentration technique is the cryogenic trapping ('cryotrapping') of trace compounds by cooling
1861 the gas sample at a temperature such that the volatile trace compounds condense but not the gas matrix
1862 (CO₂, CH₄, N₂). The gas is typically passed through a U-shaped tube (glass or stainless-steel, example 1/8"
1863 ID × 6" length) immersed in liquid cryogen, e.g., liquid nitrogen (−196 °C) or liquid argon (−186 °C) when
1864 dealing with air samples [24]. When dealing with methane/carbon dioxide samples (landfill gas, biogas,
1865 biomethane), the cryogen temperature should be higher than the methane boiling point (−161.5 °C at 1 atm)
1866 and carbon dioxide freezing point (−78.5 °C at 1 atm) to avoid CH₄ and CO₂ condensation. For instance,
1867 Feldmann et al. [191], [192] used an acetone/liquid nitrogen cryogen temperature of −80 °C, or an ace-
1868 tone/dry ice slush at −78 °C [193], [194] to sample landfill and sewage gases.

1869 Cryotrap usually do not contain adsorbent or absorbent material, but can be packed with some untreated
1870 quartz wool, glass beads or other light inert silica material (e.g., diatomite [191]), that is secured between
1871 quartz or glass wool plugs, to increase the cryogenic surface area and thus the trapping efficiency [24]. The
1872 absence of sorbent material in the tube allows to recover the trapped analytes by heating the tube at a
1873 moderate temperature (e.g., 40-100 °C) [22], [24] which nondestructively regasifies the analytes. The re-
1874 covered analytes are then transferred either to a refocusing trap (itself a cryotrap, e.g., [65], [193]) and then
1875 to the analytical unit, or directly to the analytical unit, typically a gas chromatograph (GC). The main draw-
1876 back of cryotrapping is the formation of water ice blocks in the cryotrap tube when sampling humid gases,
1877 obstructing further gas flow. Upon thermal desorption of the tube, ice returns to the liquid/vapor state and
1878 this water may be transferred to the analytical system, leading to interferences. This shortcoming can be
1879 avoided by drying the gas before cryotrapping (e.g., using anhydrous calcium chloride tubes [191], [192]
1880 or by passing the gas through an empty glass tube at −20 °C to condense water and dry the gas [16], [65],
1881 [195]) or by adding a second 'analytical' cryogenic trap (refocusing trap) at the entry of the analytical
1882 device [24]: the first 'sampling' cryotrap, where on water potentially collected, is slowly heated so that
1883 water vapor is evacuated and prevented from being transferred to the second refocusing trap, while targeted
1884 analytes are transferred [196]. Since stable storage of sampled cryotrap is delicate and energy-consuming,
1885 cryotrap are sampled while directly hyphenated with the analytical system. This renders *in situ* field utili-
1886 zation burdensome if not infeasible in view of the need for substantial volumes of liquid cryogen, pumps
1887 and associated power supplies on site, and of hazards related to the transport of cryogen [17], [22]. Cry-
1888 otrapping hyphenated with gas chromatography – inductively coupled plasma – mass spectrometry (CT-
1889 GC-ICP-MS) was introduced in the 1990s to improve sampling and characterization approaches for (in)or-
1890 ganic volatile metal(loid) species in environmental gas samples, wherein they are typically thermodynam-
1891 ically unstable [194]. CT-GC-ICP-MS enables, in one-stage cryogenic sampling, the concomitant kinetic
1892 stabilization and preconcentration of the metal(loid) species and has proven to be the most robust and sen-
1893 sitive technique to separate, detect and semiquantify distinct volatile metal(loid) species in complex gases,
1894 even those such as biogas containing ICP-interfering CO₂ [17], [25], [191], [192], [197], [198].

1895 Table 6 reviews the studies that used CT-GC-ICP-MS to preconcentrate (in)organic volatile metal(loid)
1896 species in landfill gas, biogases and natural gas. Feldmann et al. [15], [22], [191]–[194], [198]–[201] pio-
1897 neered this domain. As CT-GC-ICP-MS is not field-deployable, gases are often first field sampled in Tedlar
1898 bags and then transported to the laboratory for ensuing transfer to the CT-GC-ICP-MS unit (Table 6). Since
1899 most volatile metal(loid) species sampled in Tedlar bags were demonstrated to be stable for at least 24 h

1900 when stored at 20 °C [22], this sampling approach is an attractive compromise to benefit from the cryogenic
1901 preconcentration. Generally, Tedlar bags should be shielded from light to prevent UV-induced degradation
1902 of the samples, stored at 4 °C and analyzed as soon as possible [193], [194]. If cryotrap are sampled directly
1903 *in situ*, they should be gas-tightly closed and stored in liquid nitrogen (−196 °C) [192] or in a dry atmosphere
1904 cryogenic container [16], [65], [195] until analysis. The most often determined compounds include hydrides
1905 and alkylated species of As, Bi, Cd, Hg, Pb, Se, Sb, Sn, Te. Carbonyls of Ni, Mo and W (Ni(CO)₄, Mo(CO)₆
1906 and W(CO)₆) were also evidenced in landfill gas and sewage sludge biogas [193], [194] (Table 6). To
1907 efficiently trap the most volatile metal(loid)s, such as stannane (SnH₄), from landfill or sewage gas, cry-
1908 otrapping at −196 °C can be necessary [192], [200]. At such low temperature, CO₂ ice-blocks in the cryotrap
1909 can be avoided by placing a NaOH-pellet cartridge, which retains CO₂, upstream of the cryotrap. Methane
1910 is not retained by NaOH but is also not efficiently condensed in the −196 °C cryotrap and does not cause
1911 major interferences in the ICP. The NaOH cartridge can, however, react with some volatile metal(loid)s,
1912 especially antimony ones (trimethylantimony, stibine), which decreases their recovery [198], [200].

1913 In addition to volatile metal(loid) species, cryotrapping has also been occasionally used for the preconcentra-
1914 tion of siloxanes and VOCs in landfill gas and sewage sludge biogas, which are first sampled in gas
1915 sampling bags [202] or canisters [14]. Cryotrap packed either with a silicon-containing material (3% SP-
1916 2100 on Supelcoport, 80/100 mesh) or with a silicon-free material (5% Carbowax on Carbopack, 60/80
1917 mesh) were used at −100 °C, and desorption of the traps to 165 °C enabled the determination of trimethylsi-
1918 lanol and siloxanes in the ng·m⁻³ to µg·m⁻³ range using either the silicon-material or the silicon-free material
1919 in the cryotrap [202]. Another cryotrap consisting of a nickel tube packed with fine glass beads was used
1920 at −85 °C and desorbed at 250 °C [14]. More than 80 VOCs and organosilicon compounds were identified,
1921 including the following: alkanes, terpenes, aromatics, ketones, alcohols, furans, trimethylsilanol and silox-
1922 anes.

Table 6: Review of the applications of cryotrapping – gas chromatography – inductively coupled plasma – mass spectrometry (CT-GC-ICP-MS) for the determination of traces of (in)organic volatile metals and metalloids in biogas, landfill gas and natural gas.

LOD: limit of detection. WWTP: wastewater treatment plant (anaerobic digestion of WWTP sludge). AD: anaerobic digestion

Sampled gas	Sampling conditions	Cryotrap	Targeted compounds	Compounds identified	LOD	Reference
Landfill gas	20 L gas; 20 mL·min ⁻¹ ; CaCl ₂ drying tube upstream cryotrap	– 80°C; packed with Supelcoport (10% SP-2100, 60/80 mesh, Supelco)	Volatile metals and metalloids	Volatile species (hydrides and alkylated) of As, Bi, Hg, Sb, Sn, Te (ng to µg·m ⁻³)	Not available	[191]
Landfill gas, WWTP biogas	20 L gas; CaCl ₂ or Mg(ClO ₄) ₂ drying tube upstream cryotrap	2 cryotrap in series; – 80°C; packed with Supelcoport (10% SP-2100, 60/80 mesh, Supelco)	Volatile metals and metalloids	Volatile species (hydrides and alkylated) of: Landfill gas: As, Bi, Hg, Pb, Sb, Se, Sn, Te WWTP biogas: As, Bi, Cd, Hg, Pb, Sb, Sn, Te (ng to µg·m ⁻³)	Not available	[192]
Landfill gas	Tedlar bag (4 L) with subsequent transfer to cryotrap	– 78°C; packed with Chromosorb (10% SP-2100, 60/80 mesh, Supelco)	Volatile metals, metalloids and transition metals	Volatile species (hydrides and alkylated) of As, Bi, Hg, Pb, Sb, Se, Sn, Te; Transition metal carbonyls: Mo(CO) ₆ , W(CO) ₆ (Mo: 0.2 – 0.3 µg·m ⁻³ ; W: 0.005 – 0.01 µg·m ⁻³)	Not available	[193]
WWTP biogas	Tedlar bag (80 L) with subsequent transfer to cryotrap	– 78°C; packed with Chromosorb (10% SP-2100, 60/80 mesh, Supelco)	Volatile transition metal carbonyls	Ni(CO) ₄ (0.5 – 1.0 µg·m ⁻³); Mo(CO) ₆ (3.0 – 3.6 µg·m ⁻³); W(CO) ₆ (0.01 – 0.015 µg·m ⁻³)	Ni: 0.01 µg·m ⁻³ gas	[194]
Landfill and WWTP biogas	4 – 20 L	–78°C or –80°C; packed with 10% SP-2100 on either Chromosorb or Supelcoport	Volatile bismuth species	Trimethylbismuth (Bi(CH ₃) ₃ , up to 25 µg·m ⁻³)	Not available	[201]
Landfill gas and WWTP biogas	Tedlar bag with subsequent transfer to cryotrap	– 78°C; packed with Chromosorb (10% SP-2100, 45/60 mesh, Supelco)	Volatile metals and metalloids	Volatile species (hydrides and alkylated) of Sb, Sn, Bi species	~ µg·m ⁻³ gas	[15]
WWTP biogas	Tedlar bag (10 L) with subsequent transfer to cryotrap	–80°C; fused silica column	Volatile metals and metalloids	Trimethylantimony (5 ng·L ⁻¹); trimethylbismuth (18 ng·L ⁻¹); dimethyltellurium	Not available	[22]
Landfill gas	Tedlar bag (5 – 10 L) with subsequent transfer of 500 mL to cryotrap	–80°C; fused silica column	Volatile metals and metalloids	Volatile alkylated species of As, Bi, Pb, Sn, Sb, Te	Not available	[199]

Table 6: continued

Sampled gas	Sampling conditions	Cryotrap	Targeted compounds	Compounds identified	LOD	Reference
Experimental AD biogas	NaOH-pellets cartridge to absorb CO ₂ and H ₂ O upstream cryotrap	-196°C	Volatile metals and metalloids	Volatile species (hydrides and alkylated) of: As, Sb, Sn	Not available	[198], [200]
Natural gas	if not: Pressurized stainless-steel gas cylinder (SilcoSteel® surface treatment) with subsequent depressurization and transfer of 50 mL to the cryotrap	-80°C	Volatile arsenic compounds	Trimethylarsine (TMA) <18 µg·m ⁻³ gas	0.2 µg TMA · m ⁻³ gas	[17]
Natural gas	Pressurized stainless-steel gas cylinder (SilcoSteel® surface treatment) with subsequent depressurization and transfer of 50 mL to the cryotrap	-120°C; SilcoSteel® tubing	Volatile arsenic compounds	Trimethylarsine (TMA) 3 – 130 µg·m ⁻³ gas	0.2 µg TMA · m ⁻³ gas	[25]
Landfill gas	Pressurized stainless-steel gas cylinder (Sulfinert™ surface treatment) with subsequent depressurization and transfer of 50 mL to the cryotrap	-80°C; SilcoSteel® tubing	Volatile (in)organic arsenic compounds	Volatile alkylated arsenic species (0 – 15 µg As · m ⁻³ gas)	0.1 ng As · m ⁻³ gas	[65]
Landfill gas	Tedlar bag (10 L) with subsequent transfer to a H ₂ O-condensation tube (-20°C) before transfer to the cryotrap	-80°C; Packed with glass wool	Volatile (in)organic tin compounds	Volatile alkylated tin species 0.01 – 20 µg Sn · m ⁻³ gas	0.25 ng Sn · m ⁻³ gas	[195]
Compost (pine shavings, duck feathers, duck excreta) biogas	Tedlar bag (10 L) with subsequent transfer to a H ₂ O-condensation tube (-20°C) before transfer to the cryotrap	-80°C; Packed with silanized glass wool	Volatile metals and metalloids	Volatile alkylated species of As, Bi, Pb, Sb, Se, Sn, Te (Se and Te: 0.01 – 2.3 µg·m ⁻³ gas)	Bi: 1.2 pg·m ⁻³ gas Se: 799 pg·m ⁻³ gas	[16]

1956 **4. Conclusions and recommendations**

1957 This review highlighted the diversity of available gas sampling techniques, including whole gas sampling
1958 and gas sampling with preconcentration of trace compounds. Most of these techniques have been applied
1959 for biogas and biomethane sampling, as recently reviewed by Bragança et al., 2020 [203]. Importantly, as
1960 stressed by Arrhenius et al. [4], the above discussions suggest that there is no universal sampling vessel or
1961 preconcentration technique able to quantitatively sample and recover all (families of) trace compounds. The
1962 materials used in the sampling chain (tubing, polymer film and valve fitting material of gas bags, pas-
1963 sivation treatment in stainless-steel cylinders and canisters, adsorbent material and sorbent bed retaining
1964 hardware in sorbent tubes; absorption solvent in impingers, packing material in cryotrap...), the pressure
1965 at which gas is sampled, the transport and storage conditions of samples (duration, temperature, humidity,
1966 exposure to light, etc.), the gas composition and trace compounds nature and concentrations, all influence
1967 the integrity, stability and recovery of trace compounds in and from their sampling unit. High boiling and
1968 polar compounds are, for instance, less stable in whole gas sampling vessels owing to their propensity for
1969 wall sorption and dissolution in condensed water, respectively. The stability of volatile metal(loid) com-
1970 pounds in whole gas vessels may depend on the central metal atom. Reactive analytes could undergo con-
1971 version or degradation reactions with other sampled compounds, especially inside whole gas sampling ves-
1972 sels. In those vessels, the initial sampled analyte concentration and moisture level as well as the sampled
1973 volume and the sample pressure critically influence wall sorption effects.

1974 In addition, this review suggests that most sampling and preconcentration techniques are dedicated to gas
1975 systems at near atmospheric pressure. With the exception of high-pressure impinger prototypes [46], the
1976 current techniques do not allow the direct preconcentration of trace compounds from pressurized gases,
1977 such as grid biomethane, *in situ* on the gas pipes at the working pressure to avoid drawbacks and shortcom-
1978 ings diverted from the depressurization of gas samples.

1979 If a singular trace compound or chemical family is targeted, the most appropriate sampling chain can be
1980 chosen based on literature and on preliminary validation experiments. Nonetheless, when a global screening
1981 of trace compounds in a gas sample is desired, coupling several sampling methods is perhaps the best com-
1982 promise to increase the chances that each considered sampling method suitably retains a given family of
1983 trace compounds. The following general recommendations can be drawn from the above to optimize sam-
1984 pling procedures:

- 1985 • The sampling vessel or preconcentration unit should be chosen based on the preliminary evaluation of
1986 the short-term (~24 h) storage stability and recovery of targeted analytes in/from that sampling unit and
1987 of the achievable analytical detection limits. Reference, calibrated gas mixtures prepared in biogas ma-
1988 trices and containing model targeted compounds should be used to validate the methods. Suitable meth-
1989 ods for biogas should also be appropriate for biomethane, as this purified gas is dry and should contain
1990 lower concentrations of trace compounds than biogas. However, more stringent detection limits are
1991 required for biomethane.
- 1992 • Tubing and connectors used in the field sampling chain and in the laboratory analytical chain should
1993 be of inert and clean materials and leak-free to avoid trace compound losses. Polytetrafluoroethylene
1994 (PTFE) tubing is generally advised because it is considerably less adsorptive than stainless-steel, copper

1995 or Tygon tubing. Silicon tubing should especially be avoided when targeting siloxanes, for which sili-
 1996 con-free tubing must be used. When stainless-steel collection or tubing material is used, it should be
 1997 surface-treated or coated with appropriate passivation technologies to limit surface wall sorption and
 1998 reactions with the stainless-steel iron.

- 1999 • An inert particle filter (e.g., ~5 µm or 30 µm, PTFE) may be installed upstream of the sampling chain
 2000 to prevent dust particles from the gas from fouling or damaging valves, obstructing flow paths, altering
 2001 flow rates and entering the sampling unit.
- 2002 • The field sampling chain should be as short as possible by using tubing as short as possible to limit
 2003 trace compound sorption losses.
- 2004 • The field sampling chain should be flushed with the gas to sample for several minutes to hours before
 2005 effective sampling to condition and ‘accustom’ the tubing to the trace compounds and saturate potential
 2006 sinks (sorption sites).
- 2007 • Gas samples should be analyzed as soon as possible after sampling, ideally within 24 h, to avoid or
 2008 minimize artifacts and analyte losses during storage phases. If possible, direct *in situ* analysis should
 2009 be performed, e.g., using field-portable gas chromatographs.
- 2010 • If sample storage is inevitable, the gas sample should be stored at cold temperatures (from <0 °C for
 2011 adsorbent tubes to <20 °C for Tedlar bags), shielded from sunlight to avoid UV-induced degradation
 2012 reactions and stored in a dry, solvent-free and vapor-free environment.

2013 To conclude, Table 7 displays an overview of important features of gas sampling techniques with and with-
 2014 out enrichment.

Table 7: Global features of gas sampling techniques: whole gas sampling and gas sampling with enrichment.

Sampling technique	Whole gas sampling			Sampling with enrichment				
	No analyte breakthrough; fast sampling; only defined gas volumes can be sampled; especially suitable for very volatile permanent gases (N ₂ , CO ₂ , CH ₄ , O ₂ ...)			Breakthrough possible; time-consuming; large gas volumes can be sampled; flammable gas matrix (CH ₄) not sampled; especially suitable for trace compounds				
Sampling support	Gas bag	Passivated cylinder	Passivated canister	Adsorbent tubes	Solid Phase Microextraction	Absorption (impinger)	Cryogenic trapping	Amalgamation and Chemotrapping
Allowed sampling pressure	Slightly above P _{atm}	≤ 344 bar _a	≤ 2.75 bar	Slightly above P _{atm}	P _{atm}	P _{atm} ; ≤ 100 bar _a [46]	Slightly above P _{atm}	Slightly above P _{atm}
Maximal sampleable gas volume (†)	100 L	3785 cm ³ at 124 bar _a , max [77]	Up to 100 L at max 2.75 bar _a	No theoretical limit. Analytically relevant volume function of analyte breakthrough volume	Not applicable (exposure time)	No theoretical limit. Analytically relevant volume function of analyte breakthrough volume		
Advantages \times Disadvantages	Inexpensive, easy use \times Sorption losses on vessel walls	Pressurized sampling \times Sorption losses on vessel walls; expensive	Easy use \times Sorption losses on vessel walls; expensive	Small size; easy handling, transport and storage; high storage stability; possibility of multibed for enlarged affinities \times No repeated sample analysis; trained personnel required	Small size; easy handling; fast \times Fragile; not for field utilization unless field-GC	\times Installation time-consuming; handling of solvents; cooling bath needed; trained personnel required	Reference method for volatile metal(loid)s \times Energy intensive (cryogen); cryogen handling; trained personnel needed; not field-deployable	Specific for given elements e.g., Hg, As \times Complex preparation; trained personnel required
Sampleable chemical families	(H)VOC VSC, VSiC VMC	VOC VSC, VSiC VMC	(H)VOC VSC, VSiC	(H)VOC VSC, VSiC VMC	(H)VOC VSC, VSiC	VOC VSIC VMC	VSIC VMC	VMC
Reusable	Not recommended	Yes, with cleaning (but old cylinders give artifacts [80])	Yes, with cleaning (but older canister do not keep analytes as stable as new canisters do [103])	Yes, if thermally desorbed; no if solvent-desorbed	Yes (thermal reconditioning)	No	Yes (thermal reconditioning)	Yes (thermal reconditioning)

(H)VOC: (halogenated) volatile organic compounds; VSC: volatile sulfur compounds; VSIC: volatile silicon compounds; VMC: volatile metal(loid) compounds.

(†) Maximal sampleable gas volumes for whole gas sampling vessels indicate standard commercially available vessel sizes. Custom-sized bags, cylinders and canisters are alternatives.

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Note

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