Development of an analysis method for the stability study of gaseous reference materials of siloxanes in biomethane

By
Paola Donata

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University of Applied Sciences Leiden

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Student
Paola Donata
1090801

VSL
Thijsseweg 11
2629 JA Delft
The Netherlands
tel. +31-15-2691500
fax +31-15-2612971
www.vsl.nl

Supervisors
Adriaan van der Veen, Ph.D.
Iris de Krom, Ph.D.

Internship period
5 June 2018 - 5 December 2018

Institution and education
Hogeschool Leiden
Zernikedreef 11
2333 CK Leiden
The Netherlands
Applied Sciences Department
Chemistry, specialisation in Analytical Chemistry

School Supervisor
Ruud Bakker, Ph.D.

Submission date
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Samenvatting

In de afgelopen zes jaar is er veel aandacht besteed aan de ontwikkeling van meetstandaarden voor het siloxaangehalte in biomethaan en opgewaardeerde biogas. Biogas is wereldwijd van toenemend belang als energiedrager. Het vormt een milieuvriendelijk alternatief voor aardgas en draagt bij tot de vermindering van de uitstoot van broeikasgassen. Siloxanen zijn siliciumhoudende vluchtige organische stoffen, die in biomethaan en opgewaardeerd biogas voorkomen. Het is een groep van de meest voorkomende onzuiverheden in biomethaan en opgewaardeerd biogas, zelfs na een geschikte behandeling van het ruwe biogas.

VSL neemt deel aan het project 'Metrology for Biomethane' binnen het European Metrology Programme for Innovation and Research (EMPIR). Dit project is gericht op het ontwikkelen en valideren van traceerbare meetstandaarden voor biomethaan. Een van de doelen is om "te rapporteren over de verbeterde stabiliteit van de meetstandaarden, een gevalideerde kalibratiemethode voor het meten van het totale silicium- en siloxanengehalte in biomethaan en een relatieve vergrote onzekerheid van 3 %". Voor dit onderzoek werd het criterium van 3 % in aanmerking genomen voor de relatief vergrote onzekerheden.

Het doel van dit onderzoek was om een methode te ontwikkelen voor de analyse en stabiliteitsstudie van gasvormige referentiematerialen van siloxanen in biomethaan. De subdoelen waren om de resultaten van geanalyseerde gasmengsels van een ringonderzoek die gemeten zijn op twee verschillende GC/FID-systemen met elkaar te vergelijken, een stabiliteitsonderzoek doen door de gasmengsels van het ringonderzoek te analyseren en te bepalen als deze nog stabiel zijn na bijna twee jaar, een methode ontwikkelen voor een GC-systeem met een Barrier Ionization Discharge (BID) detector en het GC/FID systeem met de GC/BID te vergelijken.

De resultaten van geanalyseerde gasmengsels van een ringonderzoek die gemeten zijn op twee verschillende GC/FID-systemen (GC-1 en GC-10) zijn met elkaar vergeleken. Er werd geconcludeerd dat GC-10 net zo goed presteert als GC-1. De pieken van de chromatogrammen zijn goed gescheiden en goed geïntegreerd.

Er werd een stabiliteitsonderzoek op lange termijn gedaan door gasmengsels van het ringonderzoek te analyseren en te bepalen als deze nog stabiel zijn na bijna twee jaar. De datapunten van de analyses tijdens de ringonderzoek hadden al een opwaartse trend en de hoeveelheid molfracties van de siloxanen veranderde gedurende één jaar in toenemende mate, en deze trend zette zich voort na een periode van bijna twee jaar.

Er werd een methode ontwikkeld voor een nieuwe GC-systeem met een BID detector. De pieken van de chromatogrammen waren goed gescheiden en goed geïntegreerd. Het mengsel dat lagere fracties van de siloxanen bevat (ppb niveau), vertoont voor L2 en L3 een herhaalbaarheid en reproduceerbaarheid lager dan 3 %. De mengsels met hogere fracties van de siloxanen (ppm niveau) hadden, met uitzondering van de reproduceerbaarheid van D5, voor alle componenten een herhaalbaarheid en reproduceerbaarheid lager dan 3 %.

De resultaten van het siloxaangehalte in methaan gemeten op een GC/FID werden vergeleken met het GC/BID-systeem. Op basis van de resultaten van de herhaalbaarheid en reproduceerbaarheid om het verschil tussen de systemen te vergelijken, is te zien dat de nieuwe detector, de BID detector, net zo gevoelig is als de FID voor de gasmengsels die hogere molfracties van de siloxanen bevatten. Het mengsel met lagere molfracties van de siloxanen kon wel gemeten worden op de GC/BID, terwijl dit niet mogelijk was op de GC/FID omdat het mengsel onder de detectielimiet van het systeem viel.

Acknowledgements

This thesis work carried out at the Van Swinden Laboratory is an effort in which, directly or indirectly, different people participated, reviewing, correcting, having patience, giving encouragement, accompanying in hard times and in moments of happiness. This work has allowed me to take advantage of the competence and experience of many people that I want to thank in this section.

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List of abbreviations

BID	Barrier Ionization Discharge
C8	n-octane
D3	Hexamethylcyclotrisiloxane
D4	Octamethylcyclotetracyclosiloxane
D5	Decamethylcyclopentasiloxane
EM	End Mixture
EMPIR	European Metrology Program for Innovation and Research
FEP	Fluorinated Ethylene Propylene
FID	Flame Ionization Detector
GC	Gas Chromatography
ISO	International Organization for Standardization
L2	Hexamethyldisiloxane
L3	Octamethyltrisiloxane
LM	Liquid Mixture
MM	Mother Mixture
MSD	Mass Spectrometry Detector
m/z	Mass-to-charge ratio
ppm	Parts per million
prep	From preparation
PSM	Primary Standard Materials
PT	Proficiency Test
RF	Response Factor
RRF	Relative Response Factor
SI	Système International
t_r	Elution time
VMS	Volatile Methylsiloxanes
VOC	Volatile Organic Compounds
VSL	Van Swinden Laboratory

List of symbols

μ Average at time zero

μ_j Added mass of liquid j (j= 1,2...d, d represents the number of liquids used to make the mixture)

τ Standard deviation between the groups

σ Standard deviation within the groups

σ^2 Repeatability variance

ε_{ij} Random error due to repeatability of measurement

$\bar{a}$ Average of the peak areas

α Slope

A Slope of instability of the relative response factor

B_i Bias in datum i (a reproducibility effect)

M_i Molar mass of component x_i

$\bar{M}$ Molar mass of end mixture

m_i Added mass of component $_i$

m_c Total mass of the mixture

N Normal distribution

p Pressure

q Number of components

r Response factor

$s_{r,\text{rel}}$ Repeatability as a percentage of the mean

$s_{R,\text{rel}}$ Reproducibility as a percentage of the mean

$s_r^{\,2}$ Repeatability variance

s_r Standard deviation of the repeatability

$s_L^{\,2}$ Between-laboratory variance

$s_R^{\,2}$ Reproducibility variance

s_{rel} Standard deviation of the mean

U Uncertainty

U_{rel} Relative uncertainty of the amount-of-substance fraction

$U_{\text{rel}}(x)$ Uncertainty of the gravimetric amount-of-substance fraction of the compounds in the gas mixtures

v_{ij} Amount-of-substance fraction of component i in liquid j

w_i Mass fraction

x Amount-of-substance fraction

1 Introduction

Van Swinden Laboratory (VSL) is the Dutch National Metrology Institute. VSL provides measurement services and calibrates instruments for customers. VSL is also responsible for the management and development of the national primary measurement standards [3]. The Chemistry group is active in the measurement of the composition of gases, air, and the production of gaseous reference materials.

Accurate measurement of chemical (gas) compositions is important in many different sectors. VSL possesses a wide range of self-developed 'Primary Standard Materials' (PSMs), to provide traceability for preparing reference materials and for conducting calibrations. These PSMs are gas mixtures with very accurately known compositions, which are traceable to SI units and which are routinely checked for quality and stability.

For about six years, considerable effort has been put into the development of measurement standards for the siloxane content in biomethane and upgraded biogas [1]. Biogas is of increasing importance worldwide as an energy vector. It presents an environment-friendly alternative for natural gas and contributes to reducing the emission of greenhouse gases.

However, biogas can contain impurities not found in traditionally distributed natural gases, which can have adverse effects on the integrity of the infrastructure, the safety and performance of end-use equipment, and even on the health of the end user. One of these impurities is siloxanes. Siloxanes are silicon-containing volatile organic compounds, which occur in biomethane and upgraded biogas. It is a group of the most commonly encountered impurities in biomethane and upgraded biogas, even after appropriate treatment of the raw biogas.

These efforts have set the stage to organize a first proficiency test (PT) for siloxane content, aiming at evaluating the performance of laboratories determining the contents of siloxanes in biomethane and upgraded biogas.

Laboratories strive for excellent quality of instruments, procedures and measurement capacities. Audits are held regularly to ensure consistent quality. However, systematic deviations that arise are not detected by these audits. Different accreditation organisations and ISO/IEC 17025 [4] therefore demand participation in what are known as proficiency tests, in which the measurement results are compared anonymously to those from other laboratories and deviations are tracked down. During a proficiency test, the same measurements and data analyses are conducted by all participating laboratories. The results are compared and assessed against an independent reference value, and the participants receive their own data so that they can compare their results anonymously with those from other laboratories. The data are handled confidentially and are only made available to the laboratory itself.

Initially, the main objective of this research was to gravimetrically prepare gas mixtures containing the 5 most volatile siloxanes L2 (hexamethyldisiloxane), L3 (octamethyltrisiloxane), D3 (hexamethylcyclotrisiloxane), D4 (octamethylcyclotetracyclosiloxane) and D5 (decamethylcyclopentasiloxane) and n-octane as internal standard and to evaluate the laboratory performances on the determination of the siloxanes. This includes the homogeneity testing and stability of the gas mixtures, establishing reference values of each siloxane and computing a consensus value from the laboratory data. However, this did not go as planned as during the gas mixture preparation there was some unexpected complications and not all of the planned gas mixtures could be prepared in time.

To accurately determine amount-of-substance fractions, assess the contents of siloxanes in biomethane and upgraded biogas, and relate measurement records from many laboratories and researchers, it is essential to have good calibration standards, that would be stable for at least the period of the PT, and a good method for analyzing these components. For the long-term stability

test of the siloxanes content in biomethane, gas mixtures containing the five most volatile siloxanes named above have already been evaluated for a period of six months for a pilot round of the Proficiency Test in 2017. The measurement data underlying the reference values showed appreciable reproducibility effects between the data points that are good enough for operating a proficiency test [1]. The focus of this research is now set for a next challenge, which is to evaluate if these gas mixtures are still stable after almost two years. For evaluating the long-term stability of the siloxanes content in biomethane, a Bayesian hierarchical model is going to be used instead of the classical statistics given in ISO Guide 35 [5] and ISO 13528 [6]. A Bayesian model better warrants the characterisation of the dispersion.

In addition to the traditional Gas Chromatography system with a flame ionization detector (GC/FID) used for the analysis of siloxanes in biomethane, there is a new type of detector, the Barrier Ionization Discharge (BID) detector, for Gas Chromatographs (GCs) that is going to be evaluated. The repeatability and reproducibility of the system are going to be determined in accordance with ISO 5725-2 [7]. The application is going to be assessed for the analysis of siloxanes mixtures already measured on the traditional Gas Chromatography system with a flame ionization detector. It is interesting to evaluate if GC/BID could be an alternative to using a traditional GC-system in the future, to get better results.

In this context, the 'Metrology for Biomethane' project was started within the European Metrology Program for Innovation and Research (EMPIR), in which VSL takes part of. This project aims to develop and validate traceable measurement standards for biomethane. One of the goals is to "report on the improved stability of the measurement standards, a validated calibration method for the measurement of the total silicon and siloxanes content in biomethane and a relative expanded uncertainty of 3 %" [8]. For this thesis, this criterion will be taken into account.

The main objective described in this thesis is to develop a method for the analysis and stability study of gaseous reference materials of siloxanes in biomethane.

The sub-objectives are:

- To compare the results of the stability study of the gas mixtures from the pilot round of the proficiency test measured on two different GC/FID-systems

- To evaluate the long-term stability of the siloxanes content in biomethane and to determine if these gas mixtures are still stable after almost 2 years

- To develop a method and determine the repeatability and reproducibility of the GC/BID-system using the approach of ISO 5725-2 [7]

- To compare the results of the siloxane content in methane measured on a GC/FID, with the new GC/BID-system

2 Theoretical background

2.1 Biomethane

2.1.1 From biogas to biomethane

Biomethane is a substitute for natural gas which can be produced by anaerobic digestion of organic matter such as agricultural biomass, agro-industrial waste, and the Organic Fraction Municipal Organic Waste. Biomethane is obtained in two phases: raw biogas production following by a process called upgrading. Upgrading is the removal of non-compatible components such as carbon dioxide (CO_2), hydrogen disulfide (H_2S) and water (H_2O). Biomethane is a renewable source of energy that can answer to emission reduction goals by exploiting existing gas networks and contributing to increasing domestic production of methane. Because the same amount of CO_2 is produced from the natural decomposition of the organic matter that creates biomethane, the CO_2 released by combustion does not increase atmospheric CO_2 [9]. Biogas upgrading and the production of biomethane nowadays is a progressive process of gas separation. There are a number of different technologies available to produce biomethane of satisfactory quality to act as a vehicle fuel or to be injected into the natural gas grid. Biogas from sewage digesters usually contain from 55 % to 65 % methane, 35 % to 45 % CO_2 and less than 1 % nitrogen, biogas from organic waste digesters usually contains from 60 % to 70 % methane, 30 % to 40 % CO_2 and less than 1 % nitrogen, while in landfills methane content is usually from 40 % to 55 %, CO_2 from 30 % to 40 % and nitrogen from 5 % to 15 % [10]. Besides the main components, biogas also contains impurities such as sulphur components, halogenated hydrocarbons (only in landfills) and siloxanes. Although the amounts of trace compounds are low compared to methane, they can have environmental impacts such as stratospheric ozone depletion, the greenhouse effect and/ or the reduction in air quality and can also be detrimental to the natural gas infrastructure.

As mentioned before, biogas upgrading is a gas separation task which ends up in a methane-rich product gas stream with a certain specification [11]. Depending on the composition of the raw biogas, this separation task comprises the separation of carbon dioxide, the drying of the gas, the removal of trace substances as well as the compression to a pressure needed for the future gas application. To give a short overview of the separation task and the gas streams involved, a basic flowsheet of biogas upgrading is given in Figure 2.1.
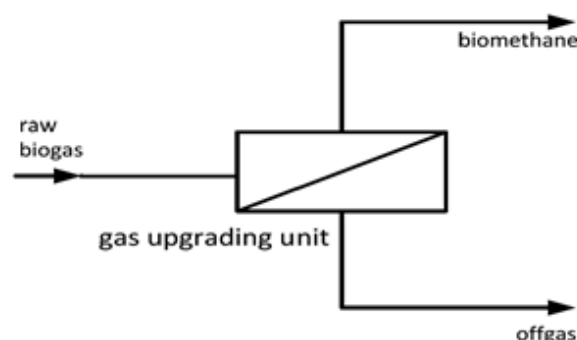
Figure 2.1: Basic flowsheet of biogas upgrading [2].

The raw biogas is split into two gas streams during the upgrading: the methane-rich biomethane stream and the carbon dioxide-rich offgas stream. The offgas stream will still contain a certain amount of methane, depending on the methane recovery of the technology that is used.

2.1.2 Siloxanes

At high temperatures, siloxanes present in biogas are oxidized into microcrystalline silicon dioxide. Silicon dioxide collects in deposits on valves, cylinder walls, and liners [12]. In internal combustion engines deposits on pistons and cylinder heads are extremely unpleasant and even a small amount is enough to cause engine power reduction and damage to the engine.

The subgroup of silicon-containing Si-O bonds with organic side groups bonded to Si are called siloxanes. As their name indicates, siloxanes consist of a backbone of alternating silicon and oxygen atoms, with side chains at the silicon atoms that are usually alkyl groups ("sil-ox-anes"). The structure of a siloxane can be linear or cyclic. Siloxanes have the abbreviation L if the structure of the compound is linear and D if the structure is cyclic [13]. An example of a linear and a cyclic siloxane is shown in Figure 2.2. Most siloxanes possess a rather unusual combination of chemical properties, including both hydrophobicity and volatility. The water solubility of the cyclic and linear dimethylsiloxanes is very low and decreases an increasing number of siloxane units. The use of siloxanes is increasing, for example, in household/ industrial cleaning products because volatile methylsiloxanes (VMS) solvents are aroma-free and widely available, and because they are not part of the volatile organic compound (VOC) regulations, they are not considered a health hazard to humans [14]. The current specification for the silicon concentration in biomethane and upgraded biogas is in the order of $0.1\,\mathrm{mg\,m^{-3}}$ [15, 16]. Organic silicon compounds end up in landfills from sources as empty cosmetic bottles and other containers in which some of the product remains, through landfilling of wastewater treatment sludge, and from packaging, etc. Degradation of high molecular silicon-organic compounds in landfills may also form widespread use, siloxanes are commonly found in air, water, sediment, sludge, and the concentration variation can be high. The structure of the siloxanes used for this research are shown in Figure 2.3.
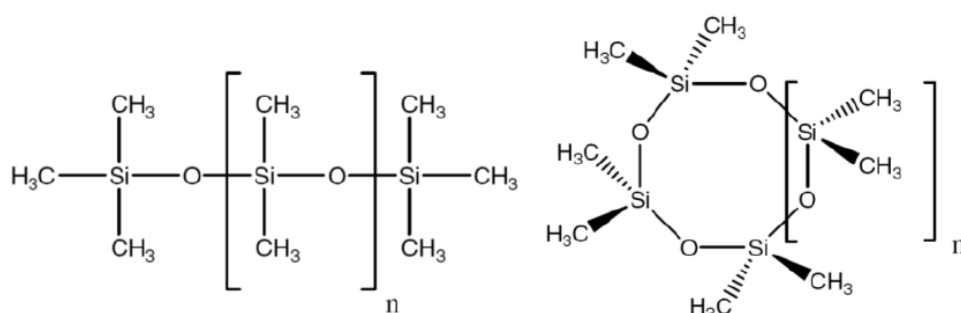
Figure 2.2: Structures of linear (left) and cyclic (right) siloxanes. When n=1, the left siloxane is L3 and the right siloxane is D4.
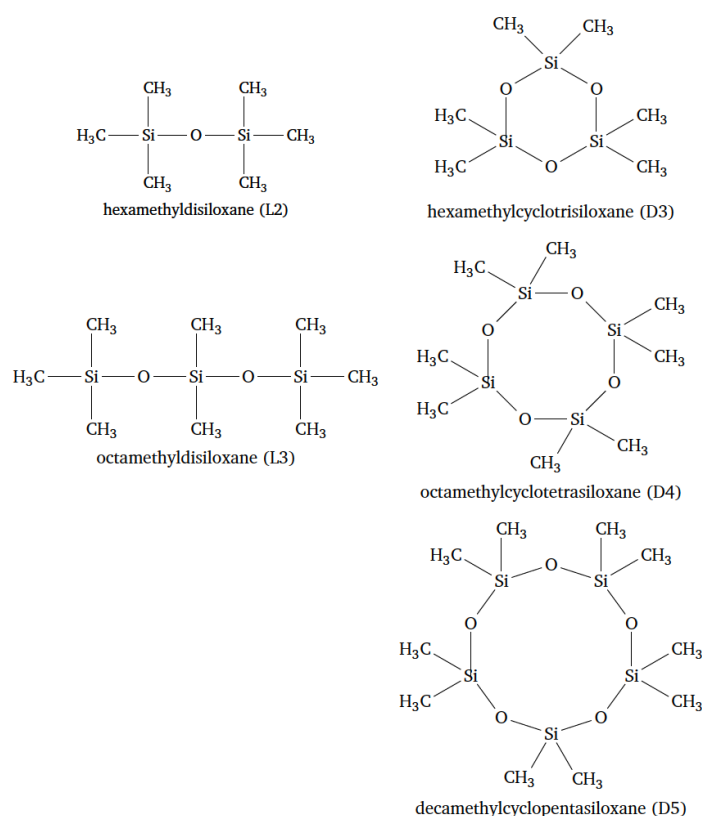
Figure 2.3: Structures of the siloxanes used in this thesis [1].

2.2 Bayesian Statistics

Bayesian statistics is a theory in the field of statistic based on Bayesian probability theory, one of the interpretations of probability. In doing so, opportunities are constantly reviewed based on new information that has become available [17].

Bayesian inference use Bayes' theorem to combine the prior probabilities and the likelihood from the data to get the posterior probability of the event.

The primary difference between the Bayesian and frequentist approaches to statistical inference is denoted in the way they interpret probability, represent the unknown parameters, acknowledge the use of prior information and make the final inferences [18].

The frequentist approach to statistics considers probability as a limiting long-run frequency. The Bayesian approach considers probability as a measure of the degree of personal belief about the value of an unknown parameter. Therefore, it is possible to give the probability to any event or proposition that we are uncertain about, including those that are not repeatable [18, 19].

A key feature of the Bayesian approach to statistics is the use of prior information in addition to the sample data. A correct Bayesian analysis will always contain valid prior information, which will help to support inferences about the true value of the parameter and ensure that relevant information about it is not wasted [20].

A Bayesian analysis incomporates two sources of information about the unknown parameters of interest. The first of these is the sample data, expressed formally by the likelihood function. The second is the prior distribution, which represents additional information that is available to the investigator [20].

2.3   Gas Chromatography (GC)

2.3.1   Principle

Gas Chromatography is a widely used chromatography technique in analytical chemistry for separating chemical substances based on boiling point and on the interaction with the stationary phase. The method consists of injecting a volatile liquid or gaseous sample through a septum into a heated port, in which it rapidly evaporates. Vapour is swept through a column by an inert gas, such as helium, that acts as carrier gas. Once the gaseous compounds reach the column, it is separated based on the interaction with the stationary phase. Compounds that have greater affinity with the stationary phase spend more time in the column and, thus, eluate later and have longer retention time (t_r) than samples that have higher affinity for the mobile phase. A chromatogram with the elution order of the siloxanes and internal standard used for the research is shown Figure 2.4. A table with the elution order of the components with the retention times can be found in Appendix A.1. Affinity for the stationary phase is mainly driven by intermolecular interactions and the polarity of the stationary phase can be chosen to maximize interactions and, thus, the separation. The column must be hot enough to provide sufficient vapour pressure for analytes to be eluted in a reasonable time [21]. As the components elute from the column, they can be quantified by a detector and/or be collected for further analysis. In order for the analytes to be gaseous, the detector must be maintained at a higher temperature than the column. Ideal peaks are Gaussian distributions and symmetrical. Asymmetrical peak features such as fronting or tailing, can be due overloading the column, injection problems, or the presence of adsorptive functional groups such as carboxylic acids.
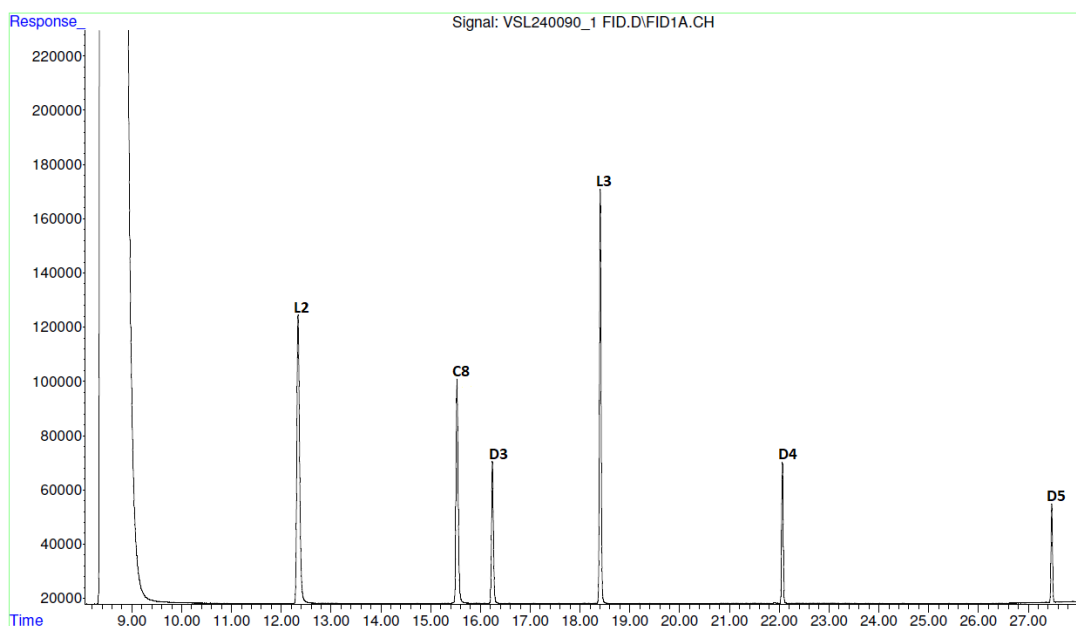

Figure 2.4: Chromatogram showing the elution order of the 5 siloxanes and n-octane.

2.3.2 Flame Ionization Detector (FID)

Flame ionization detector passes sample through a small hydrogen-air diffusion flame. Carbon atoms (except carbonyl and carboxyl carbons) produce CH radicals, which are thought to produce CHO^+ ions and electrons in the flame. Ions are detected using a metal collector which is biased with a high Direct Current voltage [21]. The current produced is proportional to the amount of sample being burned. This current is converted to voltage, amplified, filtered to remove high-frequency noise, and finally converted to a digital signal. FID is one of the most sensitive general detectors for Gas Chromatography with a limit of detection in picogram range. The response is linear over seven orders of magnitude, giving it a large linear range [21].

2.3.3 Mass Spectrometry Detector (MSD)

In mass spectrometry, a small amount of a compound is evaporated. The vapour leaks into the ionization chamber where a pressure of about 10^{-7} mbar is maintained. The molecules are ionized by an electron-beam. This electron beam is produced by a heated cathode called the filament. Ionization is achieved by inductive effects and by loss of valence electrons, mainly positive ions are produced. This molecular ion undergoes fragmentation and each primary product ion derived from the molecular ion can, in turn, undergo fragmentation, and so on. The ions are separated in the mass spectrometer according to their mass-to-charge ratio (m/z) and are detected in proportion to their abundance. As a result, a mass spectrum of the molecule is produced. In the spectrum of a pure compound, the molecular ion, if present, appears at the highest value of m/z and gives the molecular mass of the compound [22]. The mass spectrum is sensitive and provides both qualitative and quantitative information.

2.3.4 Barrier Ionization Discharge (BID)

Recently, the Barrier Ionization Discharge (BID) detector was developed, which is claimed to be twice more sensitive than flame ionization detector (FID). The BID detector is a universal detector able to detect all types of organic and inorganic compounds except for helium and neon (with an ionization potential of 21.6 eV). The operating principle is based on the ionization of the analytes by high purity helium plasma, which has an ionization potential of 17.7 eV, generated by a quartz dielectric chamber at atmospheric pressure [23].
An interesting feature of the BID is that the helium plasma generated in this process has a low temperature, which favors the reduction of the noise in the detector; because it restricts the causes of plasma fluctuations that is fluctuation in the generation and degasification temperature of the plasma generating walls.
Figure 2.5 shows a schematic representation of the BID. Compounds that elute from the GC column are ionized by the photons emitted by the plasma and proceed towards the collecting electrodes to be detected. There is a layer of quartz covering the surface of electrodes, which avoids degradation of the electrodes and allows greater stability of the detector [24].
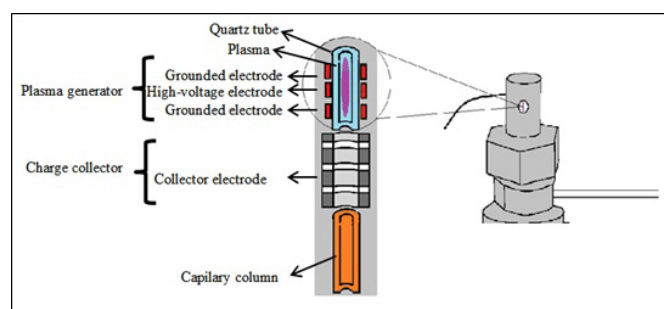
Figure 2.5: Schematic representation of the BID.

3 Experimental

3.1 Liquid Mixture preparation

A liquid mixture robot (LMR) was used for the automated preparation of liquid mixtures and dilutions (Figure 3.1). The user makes a recipe and the LMR prepares the liquid mixture using the recipe. On the left side of the robot the stock vials are placed, containing the (pure) components. At least two vials are always required, one for flushing the syringe and one vial from which the required amount of liquid is extracted. In addition to being flushed with the component, there is also rinsing with methanol. After the syringe has been rinsed three times with methanol, the needle is placed in a vial that is connected to a vacuum pump. As a result, all the methanol is removed from the syringe. Afterwards, the syringe will be flushed with the pure component. The sample mixture is prepared in a 4.5 or 10 ml vial. The volume of the mixture may not exceed 85 % of the total volume. In addition to the sample vial, a reference vial is also weighed to observe the possible drift of the balance. Each weighing is performed nine times, removing the first five weighings from the results. In the validation of the liquid robot was concluded that the robot does not provide lower uncertainties, but it does allow for more robust measurements. By using the robot, human errors are excluded when making liquid mixtures.

The gas mixtures were gravimetrically prepared in accordance with ISO 6142-1 [25] by first preparing a liquid mixture of the siloxanes L2, L3, D3, D4, D5 and n-octane. Using a gravimetric method, the individual components are weighed. The weighing process is one of the most accurate physical measuring processes that exist. That is why high precision liquid mixtures can be produced by this method. Some key properties of the components used for the liquid- and gas mixtures with their VSL codes are summarised in Table 3.1.
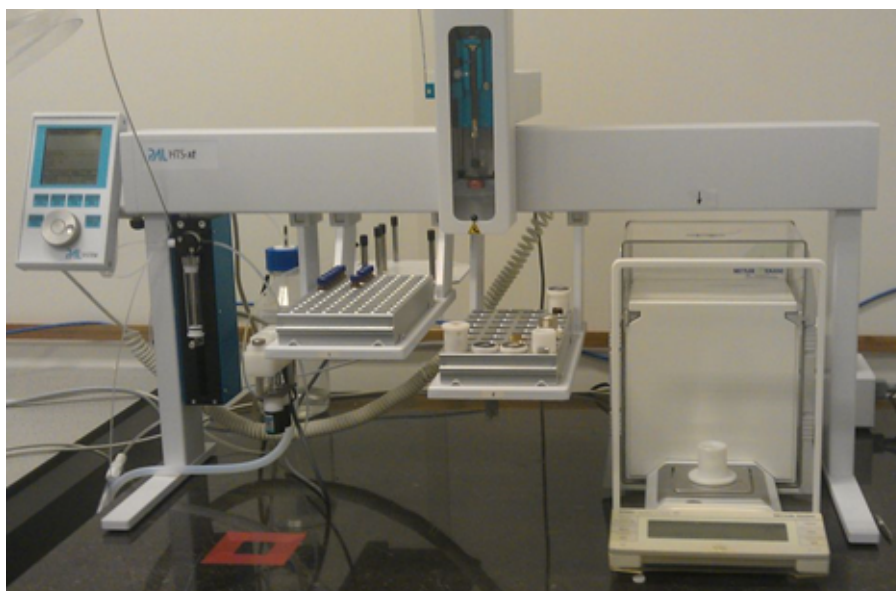
Figure 3.1: Picture of the LMR set-up.

Table 3.1: Overview of the components and liquids used in the gas mixtures.

Compound name	Abbreviation	Molecular formula	VSL code
Hexamethyldisiloxane	L2	$C_6H_{18}OSi_2$	AD089V-01
Octamethyltrisiloxane	L3	$C_8H_{24}O_2Si_3$	AD985V-01
Hexamethylcyclotrisiloxane	D3	$C_6H_{18}O_3Si_3$	AD897V-01
Octamethylcyclotetrasiloxane	D4	$C_8H_{24}O_4Si_4$	AD728V-01
Decamethylcyclopentasiloxane	D5	$C_{10}H_{30}O_5Si_5$	AD508V-02
n-Octane	C8	C_8H_{18}	SA392V-01

3.1.1 Converting the mass fraction to amount-of-substance fraction

After preparing the liquid mixtures, the masses, molar masses, and purity data are combined as amount-of-substance fractions.

An example of liquid mixture with the code "LM0100", in which the mass and mass fraction of component i is calculated with the LMR program, is shown in Table 3.2.
Equation 3.1 gives m_i, which is the added mass of component i, v_{ij} is the mass fraction of component i in liquid j, μ_j is the added mass of liquid j (j= 1,2...d, d represents the number of liquids used to make the mixture)

$$m_i = \sum_{j=1}^{d} v_{i,j} \cdot \mu_j \tag{3.1}$$

The total mass m_c of the mixture is calculated as

$$m_c = \sum_{j=1}^{d} \mu_j \tag{3.2}$$

The mass fraction w_i is given by equation 3.3, in which all the equations above are processed

$$w_i = \frac{m_i}{m_c} \tag{3.3}$$

The amount-of-substance fraction x of component $_i$ can be calculated afterwards with equation 3.4, using the molar mass. The mass fraction is represented as w_i ($_l$= 1,2 ... q, where q denotes the number of components and runs for all components in the mixture) and $\bar{M}$ is the molar mass of all components in the mixture.

$$x_i = \frac{w_i/M_i}{\sum_{l=1}^{q} w_i/\bar{M}} \tag{3.4}$$

The molecular weight of the complete liquid mixture (also known as average molar mass) is calculated using equation 3.5. Where $\bar{M}$ is the molar mass of end mixture, q the number of components, x_i the amount-of-substance fraction of component $_i$, M_i is the molar mass of component x_i.

$$\bar{M} = \sum_{i=1}^{q} x_i \cdot M_i \tag{3.5}$$

The uncertainty of the calculated amount-of-substance fraction (u_x) is calculated using the spreadsheet LMRMixComp based on ISO 6142-1 [26] and ISO 19229 [27]. In this spreadsheet the weighing data are entered in mass fraction with the associated uncertainties of the balance, evaporation and the density of air. The spreadsheet then calculates the uncertainty of the component and the mole fraction in the sample via matrix calculations.

Table 3.2: Calculated masses and amount-of-substance fractions for liquid mixture LM0100.

Compound	Mass (g)	Mass fraction (g/g)	Molar mass (g/mol)	Amount-of-substance fraction (mol/mol)
L2	0.65789	0.25017	162.377	0.30139
L3	0.63560	0.24169	236.520	0.19990
D3	0.59558	0.22647	222.460	0.19915
D4	0.22999	0.08745	296.614	0.05768
D5	0.20141	0.07659	370.767	0.04041
C8	0.30937	0.11764	114.228	0.20147

3.2 Gas Mixture Preparation

For the proficiency test, two liquid mixtures (LMs) were prepared. From these LMs, two mother gas mixtures were prepared. Each mother mixture was diluted gravimetrically ten times with methane gas to obtain five end mixtures (in total ten end mixtures) with amount-of-substance fractions as shown in Figure 3.2 for the mixtures from 2016 and Figure 3.3 for the mixtures planned for 2018. In Table 3.3 and Table 3.4 the sample numbers are shown for the different liquid and gas mixtures prepared in 2016 and planned for 2018.

Liquid mixture		Mother mixture		End mixture	
•C8	0.17 mol/mol	•C8	20 ppm	•C8	2 ppm
•L2	0.35 mol/mol	•L2	40 ppm	•L2	4 ppm
•L3	0.22 mol/mol	•L3	25 ppm	•L3	2.5 ppm
•D3	0.14 mol/mol	•D3	16 ppm	•D3	1.6 ppm
•D4	0.07 mol/mol	•D4	8 ppm	•D4	0.8 ppm
•D5	0.03 mol/mol	•D5	4 ppm	•D5	0.4 ppm
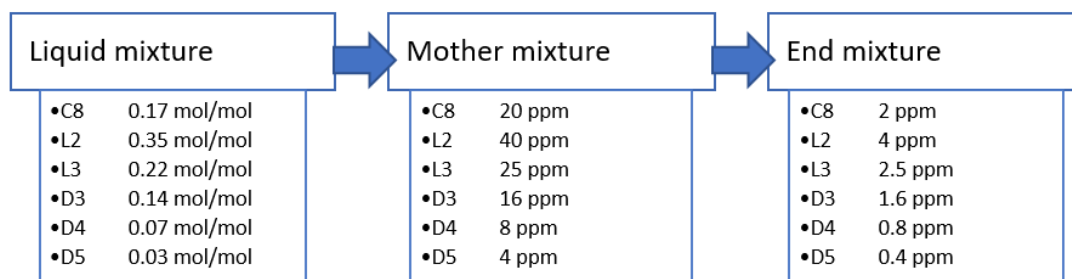
Figure 3.2: Diagram showing the preparation route with nominal compositions for the prepared gas in 2016

Liquid mixture		Mother mixture		End mixture	
•C8	0.20 mol/mol	•C8	20 ppm	•C8	2 ppm
•L2	0.30 mol/mol	•L2	30 ppm	•L2	3 ppm
•L3	0.20 mol/mol	•L3	20 ppm	•L3	2 ppm
•D3	0.20 mol/mol	•D3	20 ppm	•D3	12 ppm
•D4	0.06 mol/mol	•D4	6 ppm	•D4	0.6 ppm
•D5	0.05 mol/mol	•D5	5 ppm	•D5	0.5 ppm
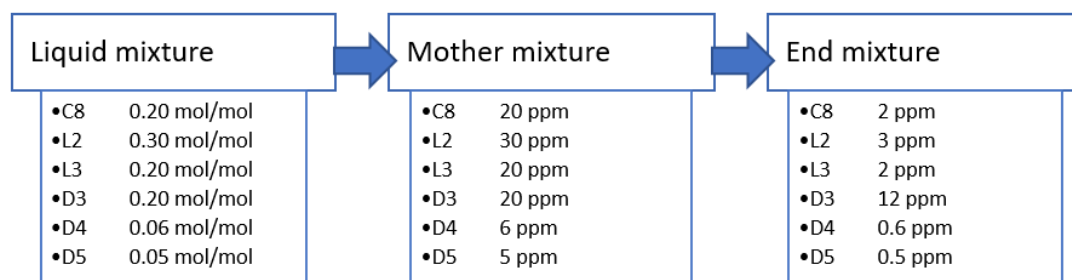
Figure 3.3: Diagram showing the preparation route with nominal compositions for the gas mixtures to be prepared in 2018

Table 3.3: Overview of the mixtures prepared in 2016 [1].

Liquid mixture	Mother mixture		PT mixture	
Number	Code	Dilution	Code	Dilution
LM0035	VSL602787	40 ppm L2 from LM1	VSL244195	4 ppm L2 from MM1
			VSL244251	4 ppm L2 from MM1
			VSL144866	4 ppm L2 from MM1
			VSL145000	4 ppm L2 from MM1
			VSL144853	4 ppm L2 from MM1
LM0037	VSL240090	40 ppm L2 from LM2	VSL144858	3 ppm L2 from MM2
			VSL144902	4 ppm L2 from MM2
			VSL144859	4 ppm L2 from MM2
			VSL145002	4 ppm L2 from MM2
			VSL145006	4 ppm L2 from MM2

Table 3.4: Overview of the mixtures planned in 2018.

Liquid mixture	Mother mixture		PT mixture	
Number	Code	Dilution	Code	Dilution
LM0099	VSL345051	30 ppm L2 from LM1	EM1	3 ppm L2 from MM1
			EM2	3 ppm L2 from MM1
			EM3	3 ppm L2 from MM1
			EM4	3 ppm L2 from MM1
			EM5	3 ppm L2 from MM1
LM0100	VSL165090	30 ppm L2 from LM2	EM1	3 ppm L2 from MM2
			EM2	3 ppm L2 from MM2
			EM3	3 ppm L2 from MM2
			EM4	3 ppm L2 from MM2
			EM5	3 ppm L2 from MM2

Before starting with the gas mixtures preparation, all cylinders were flushed using nitrogen (Air products, 6.0) (6 x 15 bar and two hours vacuum). Then, the cylinders were vented to the nitrogen present and evacuated overnight with help of a vacuum turbo pump ($p \approx 2$ x10^{-7} mbar). The two LMs, that were prepared with the Liquid Mixture Robot, were injected with a syringe into different 5 L gas cylinders (aculife IV), then vaporized and diluted with methane, to obtain mother mixtures. Both the syringe and the gas cylinder were weighed before and after injection to determine the exact mass and calculate the amount-of-substance fractions of the components [28]. The mother mixtures are diluted to obtain final mixtures with the siloxane fractions at the desired levels. For the dilution of the mixtures as little tubing as possible must be used to prevent reaction or adsorption of the siloxanes to the tubing.

After evacuating, the cylinders were weighed. After completing a weighing, the computer program advises the amount of mixture to be introduced (both the pressure and the mass). The introduction of a mixture takes place at a filling station (see Figure 3.4).
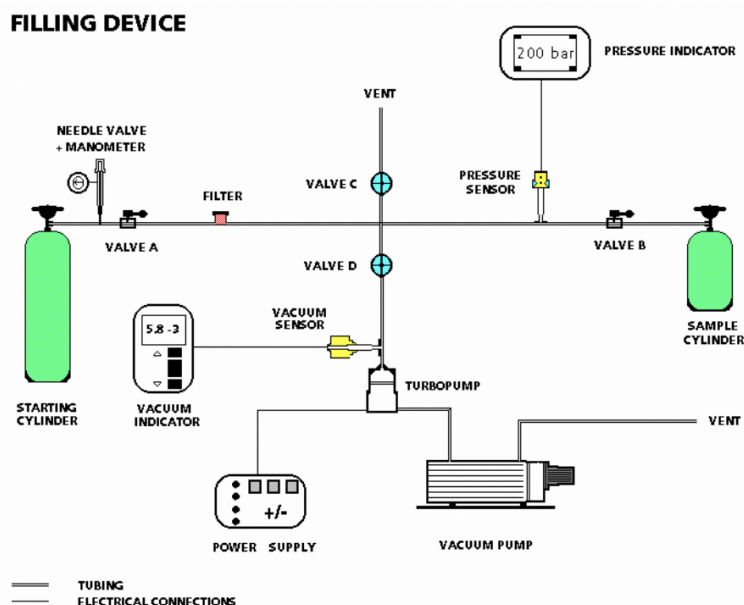

Figure 3.4: Schematic drawing of the filling station.

The cylinder on the left in Figure 3.4 is the mother cylinder (starting cylinder) and the cylinder on the right (sample cylinder) is the end cylinder. A vacuum pump and a blow-off valve can be seen in the middle. The sample cylinder is placed on a balance, so that mass increase can be observed by inserting the component, in order to be able to "target". A leak test was performed by placing 15 bar pressure on the tubing and checking whether the pressure remains constant for 15 minutes. The tubing is heated (60°C to 70°C) to remove absorbed water and to prevent absorption of the component during insertion and flushed eight times using vacuum ($p \approx 2 \times 10^{-5}$ mbar) and pressure (> 15 bar, gas from the mother mixture). To saturate the tubing with the mother mixture, a 9th and 10th flushing is introduced, without evacuation. After a few minutes the system is de-pressurised and then filled again with gas of the mother cylinder. After de-pressurising one last time, the black valve is closed towards the vacuum pump (see Figure 3.5: the left valve in the left set-up) and the balance is tared with the end mixture cylinder on top. The mother cylinder is opened followed by the end cylinder after slowly inserting, to ensure that the evaporated liquid does not absorb on the tubing, the desired quantity according to the balance both cylinders are closed again. A picture of the set-up can be found in Figure 3.5.

After weighing the cylinder of the end mixture, the mixture is diluted with methane. Every step was weighed with an automatic weighing device in order to calculate the exact prepared composition. After preparation, each mixture was homogenized for two hours. In Figure 3.2 and Figure 3.3 the fractions per component in the liquid mixture can be found. Part of the liquid mixture is injected into a cylinder which is then filled with methane gas to obtain the mother mixture.

The mother mixture is diluted gravimetrically ten times with methane gas to obtain several end mixtures.

Figure 3.5: Picture of the set-up (left), including heating of the tubing (right).

3.3   Analysis

3.3.1   Flushing procedure gas cylinders

Before starting with the analysis of the gas mixtures, all cylinders had to be equipped with a pressure regulator. By using a regulator, the pressure of the outgoing gas flow can be regulated. After each gas cylinder was equipped with a regulator and flow rate, the regulators were flushed. It is very important that the regulators are flushed properly, as they may still be contaminated by previous use. The general flushing procedure for the regulator is as follows: first, the regulator is pressurized and by opening and closing the cylinder valve five to eight times, the regulator is flushed. Then, the regulator had to be vented and by pressurizing and filling the regulator with the gas mixture and venting it afterwards, the regulator was flushed with the gas mixture. This procedure must be done five times in a row. The cylinder valve must always be left closed and the regulator pressurized so that air pollution is prevented. For siloxanes and other components which have a low vapour pressure, there is an adjusted flushing procedure for the regulators. The regulators were flushed slowly to prevent components from condensing. Immediately after the gas cylinder was equipped with a regulator; the pressurized regulator was flushed five to eight times. Then, a pressure gauge, a needle valve, and a flow meter are connected to the regulator. The regulator must be vented and filled with the gas mixture. Afterwards, the regulator must be pressurized with two bar and the needle vent has to be set up until a flow of 90-100 ml/min is reached. Eventually, all the gas is flushed out of the regulator This procedure was performed four to five times in a row. The flushing procedure of the regulator must be carried out more than once a day. To ensure that the regulators are flushed properly, this procedure was started five days before the analysis.

3.3.2   Connecting the gas cylinders to the GC

After the regulators were flushed, the gas cylinders were ready to be connected to the Gas Chromatograph. The gas mixture must be offered to the GC at 1 bar. For this reason, the regulator was tightened to 1 bar with the aid of the manometer and the valve.
FEP (Fluorinated Ethylene Propylene) tubings were used to connect the gas cylinders to a multi-position valve connected with the gas chromatograph. As soon as the cylinders were connected to the GC, the pipes had to be flushed using a short GC program. During the execution of this flushing procedure, a leak check was performed. The connections were checked for possible gas leaks using Snoop®. Snoop® is deionized water with a surfactant that forms gas bubbles as soon as a gas leak is detected [29]. After the flushing procedure was completed and possible gas leaks were rectified, the analysis was ready to get started.

3.3.3   Analysis method

An Agilent 5975B Gas Chromatograph with a flame ionization detector (GC/FID) with gas autosampler and a pressure controlling device was used for all analyses. A mass spectrometry detector (MSD) was used for the identification of the siloxanes. A picture of the GC is shown in Figure 3.6.

Figure 3.6: The Agilent 5975B GC with gas autosampler and pressure controlling device used for the analyses.

3.4 A comparison of two GC/FID-systems

The gas mixtures analysed between September 2016 and March 2017 for the pilot round of the Proficiency Test were performed on an Agilent 7890A Gas Chromatograph with a flame-ionization detector (GC-1) with gas autosampler and a pressure controlling device. The settings used for the analytical method are listed in Table 3.5.

Table 3.5: Specifications of the method on GC-1.

Method parameter	GC/FID
Column	Polydimethyl siloxane (PDMS), 30 m x 0.35 mm x 5 μm
Injection	Direct injection to the column
Oven settings	35°C (hold 6 min), 10°C min^{-1} to 200°C (hold 8.5 min)
Detector settings	190°C H$_2$ flow rate 35 mL min^{-1} Air flow rate 350 mL min^{-1} Make up N$_2$ flow rate 20 mL min^{-1}

The gas mixtures analysed between June 2018 and August 2018 were performed on an Agilent 5975B Gas Chromatograph with a flame-ionization detector (GC-10) with gas autosampler and a pressure controlling device. The settings used for the analytical method are listed in Table 3.6. The mixtures measured on the GC-1 and GC-10 are listed in Table 3.7. The last two mixtures listed (VSL602787 and VSL240090) are the two mother mixtures. The exact composition of these gas mixtures are summarised in Appendix B.1.

Table 3.6: Specifications of the method on GC-10.

Method parameter	GC/FID	GC/MSD
Column	Capillary DB-1ms UI 60 m x 0.25 mm x 0.25 μm	Capillary DB-1ms UI 60 m x 0.25 mm x 0.25 μm
Injection	Direct injection to the column	Direct injection to the column
Oven settings	40°C (hold 5 min), 5°C min^{-1} to 130°C (hold 3 min), 20°C min^{-1} to 210°C (hold 10 min)	40°C (hold 5 min), 5°C min^{-1} to 130°C (hold 3 min), 20°C min^{-1} to 210°C (hold 10 min)
Detector settings	190°C H$_2$ flow rate 30 mL min^{-1} Air flow rate 350 mL min^{-1} Make up N$_2$ flow rate 35 mL min^{-1}	190°C H$_2$ flow rate 30 mL min^{-1} Air flow rate 350 mL min^{-1} Make up N$_2$ flow rate 10 mL min^{-1}

Table 3.7: Gas cylinders measured on GC-1 and GC-10 (+ means the cylinder is inclulded and - means the cylinder is not included).

Cylinder code	GC-1	GC-10
VSL244195	+	+
VSL244251	+	+
VSL144866	+	-
VSL145000	+	+
VSL144853	+	+
VSL144858	+	+
VSL144902	+	+
VSL144859	+	+
VSL145002	+	+
VSL145006	+	+
VSL602787	+	-
VSL240090	+	+

3.4.1 Response factor

To compare the two GC/FID-systems with each other, the response- and relative response factors (RF and RRF) are calculated.

The basis for the assessment of the stability of the amount-of-substance fractions is the peak area ratio of the component of interest and the internal standard (C8). This ratio is assumed to be insensitive to instrument drift and effects of, e.g., the ambient pressure fluctuations.

The amount-of-substance fraction of a component k is calculated as

$$x_k = \frac{A_k}{r_{\text{IS}}} \frac{r_{\text{IS,cal}}}{r_{k,\text{cal}}} \tag{3.6}$$

where r denotes the response factor ($r = A/x$), x the amount-of-substance fraction, and IS the internal standard (n-octane). The second part of the equation refers to the measurement used for calibrating the GC/FID; the first part to a measurement in the stability study. Thus, all amount-of-substance fractions of a component are obtained with the same calibration.

3.5   Stability study

For evaluating the long-term stability of the siloxanes content in biomethane, a Bayesian hierarchical model is used instead of the classical statistics given in ISO Guide 35 [5] and ISO 13528 [6]. A Bayesian model better warrants the characterisation of the dispersion. Reference material development is often paired with the development of methods for preparation, calibration of equipment, and measurement of the quantities of interest. Current guidance expects that measurement methods used in stability study for assessing the behaviour over time of reference and proficiency test materials have been rigorously validated. In the development of an approach for a proficiency test about the content of siloxanes in biomethane and upgraded biogas, the development of the measurement method was done in parallel to the production of a batch of gas mixtures to be used as transfer standards. A Bayesian model was developed that enables separating stability effects of the material properties from repeatability and reproducibility effects of the measurement method [30, 31].

The gas mixtures have been analysed eight times, five times between September 2016 and March 2017, and three times between June 2018 and August 2018.

After analysing the gas mixtures, the relative standard deviation of the mean is calculated by the standard deviation divided by the corresponding mean ($s_{rel} = s/\bar{a}\cdot$).

The amount-of-substance fraction x is calculated as

$$x = \frac{\bar{a}}{\bar{i}_{\bar{a}}} \cdot x_{\text{prep}}$$

The calculated relative uncertainty of the amount-of-substance fraction $U_{\text{rel}}(x)$ is calculated as

$$U_{\text{rel}}(x) = \sqrt{U_{\text{rel,prep}}(x)^2 + s_{\text{rel}}^2}$$

Where the uncertainty of the gravimetric amount-of-substance fraction of the compounds in the gas mixtures $U_{\text{rel, prep}}(x)$ is calculated with the equation

$$U_{\text{rel,prep}}(x) = \frac{U_{\text{x, prep}}}{x_{\text{prep}}}$$

Finally, the uncertainty U is calculated as

$$U = U_{\text{x, rel}} \cdot x$$

A mixed-effects model for a stability study in the production of reference materials is generated

$$x_{ij} = \mu + B_i + A \cdot t_i + \varepsilon_{ij} \qquad (3.7)$$

for datum i and replicate j, where x_{ij} denotes the relative response factor, B_i the bias in datum i (a reproducibility effect), μ the expected value, A the slope of instability of the relative response factor at time t_i , and ε_{ij} the random error due to repeatability of measurement. This mixed-effects model accounts not only for (1) the repeatability of measurement, (2) the possible degradation of the mixture composition, but also for a possible excess variance in the data. In this sense, it is an augmented form of the model that has been used so far [32].

In the mixed-effects model, the following assumptions are made:

$$B_i \sim N(0, \tau^2)$$
$$A_i \sim N(\alpha, \sigma_\alpha^2)$$
$$\varepsilon_{ij} \sim N(0, \sigma^2)$$

The mixed-effects model above is the same as in a classical statistical model. The parameters in the model are therefore μ, τ, σ, and α. Where the symbol N means "normal" and "$\sim$" means "is distributed as". The mixed-effects model is used in a Bayesian analysis. Weakly informative priors have been assigned to the following parameters to regularise the calculations so that there is no/little effect on the outcome:

$$\mu \sim N(\mu_0, (0.2\mu_0)^2)$$
$$\alpha \sim N(0, (0.20\mu_0)^2)$$
$$\sigma_\alpha \sim Cauchy(0, 0.05\mu_0)$$
$$\tau \sim Cauchy(0, 0.1\mu_0)$$
$$\sigma \sim Cauchy(0, 0.05\mu_0)$$

The criterion for stability is:

$$|\alpha| \leq 2 \cdot u(\alpha)$$

The Cauchy distribution is a t-distribution with one degree of freedom. These probability distributions have limited influence of the estimated and standard deviations of the model parameters, but enhance the performance of the computational method. The calculations were performed in R [33] using the package rstan [34]. The Markov Chain Monte Carlo method, four chains of each 20 000 iterations were used, preceded by 10 000 interations in the 'warm-up' phase.

3.6 Repeatability and reproducibility

In addition to the Bayesian hierarchical model used for the long-term stability study, the repeatability and reproducibility parameters were used to evaluate the precision of the analytical method. The repeatability variance, between-day variance and reproducibility variance are calculated using the approach of ISO 5725-2 [7].

The repeatability is a measure of the dispersion of measurement values obtained with the same method on the same sample material under the same conditions. The method reproducibility defines the closeness between measured values obtained from an independent measurement using the same instrument and under the same analytical conditions by the same operator and within a short time interval.

The nine gas mixtures listed in Table 3.7 for the GC-10 were analysed to determine the repeatability and the reproducibility of the analytical method. Seven repeated injections were conducted on June 7, June 22 and August 8, 2018. The first analysis result of each analysis was removed from the results. The method was validated with the remaining 18 analysis results.

The repeatability variance in calculated as

$$s_r^2 = \frac{\sum_{i=1}^{p}(n_i - 1),\ s_i^2}{\sum_{i=1}^{p} n_i - p}$$

The standard deviation of the repeatability was then calculated by

$$s_r = \sqrt{s_r^2}$$

To express the repeatability as a percentage of the mean ($s_{r,\text{rel}}$), the following equation is used

$$s_{r,\text{rel}} = s\%_{\ within} = \frac{s_r}{\bar{m}}$$

The between-day variance is calculated as

$$s_L^2 = \frac{s_d^2 - s_r^2}{\bar{\bar{n}}}$$

where

$$s_d^2 = \frac{1}{p-1}\sum_{i=1}^{p} n_i(\bar{y}_i - \bar{\bar{y}})^2$$

The reproducibility variance

$$s_R^2 = s_r^2 + s_L^2$$

$$s_R = \sqrt{s_r^2 + s_L^2}$$

To express the reproducibility as a percentage of the mean ($s_{R,\text{rel}}$), the following equation is used

$$s_{R,\text{rel}} = \frac{s_R}{\bar{m}}$$

3.7 Method development on the GC/BID

A Shimadzu Nexis GC-2030 Gas Chromatograph with a Barrier Ionization Discharge detector (GC/BID) with gas autosampler and a pressure controlling device was used for all analyses. The method development for siloxanes on the GC/BID was carried out using the four gas mixtures VSL348568, VSL144853, VSL144858 and VSL244251, containing the five most volatile siloxanes L2, L3, D3, D4 and D5. The matrix gas of these cylinders was methane and besides the five siloxanes, the cylinder also contained n-octane as internal standard. The exact composition of these gas mixtures are summarised in Appendix C.1. For the method development, the elution order of the six components were already known, because the same column (DB1-MS) was used for both GC/FID and GC/BID alayses. The DB1-MS column separates the components by boiling point. Based on an existing method, that was used on the GC/FID, a method was subsequently developed. By varying in different parameters, it was examined what effect this had on the chromatogram and whether this was a positive change. Finally, the best method was developed by changing the oven program and the split ratio of the existing GC/FID method listed in Table 3.6 on page 16. And also by trying different values of the discharge flow.

Fifteen repeated injections were conducted on November 5, November 12 and November 19, 2018. The first five analysis result of each analysis was removed from the results. The method was validated with the remaining 30 analysis results. The precision of the analytical method has been evaluated using the repeatability and reproducibility parameters.

3.8 A comparison of the GC/FID and GC/BID

3.8.1 Standard deviation

For the comparison of the two GC-systems, the gas mixture VSL144858 (analysed on both the GC/FID and GC/BID) was used. The gas mixture VSL348568, with a lower amount-of-substance fractions (in ppb levels), will also be used even though this cylinder was only analysed on the GC/BID. The amount-of-substance fractions of the mixture was below the detection limit of the GC/FID system (GC-10).

In order to be able to compare the two GC systems, the relative standard (s_{rel}) deviation is used to compare the difference between the systems after one analysis. The repeatability and reproducibility is used to compare the systems after three analysis days.

The relative standard deviation, s_{rel}, where s denotes the standard deviation of the peak areas and $\bar{a}$ the average of the peak areas, is calculated as

$$s_{rel} = \frac{s}{\bar{a}}$$

The calculations of the repeatability ($s_{r,\mathrm{rel}}$) and reproducibility ($s_{R,\mathrm{rel}}$) are given in Chapter 3.5.

As already mentioned in the introduction, one of the goals of the "Metrology for Biomethane" project is to achieve a relative expanded uncertainty of 3 % for the silicon and siloxane content in biomethane.

4 Results and discussion

4.1 A comparison of two GC/FID-systems

The following results (Figures 4.1 - 4.10) show the relative response factors (R) next to each other per component for GC-1 (left) and CG-10 (right). The different coloured shapes in the figures, stands for the different days of analysis.

The last three analyses on the GC-10 exhibit a greater dispersion between the gas mixtures compared to the analyses on GC-1. A reason for this could be that GC-1 had 15 different data points and the five best point were selected. On the GC-10 there were only 3 analysis days and were therefore all used.

For the last three analyses on the GC-10, it is noticeable that the first analysis day (the black squares) deviates from the two other analysis days (red dots and purple triangles). To find the cause of the deviating data points of the first analysis day (the black squares), the retention times, peak shapes in the chromatograms and the integration of the peaks were checked. Everything seemed to be right, so it is still unexplainable why the first analysis day differs from the other two.
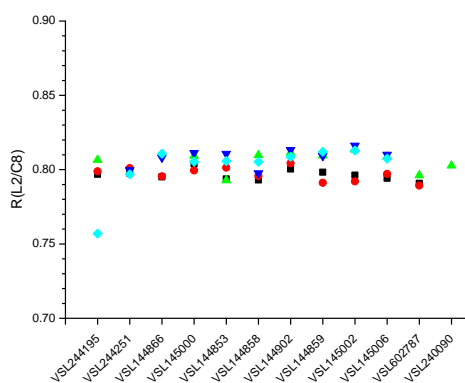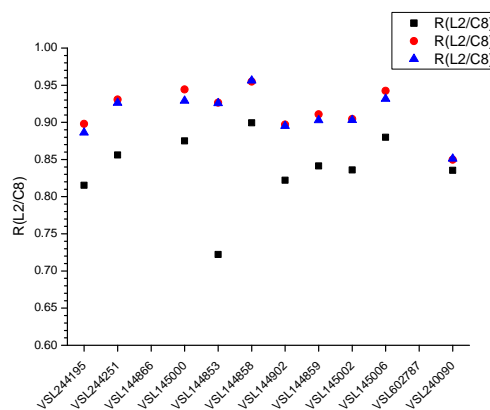

Figure 4.1: RRF of L2 on GC-1
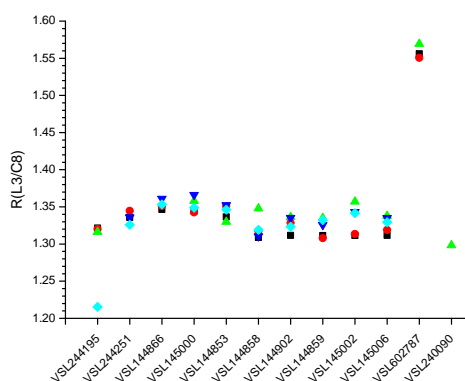

Figure 4.2: RRF of L2 on GC-10
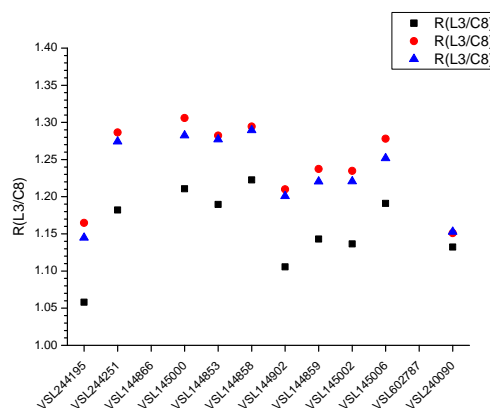

Figure 4.3: RRF of L3 on GC-1

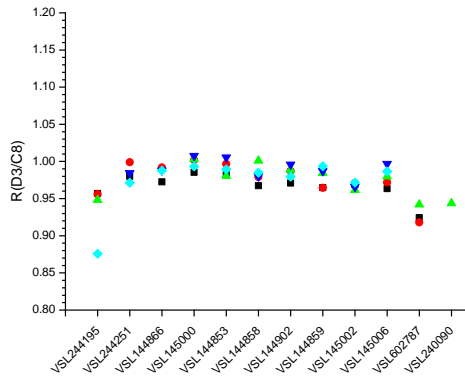Figure 4.4: RRF of L3 on GC-10

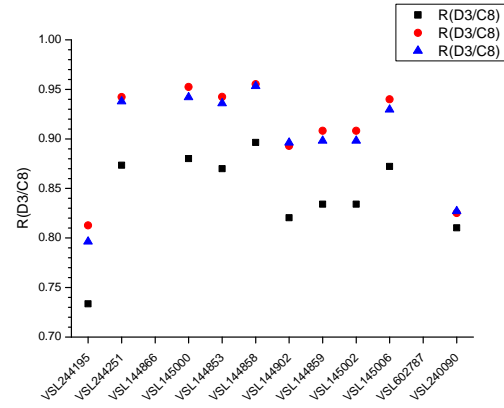Figure 4.5: RRF of D3 on GC-1

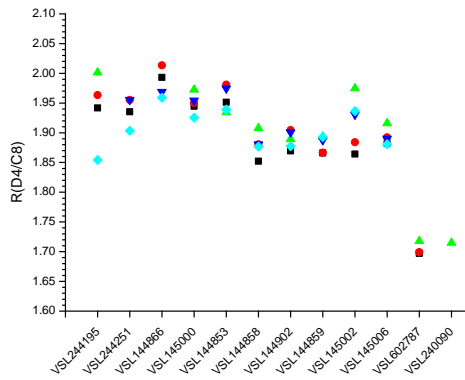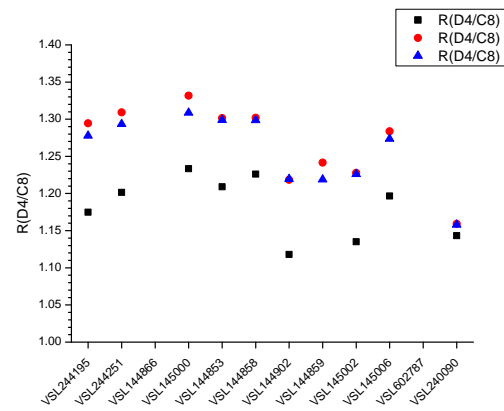Figure 4.6: RRF of D3 on GC-10

Figure 4.7: RRF of D4 on GC-1
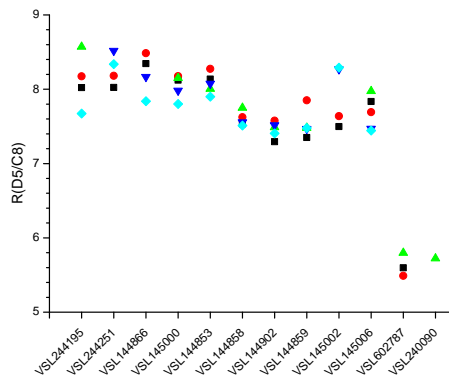

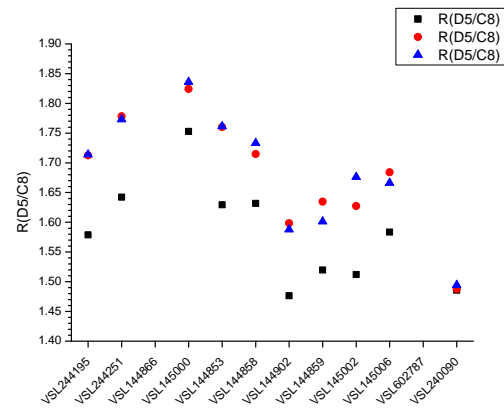Figure 4.8: RRF of D4 on GC-10

Figure 4.9: RRF of D5 on GC-1

Figure 4.10: RRF of D5 on GC-10

4.2 Stability study

4.2.1 Density

For evaluating the long-term stability of the siloxanes content in biomethane, a Bayesian hierarchical model was used instead of the classical statistic. A Bayesian model better warrants the characterisation of the dispersion.

The results of the density study per component for the gas mixtures VSL145000 are summarised in Figures 4.11 - 4.15. Bayesian model provides sample at the probability density function of the parameters. The prime interest are μ, $s(\mu)$, τ, σ, α, and $s(\alpha)$ which can be computed from the output probability default.

Based on the shapes of the curves of the μ (black curve) and the α (green curve), a similar shape as the t-distribution can be observed. The τ has a more skewed shape, and the σ a narrow curve. The average of the distributions was used subsequently in the stability assessment.

Remarkable is that the slope (α) for L2 and D4 starts in the minus (x-axis) in contrast to siloxanes L3, D3 and D5.
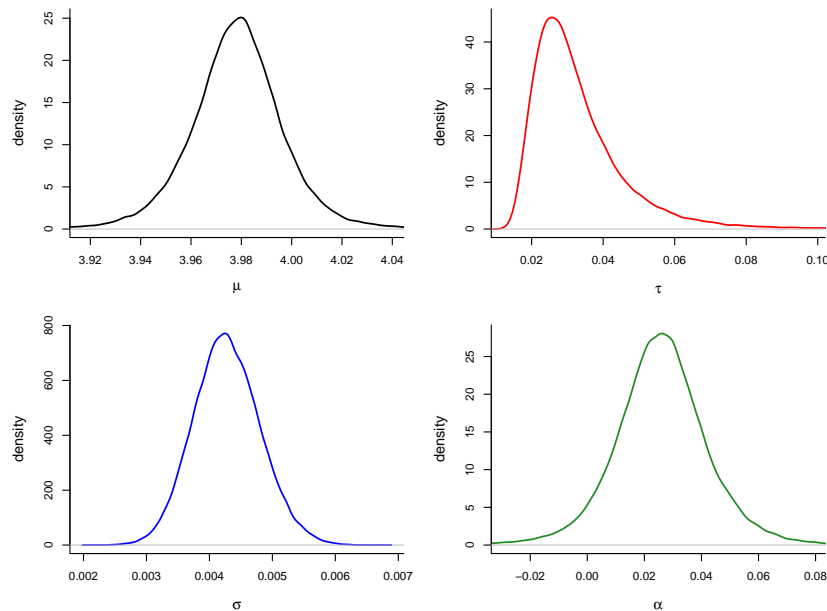

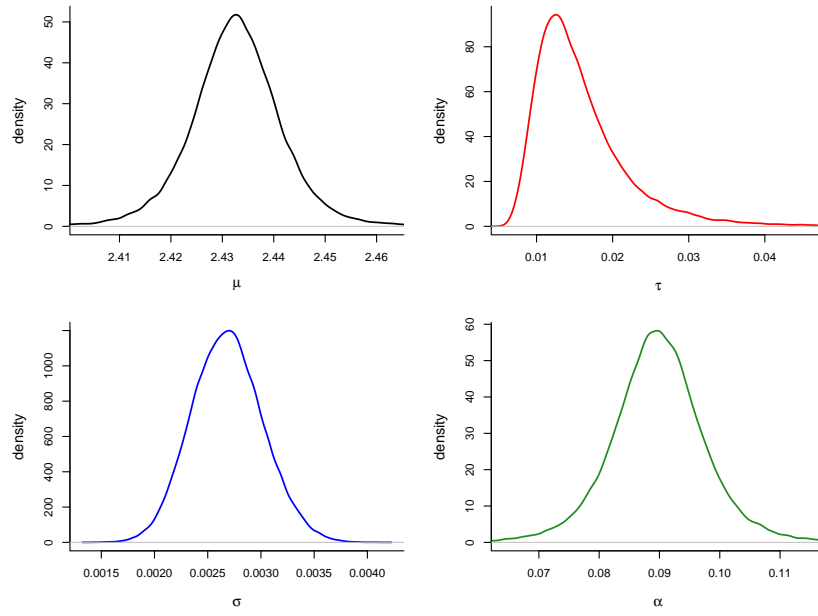Figure 4.11: Density plot for L2 in gas mixture VSL145000

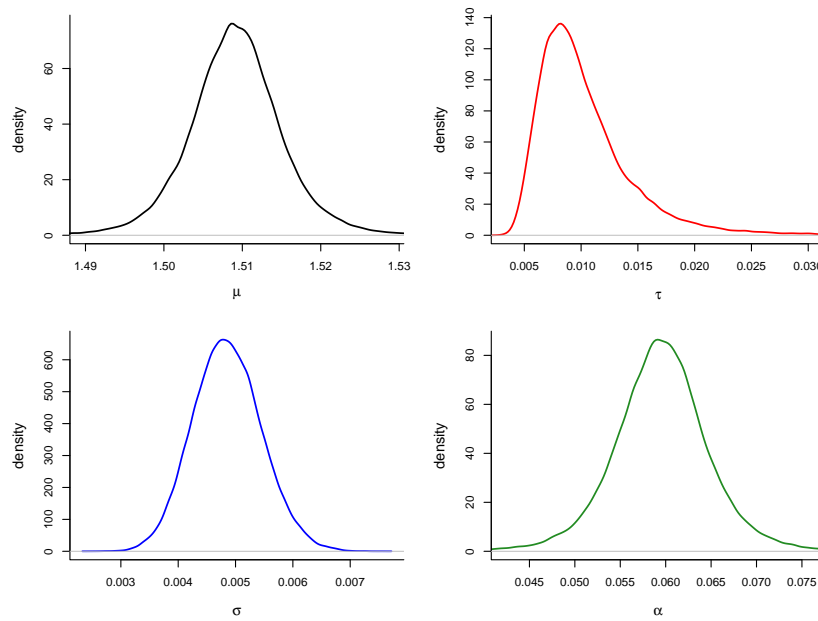Figure 4.12: Density plot for L3 in gas mixture VSL145000

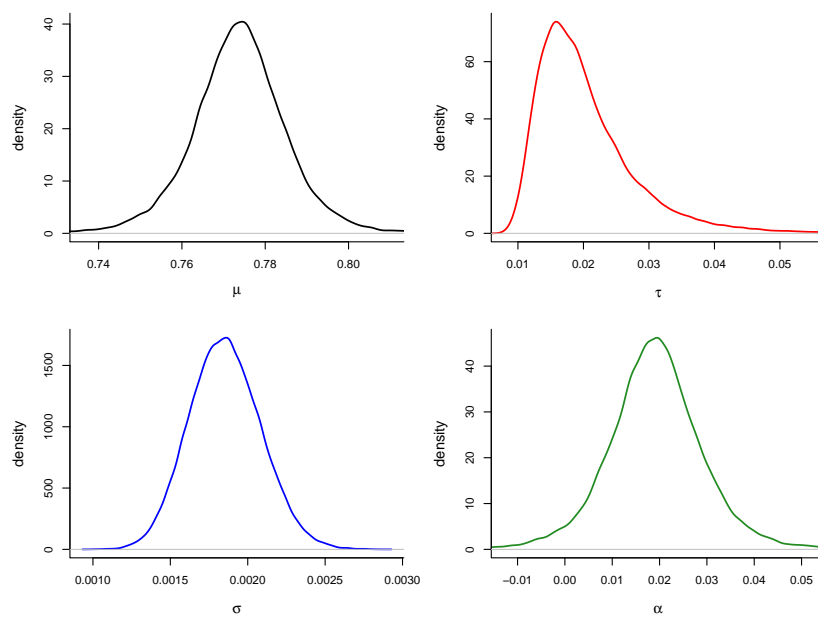Figure 4.13: Density plot for D3 in gas mixture VSL145000

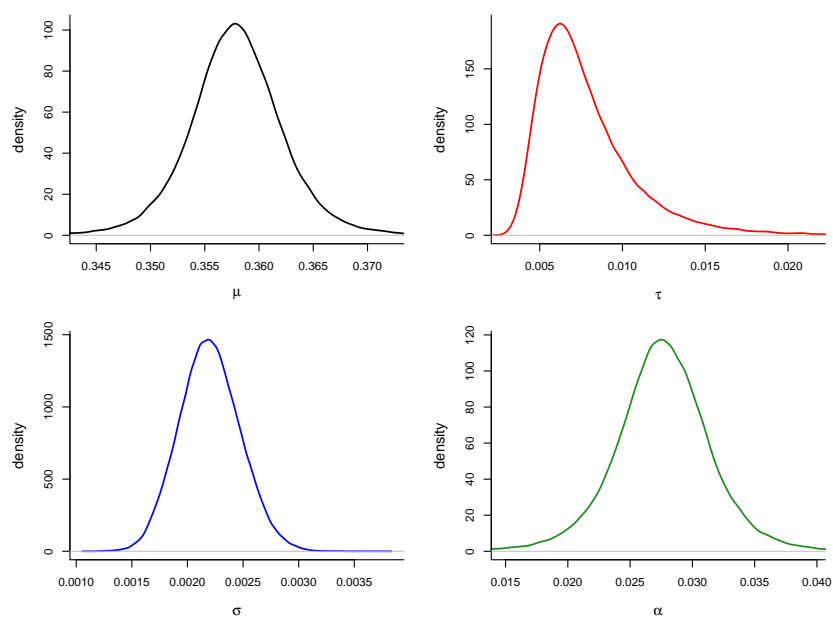Figure 4.14: Density plot for D4 in gas mixture VSL145000

Figure 4.15: Density plot for D5 in gas mixture VSL145000

4.2.2 Stability

To determine if the gas mixtures are still stable after almost two years, a stability study was conducted with n-octane as internal standard.

For the long-term stability test of the siloxanes content in biomethane, the gas mixtures have already been evaluated for a period of six months for a pilot round of the proficiency test in 2017. The measurement data underlying the reference values showed appreciable reproducibility effects between the data points that are good enough for operating a proficiency test [1].

The results of the stability study are summarised in Figures 4.16 - 4.20. The expended uncertainties indicated in the figures indicate those from propagating the uncertainties from calibration and measurement. The calculated uncertainty from the gravimetric gas mixture preparation has a negligible influence on the overall uncertainty.

The results for the last two analysis days for L2 (Figure 4.16) show an upward trend in the data compared with the first five analyses. Mixture VSL144866 was not analysed for the stability study. The slope of the regression line computed with the model given in equation 3.7 is insignificant for all mixtures.

The results for L3 (Figure 4.17) show a similar pattern as those for L2, but the slope is, except for mixture VSL244195, significant for all the mixtures.

The results for D3 (Figure 4.18) show a similar pattern as those for L2. The slope is significant for the mixtures VSL144858, VSL144902, VSL144859, VSL145002, and VSL145006.

The results for D4 (Figure 4.19) show similar patterns as those for L2.

The results for D5 (Figure 4.20) show similar patterns as those for D3. Mixtures VSL145000, VSL145002, and VSL144859 show a significant trend.

For all the gas mixtures, the amount-of-substance fractions run up and that is strange, because either a horizontal trend (if the mixtures are stable) line or a downward trend (if the mixtures are not stable anymore) is expected.

The GC was calibrated with calibration mixtures containing one siloxane and the internal standard, n-octane. The results of the calibration mixtures show data points for analysis days three to five that were already increasing. Thus, if the ten proficiency test mixtures are measured again after a period of almost two years (data points six to eight), and the calibration mixtures also expire, higher values of the fractions will be obtained for the mixtures that have been measured.

For the gas mixture preparations, Aculife IV-treated aluminum cylinders were used. It is known that the cylinders are silanized with polydimethylsiloxane (PDMS) [35]. This may be an explanation for the upward trend of the amount-of-substance fractions, because the main components of interests in the gas cylinders are siloxanes (silicon-containing Si-O bonds) and PDMS also contains silicon.

An idea is to make fresh calibration mixtures every time before measuring, so that the differences in behavior of the components are monitored.
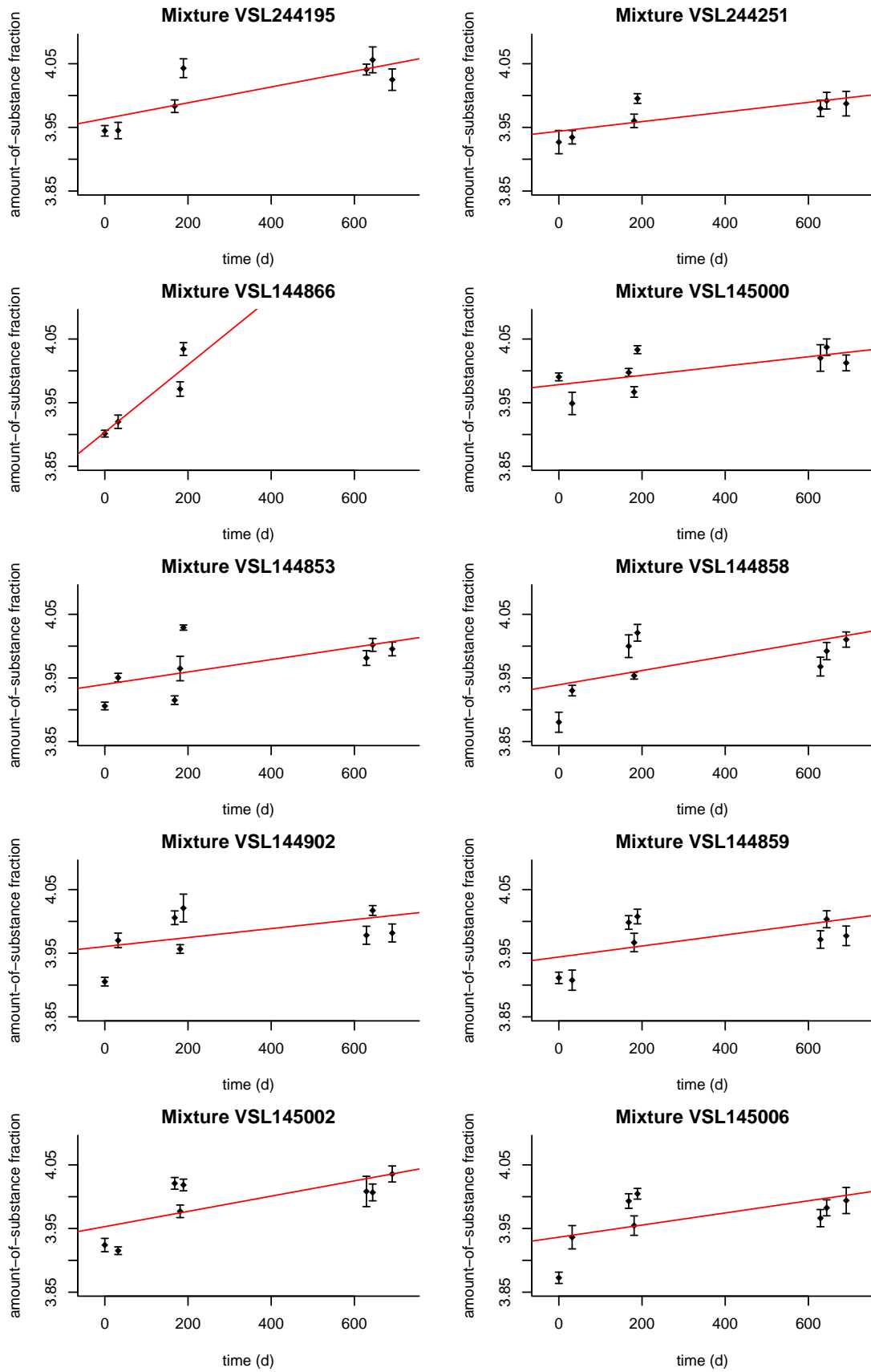
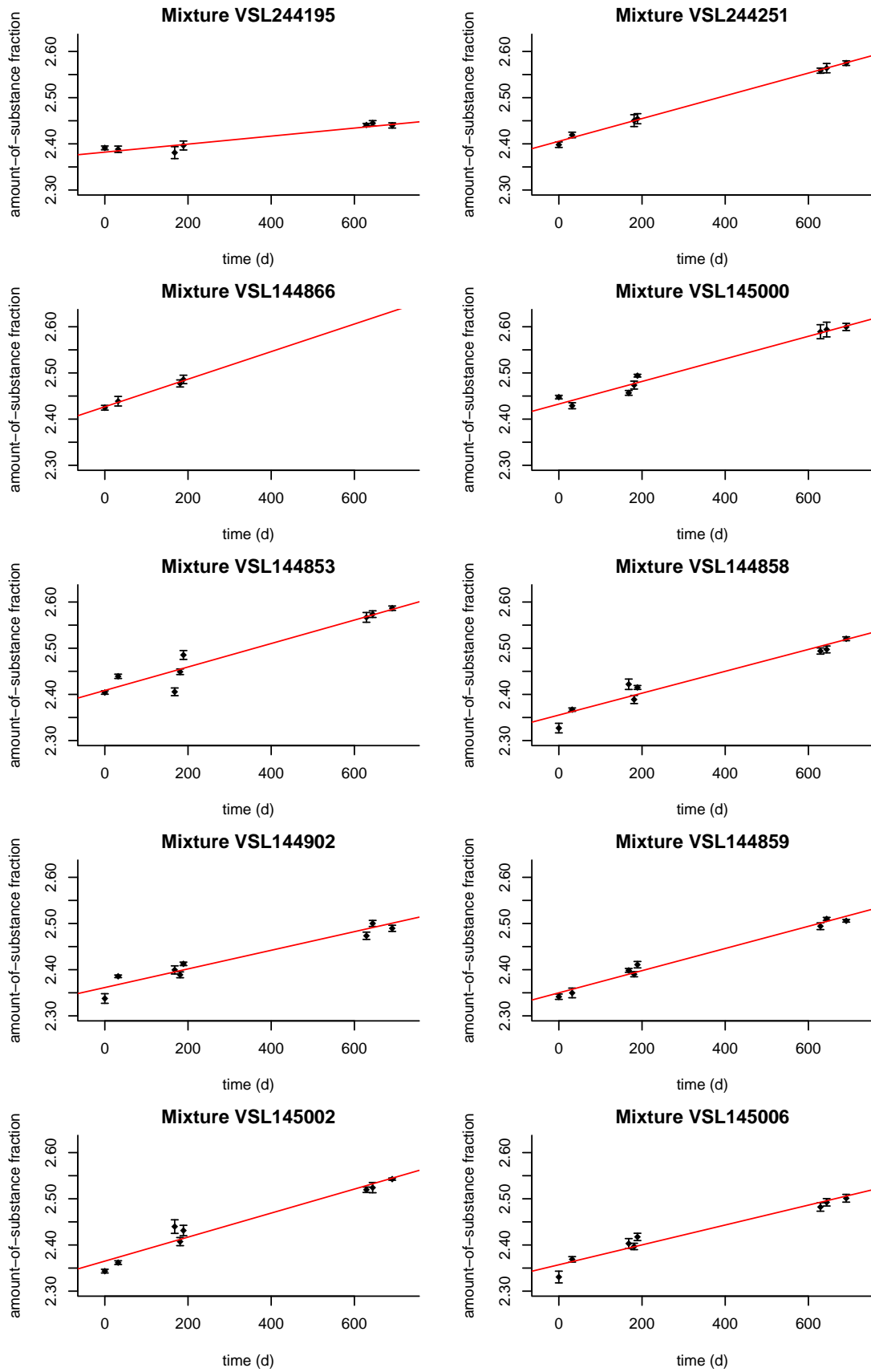Figure 4.16: Stability study results for L2
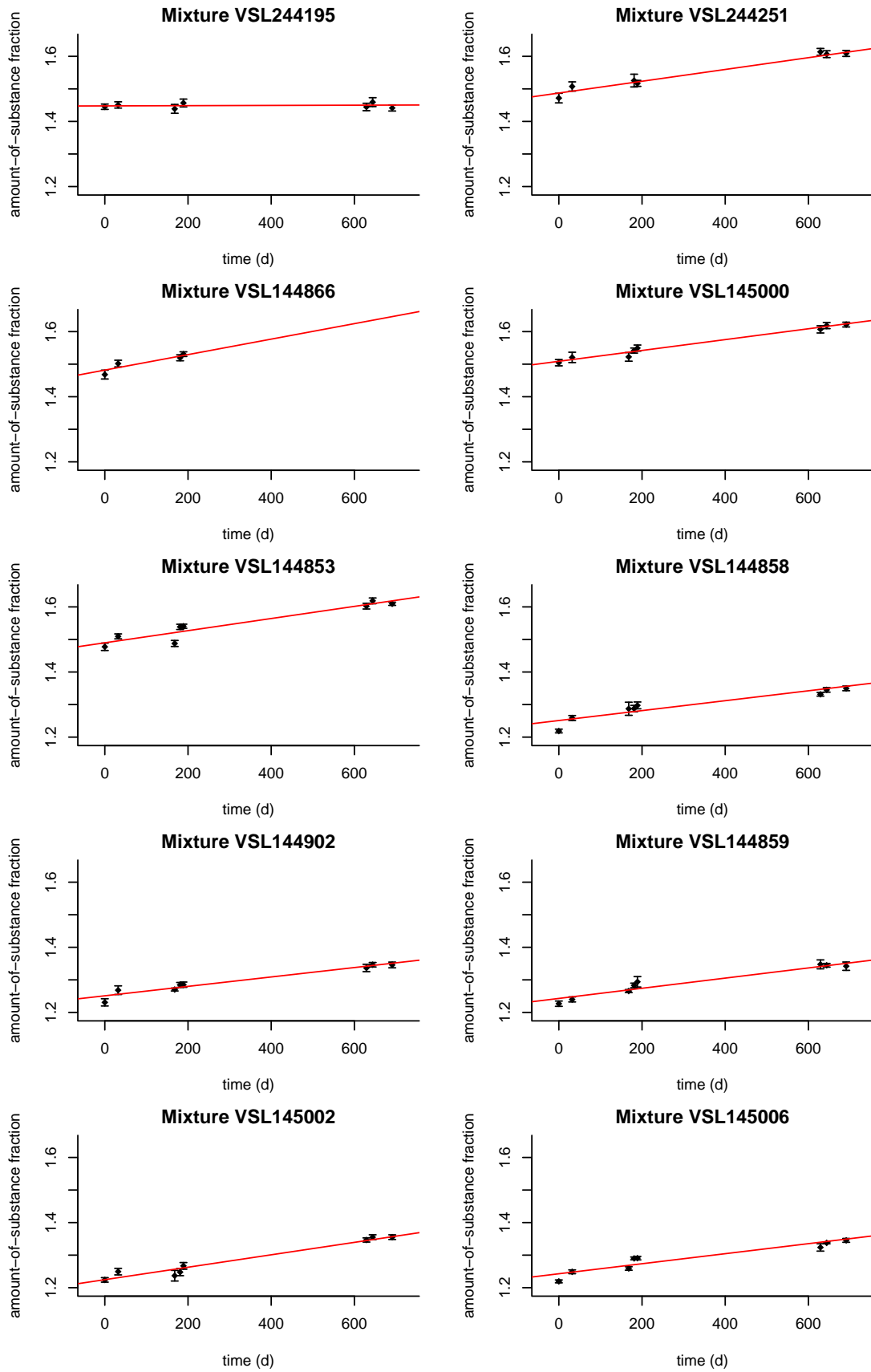
Figure 4.17: Stability study results for L3

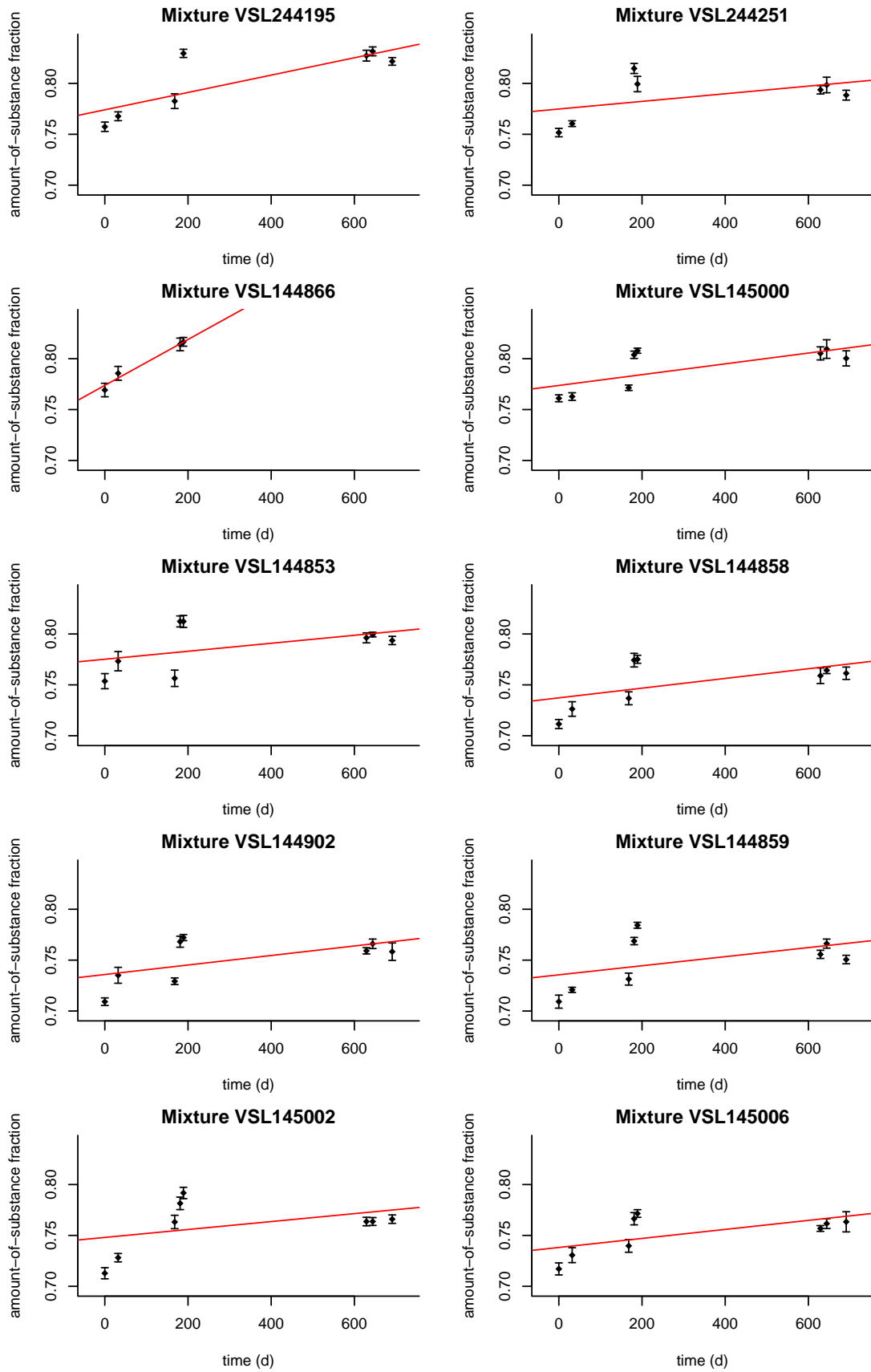Figure 4.18: Stability study results for D3
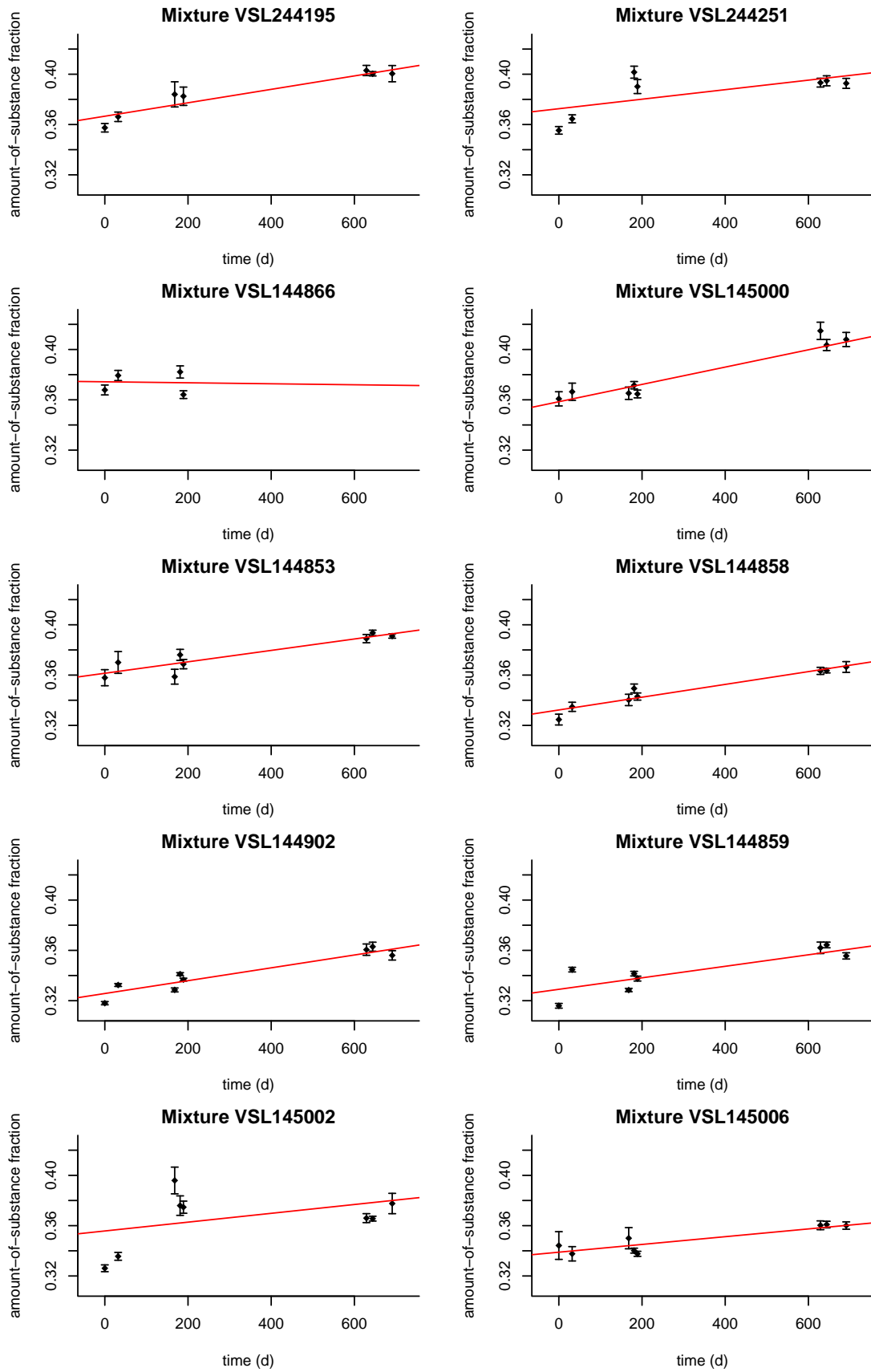
Figure 4.19: Stability study results for D4

Figure 4.20: Stability study results for D5

4.2.3 Repeatability and reproducibility

The nine gas mixtures from Table 3.7 were analysed to determine the repeatability and the reproducibility of the method. Seven repeated injections were conducted on June 7, June 22 and August 8, 2018. The first analysis result of each analysis was removed from the results. The method was validated with the remaining 18 analysis results. Table 4.1 and 4.2 summarises the repeatability and reproducibility ('lack of', expressed as a percentage of the average) per component, per cylinder.

The following results (Figures 4.28-4.33) shows the repeatability ($s_{r,\mathrm{rel}}$) and reproducibility ($s_{R,\mathrm{rel}}$) per component, per cylinder. The values shown are based on the three data sets (n = 6), which have been analysed between June 7 and August 8, 2018.
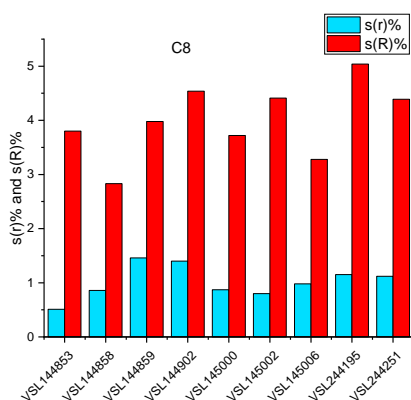
Figure 4.21: $s_{r,\mathrm{rel}}$ and $s_{R,\mathrm{rel}}$ for C8
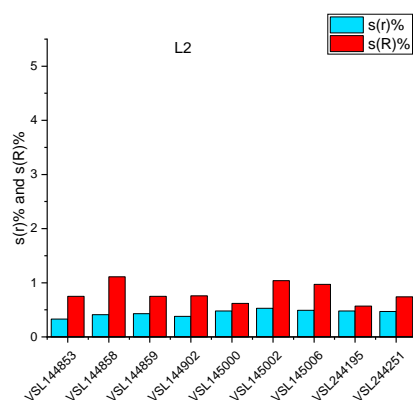

Figure 4.22: $s_{r,\mathrm{rel}}$ and $s_{R,\mathrm{rel}}$ for for L2
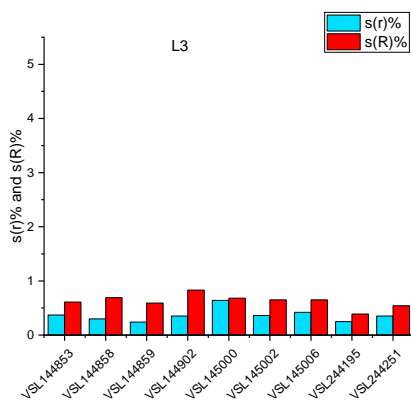
Figure 4.23: $s_{r,\mathrm{rel}}$ and $s_{R,\mathrm{rel}}$ for for L3
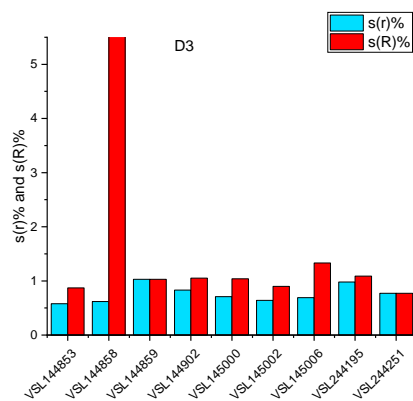
Figure 4.24: $s_{r,\mathrm{rel}}$ and $s_{R,\mathrm{rel}}$ for for D3
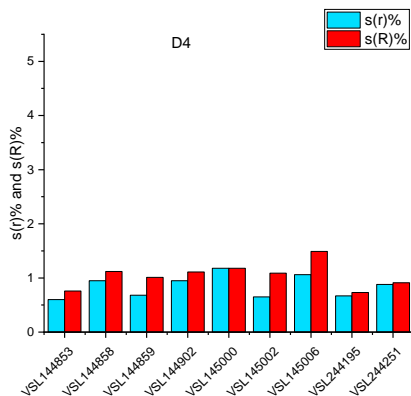
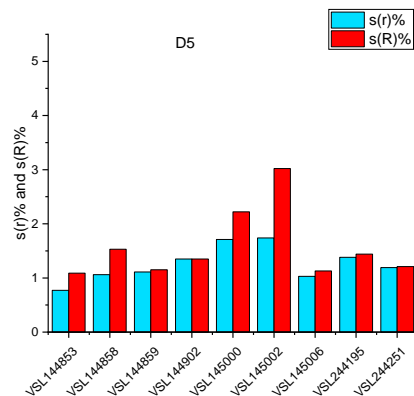Figure 4.25: $s_{r,\text{rel}}$ and $s_{R,\text{rel}}$ for D4

Figure 4.26: $s_{r,\text{rel}}$ and $s_{R,\text{rel}}$ for D5

Table 4.1: The repeatability and reproducibility per component, per mixture.

	VSL144853		VSL144858		VSL144859		VSL144902		VSL145000	
	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$
C8	0,51	3,80	0,86	2,83	1,46	3,98	1,40	4,54	0,87	3,72
L2	0,33	0,75	0,41	1,11	0,43	0,75	0,38	0,76	0,48	0,62
L3	0,37	0,61	0,30	0,69	0,24	0,59	0,35	0,83	0,64	0,68
D3	0,58	0,87	0,62	27,42	1,03	1,03	0,83	1,05	0,71	1,04
D4	0,60	0,76	0,95	1,21	0,68	1,01	0,95	1,11	1,18	1,18
D5	0,77	1,09	1,06	1,53	1,11	1,15	1,35	1,35	1,71	2,22

Table 4.2: The repeatability and reproducibility per component, per cylinder.

	VSL145002		VSL145006		VSL244195		VSL244251	
	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$	$s_{r,\text{rel}}$	$s_{r,\text{rel}}$	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$
C8	0,80	4,14	0,98	3,28	1,15	5,04	1,12	4,39
L2	0,53	1,04	0,49	0,97	0,48	0,57	0,47	0,74
L3	0,36	0,65	0,42	0,65	0,25	0,39	0,35	0,54
D3	0,64	0,90	0,69	1,33	0,98	1,09	0,77	0,77
D4	0,65	1,09	1,06	1,49	0,67	0,73	0,88	0,91
D5	1,74	3,02	1,03	1,13	1,38	1,44	1,19	1,21

A previous student performed analyses of siloxane mixtures on the GC/FID (GC-10) between August 2017 and January 2018 and determined the repeatability and reproducibility of the method analysis [36]. Table 4.3 summarises the repeatability and reproducibility per component of the analyses. Figure 4.27 shows the repeatability ($s_{r,\text{rel}}$) and reproducibility ($s_{R,\text{rel}}$) per component. The blue bars represent the repeatability and the red bars represent the reproducibility.
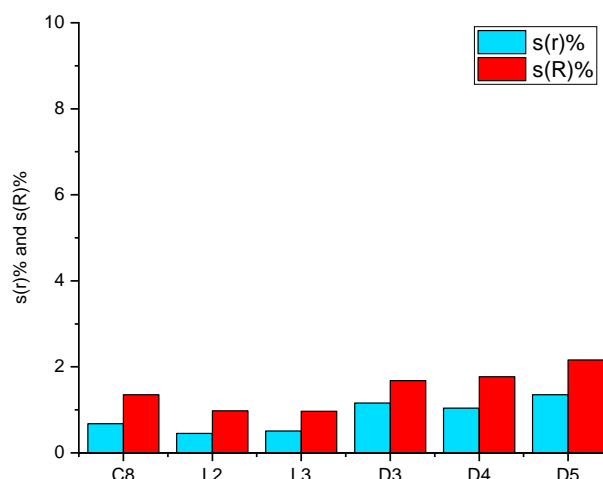
Figure 4.27: $s_{r,\text{rel}}$ and $s_{R,\text{rel}}$ of previous analyses on GC/FID

Table 4.3: The repeatability and reproducibility of previous analyses on GC/FID.

	GC/FID	
	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$
C8	0.68	1.35
L2	0.45	0.98
L3	0.51	0.97
D3	1.16	1.68
D4	1.04	1.77
D5	1.35	2.16

Comparing this year analysis results with the results for repeatability and reproducibility of the analysis method of the previous student, the results for repeatability and reproducibility for C8 show a deterioration for all gas mixtures.

The results for repeatability for L2 have all deteriorated, except for gas mixture VSL144853, VSL144858, VSL144859 and VSL144902. For reproducibility, they are all improved, except for gas mixture VSL144858.

The results for repeatability and reproducibility for L3 have all been improved, except for the repeatability of mixture VSL145000.

The results for repeatability and reproducibility for D3 have all been improved, except for the repeatability of mixture VSL144858.

The results for repeatability and reproducibility for D4 have all been improved, except for the repeatability of mixture VSL145000.

The results for D5 have been improved for repeatability for all mixtures, except for VSL145000, VSL145002 and VSL244195. The reproducibility has also been improved for the gas mixtures, except for mixture VSL145000 and VSL145002.

In general, all results for repeatability are lower than 3 %. Except for C8, mixture VSL144858 for D3 and mixture VSL145002 for D5, the results for the reproducibility are also below 3 %. To improve the reproducibility of C8 in the gas mixtures, the amount-of-substance fractions of C8 can be doubled. If the concentration is doubled, the peak also becomes twice as large and the peak area becomes larger. Another option is to use iso-octane as an internal standard instead of n-octane. Iso-octane is much more volatile and could provide better performance than the n-octane.

4.3   Method development on the GC/BID

As already mentioned in Chapter 3.7 on page 20, based on an existing method that was used on the GC/FID, a method was subsequently developed for the GC/BID. By varying in different parameters, it was examined what effect this had on the chromatogram and whether this was a positive change. Finally, the best method was developed by changing the oven program and the split ratio of the existing GC/FID method. And also by trying different values of the discharge flow. The settings of the analytical method developed for analysing siloxanes in biomethane are listed in Table 4.4. An example of a chromatogram is given in Figure 4.28. During the method development, the identity of the peaks was determined using the elution sequence of the measured gas mixtures on the GC/FID. The chromatograms are included in Appendix Figure C.1-Figure C.4. Table 4.5 indicates the elution order of the components. The retention times are rounded to one decimal.

Table 4.4: Specifications of the method on GC/BID.

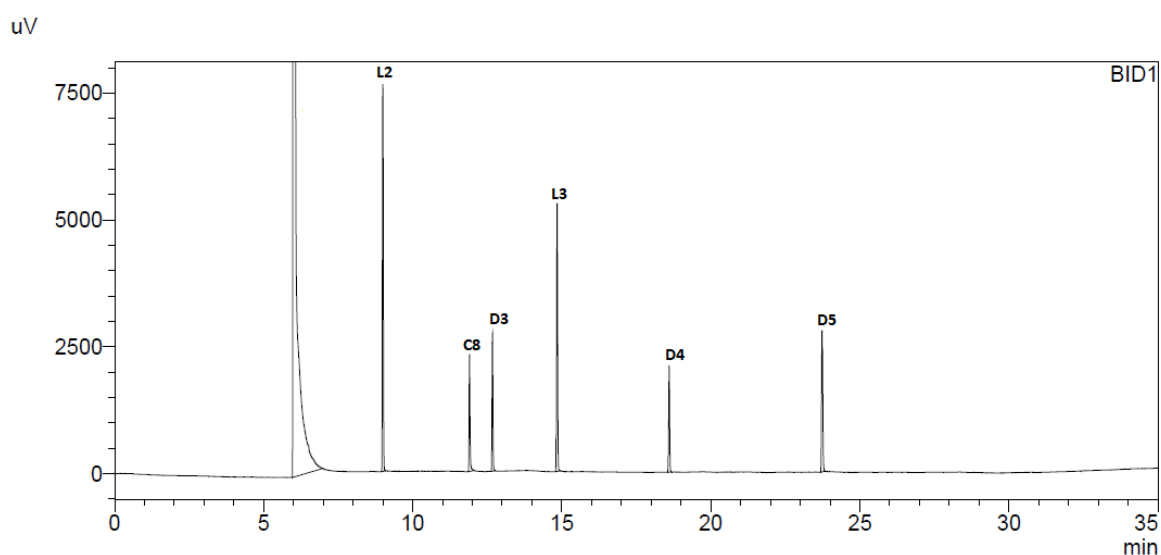| Method parameter	GC/BID
Column	Capillary DB-1ms UI 60 m x 0.25 mm x 0.25 μm
Injection	Split 1:100
Oven settings	40°C (hold 5 min), 5°C min^{-1} to 130°C (hold 3 min), 20°C min^{-1} to 210°C (hold 10 min)
Detector settings	250°C He flow rate 30 mL min^{-1}

Figure 4.28: Chromatogram showing the elution order of the 5 siloxanes and n-octane.

Table 4.5: Elution order of the components

Compound	Retention time (min)
L2	9.0
C8	12.0
D3	12.7
L3	14.9
D4	18.6
D5	23.8

The method has been validated based on repeatability, reproducibility analysing the four gas mixtures VSL348568, VSL144853, VSL144858 and VSL244251. Fifteen repeated injections were conducted on November 5, November 12 and November 19, 2018. The first five results of each analysis was removed from the results. The method was validated with the remaining 30 analysis results.

Table 4.6 summarises the repeatability and reproducibility ('lack of', expressed as a percentage of the average) per component, per cylinder. An example for the calculation of the repeatability and reproducibility is given in Chapter 3.6 on page 20.

The following results (Figures 4.12 - 4.17) show the repeatability ($s_{(r)}$%) and reproducibility ($s_{(R)}$%) per component, per mixture. The blue bars represent the repeatability and the red bars represent the reproducibility. The mixture VSL348568 has a lower amount-of-substance fraction than mixtures VSL144853, VSL144858 and VSL244251. For this reason, VSL348568 was only analysed on the GC/BID. The amount-of-substance fractions of the mixture was below the detection limit of the GC/FID system (GC-10).

It is noticeable that the mixture VSL348568, containing the lower amount-of-substance fractions of the siloxanes, has higher percentages for both the repeatability and reproducibility for all components. The results for L2 and L3 show a repeatability and reproducibility lower than 3 %. The remaining three mixtures, with higher amount-of substance-fractions, all have low repeatability percentages and higher reproducibility percentages. The measurement data for the mixtures VSL144853, VSL144858 and VSL244251, underlying the reproducibility and repeatability values show appreciable results for all components. Except for the reproducibility of D5 for these mixtures, all components have a repeatability and reproducibility lower than 3 %.
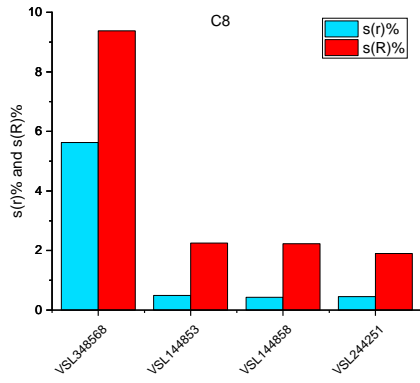
Figure 4.29: $s_{r,\text{rel}}$ and $s_{R,\text{rel}}$ for C8
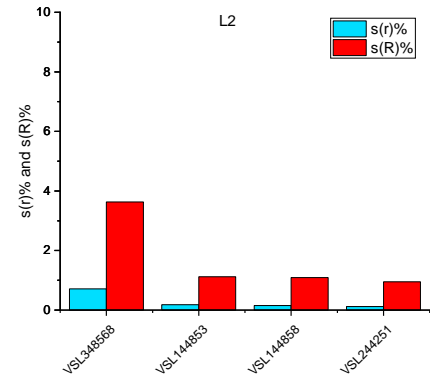
Figure 4.30: $s_{r,\text{rel}}$ and $s_{R,\text{rel}}$ for L2
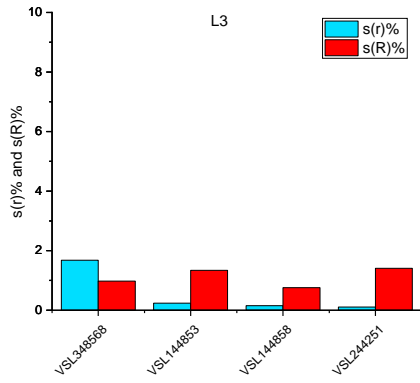
Figure 4.31: $s_{r,\text{rel}}$ and $s_{R,\text{rel}}$ for L3
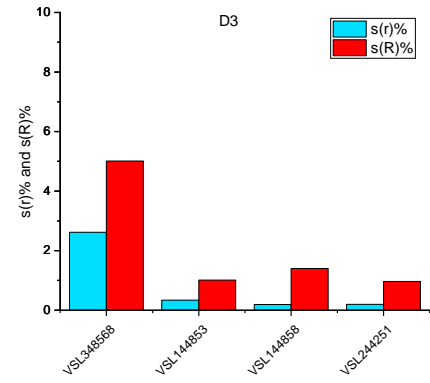
Figure 4.32: $s_{r,\text{rel}}$ and $s_{R,\text{rel}}$ for D3
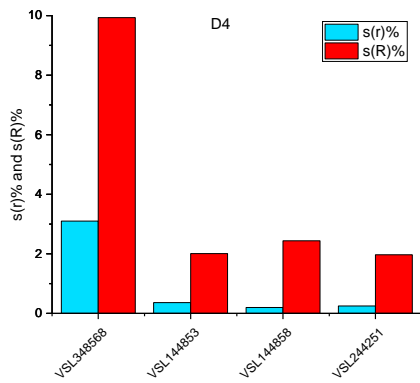
Figure 4.33: $s_{r,\text{rel}}$ and $s_{R,\text{rel}}$ for D4
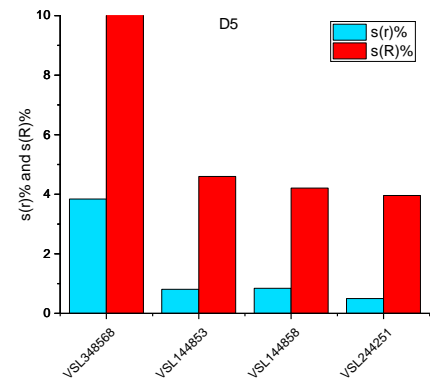
Figure 4.34: $s_{r,\text{rel}}$ and $s_{R,\text{rel}}$ for D5

Table 4.6: Summary of the repeatability and reproducibility per component, per mixture on GC/BID.

	VSL348568		VSL144853		VSL144858		VSL244251	
	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$
C8	5.63	9.38	0.49	2.25	0.43	2.23	0.45	1.90
L2	0.71	3.63	0.18	1.12	0.15	1.09	0.12	0.95
L3	1.68	1.98	0.24	1.34	0.15	1.76	0.11	1.41
D3	2.62	5.01	0.34	1.01	0.19	1.40	0.20	0.97
D4	3.10	9.93	0.36	2.01	0.20	2.44	0.25	1.97
D5	3.84	21.24	0.81	4.60	0.84	4.21	0.50	3.69

4.4   A comparison of the GC/FID and GC/BID

The following results in Table 4.7 summarises the relative standard deviation (s_{rel}) per component, for the mixtures VSL144858 and VSL348568 analysed on November 5, 2018. The mixture VSL348568, with a lower amount-of-substance fractions, was only analysed on the GC/BID. The amount-of-substance fractions of the mixture was below the detection limit of the GC/FID system (GC-10).

Figure 4.35 shows the relative standard deviation (s_{rel}) per component. The blue bars represent the s_{rel} of the analysis of the mixture VSL144858 on the GC/FID, the yellow bars represent the s_{rel} of the analysis of the mixture VSL144858 on the GC/BID, and the red bars represent s_{rel} of the analysis of the mixture VSL348568 on the GC/BID.
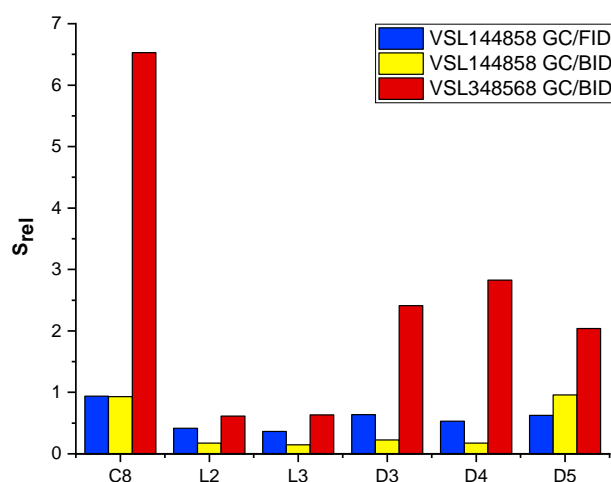
Figure 4.35: s_{rel} per component, per mixture on GC/FID and GC/BID.

Table 4.7: Summary of s_{rel} per component, per mixture on GC/FID and GC/BID.

	VSL144858		VSL348568
	s_{rel} **GC/FID**	s_{rel} **GC/BID**	s_{rel} **GC/BID**
C8	0.937	0.391	6.530
L2	0.415	0.175	0.612
L3	0.364	0.146	0.635
D3	0.636	0.226	2.412
D4	0.513	0.176	2.282
D5	0.626	0.958	2.038

Overall, the s_{rel} for all the components are below the 3 %. And one of the goals of the "Metrology for Biomethane" project is to achieve a relative expanded uncertainty of 3 % for the silicon and siloxane content in biomethane.

The results for mixture VSL144858 show for the components C8, L2, L3, D3 and D4, a smaller s_{rel} for the analysis on the GC/BID, but a larger s_{rel} for D5.

The results for mixture VSL348568 show a larger s_{rel} for all component, in contrast to mixture VSL144858 for both GC/FID and GC/BID.

As already mentioned, a previous student performed analyses of siloxane mixtures on the GC/FID (GC-10) between August 2017 and January 2018 and determined the repeatability and reproducibility of the analysis method. Table 4.8 summarises the repeatability and reproducibility per component of the analyses measures on the GC/FID (GC-10). Table 4.9 summarises the repeatability and reproducibility of the analysis method for the GC/BID.

Table 4.8: The repeatability and reproducibility of previous analyses on GC/FID.

	GC/FID	
	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$
C8	0.68	1.35
L2	0.45	0.98
L3	0.51	0.97
D3	1.16	1.68
D4	1.04	1.77
D5	1.35	2.16

Table 4.9: The repeatability and reproducibility per component, per mixture on GC/BID.

	VSL348568		VSL144853		VSL144858		VSL244251	
	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$	$s_{r,\text{rel}}$	$s_{R,\text{rel}}$
C8	5.63	9.38	0.49	2.25	0.43	2.23	0.45	1.90
L2	0.71	3.63	0.18	1.12	0.15	1.09	0.12	0.95
L3	1.68	1.98	0.24	1.34	0.15	1.76	0.11	1.41
D3	2.62	5.01	0.34	1.01	0.19	1.40	0.20	0.97
D4	3.10	9.93	0.36	2.01	0.20	2.44	0.25	1.97
D5	3.84	21.24	0.81	4.60	0.84	4.21	0.50	3.69

Comparing the results of the repeatability and reproducibility of the GC/FID and GC/BID with each other, gas mixture VSL348568 (with lower amount-of substance fractions) measured on the GC/BID has higher percentages for both repeatability and reproducibility. The remaining three mixtures have improved in repeatability on the GC/BID, but has larger reproducibility percentages than the GC/FID. Component D3 is the only one that has improved in repeatability on the GC/BID for mixtures VSL144853, VSL144858 and VSL244251.

The results for mixtures VSL144853, VSL144858 and VSL244251 show, except for the reproducibility for component D5 in all the three mixtures, for all components a repeatability and reproducibility lower than 3 %.

Based on the results of the repeatability and reproducibility to compare the difference between the systems, the new detector, the Barrier Ionization Detector (BID), is just as sensitive as the FID. It is interesting to see that gas mixture containing the lower amount-of-substance fractions of the siloxanes, could be measured on the GC/BID, while this was not possible on the GC/FID because the mixture fell below the detection limit of the GC-10. BID is interesting for components with with lower amount-of substance fractions that cannot be measured on a GC/FID, for example Volatile Organic compounds (VOCs) and Nitrous oxide (N_2O).

5   Conclusions

The main objective of this thesis was to develop a method for the analysis and stability study of gaseous reference materials of siloxanes in biomethane. To achieve the main objective, four sub-objectives were set. For this research, a criterion of 3 % was taken into account for the relative expanded uncertainties.

The first sub-objective was to compare the results of the stability study of the gas mixtures from the pilot round of the proficiency test measured on two different GC/FID-systems. GC-10 performs at a higher level just as well as GC-1. The peaks from the chromatogram are well separated and well-integrated.

The second sub-objective was to evaluate the long-term stability of the siloxanes content in biomethane and to determine if these gas mixtures are still stable after almost 2 years. The measurement data underlying the reference values for a pilot round of the proficiency test in 2017 showed appreciable reproducibility effects between the data points that are good enough for operating a proficiency test. The data points of the analyses during the proficiency test already had an upward trend and the amount-of-substance fractions of the siloxanes had an increasing change over a period of one year, and this trend continued after a period of almost two years.

The third sub-objective was to develop a method and determine the repeatability and reproducibility of the GC/BID-system using the approach of ISO 5725-2 [7]. A method on the GC/BID was developed very similar with GC-10. The peaks from the chromatograms were well separated and well-integrated. The precision of the analytical method has been evaluated using the repeatability and reproducibility standard deviations parameters. The mixture containing the lower amount-of-substance fractions of the siloxanes show a repeatability and reproducibility standard deviation for L2 and L3 lower than 3 %. The measurement data for the mixtures containing higher amount-of-substance fractions of the siloxanes, except for the reproducibility of D5 for these mixtures, all components have a repeatability and reproducibility standard deviations lower than 3 %.

The fourth sub-objective was to compare the results of the siloxane content in methane measured on a GC/FID, with the new GC/BID-system. Based on the results of the repeatability and reproducibility to compare the difference between the systems, the new detector, the Barrier Ionization Detector (BID), is just as sensitive as the FID. Only D3 has been improved with the GC/BID for all mixtures containing higher amount-of-substance fractions of the siloxanes. The gas mixture containing the lower amount-of-substance fractions of the siloxanes, could be measured on the GC/BID, while this was not possible on the GC/FID because the mixture fell below the detection limit of the GC-10.

6 Recommendations

For a follow-up study of the mixtures with siloxanes content, some tests should be done to improve the results.

For the long-term stability study, fresh calibration mixtures should be made every time before measuring, so that differences in behavior of the components are monitored.

To improve the repeatability and reproducibility of C8 in the gas mixtures, the amount-of-substance fractions of C8 can be doubled. If the concentration is doubled, the peak also becomes twice as large and the peak area becomes larger. This can help improve the repeatability and reproducibility of n-octane. Another option is to use iso-octane as an internal standard instead of n-octane. Iso-octane is much more volatile and could provide better performance than the n-octane.

To improve the repeatability and reproducibility of the mixture with lower amount-of-substance fractions of the siloxanes on the GC/BID, an optimal split ratio should be determined. If the split ratio is reduced from 1:100 to say 1:50, the peak areas will become larger and as a result better repeatability and reproducibility.

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A Appendices

A.1 Gas Chromatography (GC)

Table A.1: Elution order of the components analysed on GC-10

Compound	Retention time (min)
L2	12.3
C8	15.6
D3	16.3
L3	18.4
D4	22.1
D5	27.5

B A comparison of two GC/FID-systems

B.1 Composition of the gas mixtures used for this research

Table B.1: Overview of the exact composition of the gas mixtures in amount-of-substance fractions (mol/mol) used for analyses on the GC/FID (GC-1 and GC-10).

Mixture	L2 (mol/mol)	L3 (mol/mol)	D3 (mol/mol)	D4 (mol/mol)	D5 (mol/mol)	C8 (mol/mol)
VSL244195	$3.9991 \cdot 10^{-7}$	$2.5151 \cdot 10^{-7}$	$1.6097 \cdot 10^{-7}$	$8.0741 \cdot 10^{-8}$	$3.9707 \cdot 10^{-7}$	$2.0225 \cdot 10^{-7}$
VSL244251	$3.9778 \cdot 10^{-6}$	$2.5018 \cdot 10^{-6}$	$1.6011 \cdot 10^{-6}$	$8.0312 \cdot 10^{-7}$	$3.9496 \cdot 10^{-7}$	$2.0118 \cdot 10^{-6}$
VSL144866	$3.9908 \cdot 10^{-6}$	$2.5099 \cdot 10^{-6}$	$1.6064 \cdot 10^{-6}$	$8.0574 \cdot 10^{-7}$	$3.9625 \cdot 10^{-7}$	$2.0184 \cdot 10^{-6}$
VSL145000	$4.0001 \cdot 10^{-6}$	$2.5158 \cdot 10^{-6}$	$1.6101 \cdot 10^{-6}$	$8.0762 \cdot 10^{-7}$	$3.9717 \cdot 10^{-7}$	$2.0231 \cdot 10^{-6}$
VSL144853	$3.9922 \cdot 10^{-6}$	$2.5108 \cdot 10^{-6}$	$1.6069 \cdot 10^{-6}$	$8.0602 \cdot 10^{-7}$	$3.9638 \cdot 10^{-7}$	$2.0191 \cdot 10^{-6}$
VSL144858	$4.0001 \cdot 10^{-6}$	$2.4984 \cdot 10^{-6}$	$1.3640 \cdot 10^{-6}$	$7.9746 \cdot 10^{-7}$	$3.8913 \cdot 10^{-7}$	$2.0043 \cdot 10^{-6}$
VSL144902	$3.9977 \cdot 10^{-6}$	$2.4969 \cdot 10^{-6}$	$1.3631 \cdot 10^{-6}$	$7.9698 \cdot 10^{-7}$	$3.8889 \cdot 10^{-7}$	$2.0031 \cdot 10^{-6}$
VSL144859	$3.9998 \cdot 10^{-6}$	$2.4982 \cdot 10^{-6}$	$1.3639 \cdot 10^{-6}$	$7.9740 \cdot 10^{-7}$	$3.8910 \cdot 10^{-7}$	$2.0042 \cdot 10^{-6}$
VSL145002	$4.0027 \cdot 10^{-6}$	$2.5000 \cdot 10^{-6}$	$1.3649 \cdot 10^{-6}$	$7.9799 \cdot 10^{-7}$	$3.8939 \cdot 10^{-7}$	$2.0057 \cdot 10^{-6}$
VSL145006	$3.9989 \cdot 10^{-6}$	$2.4976 \cdot 10^{-6}$	$1.3635 \cdot 10^{-6}$	$7.9722 \cdot 10^{-7}$	$3.8901 \cdot 10^{-7}$	$2.0037 \cdot 10^{-6}$
VSL602787	$3.9887 \cdot 10^{-5}$	$2.0586 \cdot 10^{-5}$	$1.6055 \cdot 10^{-5}$	$8.0532 \cdot 10^{-6}$	$3.9604 \cdot 10^{-6}$	$2.0173 \cdot 10^{-5}$
VSL240090	$4.0188 \cdot 10^{-5}$	$2.5100 \cdot 10^{-5}$	$1.3703 \cdot 10^{-5}$	$8.0119 \cdot 10^{-6}$	$3.9095 \cdot 10^{-6}$	$2.0137 \cdot 10^{-5}$

C Method development on the GC/BID

C.1 Composition of the gas mixtures used for this research

Table C.1: Overview of the exact composition of the gas mixtures in amount-of-substance fractions (mol/mol) used for the method development on GC/BID.

Mixture	L2 (mol/mol)	L3 (mol/mol)	D3 (mol/mol)	D4 (mol/mol)	D5 (mol/mol)	C8 (mol/mol)
VSL348568	$3.9991 \cdot 10^{-7}$	$2.5151 \cdot 10^{-7}$	$1.6097 \cdot 10^{-7}$	$8.0741 \cdot 10^{-8}$	$3.9707 \cdot 10^{-7}$	$2.0225 \cdot 10^{-7}$
VSL144853	$3.9922 \cdot 10^{-6}$	$2.5108 \cdot 10^{-6}$	$1.6069 \cdot 10^{-6}$	$8.0602 \cdot 10^{-7}$	$3.9638 \cdot 10^{-7}$	$2.0191 \cdot 10^{-7}$
VSL144858	$4,0001 \cdot 10^{-6}$	$2.4984 \cdot 10^{-6}$	$1.3640 \cdot 10^{-6}$	$7.9746 \cdot 10^{-7}$	$3.8913 \cdot 10^{-7}$	$2.0043 \cdot 10^{-6}$
VSL244251	$3.9778 \cdot 10^{-6}$	$2.5018 \cdot 10^{-6}$	$1.6011 \cdot 10^{-6}$	$8.0312 \cdot 10^{-7}$	$3.9496 \cdot 10^{-7}$	$2.0118 \cdot 10^{-6}$

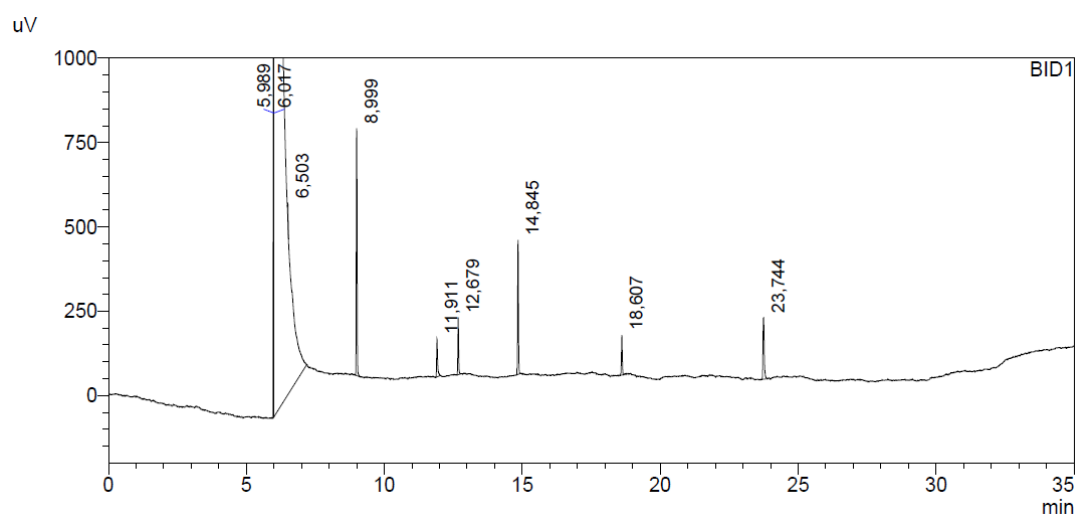## C.2 Chromatograms of the gas mixtures analysed on the GC/BID

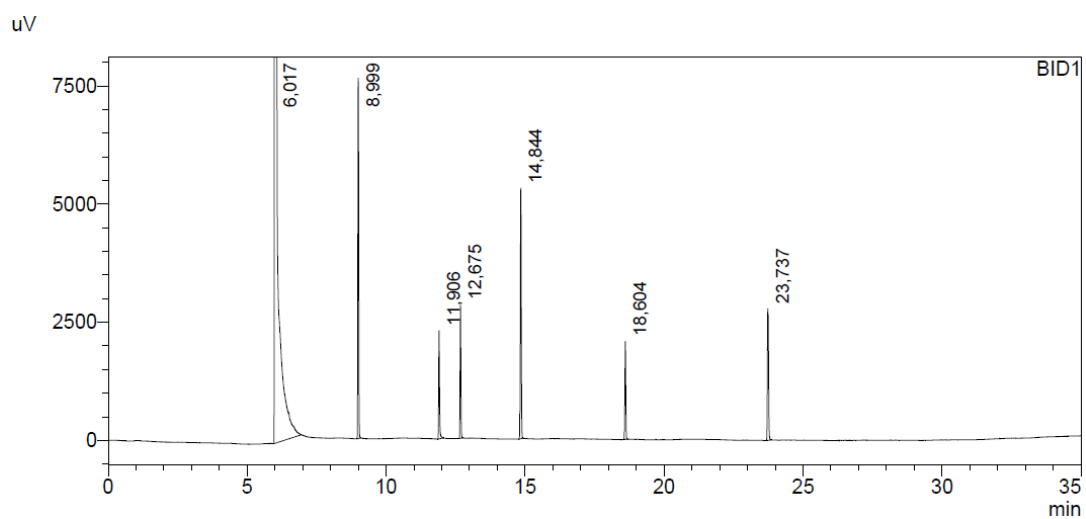Figure C.1: Chromatogram of gas mixture VSL348568.

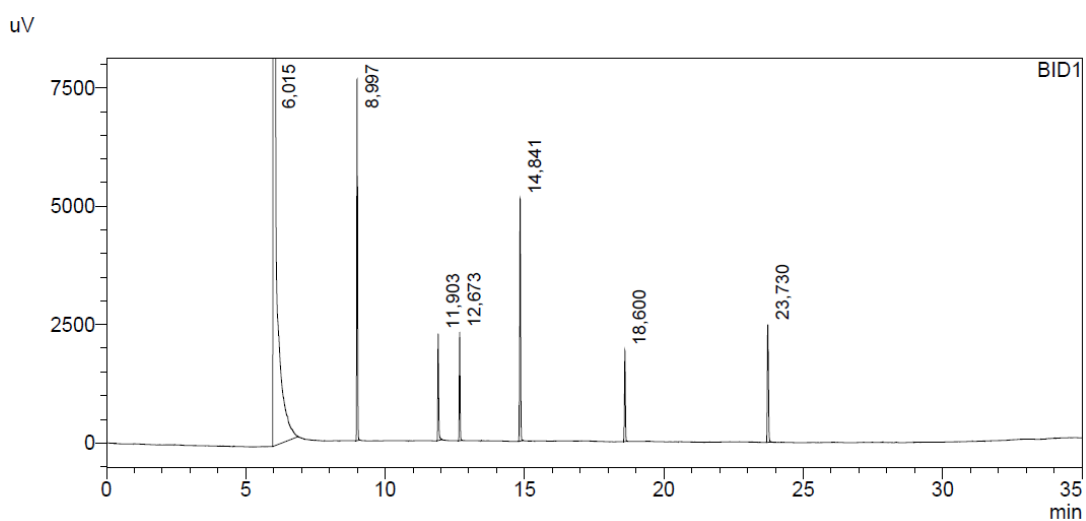Figure C.2: Chromatogram of gas mixture VSL144853
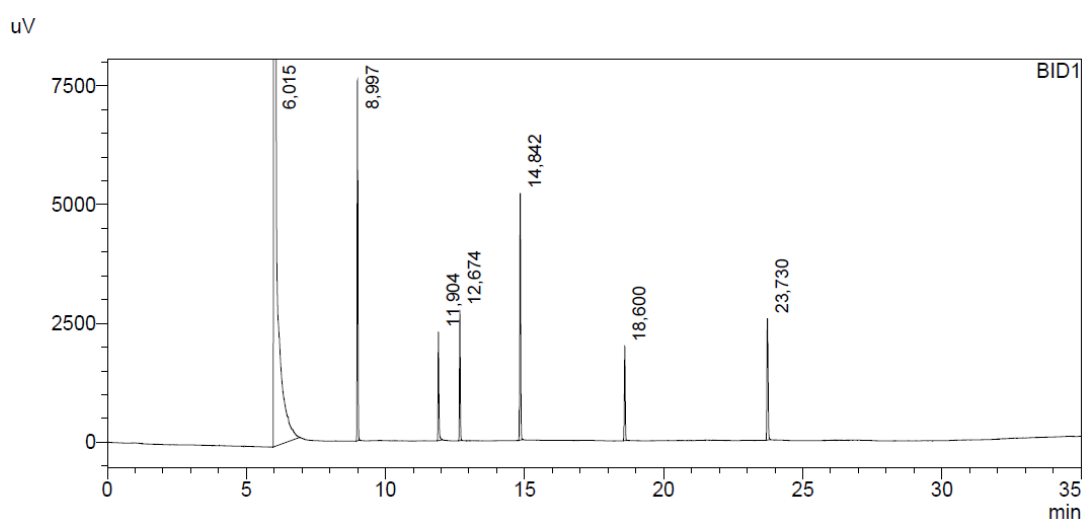

Figure C.3: Chromatogram of gas mixture VSL144858

Figure C.4: Chromatogram of gas mixture VSL244251