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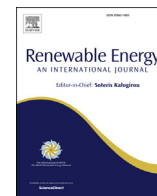
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Sampling, on-line and off-line measurement of organic silicon compounds at an industrial biogas-fed 175-kWe SOFC plant

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ABSTRACT

The use of biogas in the energy sector requires efficient removal of harmful trace levels of impurities. Reliable and robust online analytical equipment to measure these impurities is necessary and must be validated using offline techniques. In this work, total silicon and siloxanes were measured at an industrial solid oxide fuel cell fed by biogas. SOFC anodes are sensitive to silicon-based contaminants even at parts-per-billion levels. Online measurements of total silicon were carried out using a nondispersive infrared sensor (NDIR). Different sampling methods, including chemical adsorption, liquid quenching, and solid-phase adsorption were used at six biogas sampling points. Organic silicon compounds in the samples were determined by offline methods including GC-FID and GC-ICP-MS. The online analyzer's performance was satisfactory in both untreated biogas, where it agreed within the error margin of the most reliable offline technique used, and in clean biogas, where <0.1 mg$_{Si}$/m^3 siloxanes were detected. Several operational issues with different offline sampling and analytical methods are discussed, as is the performance of the sorbent-based biogas cleaning system used.

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1. Introduction

Biogas produced from anaerobic digestion of organic matter represents a growing renewable energy resource, delivering up to 127 TJ of heat and 61 TWh of electricity in the EU in 2015 [1]. While biogas production capacity grows, there has been a simultaneously growing interest in converting biogas to electricity with high efficiency (up to 60% LHV) through the use of high-temperature fuel cells, especially for small- or medium-scale facilities (≤1 MWe) where combustion engines are relatively inefficient (≤40% LHV) [2]. Successful long-duration field operation of these systems in recent years (for example, in Spain [3] and in Italy [4]) have enabled both a validation of the operability of the biogas-fuel cell combination, as well as provided a chance to study and resolve operational issues. Two key practical implementation challenges for these systems are the consistent removal and detection of harmful trace compounds in biogas, to which fuel cells are especially sensitive [2,5].

The primary components of biogas are methane (molar fraction ≤ 70%) and carbon dioxide (molar fraction ≤ 45%). In addition, biogas contains many impurities such as trace oxygen and nitrogen, aromatic hydrocarbons, and halogen-, sulfur- and silicon-containing compounds, as summarized in several reviews [2,6,7]. At high temperatures, silicon-containing compounds such as siloxanes are transformed into abrasive silica [8]. SOFC anodes can even be affected at very low siloxane concentrations (even at 69 ppb$_v$ of siloxane D4, corresponding to 0.340 mg$_{Si}$/m^3) [9]. Therefore, reliable monitoring techniques for siloxanes in low concentrations in biogas are essential, and gas cleaning systems are also required to achieve high biogas quality. At the moment, neither of these two systems—monitoring techniques and biogas cleaning systems—are well-understood or standardized for low-concentration siloxanes in biogas. Moreover, many validations of analytical equipment are done using model gases, which do not include the other impurities and moisture found in real biogas; all of these can strongly affect measurements and validation must be completed in the field.

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7. Nomenclature

ATD	Analytical Thermal Desorption
BEC	Blank-equivalent concentration
b.d.l.	Below Detection Limit
CD	Chemical Desorption
FID	Flame Ionization Detector
GC	Gas Chromatograph
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LQ	Liquid Quench (sampling technique)
LoD	Limit of detection
LoQ	Limit of quantification
MS	Mass spectrometry
ppmv, ppbv	Parts per million/billion on a volume basis, equivalent to a 1E-6 mol/mol and 1E-9 mol/mol, respectively, for ideal gas mixtures (assumed here for all gaseous mixtures)
SCD	Sulfur chemiluminescence detector
STP	Reference state for volumetric measurements of gases, 0 °C and 1 bar
SOFC	Solid Oxide Fuel Cell
SPA	Solid-Phase Adsorption (sampling technique)
WWTP	Waste Water Treatment Plant

In this study, we aim to fill this gap by evaluating the performance of an online analytical device for the measurement of total silicon against different sampling and offline analytical techniques, in both untreated and clean biogas. This evaluation is done in the field, at the site of the first European industrial-sized (175 kWe) biogas-fed Solid Oxide Fuel Cell (SOFC) plant, where biogas is cleaned by a series of adsorption steps to protect the fuel cell modules. This study therefore additionally provides quantitative data on the operation of a full-scale biogas cleaning system for siloxane and other trace compound removal. First, the state of the art in siloxane measurement and removal in biogas is summarized. The sampling site, approach, and methodology is described. For the offline analysis done in this work, raw and clean biogas samples have been collected from six sampling points at the SOFC plant using three different sampling methods: Tenax tubes, solid absorption, and a continuous liquid quench sampling system (LQSS). The collected samples were analyzed by different techniques including GC-FID, GC-MS and GC-ICP-MS. Results are compared to total Si as measured by the Qualvista online analyzer (QBM-100) [10]. Other contaminants, especially sulfur compounds, were quantified as well. The results of the different methods for sampling and analysis have been compared and the performance of the online technique has been evaluated.

2. Background: state of the art

Sampling methods and analysis techniques for siloxane concentration measurement are still in the process of being developed and standardized. Although international standards are beginning to be applied for biomethane (i.e., biogas from which CO_2 has been separated) for injection in the natural gas grid (EN 16723-1 [11]) or as automotive fuel (EN 16723-2 [12]), no such standards exist for direct biogas use in fuel cells. Not only are fuel cells more sensitive to contaminants than some other applications, but biogas is also generally "dirtier" than biomethane, as it contains a wide range of variable impurities. In the literature, several studies have been reported investigating different sampling methods and analysis techniques on different biogas matrices. Sampling methods

including using canister [13,14], cylinders [14,18], liquid solvents [17], sorbent tubes [13–16,18], sampling bags [13,14,16,18] and impingers [13,14,16] have been employed to sample biogas containing sulfur and siloxane compounds. Generally, the offline analysis of siloxanes was carried out using gas-chromatography-based techniques such as GC-FID (gas chromatography flame ionization detector) or GC-MS (GC mass spectrometry) which has a comparatively lower LOD (limit of detection) [13], and has been used to analyze siloxanes in liquid wastewater samples [14] as well as in gas-phase biogas samples [15]. Ghidotti et al., for instance, used a solid-phase micro-extraction (SPME) followed by GC-MS for the measurement of different siloxanes in biogas and biomethane from anaerobic digesters and wastewater treatment plants. The method was compared to indirect gas sampling using sorbent tubes and followed by solvent extraction and GC-MS [16]. For compound-rich matrices, such as raw biogas, the mass spectra corresponding to siloxanes are highly affected by interferences. Simple mass spectra, high sensitivities and low LOD can be achieved using other coupled techniques such as GC-ICP-MS (gas chromatography inductively coupled plasma mass spectrometry), as reviewed for general trace compound measurements by Easter et al. [17], established for siloxane measurements in a clean solvent by Agilent [18], and demonstrated in real biogas samples with the full gas matrix complexity by Foppiano et al. [19].

Reliable online (and/or inline) analytical techniques are a crucial tool to protect the downstream plant equipment. Such online systems are especially important for long-term industrial use to insure efficient and stable operating of biogas plant. Unfortunately, only few online techniques with moderate LOD values, including PTR-MS [20] and FT-IR [21] were reported in the literature for the siloxane measurement. Additionally, establishing appropriate methods for such online analytical equipment need prospective and continuous validation using other advanced offline techniques, and this has not been reported to a significant extent in the scientific literature today. This work therefore fills a gap in the knowledge on online siloxane analyzers for use in real biogas, especially in comparison with existing offline methods.

To remove siloxanes from biogas, several high-surface area adsorbent materials including unmodified activated carbon [22], modified activated carbon [23], molecular sieves [24], silica gel [25], or zeolites [23] can be employed. Techniques have been reviewed by de Arespacochaga et al. [26]; comparisons between different sorbent types (silica gel, molecular sieve, activated carbon) were tested by Kajolinna et al. [24]. The presence of moisture in the biogas can dramatically reduce sorbents' siloxane capacity, as demonstrated for example by Sigot et al. in silica gel [25]. Simultaneous removal of siloxanes, sulfur compounds, and other contaminants, while desirable in principle, generally results in competitive effects which can lead to early breakthrough of adsorbent beds, as reported in a lab-based setting by Papurello et al. [27] and in the field by Calbry-Muzyka et al. [23]. Thus, two or more targeted biogas treatment steps may be needed. Only very sparse information is available in the literature on siloxane removal for full-scale biogas/SOFC systems. This work therefore fills a gap in this secondary topic by reporting on the performance of the sorbent-based cleaning system which is used as a test case for siloxane sampling and analytical equipment.

3. Methods

3.1. Plant description

The biogas cleaning system analyzed in the framework of the present work is the one installed at the DEMOSOFC plant, in the Turin premises in Italy. The DEMOSOFC plant is the first European

industrial-size biogas-fed Solid Oxide Fuel Cell (SOFC) plant [4]. The plant consists of a 175 kWe SOFC system (composed of three modules) fed by biogas from sewage sludge, produced onsite from a waste water treatment plant (WWTP). The system is hosted by the SMAT Collegno WWTP. As stated in the introduction section, biogas fed to fuel cell systems should be deeply cleaned from all sulfur and silicon based contaminants since they are detrimental for the cell and can cause severe irreversible degradation [4]. The cleaning unit installed in the DEMOSOFC plant has been designed by Politecnico di Torino together with Biokomp s.r.l., the company which has also constructed the system. The biogas cleaning process is based on adsorption on commercial impregnated activated carbons. The cleaning system (adsorption vessels) are installed inside an insulated container. Each vessel can contain around 250 kg–300 kg of sorbent material and the complete cleaning system includes 6 vessels in series. The chosen materials are provided by the company AirDep® and chosen sorbents are CKC, a potassium-impregnated activated carbon, specific for sulfur (H_2S) removal and C64, another impregnated activated carbon, specific for siloxanes and VOC removal.

The sampling points available at the site, which have been used for this activity, were identified and chosen during the DEMOSOFC cleaning system design process. The sampling points were designed to monitor the biogas quality on the raw gas side (before and after the 100 m pipeline connecting the digester area to the cleaning area) and on the clean gas side. Inside the cleaning container, sampling points were designed to analyze the biogas quality before every single vessel in the first lead-and-lag block (composed of 4 vessels), followed by a final sampling point at the end of the unit, to check the biogas fed to the fuel cell system.

A layout of the cleaning system is shown in Fig. 1. The system is designed in a lead-and-lag mode: thanks to available 2-ways and 4-ways valves, the first four vessels can be switched from series mode (standard operation) to parallel mode (maintenance): in this configuration, two vessels can be isolated and the sorbents replaced, while the other two are operating. This guarantees a continuous operation without any stop for sorbents replacement. Fig. 1S in the SI (Supporting Information) shows a photograph of the biogas treatment steps.

Biogas is produced onsite from the anaerobic digestion of sewage sludge. The as-produced gas is the stored before being fed to the system. The biogas line includes a first gravel filter used to remove liquid water followed by a blower (which increases the pressure up to 400 mbar gauge) and a chiller (operating with a dew point of 10 °C); the first biogas sampling point is located after the chiller (RawGas1), outside and in an open air environment, and it is derived from the bottom of the biogas piping.

After a pipeline around 100 m long, the biogas enters the biogas cleaning container at which another raw gas sampling point is installed (RawGas2). The biogas is first sent to a siloxanes-dedicated sorbent, after which another sampling point is available (SemiClean3). The second step of the cleaning process is the H_2S-dedicated sorbent. After the first two sorbent beds (siloxanes + sulfur removal) a further sampling point is available (SemiClean4): this sampling is essential to understand when the first sorbent beds reach breakthrough and need to be replaced. After this first stage, a second identical stage is placed in series, with one first sorbent bed for siloxanes removal followed by a second one for H_2S removal. At the end of the line with the four sorbent beds, sampling point Clean5 is available. Since siloxanes belong to the most critical compounds for fuel cell operation a final polisher is also installed, which is composed of 2 siloxane sorbent beds mounted in lead-and-lag mode. After the polisher stage, the biogas is ready to be compressed, chilled and fed to the SOFC system. The last sampling point (Polish6) is where the biogas is fed to

the SOFC system.

The DEMOSOFC plant, currently composed of 2 SOFC modules (approx. 100 kWe installed), has been operating for more than 12′500 h from October 2017 until March 2020, and it is currently running. Average biogas mass flow rate during the operation has been around 9 kg/h of biogas. During the sampling campaign, the plant was equipped with one module running stably at 45 kW, with a biogas flow rate of 15 kg/h. At the time, the cleaning was already in operation for 4500 h.

3.2. Sampling and analysis approach

An overview of the samples taken at the plant over a time period of three days, along with the sampling and analysis techniques used for organic silicon compounds, is listed in Table 1, where the sampling point labels refer to those illustrated in Fig. 1. The full range of sampling points available in the plant, from completely untreated biogas to high purity biogas, was used to compare techniques across the widest range of silicon-based compound concentration available in the plant. Additionally, each sorbent-based gas cleaning step can remove other, non-silicon-based trace compounds, which could cause different levels of interference for the silicon measurement systems, so using the full range of sampling points available is preferable. The sampling of all samples at the same sampling point was completed within the same calendar day.

Other biogas trace species were also analyzed, following the methods listed in Table 2. The purpose of these measurements was to provide information about the complexity of the biogas matrix beyond silicon compounds, as co-adsorption of different trace compounds can have a significant effect on sorbent capacities for siloxanes. Quantified were a selection of sulfur compounds (H_2S, CS_2, dimethyl sulfide, 2- and 1-propanethiol, dimethyl disulfide) and of terpenes and terpenoids (limonene, alpha-pinene, para-cymene) which are commonly found in biogas.

3.3. Sampling procedures

3.3.1. Online sampling

Biogas going to the NDIR online analyzer (QBM-100) is taken from the main fuel pipeline, from the top of the pipe to avoid condensation dragging to the analyzer. In order to avoid the risk of liquid water reaching the analyzer, a water trap has also been installed on the sampling line going to the system. This set-up and connection to the NDIR analyzer are shown in Fig. 2S. Sampling lines are made of stainless steel until the analyzer premises and turns into Teflon to reach the system inlet, where they are connected to the ports through fast-connectors. The temperature of the sampling point is the one inside the biogas cleaning container, which does not vary as much as the ambient temperature because of insulation (although seasonal and day-night temperature variations are nevertheless measured). To avoid temperature-dependent problems in the analysis, NDIR analyzer is insulated and kept, through a dedicated conditioning and ventilation system, at 25 °C. The pressure in the sampling point is the one of the biogas line which is approx. 400 mbar gauge. Flow rate of the sampling line should be — according to the product specifications — between 0.5 L_{STP}/min and 0.7 L_{STP}/min; dedicated rotameters are available to set the proper flow rate, which is also measured through a dedicated flow sensor.

3.3.2. Solid-phase adsorption sampling: direct gas flow method

Coated TD-tubes with Tenax TA® as sorbent were used. The TD-tubes were conditioned before usage by being heated up to 300 °C for 2 h under nitrogen. The sampling set-up used for SPA is
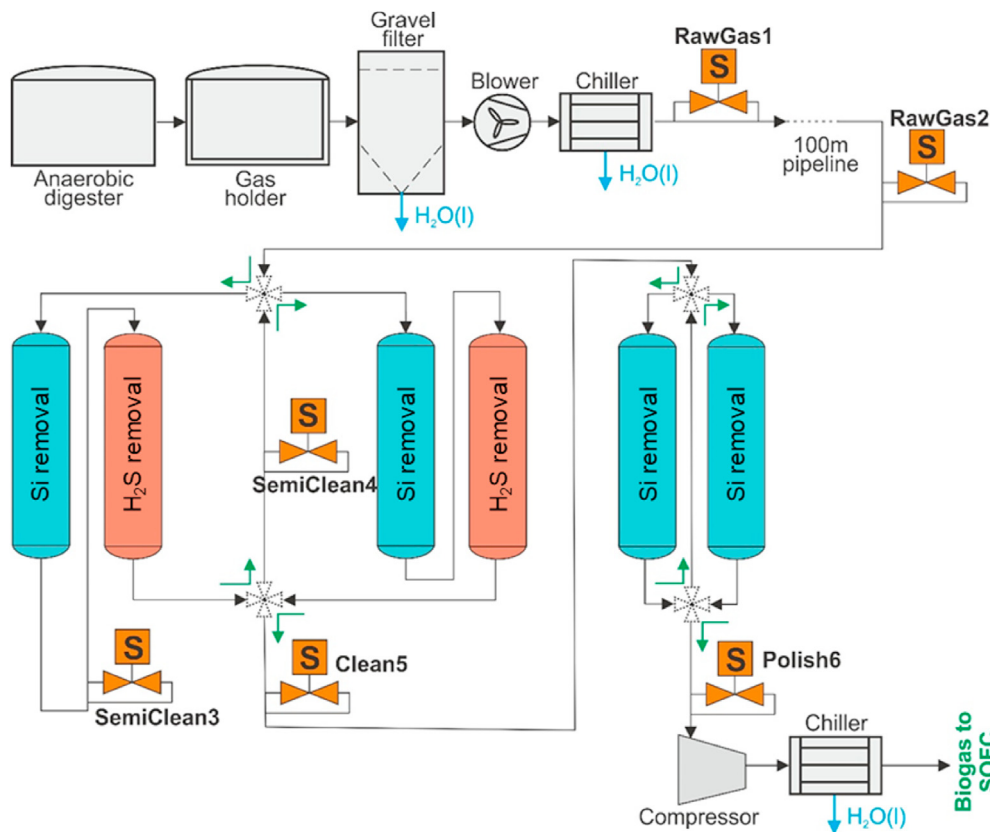
Fig. 1. Schematic overview of the biogas-SOFC plant studied in this work.

Table 1
Overview of the sampling and analysis approach used to measure organic silicon compounds in biogas in this work. Sampling point labels refer to those in Fig. 1.

Gas description	Sampling point label	Sampling technique	Analysis technique
Raw biogas	RawGas1	Adsorption on Tenax GR vials	Thermal desorption (ref. standard [28]) + GC-MS
		Adsorption in methanol	Chemical desorption (ref. standard [29]) + GC-MS
	RawGas2	Online	NDIR, in Qualvista instrument
		Liquid Quench	GC-FID
		Liquid Quench	GC-ICP-MS
		SPA	ATD + GC-FID
Biogas after 1 stage of siloxane-intended sorbent	SemiClean3	Liquid Quench	GC-FID
		Liquid Quench	GC-ICP-MS
		SPA	ATD + GC-FID
Biogas after 1 stage each of siloxane- and sulfur-intended sorbents	SemiClean4	Online	NDIR, in Qualvista instrument
		Liquid Quench	GC-FID
		Liquid Quench	GC-ICP-MS
		SPA	ATD + GC-FID
Biogas after 2 stages each of siloxane- and sulfur-intended sorbents	Clean5	Online	NDIR, in Qualvista instrument
		Liquid Quench	GC-FID
		Liquid Quench	GC-ICP-MS
		SPA	ATD + GC-FID
Clean biogas, after a further 2 steps of siloxane-intended sorbents	Polish6	Liquid Quench	GC-FID
		Liquid Quench	GC-ICP-MS
		SPA	ATD + GC-FID
		Adsorption on Tenax GR vials	Thermal desorption (ref. standard [28]) + GC-MS
		Adsorption in methanol	Chemical desorption (ref. standard [29]) + GC-MS

illustrated in Fig. 3S. First the sampling system was flushed with biogas, keeping the sampling tube isolated, for over 15 min using a flowrate much larger than the sampling flowrate (1 L_{STP}/min). To begin sampling, the SPA tube was connected to the biogas source upstream, and a membrane pump was connected downstream of the tube to regulate the flow. Three SPA tubes were used for sampling each biogas sampling point, each processing approximately 1,

2, and 5 L_{STP} of biogas using flowrates of approximately 0.05 L_{STP}/min, 0.1 L_{STP}/min, and 0.25 L_{STP}/min respectively for 20 min, as listed in Table 1S.

3.3.3. Solid-phase adsorption sampling: gas bag transfer method

The thermal desorption siloxanes analysis was performed by a dedicated external laboratory (N.S.A. - Nuovi Servizi Ambientali

Table 2
Overview of the sampling and analysis approach used to measure other (non-silicon) trace compounds in biogas. Sampling point labels refer to those in Fig. 1.

Gas description	Sampling point label	Sampling technique	Analysis technique and targeted compounds
Raw biogas	RawGas2	Colorimetry Liquid Quench Liquid Quench	Dräger tubes [30]: H_2S, mercaptans, NH_3 GC-FID: limonene, alpha-pinene, para-cymene GC-SCD: carbon disulfide, dimethyl sulfide, 2- and 1-propanethiol, dimethyl disulfide
Biogas after 1 stage of siloxane-intended sorbent	SemiClean3	Colorimetry Liquid Quench Liquid Quench	Dräger tubes: H_2S, mercaptans, NH_3 GC-FID: limonene, alpha-pinene, para-cymene GC-SCD: carbon disulfide, dimethyl sulfide, 2- and 1-propanethiol, dimethyl disulfide
Biogas after 1 stage each of siloxane- and sulfur-intended sorbents	SemiClean4	Colorimetry Liquid Quench Liquid Quench	Dräger tubes: H_2S, mercaptans, NH_3 GC-FID: limonene, alpha-pinene, para-cymene GC-SCD: carbon disulfide, dimethyl sulfide, 2- and 1-propanethiol, dimethyl disulfide
Biogas after 2 stages each of siloxane- and sulfur-intended sorbents	Clean5	Colorimetry Liquid Quench Liquid Quench	Dräger tubes: H_2S, mercaptans, NH_3 GC-FID: limonene, alpha-pinene, para-cymene GC-SCD: carbon disulfide, dimethyl sulfide, 2- and 1-propanethiol, dimethyl disulfide
Clean biogas, after a further 2 steps of siloxane-intended sorbents	Polish6	Colorimetry Liquid Quench Liquid Quench	Dräger tubes: H_2S, mercaptans, NH_3 GC-FID: limonene, alpha-pinene, para-cymene GC-SCD: carbon disulfide, dimethyl sulfide, 2- and 1-propanethiol, dimethyl disulfide

S.r.l. [31]) located in Turin, Italy, close to the DEMOSOFC plant. The sampling procedure was composed of two steps: first the biogas was collected in dedicated Tedlar® bags from sampling points RawGas1 and Polish6, then the gas from the bags was adsorbed, onsite during the sampling day, on dedicated solid materials (Tenax GR vials) using a low-flow pump (as shown in Fig. 4S). This two-step approach was required to control the flow going to the solid-phase material.

3.3.4. Methanol adsorption

The external laboratory N.S.A. also performed a siloxane analysis through a chemical desorption method. In this case, sampling was performed through direct biogas bubbling – from the sampling point – in a methanol refrigerated environment, as visible in Fig. 5S.

3.3.5. Liquid quench sampling

The liquid quench sampling process uses a system, somewhat analogous to an impinger bottle train, in which the sampled biogas is quenched by cold solvent (isopropanol) in continuous flow, producing a solvent with concentrated trace compounds and a clean gas, as shown in Fig. 6S. The two-phase mixture of clean gas and liquid solvent containing concentrated trace compounds is compressed and brought into a chilled container, where the phases are separated at 2 bar and −20 °C. The clean gas is vented and the liquid is retained in sample tubes, which are kept refrigerated until the time of analysis. The gas and liquid flows are recorded continuously during sampling, such that the concentration of gas phase contaminants in the biogas source can be calculated from the analyzed liquid phase concentration and the gas-to-liquid flow ratio (G/L). By comparison with an impinger bottle train, this system therefore allows continuous sampling operation, improved gas to liquid mass transfer during sampling [32], and improved flexibility in setting the phase separation conditions. The detailed operation of this system is given by Kaufman-Rechulski et al. [33,34].

3.4. Analysis procedures for silicon organic compounds

An overview of the analytical methods used for characterizing silicon-containing compounds in this work is shown in Table 3 and explained in detail in the subsections that follow. Note that the focus here is on analytical techniques which may have different

sampling techniques; the sampling techniques are explained in detail in section 3.3 above.

3.4.1. Online NDIR

The NDIR online analyzer takes 40 min to complete one measurement. This time includes 20 min of analysis of the clean/zero gas (zero measurement) and 20 min of analysis of the gas to be measured. The 20 min time is always composed of 10 min for filling the sensor volume and 10 min of analysis. The clean/zero gas is the biogas itself cleaned through a dedicated filter. The NDIR online analyzer measures the composition of the following sampling points (with reference to Fig. 1): RawGas2, SemiClean4 and Clean5. Raw biogas (RawGas2) is measured only once per day while SemiClean4 and Clean5 are alternately measured during the rest of the day.

The QBM-100 is factory calibrated prior to delivery to the customer. Siloxanes dedicated NDIR sensor (nondispersive infrared) is calibrated using gas mixtures at six concentration levels (8.16, 16.32, 81.6, and 163.2 mg_{D5}/m^3 of siloxane D5 in nitrogen, corresponding to 3.08, 6.16, 30.8, and 61.6 mg_{Si}/m^3, or 0.5, 1, 5, and 10 ppm_v siloxane D5) and zero gas (nitrogen). At each concentration level, four repetitions are done. The system installed in the DEMOSOFC plant was tested with D5 siloxane compound.

3.4.2. ATD + GC-FID

Calibration standards: Coated TD-tubes with Tenax TA® as sorbent were spiked with liquid or gas to obtained calibration standards. The TD-tubes were conditioned before usage by being heated up to 300 °C for 2 h under nitrogen. The liquid spiked TD-tubes contain L2, L3, D4, D5 and D6. The gas spiked TD-tubes do not contain D6 but do contain D3 next to L2, L3, D4 and D5. All standards contained n-octane (C8) as internal standard. The liquid spiked TD-tubes contained higher masses of the different siloxanes, between 1100 and 40 ng per TD-tube. The gas spiked TD-tubes contained lower masses of the different siloxanes between 270 and 14 ng per TD-tube.

Liquid spike: For the liquid spiking of TD-tubes a liquid mixture was prepared gravimetrically. The mixture is used for the manual spiking of nine TD-tubes. The uncertainty of the liquid spiked mass on the TD-tubes is 5%.

Gas spike: For the gas spiking of TD-tubes a static gas mixture is used in a high-pressure cylinder containing ppb levels of the different siloxanes in methane. The gas mixture from the cylinder

Table 3
Key operational parameters used for the different analytical techniques compared for the characterization of siloxanes in this work; details follow in this section. Sampling techniques are explained in detail in section 3.3.

Analytical technique	Key operational parameters
Online NDIR	Total measurement time 40 min: 20 min for calibration gas analysis +20 min for the gas analysis. Modified NDIR for siloxane analysis, patented by Qualvista®.
ATD + GC-FID	1st stage desorption at 300 °C for 5min, sampling flow 60 mL min^{-1}, cold trap temperature at −30 °C. heated with at least 1 °C s^{-1} to 300 °C for the 2nd stage desorption. The outlet split flow 10 mL min^{-1}. GC column DB-1MS-UI (60 m × 0.25 mm x 0.25 μm). GC oven temperature 50 °C hold 6 min, 10 °C/min to 150 °C, then 20 °C/min to 270 °C hold 5 min. FID detector at 250 °C, H$_2$ flow 30 mL min^{-1}, air flow 400 mL min^{-1} and N$_2$ flow 25 mL min^{-1}.
ATD + External lab analysis method	Adsorption on Tenax GR vials with 225 mg of material, 150 mg on the first stage and 75 mg on the second stage. Desorption temperature in the range 250–325 °C from 5 to 15 min and a flow rate in the range 30–50 ml min^{-1} (UNI EN ISO 16017). GC-MS instrument for the gas analysis.
CD external lab analysis method	Adsorption in refrigerated methanol. Extraction performed with solvents (UNI CEN/TS13649). GC-MS instrument for the gas analysis.
GC-FID of liquid quench samples	GC instrument: 7890A Agilent; column: 5% phenyl methyl siloxane stationary phase; method: start at 40 °C with 7 min hold, then 7 °C/min heating rate from 55 °C to 220 °C
GC-ICP-MS of liquid quench samples	GC instrument: 7890A Agilent; column: 5% phenyl methyl siloxane stationary phase; method: 12 °C/min heating rate from 55 °C to 200 °C ICP-MS Instrument: 7700x Agilent; RF Power 1400W; Ar Carrier Gas: 0.37 L min^{-1}; Option Gas: 60 mL (20% O$_2$ in Ar/O$_2$ mixture); ORS gases flow: He 2 mL min^{-1}, H 1 mL min^{-1}

was diluted with nitrogen to obtain the calibration standards with low masses of the siloxanes. The TD-tubes were spiked using a sampling manifold according to ISO 16017-1(2000) "Indoor, ambient and workplace air − Sampling and analysis of volatile organic compounds by sorbent TD-tube/thermal desorption/capillary gas chromatography − Part 1: Pumped sampling". The uncertainty of the gas spiked mass on the TD-tubes is 5%.

ATD-GC-FID: For the ATD-GC-FID/MSD analysis the TD-tubes were desorbed using a Perkin Elmer ATD650 thermal desorber with a two stages desorption; during the first stage the TD-tube was desorbed for 5 min at 300 °C with a sampling flow of 60 mL min^{-1} onto a cold trap packed with glass wool and TTA at −30 °C. In the second stage, the cold trap is quickly heated (at least 1 °C s^{-1}) to 300 °C, so the compounds are released and reach the gas chromatographic column where they are separated. The outlet split was 10 mL min^{-1}. The instrument used for the analyses is an Agilent technologies 7820A coupled with an FID. The GC column was a DB-1MS-UI, 60 m long, 0.25 mm internal diameter, 0.25 μm film thickness. The initial GC oven temperature was 50 °C (hold 6 min). The oven temperature was then raised with two ramp rates: to 150 °C at 10 °C/min and to 270 °C at 20 °C/min with a hold time of 5 min. The compounds were quantified using FID or MSD. The FID detector was used at 250 °C, with a hydrogen flow of 30 mL min^{-1}, an air flow of 400 mL min^{-1} and a nitrogen flow of 25 mL min^{-1}. The uncertainty for the analysis of relevant siloxanes of the standards for the sampling campaign can be found in Fig. 2S.

3.4.3. ATD + External lab analysis method

The first method used by the external laboratory for siloxane analysis is thermal desorption according to UNI EN ISO 16017−1:2002 [28]. The UNI EN ISO 16017 is referred to "sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography". The document is developed for Volatile Organic Compound (VOC) measurement in air, but it has been used from the external laboratory as a reference also for siloxanes in biogas, since no specific siloxane-related standards are available. The method applied to single compound concentration between 0.5 μg/m^3 and 100 mg/m^3. Adsorption is done on dedicated Tenax GR vials with around 225 mg of material, 150 mg on the first stage and 75 mg on the second stage. Vials should be conditioned before the use. The use of two stages vials is used to guarantee the saturation of the first one, where the analysis will be then performed. According to the UNI EN ISO 16017, desorption temperature should be in the range 250–325 °C from 5 to 15 min and a flow rate in the range 30–50 ml min^{-1}.

3.4.4. Chemical desorption (CD) lab analysis method

The second method used by the external laboratory is the chemical desorption according to UNI CEN/TS 13649:2015. The N.S.A. performed the siloxanes analysis with two methods (thermal and chemical desorption) in order to compare data and find the most reliable one. The adsorption phase is done with a bubbler by flowing a constant gas flow in refrigerated methanol. The UNI CEN/TS13649 is referred to "Determination of the mass concentration of individual gaseous organic compounds". As for the previous method, also this normative is not specific for siloxanes. The difference among the two methods is that the previous one was related to VOC measurement in air, while this is referred to VOC measurement in waste gases. In this case, solvent extraction is used, even if thermal desorption is also suggested as a second option.

3.4.5. GC-FID and GC-ICP-MS of liquid quench samples

The liquid samples collected by LQSS were measured in two different configurations using the GC-FID equipment and the coupled system GC-ICP-MS. The GC instrument (7890A, Agilent, USA) was equipped by FID detector. The liquid samples were introduced into the GC via an autosampler and the separation took place in a 5% phenyl methyl siloxane stationary phase column. To achieve a good separation of the different siloxane compounds the temperature program of the GC oven was optimized using a siloxane mixture of single standard solutions: the starting temperature was set to 40 °C (with a hold time of 7 min), then the temperature was increased from 55 °C to 220 °C by a heating rate of 7 °C/min.

For the second configuration, the same GC was coupled to an ICP-MS (7700x, Agilent, USA) with a heating rate of 12 °C/min from 55 °C to 200 °C. The line connecting the GC and the ICP-MS was heated at 300 °C. The GC and ICP-MS parameters were set by using the Agilent software OPENLAB and Mass Hunter, respectively. The latter was used to control and to carry out the GC-ICP-MS measurements of the standard solutions and samples. In order to lower the interferences (mainly raising from the two polyatomic molecules $^{14}N_2^+$ and $^{12}C^{16}O^+$) in the ICP-MS at m/z 28 (for Si) a combination of hydrogen and helium (2 mL min^{-1} and 1 mL min^{-1}, respectively) was used in Octopole Reaction System (ORS). A xenon-argon mixture (100 ppm$_v$ Xe in Ar) was added to the flow entering the ICP-MS. Before each measurement the ICP-MS parameters, including power, sampling depth, carrier gas (argon) and ORC gases (H and He) were adjusted using this mixture to obtain the highest intensity of $^{124}Xe^+$ and the lowest background signal at m/z 28.

The GC-FID and GC-ICP-MS quantification of L3, L4, D3, D4, D5 and D6 was carried out by using different single siloxane standards with concentrations ranging from 0 to 10 µg/mL and 0−500 ng/mL, respectively. All standards were prepared with the same iso-propanol solvent used for liquid quenching. The corresponding figures of merit (including the sensitivity, LOD, R^2 and blank equivalent concentration, BEC) can be found in Table 3S in SI (Supporting Information). Knowing the gas-to-liquid ratio (G/L) during the sampling on the plant site the siloxane concentrations in the biogas (in mg_{Si}/Nm^3) and the related LOD (in mg_{Si}/Nm^3) of each silicon compound and of silicon were calculated. Considering the propagation of uncertainties (including that related to FID, ICP signals and G/L ratio) the values of the relative standard deviation (RSD) were determined. A detailed description of the coupled system GC-ICP-MS and the method development can be found elsewhere [19]. The samples mentioned in Table 1 were measured by GC-FID and GC-ICP-MS separately and in two replicates each.

3.5. Procedures for other biogas trace compounds

3.5.1. GC-SCD with liquid samples

The following sulfur compounds were quantified from liquid quench samples analyzed by GC-SCD: carbon disulfide (CS_2), dimethyl sulfide (($CH_3)_2S$), 2- and 1-propanethiol (C_3H_8S), and dimethyl disulfide (($CH_3)_2S_2$). The liquid quench samples were also analyzed by GC-FID for non-silicon compounds, specifically the terpenes and terpenoids limonene ($C_{10}H_{16}$), alpha-pinene ($C_{10}H_{16}$), and p-cymene ($C_{10}H_{14}$).

The GC-SCD/FID used for this analysis is an Agilent 7890 which includes a single injector followed by two columns, one for each detector. Both columns were DB-Sulfur columns with a length of 40 m, an inner diameter of 0.32 mm, and a film thickness of 0.75 µm. The oven starting temperature was 40 °C (hold time 7 min) and rose from 55 °C to 220 °C at a rate of 7 °C/min. Agilent OpenLAB software was used for instrument control, peak detection, and data integration for the SCD results. Quantification of the tar-geted compounds was done using standards for each of the compounds prepared in the same isopropanol solvent used for liquid quenching. Four concentrations were prepared in the range of 0−2.5 µg/mL for the sulfur compounds in the GC-SCD, and in the range of 0−60 µg/mL for the terpenes in the GC-FID. Given the gas-liquid sampling ratios used in the range of 1650−1750 during sampling (corresponding to $mL_{STP,gas}$/min of sampled biogas

flowrate divided by $mL_{solvent}$/min of solvent flow during sampling), these standards cover a range of gas phase concentrations equiv-alent to 0−1.5 mg/m^3_{STP} for the sulfur compounds, and 0−35.3 mg/m^3_{STP} for the terpenes.

3.5.2. Dräger colorimetric indicators

Dräger tubes are commercially available colorimetric indicators based on known color changes of solid sorbent materials upon reaction with specified gas contaminants [30]. Quantification of the contaminant concentration is possible by passing a controlled volume of gas into the indicator using a provided sample pump, and comparing the extent of the color change to pre-calibrated demarcations on the indicator. The Dräger product names used were the *Ammonia 0.25/a* tube for NH_3, the *Mercaptan 0.1/a* tube for mercaptans, and the *Hydrogen Sulfide 1/c* tube for H_2S. Each mea-surement was repeated twice for each tube type at each biogas sampling point.

4. Results and discussion

4.1. Silicon compounds in biogas

The results of the organic silicon compound measurements at each biogas sampling point are shown in Fig. 2, with further details on the measurement outcomes in Table 4. The raw biogas mea-surements allow a direct comparison of several different sampling and analytical methods, as all except SPA sampling followed by ATD + GC-FID provided conclusive results. The clean biogas mea-surements were below the limit of detection of most of the tech-niques used. Nevertheless, SPA sampling followed by ATD + GC-FID demonstrated that the treated biogas was clean enough of silicon compounds to satisfy the fuel cell system's requirements even after the first stage of sorbent-based gas cleaning.

4.1.1. Silicon compounds in raw biogas

Results from the NDIR online analyser are shown in the first row of Table 4. Raw gas silicon content detected from the online gas analyser is in line with the values from detected with the Liquid Quenching sampling analysis via GC-ICP-MS, and similar to the value obtained via Liquid Quench followed by GC-FID. The average silicon concentration measured, during the sampling time where other offline samples were taken, is 3.5 mg_{Si}/m^3.

These online results can then be compared to the online analysis techniques. In the raw biogas, siloxanes D5 and D4 were detected by LQ sampling followed by both GC-FID and GC-ICP-MS, although only D5 was present in an amount greater than the LoQ of either technique. Siloxane D5 was quantified to be present at concentra-tions of 3.9−4.6 mg_{Si}/m^3 by LQ followed by GC-FID, and 3.3 mg_{Si}/m^3 by LQ followed by GC-ICP-MS. The GC-ICP-MS values are in line with the total Si value measured by the online analyser, and the GC-FID values are similar but slightly higher.

The differences between these two offline analysis techniques on the same LQ samples can be elucidated by examining the details of the analyses. A key difference can be observed in Figs. 3 and 4. In GC-FID, the chromatogram of the raw biogas sample shown in Fig. 3 is complex, with many peaks, some not separated from the others, even using a relatively long GC program. The retention times of the siloxane compounds are noted by overlaying the chromatogram for the mixed siloxane standard. From Fig. 3, it is clear that siloxane D5 and L4 would be well detected and quantified by GC-FID in this biogas mixture, but that L5 and D6 would not be detected accu-rately due to significant co-elution. A similar conclusion was pre-viously made during the GC-ICP-MS method development [19].

By comparison, the GC-ICP-MS chromatogram in Fig. 4 makes it clear that siloxanes L5 and D6 are not present in this mixture, a
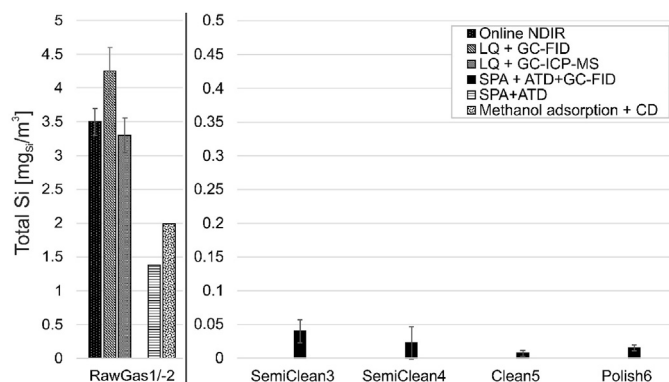

Fig. 2. Quantified total organic silicon compounds at each sampling point. The SOFC limit set by the unit's supplier is 10 ppbv siloxanes, corresponding to 0.06 mg_{Si}/m^3 if the siloxanes are mainly D5 (as in this biogas). Error bars shown refer to standard deviations of the repeated sampling and repeated analysis of each sample. Other un-certainty errors are negligible. The external lab used for methods SPA + ATD and methanol adsorption + CD did not provide any uncertainty analysis.

Table 4
Quantified organic silicon compounds and key measurement characteristics. "n.m." = not measured. "b.d.l" = below detection limit, where the superscripts refer to.

Sampling/Analysis	Sampling point label				
	RawGas1/-2	SemiClean3	SemiClean4	Clean5	Polish6
Online NDIR	3.3–3.7 mg$_{Si}$/m^3 total Si	n.m.	b.d.l.[a]	b.d.l.[a]	n.m.
LQ + GC-FID	3.9–4.6 mg$_{Si}$/m^3 D5; co-elution others.	b.d.l.[b]	b.d.l.[b]	b.d.l.[b]	b.d.l.[b]
LQ + GC-ICP-MS	3.3–3.5 mg$_{Si}$/m^3 D5; D4 detected < LoQ; others b.d.l.[c]	b.d.l.[c]	b.d.l.[c]	b.d.l.[c]	b.d.l.[c]
SPA + ATD + GC-FID	Concentration too high to be quantified	40.1 μg$_{Si}$/m^3	22.7 μg$_{Si}$/m^3	7.3 μg$_{Si}$/m^3	15.4 μg$_{Si}$/m^3
SPA + ATD	1.38 mg$_{Si}$/m^3 (sum of L3, L5, D3, D4, D5, D6)	n.m.	n.m.	n.m.	b.d.l.[d]
Methanol adsorption + CD	1.99 mg$_{Si}$/m^3 (sum of L3, L5, D3, D4, D5, D6)	n.m.	n.m.	n.m.	b.d.l.[e]

[a] LoD = 0.1 mg$_{Si}$/m^3 at 500s at 24 °C. LoD without interference compounds (chlorinated and fluorinated compounds).
[b] LoD = 0.12 mg$_{Si}$/m^3.
[c] LoD = 0.017 mg$_{Si}$/m^3.
[d] LoD = 0.0037 mg$_{Si}$/m^3.
[e] LoD = 0.037 mg$_{Si}$/m^3. Standard deviations are shown schematically in Fig. 2.
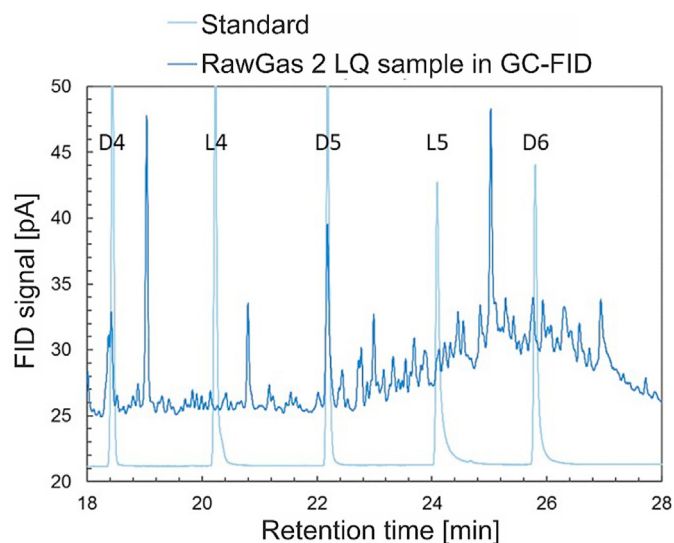
Fig. 3. Chromatogram in GC-FID for analysis of silicon compounds in the raw biogas, sampled by liquid quench. Co-elution of many non-siloxane compounds is clearly observed.
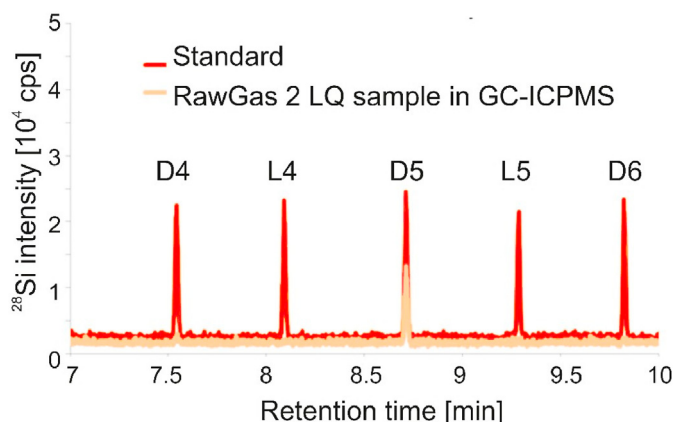
Fig. 4. Chromatogram in GC-ICP-MS for analysis of silicon compounds in the raw biogas, sampled by liquid quench. By comparison with Fig. 3 (GC-FID), co-elution of non-siloxane compounds is not detected by the ICP-MS.

conclusion which was not possible on the basis of the GC-FID results alone. A clear siloxane D5 peak is seen, confirming GC-FID results. This clarity relative to GC-FID is due to the element-specific nature of the ICP-MS detector, and allows much shorter

GC programs, as co-elution of non-silicon compounds does not have to be minimized/avoided in GC-ICP-MS as it does in GC-FID. It is also possible to assume that the D5 concentration would be overestimated in GC-FID due to the co-elution effect, which may explain the slightly higher GC-FID value of the LQ samples relative to GC-ICP-MS in Fig. 2 and Table 4.

The samples taken by SPA followed by ATD + GC-FID contained too much material, therefore, the siloxanes could not be distinguished in the chromatograms and no masses could be assigned using this method. This is unlikely to be the case for the Tenax adsorption method, as the primary siloxane compound in this biogas is siloxane D5, which is a heavy siloxane which is usually well adsorbed in solid sampling media. Here, the underestimation is currently unexplained, but could be due to condensation of D5 in the analysis process, if the transfer or analysis equipment is not properly inertized for siloxanes. However, this illustrates the care that must be taken with analyses which are completed with non-siloxane-specific methodology.

In comparison with the other solvent-absorption based sampling technique used (methanol absorption), the liquid quench technique in isopropanol gives siloxane measurements which are consistent with the online analyzer. This could be hypothesized to be due to better absorption efficiency of siloxanes in isopropanol at −20 °C and 2 bar used in the liquid quench system than in methanol as used in the methanol absorption method.

4.1.2. Silicon content in clean biogas

As concerns clean gas after the filters, the online NDIR analyzer measures silicon concentration at sampling points SemiClean4 and Clean5. Even if some noise is visible from the online NDIR results, values are always below the detection limit of the instrument (declared as 0.1 mg Si/m^3 at 500 s and 24 °C without interference compounds as chlorinated and fluorinated compounds). During normal continuous operation, the aim of the analyses in Semi-Clean4 and Clean5 are the detection of any possible breakthrough to plan the maintenance of the cleaning system. Based on these results then, no siloxanes are detected and no maintenance of the system should be necessary at the time of sampling.

These results from the online NDIR analyzer are confirmed by the measurements from the other sampling and analysis methods. The liquid quench samples were not found to contain detectable siloxanes after the first gas cleaning filter, neither using GC-FID nor GC-ICP-MS as the analysis technique. The external lab (the final two rows of Table 4) measured cleaning gas only in Polish6, with the aim of verifying the gas sent to the SOFC modules. With both the methods (Chemical and Thermal Desorption) values are below the detection limits, declared as 0.1 mg/m^3 of total siloxanes (sum of single concentrations) for chemical desorption and 0.01 mg/m^3 of

Table 5
Speciation of siloxanes identified and quantified by SPA followed by ATD + GC-FID.

Sampling point	Siloxane D3			Siloxane D4			Siloxane D5		
	Average concentration (μg/ m^3)	Stdev (μg/ m^3)	Stdev (%)	Average concentration (μg/ m^3)	Stdev (μg/ m^3)	Stdev (%)	Average concentration (μg/ m^3)	Stdev (μg/ m^3)	Stdev (%)
RawGas2	–	–	–	–	–	–	–	–	–
SemiClean3	6	5	81	13	4	30	87	36	41
SemiClean4	24	32	135	29	25	87	7	7	99
Clean5	9.5	3.3	35	9	8	86	0.9	0.3	39
Polish6	5.8	2.8	48	12	5	40	22.9	3.1	13

total siloxanes (sum of single concentrations) for thermal desorption.

The method of SPA sampling followed by ATD + GC-FID was the only one to have a detection limit low enough to detect siloxanes in the clean biogas samples, however, with high standard deviations values. Speciation of these results are shown in Table 5. The large standard deviation of the results mean that exact quantification is not possible; nevertheless, the range of values are below the limit for siloxane content set by the SOFC supplier. The supplier's limit is 10 ppb$_v$ siloxanes, corresponding to 0.06 mg$_{Si}$/m^3 if the siloxanes are mainly D5 (as in this biogas).

Comparison of retention times in chromatograms of the calibration standards and the samples showed that D3, D4 and D5 are present in the samples, while L2, L3 and D6 could not be detected if they were present the amounts are below the detection limit. According to ISO 6143:2001 Gas analysis − Comparison methods for determining and checking the composition of calibration gas mixtures, a straight-line regression model could be calculated from the gas spiked calibration standards for D3 and from the liquid spiked and gas spiked calibration standards combined for D4 and D5. Using this calibration, the mass of each siloxane could be determined in each sample. The blanks also contained traces of siloxane D4 and D5; these masses were deduced from the calculated masses. The concentration of the siloxanes at each sampling point was then determined using the sampling volume (std. L).

There are significant deviations between the samples taken at the same sampling point. The standard deviations of the data are large, ranging from 13% up to 135%. This could be caused by the reactive nature of the siloxanes. It could also be caused by trace amounts of siloxanes left in the sampling equipment from sampling event to sampling event, despite significant flushing, the use of fresh equipment wherever possible at each new sampling point, and despite efforts to sample at the cleaner biogas sampling points before the more contaminated ones.

Nevertheless, even these variations in trace amounts of measured siloxanes in the clean biogas sampling points still demonstrate three key points. First, the treated biogas entering the fuel cell is clean enough to satisfy the fuel cell's requirements for total silicon. Second, the NDIR online analyzer's measurement of correct biogas cleaning operation is confirmed by the off-line analysis performed here. Third, the biogas is demonstrated to be clean of silicon compounds even after a single sorbent-based gas cleaning step.

4.2. Other compounds in biogas and their effect on silicon measurements

The presence of the multitude of other possible trace compounds in biogas has the potential to significantly affect both the measurement of silicon-containing compounds and their removal in sorbent-based gas cleaning steps. The quantified non-silicon trace compounds in this biogas source are shown in Table 6 and 7. In these tables, each value is shown along with the limit of

quantification (LoQ) of each method. The LoQ is taken to be the first demarcation of the Dräger colorimetric indicator tubes, and for GC-based methods it corresponds to a peak with signal:noise ratio of 9−10, corresponding to three times the limit of detection (LoD) at a signal:noise ratio of 3.

The results demonstrate that this biogas contains a relatively low level of non-siloxane trace species, with trace sulfur compounds in the raw biogas at <40 ppm$_v$ and nearly entirely composed of H_2S, and effectively negligible (<1 ppm$_v$) levels of organic, non-sulfur, non-silicon compounds. By contrast, it is certainly possible for biogas sources to contain up to several 1000s of ppm$_v$ of H_2S, a few ppm$_v$ of other sulfur compounds, and several 100s of ppm$_v$ of other organic compounds [35].

Nevertheless, even in this relatively clean biogas, matrix effects still affected the quantification of siloxanes using certain techniques, via a mechanism of co-elution in gas chromatography followed by a detector which is not element-specific (GC-FID, GC-MS). This was true regardless of sampling technique used: the effect was observed in both LQ sampling followed by GC-FID and in SPA sampling followed by GC-MS. An element-specific detector, such as ICP-MS, is not affected by co-elution of non-silicon compounds. This conclusion had previously been reached in a comparison of GC-FID and GC-ICP-MS for siloxane measurements in a much more complex biogas mixture [19]; however, the fact that this co-elution effect remains significant even in the biogas source here, which contains siloxanes, H_2S, and little else, is noteworthy. Quantification of siloxanes in biogas via GC-based methods without an element-specific detector should be treated very carefully, with longer temperature programs to achieve as much separation as possible.

In Table 6 and 7, the effects of the adsorptive gas cleaning process on non-silicon compounds can also be seen. Although the first gas cleaning step was targeted for siloxane removal (see Fig. 1), Table 6 also shows that significant H_2S removal occurs in this step as well, at a removal effectiveness of 64% at the time of measurement. Other sulfur compounds and hydrocarbons were removed beyond their limit of detection as well. First, this shows that the gas cleaning system is performing well: all measured trace compounds, not only siloxanes, are removed successfully by the gas cleaning system. Secondly, this demonstrates that even sorbents which are carefully selected for the removal of a single compound or compound class are not necessarily selective for that compound in real biogas operation.

5. Conclusions

In this work, the performance for gas-phase total silicon quantification of an online NDIR analyzer mounted at a biogas plant with the aim of regulation and protection of SOFC was evaluated by comparing its readings to different sampling methods and offline techniques. Readings were compared at six different biogas sampling points, each after a different set of sorbent-based biogas cleaning steps, in order to evaluate the methods in different silicon-

Table 6
Sulfur-containing compounds quantified at each of the biogas sampling points. (*) indicates the compound was detected, but is below the limit of quantification (LoQ). '-' indicates the compound was not detected.

Units	H_2S	Mercaptans	Carbon disulfide	Dimethyl sulfide	1-propanethiol	2-propanethiol	Dimethyl disulfide
	ppm$_v$	ppm$_v$	ppm$_v$	ppm$_v$	ppm$_v$	ppm$_v$	ppm$_v$
LoQ	0.2	0.25	0.15	0.06	0.06	0.06	0.06
RawGas2	35.0	0.5	(*)	–	(*)	(*)	–
SemiClean3	12.5	(*)	–	–	–	–	–
SemiClean4	–	–	–	–	–	–	–
Clean5	–	–	–	–	–	–	–
Polish6	–	–	–	–	–	–	–

Table 7
Non-silicon, non-sulfur trace compounds quantified at each of the biogas sampling points. (*) indicates the compound was detected, but is below the limit of quantification (LoQ). '-' indicates the compound was not detected.

Units	NH_3	Limonene	Alpha-pinene	P-cymene
	ppm$_v$	ppm$_v$	ppm$_v$	ppm$_v$
LoQ	0.2	0.16	0.16	0.15
RawGas2	–	1.25	0.25	(*)
SemiClean3	–	–	–	–
SemiClean4	–	–	–	–
Clean5	–	–	–	–
Polish6	–	–	–	–

content regimes and confirm the performance of the gas cleaning itself.

The raw biogas sampling point was the only one at which measureable silicon was detected by the NDIR analyzer, at an average value of 3.5 mg$_{Si}$/m^3. This value is confirmed by offline measurements obtained by liquid quench (LQ) sampling followed by GC-ICP-MS. Other sampling and analytical combinations demonstrated either slightly higher values (LQ followed by GC-FID) which could be attributed to co-elution, or clearly lower values (SPA + ATD and Methanol adsorption + CD). The reason for the lower values is not clear, though for methanol adsorption it can be suspected to be due to loss of analyte in sampling.

After biogas cleaning steps, the online and all offline analytical methods showed that the biogas was clean enough to satisfy the fuel cell system's requirements for total silicon even after the first sorbent bed. Moreover, this gas cleaning system shows a non-selective removal of several contaminants including sulfur-containing compounds and other volatile hydrocarbons. These results are promising for future development of simpler biogas cleaning systems with fewer beds. From an analytical point of view, the results of the NDIR online analyzer's measurement in the clean gas are confirmed by the offline analysis, lending trust in the online analyzer's continued operation.

However, the complexity of the raw biogas matrix can substantially affect the performance of the other analytical methods used when combined with specific sampling methods. While SPA sampling followed by ATD + GC-FID delivers the lowest detection limits for the clean gas samples, it failed for the siloxane measurement for the raw biogas, where the total concentration of adsorbed trace compounds was too high for an accurate desorption and measurement. The relatively high uncertainty values obtained by this method are most probably due to the reactive nature of the siloxanes and/or caused by possible memory effects. Moreover, the presence of other contaminants in the raw biogas at moderate and high concentration level can lead to an overestimation of the siloxanes measured by a gas chromatograph due to the co-elution effect. This problem can be partially solved by setting long temperature programs in order to achieve as much separation as

possible. However, to overcome efficiently the co-elution effect an element-specific detector combined with GC, such as ICP-MS (instead of a FID or MS) is needed.

Finally, the choice of a reliable method which can efficiently sample siloxanes is challenging. While a liquid quench (LQ) system performs well for sampling raw biogas, physical adsorption on Tenax tubes shows better results for the clean biogas, due to achieving higher pre-concentration ratios and thus lower limits of detection in the final analysis. Solvent absorption using isopropanol at −20 °C and 2 bar used in the liquid quench system seems to have more absorption capabilities than methanol and shows consistent results with the online analyzer and LQS-GC-FID/ICP-MS systems.

In conclusion, the NDIR online analyzer's performance was found to be satisfactory in both untreated and clean biogas, the biogas cleaning system was found to remove silicon to below the limits required for the SOFC, and several operational issues with different offline sampling and analytical methods have been discussed.

CRediT authorship contribution statement

Adelaide Calbry-Muzyka: Conceptualization, Investigation, Writing − original draft, Writing − review & editing, Visualization. **Mohamed Tarik:** Conceptualization, Investigation, Writing − original draft, Visualization. **Marta Gandiglio:** Conceptualization, Investigation, Writing − original draft, Writing − review & editing. **Jianrong Li:** Conceptualization, Investigation, Writing − original draft, Writing − review & editing. **Debora Foppiano:** Investigation, Writing − original draft, Visualization. **Iris de Krom:** Investigation, Writing − original draft. **Dita Heikens:** Investigation. **Christian Ludwig:** Supervision, Resources. **Serge Biollaz:** Conceptualization, Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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