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Comparison between sampling and analytical methods in characterization of pollutants in biogas

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ABSTRACT

Different sampling methods involving the collection of biogas by Tedlar bags or adsorption tubes, and different GC–MS injection systems, loop injection or cold trap injection (with bags or by tube desorption), were compared to establish the best method to determine the minority compounds in biogas from sewage treatment plants (STPs). A study of parameters is included, such as the stability of compounds in Tedlar bags or cartridges and the adsorption effect of some less volatile compounds in the thermal desorption system (TD).

The optimized methods allowed to determine most compounds at low mg m^{-3} levels. Among them, maximum values of D5 (4.84 mg m^{-3}), decane (95–118 mg m^{-3}) and H_2S (2223 mg m^{-3}) were found in biogas samples.

1. Introduction

Biogas is a modern form of bioenergy that is derived from the anaerobic digestion of organic matter by microorganisms from sludge treatment in landfills and sewage treatment plants (STPs) [1]. Landfill-biogas utilization is a win-win solution as it creates sources of renewable energy and revenue while diminishing greenhouse gas emissions [2]. Biogas produced in these activities is rich in a mixture comprised mainly of methane (CH_4) and carbon dioxide (CO_2) and other compounds at lower levels [3–5]. Unfortunately, the presence of compounds such as volatile organic sulfur compounds (VOSCs) and siloxanes in biogas can cause severe damage to heat engines, turbines and gas treatment systems, thus reducing the economic benefits of using biogas [2,6,7]. The presence of siloxanes is due to the widespread use of these compounds in everyday products such as personal-care products and anti-foaming agents in detergents and they are considered potentially persistent, bioaccumulative and toxic [8,9]. As well as focusing on siloxanes, it is equally important to study other harmful contaminants in order to ensure fully that the specifications of biogas meet the requirements of an electricity-generating, while avoiding toxicity levels.

In order to evaluate gas purification installations at STPs, the correct quantification of biogas components is essential. Whereas analysis via GC–MS is widely agreed upon; there is no consensus on the most suitable sampling technique. However, among the different sampling strategies developed, key examples include the use of whole-air containers (canisters/bags) and sorbent tubes to trap and selectively concentrate the gas sample [10]. Air-sampling bags are widely accepted and used as a convenient portable system for the collection of biogas. They are very suitable for ultra-volatile chemicals, which are difficult to retain at ambient temperature using sorbent tubes. Among the most commonly used films, polytetrafluoroethylene (PTFE), polyethylene-terephtalate–nylon–aluminum (PET-NY-AL-CPE) and polyvinyl fluoride (PVF) are the most widely used for making bags, the last of which is registered under the brand name of Tedlar. Despite quality bags minimize undesired effects some limitations have been reported about sampling bags, such as permeation through the walls and leaks through valves, with sorption losses and adsorption effects having implications for the reusability [11,12]. Given the possible limitations of bag sampling, most recent analytical strategies favor the use of one or more sorbent focusing traps held at ambient or moderately cooler temperatures for subsequent analysis [10].

However, new trends in biogas analysis focus on the development of techniques with improved limits of detection. One such technique is thermal desorption (TD) coupled to gas chromatography–mass spectrometry (GC–MS), which is often used for the analysis of air samples [13–15]. The samples are either collected by active sampling on sorbent tubes and analyzed by dual stage desorption (by desorption from the tube and refocusing on a cold trap and final desorption from the cold trap to the GC column) or the samples are collected in canisters or Tedlar bags and the analytes are directly focused on the cold trap.

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For example, Badjagbo et al. [2] determined siloxanes using 56 L gas sampling bags with direct APCI-MS/MS and obtained limits of detection of 146 $\mu g\ m^{-3}$ (D4) and 354 $\mu g\ m^{-3}$ (D5).

Thermal desorption enables a wide range of sorbents to be used. Several sorbents have been reviewed for VOCs analysis using TD including Tenax TA, graphitized carbon blacks (GCBs) and molecular sieves [16]. The most suitable of these depends not only on the physical and chemical characteristics of the analytes but also on the sample time and volume.

The work presented here compares different analytical methods for the determination of contaminants from biogas and STPs. Gas samples were analyzed using both sampling methods, namely with Tedlar bags and sorption tubes. The gas in the Tedlar bags was then analyzed firstly by TD and GC–MS and secondly directly by GC–MS with loop injection.

2. Experimental

2.1. Reagents, supplies and equipment

Liquid standards involved mixtures of volatile organic compounds (VOCs) at 100 $mg\ L^{-1}$ in methanol (EPA 8020/8240 Aromatic Volatiles Mix, USA) (benzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, ethylbenzene, styrene, toluene, o-xylene, m-xylene and p-xylene), and mixtures of C_8–C_{20} alkane standards at 100 $mg\ L^{-1}$ in hexane.

Limonene and mercaptans (trimethylsilanol, ethyl mercaptan, dimethyl sulfide, carbon disulfide, propyl mercaptan, butyl mercaptan, dimethyl disulfide, 1-pentanethiol) were diluted in MeOH at 1000 $mg\ L^{-1}$ and siloxanes (hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5)) were diluted in n-hexane (SDS, Peypin, France) at 1000 $mg\ L^{-1}$. All compounds were obtained from Sigma-Aldrich (St. Louis, USA). All the standards were prepared on the day of use at 10 $mg\ L^{-1}$ and stored at 4 °C in 1 mL amber vials supplied by Supelco.

Standard in a cylinder mixture of gases: propane, butane, pentane, hexane, heptane, and carbonyl sulfide at 5 ppm in helium (99.80% v/v) was purchased from Carburos Metálicos (Barcelona, Spain). High levels of hydrogen sulfide were calibrated with a cylinder mixture of gases of hydrogen sulfide (0.2%) and helium (99.8%) also purchased from Carburos Metálicos (Barcelona, Spain).

For the preparation of Tedlar bag standards, a matrix similar to biogas obtained in a cylinder mixture of gases was supplied by Carburos Metálicos (Barcelona, Spain), with the following composition: methane (60% v/v), carbon dioxide (31% v/v), nitrogen (4.5% v/v), oxygen (4% v/v) and carbon monoxide (0.5% v/v).

Nitrogen gas of 99.999% purity was used to activate both the valve and thermal desorption sorbent tubes. Helium gas of 99.999% purity was used as a carrier gas for the chromatographic analysis (from Carburos Metálicos, Barcelona, Spain).

A two-bed cartridge was chosen to cover the wide range of target compounds in this study. It was a stainless steel tube (3.5-in. (89 mm) × 1/4-in. (6.4 mm) O.D.), SilcoSteel coated (which make them suitable for sampling reactive species) and containing about 400 mg of a multisorbent bed of Tenax TA and Unicarb (Markes International Limited, Llantrisant UK).

Tedlar bags (Polyvinyl fluoride films), equipped with a dual port stainless steel fitting and polypropylene septum with a nominal volume of 1.2 L (Cromlab, Barcelona, Spain), were used for bag sampling.

2.2. Sample collection

Biogas samples were taken from the pressurized line of a compressor station at the sewage treatment plant. Tedlar bag sampling was performed with bags of 1.2 L and polytetrafluoroethylene (PTFE) tubing was used to connect the sampling port and the needle valve. Prior to sampling the set-up and the PTFE tubing was flushed with biogas for 5 min, as Ajhar et al. [17] recommends this for reducing siloxane losses due to the adsorption on the valve and tubing. Bag samples were stored at room temperature.

Sorbent tube sampling was performed by adapting a PTFE tubing to the gas pipeline and then the cartridges were fitted a sampling pump (FLEC Air Pump 1001, from Markes) at a flow rate of 50 $mL\ min^{-1}$ for 10 min. The pumped biogas volume was therefore 500 mL. After collection, samples were immediately sealed with end caps fitted with PTFE ferrules and stored at 4 °C in hermetically sealable glass jars and analyzed within 3 days of collection.

2.3. Analytical methods

Three different methods (A, B and C) were applied for the determination of analytes in samples.

2.3.1. Method A (sampling with bag and loop injection in GC–MS)

Method A involves the analysis of samples in Tedlar bags by direct loop injection in GC–MS (250 μL). Filled Tedlar bags were connected to the loop by PTFE tubing. To run analysis, the valve was opened and the biogas sample was introduced into the inlet by injecting the bag for 1 min.

2.3.2. Method B (sampling with bag and injection in the cold trap followed by TD-GC–MS)

Method B involves the sampling analysis using Tedlar bags by TD-GC–MS. Tedlar bags containing biogas samples were directly connected to the TD by an Airserver (Markes, International Limited, Llantrisant, UK) via PTFE tubing. Sample bags were injected for 2 min at 100 $mL\ min^{-1}$ for a final injected volume was 200 mL. Retention of the analytes was performed by a cold trap filled with Tenax TA and Unicarb cooled to −10 °C. After flash heating the cold trap at 300 °C for 8 min, analytes were injected into the chromatographic column. A split flow of 5 $mL\ min^{-1}$ was applied in this step.

2.3.3. Method C (sampling with cartridges and TD-GC–MS)

Method C involves the sampling analysis using cartridges and followed by TD-GC–MS. Desorption of the analytes retained on the sorbent tubes was carried out in a Unity Thermal Desorption system connected to an Ultra A automatic sampler (both from Markes International Limited, Llantrisant, UK). In the first step, primary desorption, tubes were heated to 200 °C with a helium flow rate of 30 $mL\ min^{-1}$ for 5 min. This was done to desorb the analytes which were refocused on a cold trap filled with Tenax TA and Unicarb, cooled to −10 °C. A split flow was not applied in this step, so all the mass desorbed from the tubes went into the cold trap. After flashheating of the cold trap at 300 °C for 8 min, analytes were injected into the chromatographic column. A split flow of 5 $mL\ min^{-1}$ was applied in this step.

After each use, the tubes were reconditioned by thermal cleaning (100 °C, 200 °C, 300 °C and 335 °C) for 15 min at each temperature. The clean tubes were cupped with end caps fitted with PTFE ferrules, stored in hermetically sealable glass jars with desiccant material.

2.4. GC–MS conditions

Separation and detection were performed with a 7890 A gas chromatograph and 5975C inert mass spectrometer (Agilent Technologies, Palo Alto, USA) using helium gas as the carrier at a flow rate of 1.5 $mL\ min^{-1}$.

Two chromatographic conditions were optimized for the best resolution of all compounds with both injections loop and TD. Firstly, alkanes (C_3–C_7), hydrogen sulfide and carbonyl sulfide were separated into a capillary column GS-GASPRO (30 m, 0.32 mm and 1.0 μm) (Agilent Technologies Palo Alto, USA). The oven temperature of the GC was initially held at 40 °C for 2 min, then raised to 220 °C at a rate of 50 °C min^{-1} and held at that temperature for 12 min.

Secondly, the chromatographic separation of alkanes (C_8–C_{20}), mercaptans, siloxanes and VOCs was performed in a capillary column ZB-5 (60 m, 0.32 mm and 1.0 μm) (Teknokroma, Barcelona, Spain). In Method A (loop injection), the oven temperature of the GC was initially held at 36 °C for 5 min, then raised to 120 °C at a rate of 10 °C min^{-1} and then raised again to 220 °C at a rate of 20 °C min^{-1} and held at that temperature for 10 min. In Method B and C (TD), the oven temperature of the GC was initially held at 36 °C for 5 min, then raised to 120 °C at a rate of 10 °C min^{-1} and then to 220 °C at 20 °C min^{-1} and held at that temperature for 25 min.

The GC–MS interface was set at 250 °C. The mass spectrometer acquired data in scan mode with an m/z interval ranging from 35 to 290, operating at electron impact energy of 70 eV. SIM acquisition was used for siloxane determination. Qualitative identification of the target compounds was based on the match of the retention times and the ion ratios of the target quantifier and qualifier ions (Table 1).

2.5. Calibration

For gas standards, the instrumentation allowed the automatic preparation of standards from the cylinder gas through a point-of-use dynamic blending system calibration suitable for gaseous component analysis, especially for low-level components. Gas standard levels were prepared in-situ in the blending system with helium at ranges between 0.07 and 5 ppm. Only hydrogen sulfide ranges were between 4.8 and 2000 ppm. No extra step was

Table 1
Target compounds, quantifier and qualifier ions, and validation results (expressed in mg m^{-3}) for the three analytical methods studied.

Compound	Quantifier ions	Qualifier ions[a]			Method A		Method B		Method C	
					LOD	LOQ	LOD	LOQ	LOD	LOQ
Ethyl mercaptan	62	47(90)	45(82)		1.2	3.5	4×10^{-3}	0.02	2.5×10^{-3}	0.01
Dimethyl sulfide	62	47(95)	45(80)		1.2	3.5	2×10^{-4}	8×10^{-4}	1×10^{-4}	5×10^{-4}
Carbon disulfide	76	44(14)			1.2	3.5	2×10^{-4}	8×10^{-4}	1×10^{-4}	5×10^{-4}
Propyl mercaptan	76	47(58)	43(48)	61(11)	1.2	3.5	2×10^{-4}	8×10^{-4}	1×10^{-4}	5×10^{-4}
Butyl mercaptan	90	56(107)	61(24)	47(34)	1.2	3.5	2×10^{-4}	8×10^{-4}	1×10^{-4}	5×10^{-4}
Dimethyl disulfide	94	79(48)	61(9)	64(8)	1.2	3.5	4×10^{-4}	0.02	2.5×10^{-3}	0.02
1-Pentanethiol	104	55(83)	70(66)	61(22)	1.2	3.5	2×10^{-4}	8×10^{-4}	1×10^{-4}	2×10^{-4}
Carbonyl sulfide*	60	32(71)	44(7)		0.05	0.2	–	–	–	–
Hydrogen sulfide*	34	32(50)	33(45)		2.5	7.6	–	–	–	–
Benzene	78	77(23)	51(14)		1.2	3.2	8×10^{-4}	4×10^{-3}	5×10^{-4}	2×10^{-3}
Toluene	91	92(59)			1.2	3.2	2×10^{-4}	8×10^{-4}	1×10^{-4}	5×10^{-4}
Chlorobenzene	112	77(48)	114(32)	51(13)	0.4	3.2	2×10^{-4}	8×10^{-4}	1×10^{-4}	5×10^{-4}
Ethylbenzene	91	106(33)			3.2	6.0	2×10^{-4}	8×10^{-4}	1×10^{-4}	5×10^{-4}
m,p-Xylene	61	106(51)	105(23)	77(12)	0.4	3.2	8×10^{-4}	4×10^{-3}	1×10^{-4}	5×10^{-4}
Styrene	104	103(47)	78(40)		0.4	3.2	2×10^{-4}	8×10^{-4}	1×10^{-4}	5×10^{-4}
o-Xylene	91	106(49)	77(16)		0.4	3.2	2×10^{-4}	8×10^{-4}	1×10^{-4}	5×10^{-4}
1,3-Dichlorobenzene	146	148(64)	111(35)	75(21)	0.4	3.2	8×10^{-4}	4×10^{-3}	5×10^{-4}	2×10^{-3}
1,4-Dichlorobenzene	146	148(65)	111(34)	75(22)	0.4	3.2	8×10^{-4}	4×10^{-3}	5×10^{-4}	2×10^{-3}
1,2-Dichlorobenzene	146	148(64)	111(37)	75(22)	0.5	3.2	8×10^{-4}	4×10^{-3}	5×10^{-4}	2×10^{-3}
Limonene	68	93(86)	67(79)	79(45)	0.4	3.2	8×10^{-4}	0.02	2.5×10^{-3}	5×10^{-3}
Propane	29	44(57)	43(51)		0.05	0.2	–	–	–	–
Butane	43	41(37)	58(16)		0.1	0.3	–	–	–	–
Pentane	43	42(66)	72(12)		0.1	0.4	–	–	–	–
Hexane	57	41(69)	86(19)		0.1	0.3	–	–	–	–
Heptane	43	71(77)	57(65)	100(23)	0.1	0.3	–	–	–	–
Octane	43	85(64)	57(48)	114(11)	6	16	3×10^{-4}	5×10^{-4}	1×10^{-4}	2×10^{-4}
Nonane	43	57(94)	85(38)	128(6)	6	16	3×10^{-4}	8×10^{-4}	1×10^{-4}	2×10^{-4}
Decane	57	43(90)	71(48)	142(5)	8	16	3×10^{-4}	8×10^{-4}	5×10^{-5}	1×10^{-4}
Undecane	57	43(68)	71(56)	156(7)	8	16	3×10^{-4}	8×10^{-4}	1×10^{-4}	2×10^{-3}
Dodecane	57	43(67)	71(62)	170(6)	8	16	1×10^{-4}	2×10^{-4}	2×10^{-5}	1×10^{-4}
Tridecane	57	71(67)	43(65)	184(5)	2	10	1×10^{-4}	2×10^{-4}	2×10^{-5}	1×10^{-4}
Tetradecane	57	71(71)	43(62)	198(5)	8	16	1×10^{-4}	2×10^{-4}	2×10^{-5}	1×10^{-4}
Pentadecane	57	71(74)	43(63)	212(4)	8	16	2×10^{-4}	2×10^{-4}	1×10^{-4}	2×10^{-3}
Hexadecane	57	71(75)	43(61)	226(5)	8	16	2×10^{-4}	8×10^{-4}	1×10^{-4}	2×10^{-3}
Heptadecane	57	71(76)	43(61)	240(4)	8	16	1×10^{-3}	4×10^{-3}	4×10^{-4}	2×10^{-3}
Octadecane	57	71(78)	43(61)	254(4)	8	16	1×10^{-3}	4×10^{-3}	4×10^{-4}	2×10^{-3}
Nonadecane	57	71(78)	43(60)	268(3)	8	16	1×10^{-3}	4×10^{-3}	4×10^{-4}	2×10^{-3}
Eicosane	57	71(79)	43(61)	282(3)	8	16	1×10^{-3}	4×10^{-3}	4×10^{-4}	2×10^{-3}
D3	207	208	209		0.6	1.0	–	–	–	–
D4	281	282	283		0.6	1.0	–	–	–	–
D5	73	355	267		0.6	1.0	–	–	–	–

Method A: 0.25 mL of sample injection.
Method B: 200 mL of sample injection.
Method C: 500 mL of sample injection.
LOD: Limit of detection.
LOQ: Limit of quantification.

[a] The value in brackets next to the qualifier ions represents percent abundances of each ion for that compound.
* Stability not studied.

required for the calibration as the bottle was directly plugged into the injector of the equipment. Due to the easy calibration of the gas standards using this blending system, these compounds (C_3–C_7, H_2S and carbonyl sulfide) were only calibrated using this system. As they were directly injected by loop, these compounds were determined in samples using only Method A.

Liquid standards were prepared in both the Tedlar bags and tube sampling methods. Five sampling bags were used as calibration standards filled to a volume of 1.2 L with a gas mixture with a composition as similar as possible to the biogas samples. After filling the bags, between 1 and 20 μL of stock solutions prepared in hexane (siloxanes and C_8–C_{20}) and methanol (mercaptans and VOCs) were injected in the respective filled bags at different concentrations, which evaporated into the gas mixture within minutes.

For the preparation of standards in cartridges, the external liquid standards were loaded into the two-bed sorbent tubes using a Calibration Solution Loading Rig (Markes International Limited, Llantrisant, UK), which allows a 99.999% pure Helium flow (Carburos Metálicos, Tarragona, Spain) to pass through the tube at a fixed flow rate of 100 mL min^{-1}. A conventional GC syringe was used to inject 5 μL of each standard dilution into the tube through a septum and this was deposited in the sampling end of the tube. The cartridges were attached to the end of the weak sorbent in the same position as in the sample collection. As a precaution, a short time (2 min) elapsed after the injection before the needle was withdrawn from the septum.

3. Results and discussion

As mentioned above, the instrumentation allowed the blending of the compounds obtained by cylinder gas in the GC by dilution with helium. This fact encouraged us to perform the calibration of these compounds (C_3–C_7, H_2S and carbonyl sulfide) directly into the GC by loop. Therefore, these compounds were only analyzed by Tedlar bag in Method A. The linearity for these compounds was good between 0.2 and 20 mg m^{-3}, except 10–3000 mg m^{-3} (H_2S). Calibration curves showed good linearity and their determination coefficients (r^2) were above 0.999 for all the compounds. The lowest calibration level for each compound was taken as the limit of quantification (LOQ). The limit of detection (LOD) was defined as the concentration corresponding to three times the noise of the quantifier ion. LODs of 0.1 mg m^{-3} were obtained for all the compounds, except for H_2S (5 mg m^{-3}).

Liquid standards were injected by TD and loop injection and chromatographic separation was optimized in both cases. External calibration was done by direct injection of 1 μL of diluted liquid standards. Five calibration levels were used for mercaptans and VOCs at levels between 0.8 ng and 100 ng (except ethylbenzene with a linearity of 1.5–100 ng). Alkanes from undecane to eicosane showed a linearity of 4–100 ng, and siloxanes of 0.16–20 ng. Calibration curves showed good linearity and their determination coefficients (r^2) were above 0.997 for all the compounds. LODs were between 0.05 ng (siloxanes) and 2 ng for some alkanes (tridecane–eicosane).

3.1. Tedlar bag analysis

Some studies have reported limitations concerning stability in Tedlar bags due to the adsorption process and losses by diffusion during storage [11,17]. However, Tedlar bags have been widely accepted as a container for the collection of air samples.

In the present study, we monitored the stability of the analytes in the Tedlar bags daily over a four day period (Fig. 1). Bags were filled with a matrix similar to biogas and standard solutions of the

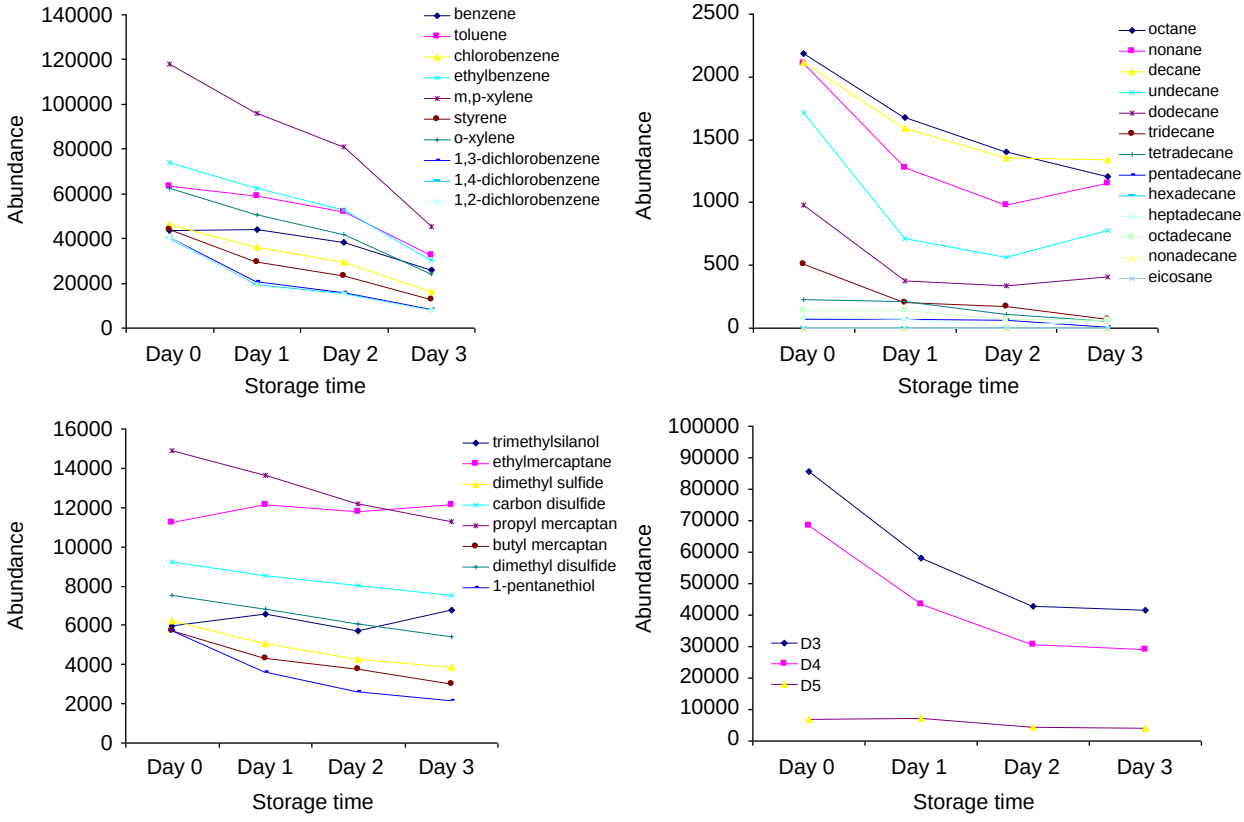

Fig. 1. Study of storage stability of compounds in Tedlar bags.

different analytes (VOCs, mercaptans siloxanes and C_8–C_{20}) were spiked into each one at a known concentration.

Tedlar bags spiked at 25 ng (VOCs and alkanes) and 4 ng (siloxanes and mercaptans) were injected directly by loop to GC–MS to study the behavior of compounds throughout the storage time. As can be seen in Fig. 1, long-term storage of compounds in this kind of Tedlar bags is not recommended. It was also noted that alkanes with high molecular weight showed a response considerably lower than expected on the first day. These results confirmed that they were more easily retained in the bag. Similar behavior was shown in literature [17,18], where some compounds showed a decrease in response (to a greater or lesser degree) through time. Despite these losses, linearity obtained from various concentrations of bag standards was good. Therefore, the authors concluded that reliable quantification can still be obtained by taking the preparation time of calibration bags into

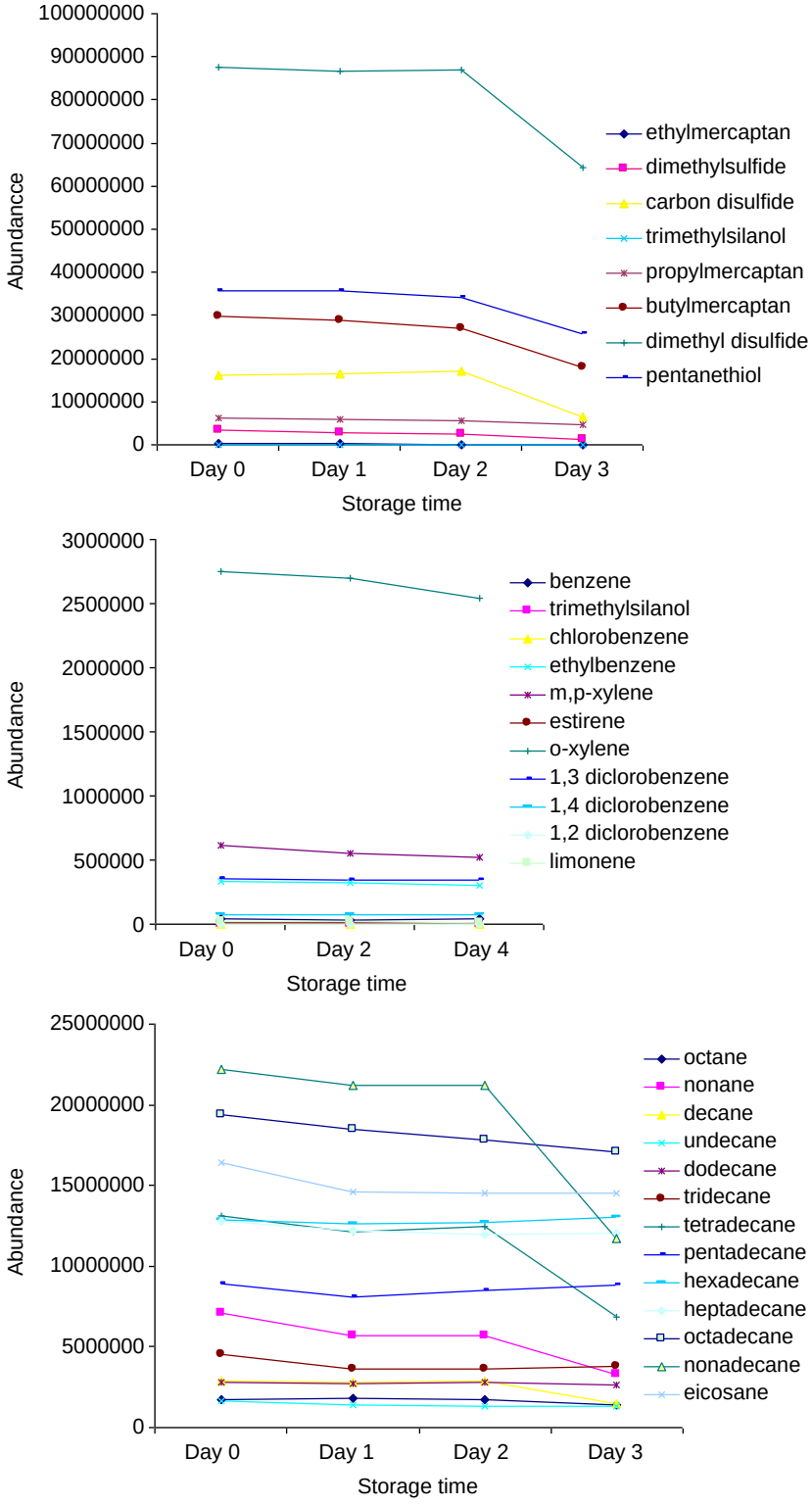

Fig. 2. Study of storage stability of compounds in sorbent tubes.

consideration. In the present study, bag samples and bag standards were analyzed after 48 h of being sampled.

In addition, our interest was focused on studying whether the adsorption effect was permanent or reversible. This would have significant implications for the common practice of reusing Tedlar bags. As recommended in reported studies about the removal of VOCs in Tedlar bags [11], the protocol followed was to clean the bags immediately after use with a rigorous flushing of N_2 10 times each. The precaution was also taken of using the same standard level for each bag during calibration. Blank samples showed benzene (2.3 ng) and some alkanes (decane, undecane, dodecane and tridecane) at levels of 3.1–9 ng. From the results found, the reuse of Tedlar bags is not recommended for determining these contaminants at low levels because blanks may compromise subsequent analysis.

Analytes from Tedlar bags were also determined by thermal desorption (200 mL). The main advantage of TD is the enhanced sensitivity that can be achieved. The suitability of TD for most of the analytes was found to be appropriate, except for siloxanes, mainly in the case of D5, because they were adsorbed in the transfer lines of the instrument. However, it can be considered as a limitation of the instrument that can be overcome with a heated interface. Under our conditions, TD allowed mercaptans to be determined since these compounds did not reach such low LODs when only 250 μL were injected by loop in GC–MS.

3.2. Tube analysis

Stability during storage was also determined in the study of sorbents. An increase of the stability of the compounds once retained was expected in comparison to Tedlar bags. Fifteen freshly cleaned cartridges were filled with 5 ng of siloxanes, alkanes, mercaptans and VOCs. Two of these were immediately analyzed and the others were sealed with metal storage caps fitted with combined PTFE ferrules and stored at 4 °C in hermetically sealable glass jars to prevent any contamination of the sorbents. Three of these cartridges were analyzed after being stored for 1 day, another three of them after 2 days, 3 more after three days and the last three after 4 days (except VOCs). Fig. 2 shows the responses with respect to the corresponding storage time. As can be seen, sorbent tubes showed insignificant storage losses of the analytes after 3 days. Only after 4 days, some compounds such as nonadecane, nonane or ethylmercaptan decreased their response by between 30% and 50%. Results found in this study were in agreement with those found by Ramírez et al. [19], who studied the stability of 90 VOCs during storage in a cartridge. In their study, all the compounds showed a complete stability after 3 days of storage and only after 7 days hexane and carbonyl sulfide increased their response, possibly due to the degradation of some analytes.

It is important to check the blanks and not to overload the sampling tube with high amounts of standards. EPA recommends ensuring levels lower than 5% of the average amounts of analytes in blank tubes [20]. In the analysis of the 10 freshly cleaned sorbent tubes involved in this study, blank signals and the artifacts of the Tenax/Carbograph 1TD tubes were tested. Blank signals coincided with the retention time and the quantifier ion of some VOCs (carbon disulfide, styrene, toluene, and chlorobenzene), siloxanes and alkanes (decane and tetradecane). The average blank levels (between 0.02 and 2.4 ng) were included in the calibration curves.

3.3. Validation

Whenever possible, all the compounds were determined using the three methods. As commented, analyte response depends on the preparation time in the bag and this effect was taken into consideration throughout the validation process of methods A and B, which use Tedlar bags. A preparation time of 48 h was selected for the bag standards for the validation of the method.

The method with loop injection (Method A), showed a linear range from 0.05 ng to 5 ng for low weight alkanes and 0.8 ng–100 ng for the rest of compounds, only with the exception of hydrogen sulfide with a linear range of 2–760 ng. In all cases, the r^2 was higher than 0.997. Table 1 shows limits of detection (LODs) and limits of quantification (LOQs) for all the compounds with the three sampling methods. When using Method A, LODs ranged between 0.1 mg m^{-3} (carbonyl sulfide) and 5 mg m^{-3} (hydrogen sulfide). Siloxanes showed a LOD of 0.6 mg m^{-3} and they were only determined by Method A because desorption problems they showed in Methods B and C. It is well known that TD of semi-volatile compounds can cause memory effects in the instrument due to the partial desorption of the analytes from the trap or their accumulation in the transfer lines.

The repeatability of bag sampling was determined from 3 measurements of a bag filled with 10 ng of standard, with

Table 2
Concentrations (mg m^{-3}) found in biogas samples ($n=3$, RSD < 25%).

Compound	[a]Concentration	[b]Concentration
Ethyl mercaptan	n.d	1.4
Dimethyl sulfide	n.d.	0.1
Carbon disulfide	n.d.	n.d.
Propyl mercaptan	< LOQ	0.48
Butyl mercaptan	0.01	0.03
Dimethyl disulfide	n.d.	n.d.
1-Pentanethiol	0.03	0.01
Hydrogen sulfide*	2223	–
Carbonyl sulfide*	< LOQ	–
Benzene	< LOQ	0.1
Toluene	1.21	1.4
Chlorobenzene	0.01	0.01
Ethylbenzene	0.05	0.05
m,p-Xylene	0.15	0.27
Styrene	< LOQ	0.1
o-Xylene	0.15	0.05
1,3-Dichlorobenzene	n.d.	n.d.
1,4-Dichlorobenzene	< LOQ	0.01
1,2-Dichlorobenzene	0.02	0.05
R-limonene	0.03	0.02
Hexamethylcyclo-trisiloxane(D3)	< LOQ	–
Octamethylcyclo-tetrasiloxane (D4)	3.25	–
Decamethylcyclo-pentasiloxane (D5)	4.84	–
Propane*	< LOQ	–
Butane*	n.d.	–
Pentane*	5.01	–
Hexane*	n.d.	–
Heptane*	n.d.	–
Octane	2.78	3.8
Nonane	10.4	12.5
Decane	118	95
Undecane	1.27	1.5
Dodecane	0.25	0.2
Tridecane	0.13	0.10
Tetradecane	0.03	0.02
Pentadecane	< LOQ	0.005
Hexadecane	< LOQ	0.01
Heptadecane	n.d.	< LOQ
Octadecane	n.d.	n.d
Nonadecane	n.d.	n.d
Eicosane	n.d.	n.d.

n.d.: Non detected.
LOQ: Limit of quantification.
GC–MS: Gas chromatography-mass spectrometry.
TD-GC–MS: Thermal desorption-gas chromatography–mass spectrometry.
[a] Methods A and B.
[b] Method C.
* Stability not studied.

results between 0.5% and 10%. Similar values of repeatability were obtained through the direct injection of gas mix cylinder at a concentration of 2.19 ppm. Reproducibility between days showed values of RSD lower than 20%.

Mercaptans, VOCs and alkanes C_8–C_{20}, could be determined by TD using both Tedlar bags (Method B) and tubes (Method C), with lower LODs. For example, with Method C, the linear range for most of the compounds was from 0.1 ng to 100 ng with r^2 being higher than 0.997. The validation for sorbent tubes (Method C) was performed by loading the sorbents with 5 μL of standards at 25 ng. Similarly to the bag study, the method was validated after 48 h of spiking the tubes. As can be seen in Table 1, TD (Tedlar and tube) showed LODs between 2×10^{-5} and 4×10^{-3} mg m^{-3} and LOQs between 1×10^{-4} and 0.02 mg m^{-3}. Similar levels were reported by Ramírez et al. [21], who obtained MDLs for 2.64 L of sample ranging between 4×10^{-4} and 0.4 μg m^{-3} for VOC determination in air samples using a tube sampling method.

The repeatability of the method was calculated as the %RSD of the analysis of three replicates of tubes filled with 25 ng of standards mixture. Values ranged from 1% for most VOCs and

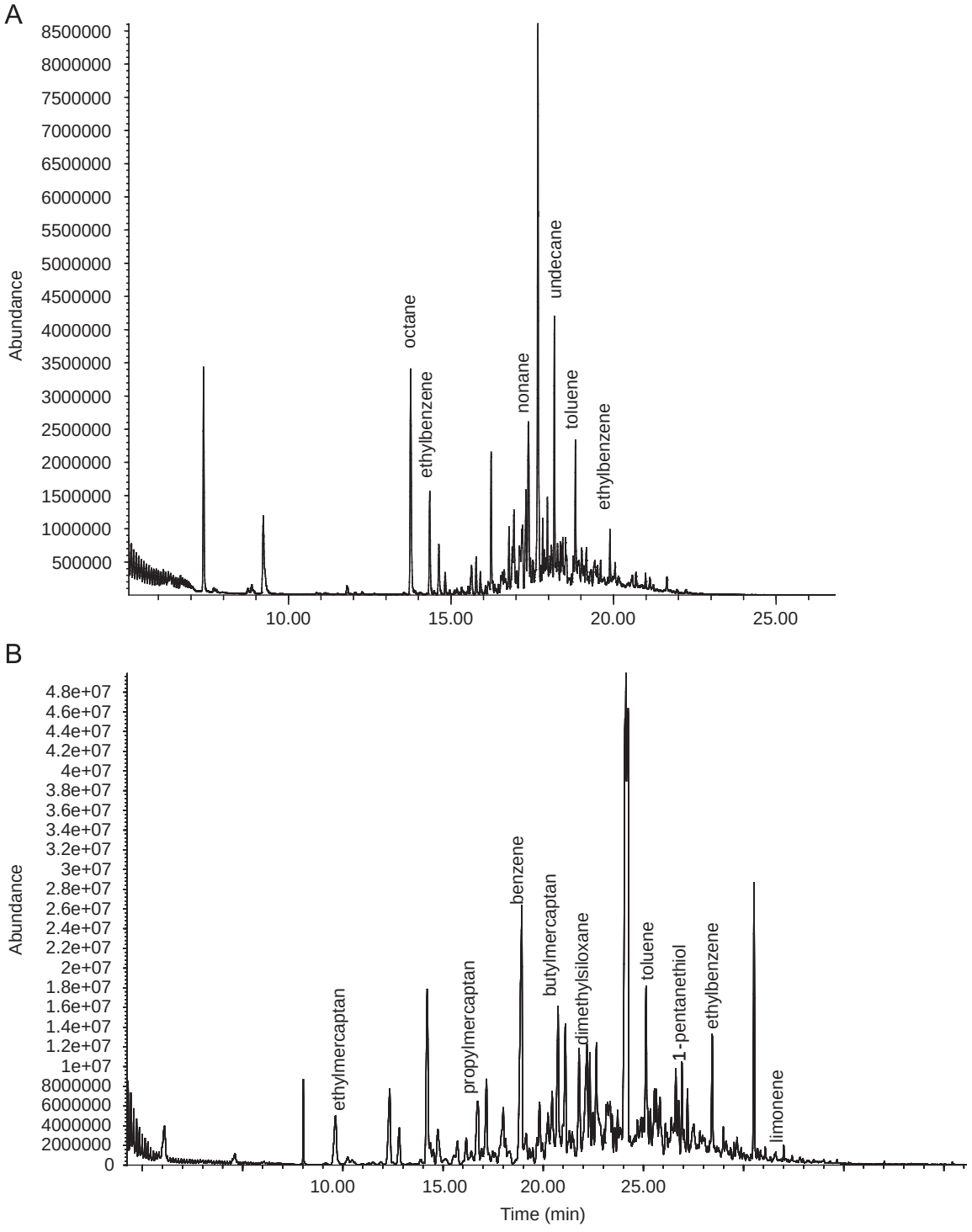

Fig. 3. Total ion chromatograms of a sample analyzed by TD with bag (A) and with tube (B). Some of the most representative compounds are marked.

alkanes to 15% for pentadecane and heptadecane. Values of reproducibility between days showed values of RSD lower than 17%.

3.4. Analysis of samples

The methods developed were applied in order to analyze biogas samples from a wastewater treatment plant. For all the compounds (mercaptans, VOCs and high molecular weight alkanes) except siloxanes and gas compounds, TD with bag or tube sampling was the best option.

As commented above, siloxanes were not desorbed correctly in our instrument, which showed limitations in temperature due to the loop. These compounds and C_3–C_7, H_2S and carbonyl sulfide were analyzed using Tedlar bag sampling injected directly to GC–MS by loop (Method A).

Table 2 shows the results found for biogas samples using both Tedlar bag (200 mL) and tube sorbent sampling (500 mL). As can be seen, despite siloxanes not being determined by TD, the LODs obtained in Method A allowed these compounds to be determined by GC–MS. As can be seen, D4 and D5 showed the highest concentrations (3.25 and 4.84 mg m^{-3}, respectively), indicating that they should be removed in the STP treatments to prevent combustion engine damage. Up to maximum values of D4 (12 mg m^{-3}) have been found in landfill gas by Narros et al. [22], and slightly lower levels of D4 and D5 (below 0.87 mg m^{-3} and 1.27 mg m^{-3}, respectively) have been reported in STPs in Finland [6].

Volatile sulfur compounds are responsible for the frequent unpleasant smells associated with STPs and may contribute to corrosion in combustion engines generating harmful emissions. Among these compounds, the highest levels recorded were for H_2S (2223 mg m^{-3}). These results were in agreement with results reviewed by Rasi et al. [3], who indicated that the high content was probably a result of the high quantity of sulfates in the STPs. Mercaptans showed lower values, with maximum values of 1.4 mg m^{-3} for ethyl mercaptan. Alkanes were found at levels of 2.78–3.8 mg m^{-3} (octane), 10.4–12.5 mg m^{-3} (nonane) and 118 mg m^{-3} (decane). The highest molecular weight compounds showed lower values, even values below LOQ.

The higher sensitivity of the Method C allowed pentadecane, hexadecane and heptadecane to be detected at levels between 0.005 and 0.01 mg m^{-3} using tube sampling. Fig. 3 shows a chromatogram with the most representative contaminants in biogas obtained by TD using a sorbent tube. In general, VOCs were found at lower levels with maximum values of 2.5 mg m^{-3} of toluene and 0.5 mg m^{-3} m,p-xylene, whereas 1,3 dichlorobenzene was not found in biogas samples.

4. Conclusions

This study compares the performance of three analytical methods for determining biogas components. Two approaches were attempted with GC–MS using a loop and TD. The TD method allowed the possibility of injecting Tedlar bag samples and sorbent tubes, decreasing the limits of detection. Based on the experimental results, some gas compounds and siloxanes were determined using the Tedlar sampling bags by direct injection by loop to GC–MS with good LODs and LOQs. However, VOCs, mercaptans and alkanes with high molecular weight were determined by TD using the tube sorbent and Tedlar bags. Tedlar bags are easy for sampling, but not always are they able to avoid loss of analites through their walls. Therefore, as a precaution, standards and samples should be analyzed after the same preparation time to avoid possible quantification errors. Sorbent tubes are an excellent sampling alternative because of their storage stability. Performance in real samples showed the presence of most of the studied compounds in biogas from STP.

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