

COMPACT SAMPLER FOR LNG/LBG TRUCKS REFUELING STATIONS

REPORT 2020:706



BIODRIVMEDEL FÖR SVERIGE 2030



Compact sampler for LNG/LBG trucks refueling stations

The use of Liquefied Natural gas and Liquefied Biogas
are a convenient path towards lower emissions

ARON HAKONEN AND ANDERS KARLSSON

ISBN 978-91-7673-706-4 | © Energiforsk November 2020

Energiforsk AB | Phone: 08-677 25 30 | E-mail: kontakt@energiforsk.se | www.energiforsk.se

Foreword

The project has been conducted within the Energiforsk programme Biofuels for Sweden 2030 (Biodrivmedel för Sverige 2030), with the goal to contribute to the development of biofuels for the transportation sector and a fossil free transportation fleet by 2030.

The programme has been financed by EON Gas Sverige AB, Gasnätet Stockholm AB, Göteborg Energi AB, Neste AB and the Region Skåne.

Within this project, a compact sampler for LNG/LBG trucks refueling stations has been developed and tested. The roll-out of LNG and LBG as transport fuels requires reliable determination of their composition and physical properties. This project has developed and tested a dual gas composition/liquid phase particle sampler for LNG/LBG at a commercial refueling station. The report has been produced by Aron Hakonen and Anders Karlsson at RISE.

The reference group for the project had the following members: Nadège Leclercq and Dominique Soleri (Westport Fuel Systems), Madeleine Ekström (Scania), Lucas Megas (Volvo), Lars Ohlson (Fordonsgas), Bertrand Lecointe (IFP Energies Nouvelles), Philippe Heisch (Cryostar), Johan Zakrisson (EON). The reference group is gratefully acknowledged for invaluable contribution to the project.

Stockholm November 2020
Bertil Wahlund Energiforsk AB

These are the results and conclusions of a project, which is part of a research programme run by Energiforsk. The author/authors are responsible for the content.

Sammanfattning

LNG (flytande naturgas) and LBG (flytande biogas) är miljömässigt fördelaktiga när de används för långväga tung transport. Användandet av dessa bränslen kan vara det mest genomförbara alternativet för en snabb omställning av tunga transporter mot ett hållbart samhälle och målen för Agenda 2030 genom systematisk minskning av utsläppen av föroreningar samtidigt som bullernivåer kan minskas. Utbyggnaden av LNG och LBG som transportbränslen kräver dock pålitlig bestämning av deras sammansättning och fysiska egenskaper för att säkra bränslekvaliteten och utsläppsnivåerna.

Som visats i aktuella vetenskapliga publikationer och tekniska rapporter är det mycket utmanande att ta ett representativt prov av LNG/LBG för efterföljande analys i ett laboratorium. Detta kräver korrekt förångning av bränslet samtidigt som man undviker partiell förångning och förlust av bränslekomponenter och partiklar. I ett tidigare projekt, genomfört av RISE, utvecklades en förångare för LNG/LBG-provtagning vid småskaliga tankstationer. Målet med det aktuella projektet var att bygga vidare på denna design och konstruera och testa en provtagare som skulle vara kompakt och transportabel för samtidig insamling av gasprover och fasta partiklar. Den utvecklade provtagaren testades vid en kommersiell tankstation. En stor förbättring jämfört med det tidigare utvecklade systemet var att nära teoretisk LNG-rörledningstemperatur (-160°C) uppnåddes i mätsystemet på cirka 10 minuter, vilket ledde till minimal förförångning och potential för snabba, sanna och repeterbara mätningar. Under det slutliga testet provtogs LNG/LBG motsvarande cirka 10 och 5 Nm^3 förångad gas för partiklar respektive gas. Fasta partiklar kvantifierades till 0,2 mg/Nm^3 gas, av vilket en stor andel identifierades som metall, metalloxid och kiseldioxid. Mätningar av gassammansättning uppvisade god repeterbarhet, med en relativ standardavvikelse av 0,3 % för huvudkomponenten metan (99,0 %), 2,0 % för etan (615 ppm). Sammanvägd relative standardavvikelse för alla mätbara komponenter var lägre än 1,0 %.

Summary

LNG (liquified natural gas) and LBG (liquified biogas) are environmentally beneficial when used for long-distance road transport. Their use may be the most feasible alternative for a rapid conversion of heavy-duty transports towards a sustainable society and the goals of Agenda 2030, by stringent reduction of pollutant emissions while at the same time reducing noise levels. However, the roll-out of LNG and LBG as transport fuels requires reliable determination of their composition and physical properties in order to secure the quality and emission levels.

As learned from current state-of-art, it is highly challenging to take a representative sample of LNG/LBG for subsequent analysis in a laboratory. This requires the proper vaporization of the fuel while avoiding partial vaporization and loss of fuel constituents and particles. In a previous project, a vaporizer for LNG/LBG-sampling at small scale refuelling stations was developed at RISE. The goal of the present project was to build on this design, and construct and test a sampler/vaporizer that would be compact and transportable for the simultaneous collection of gas samples and solid particles. The developed sampler was tested at a commercial refueling station. One major improvement over the previously developed system was that close to theoretical LNG pipeline temperature ($-160\text{ }^{\circ}\text{C}$) was achieved in the measurement system in about 10 min, leading to minimal pre-vaporization and potential for fast, true and repeatable measurements. During the final test LNG/LBG corresponding to approximately 10 and 5 Nm^3 vaporized gas was sampled for particles and gas, respectively. Solid particles were quantified to 0.2 mg/Nm^3 gas, with major number of particles being metal, metal oxide and silica. The gas composition measurements demonstrated a repeatability, defined as %RSD, of 0.3 % for main component methane (99.0 %), 2.0 % for ethane (615 ppm) and pooled standard deviation for all measurable components were below 1.0 %.

List of content

1	Introduction	7
2	Materials and methods	10
2.1	Sampling station	10
2.2	Sampling device	10
2.3	Analytical methods	13
2.3.1	SEM-EDX measurements for morphology and elemental analysis	13
2.3.2	Gas analysis	13
2.3.3	Microscopy	13
3	Results and discussion	14
3.1	Samplings at an LNG/LBG refueling station	14
3.2	Gas sampling results	15
3.3	Particle sampling	17
3.3.1	Microscopy	17
3.3.2	Scanning electron microscopy (SEM-EDX)	20
3.1	Remarks	26
4	Outlook and conclusions	27
4.1	Future work	27
4.2	Conclusions	27
5	References	28

1 Introduction

The use of Liquefied Natural Gas (LNG), possibly together with Liquefied Biogas (LBG), may be the most convenient way to rapidly and significantly reduce emissions and convert to more sustainable fuels and transports (1-3), and has the potential for contributing to achieving European Union's policy objectives regarding greenhouse gas reduction, air quality goals and crude oil dependency (4-6). To meet these objectives, an adequate LNG/LBG infrastructure has been developed in Europe through for example the research project LNG Blue Corridor which both addressed LNG fuels logistics and LNG vehicle technology (7, 8). Over 300 LNG/LBG stations are now in operation across Europe (<https://www.ngva.eu/>), with many more under construction or planned for the next few years. The number of LNG trucks is also growing rapidly in Europe, now with more than 11000 LNG trucks in operation (<https://www.ngva.eu/medias/2019-in-numbers-gas-in-transport-to-satisfy-european-consumers/>). Overall, a close cooperation between politics, research and industry will be necessary to establish the proposed measures and realize the full market entry of LNG (4).

In the vehicle, fuel is stored as a liquid. The fuel must be supplied to the engine in gaseous form at specified pressure and temperature under controlled conditions. Truck engines are based on different technologies which have different critical design criteria. Depending on the technology the engine is therefore more or less sensitive to different fuel qualities or specific parameters. Consequently, it is essential to be able to perform accurate measurements of the composition of the fuel which in turn also allows to accurately calculate physical properties such as calorific value, methane number, wobbe index, density etc. of the fuel. These properties enable optimal engine performance.

However, due to little knowledge and control over the commercial LNG being sold, there is a demand for a convenient on-site sampler for both gaseous samples and particles in the LNG, to verify quality and ensure consumer safety (9-11). In particular, the LNG fuel quality may be compromised by destructive particles for engines which causes premature wear and potentially engine failures (9, 12).

One of the newly developed technologies is the High Pressure Direct Injection second generation system (Westport™ HPDI 2.0). One unique feature of the HPDI system is a high-pressure pump located in the LNG tank. Solid small particles, if present, could lead to premature wear of the LNG pump system. Therefore, the fuel needs to be delivered clean and fueling stations need to implement new LNG filters to fulfil this fuel purity requirement. The development of a method to quantify particles in LNG is also necessary in order to gather information of the fuel purity, which in turn will support the development of an appropriate filtration solution and help define necessary filter maintenance intervals.

Currently, the physical properties of LNG/LBG are calculated from the composition. The most accurate method to measure the composition is by gas chromatography (GC) following the methods described in the international standards (the ISO 6974 series). However, the sampling of a liquefied gas into a homogenous gaseous state required for GC analysis is highly challenging and it

currently doesn't exist any commercial solutions to properly vaporize and sample LNG/LBG at a station.

In the EMRP project ENG60 (LNGII: Metrological support for LNG custody transfer and transport fuel applications) a vaporizer for LNG/LBG was developed. The main purpose for the vaporizer was to obtain representative gaseous samples of the LNG for subsequent determination of composition with gas chromatography. One difficulty to overcome was the risk of pre-evaporation/bubble formation due to ambient heat transfer, which would fractionate the sample and change the composition (methane and nitrogen are enriched in gas bubbles compared to the liquid phase, relative to ethane, propane, butane etc.). By thorough insulation of the "cold side" of the vaporizer and optimization of flows, repeatability was achieved and less than 5% relative standard deviation observed for methane, ethane and propane concentration (10), which would also indicate a fit for purpose measurement uncertainty (trueness could not be tested as LNG standards were unavailable). However, it took a long time (>2h) to cool the "cold side" to reach the goal temperature (as in the station cistern), if at all possible depending on ambient conditions (warm, windy etc.). The station connection point (ball valve) was also a weak point as it could not be insulated (needs to be free to operate). The project was expanded to also include particle sampling. For this a filter path was added to the outlet of the vaporizer (for collection of particles for subsequent characterization and quantification at lab), and also an optical particle counter (for online measurements). It was however found that particle losses were substantial (in valves, pipe bends etc.) and to get all particles on the filter a cumbersome wash procedure of the entire vaporizer at lab after sampling had to be implemented (9).

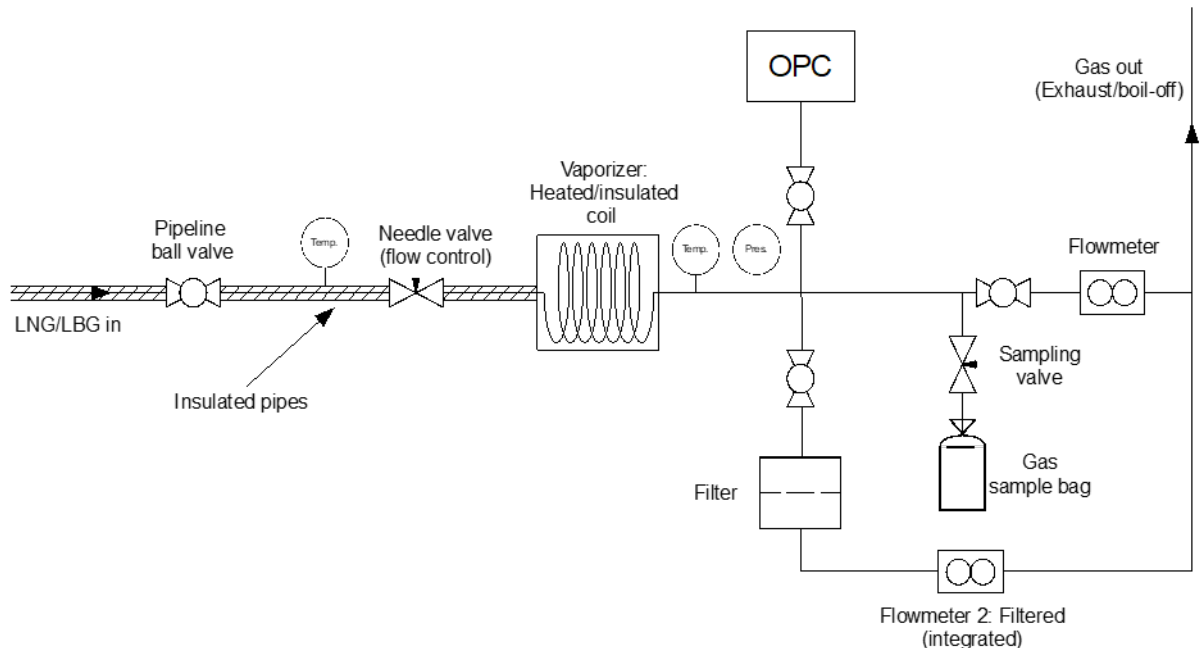


Fig. 1 Schematics of the vaporizer developed in the EMRP project ENG60 (LNGII: Metrological support for LNG custody transfer and transport fuel applications).

Figure 1 schematically shows the previously developed sampling system. The vaporizer was connected to the ball valve of the station (LNG pipe/tank, suitable connection point varies between different stations). The flow (through insulated stainless steel pipes) was controlled by the ball valve at the connection point and a needle valve on the vaporizer for more precise control. These valves were located on the cold side, where it is necessary to avoid pre-evaporation/bubble formation. To ensure that this did not happen, the temperature on the cold side was monitored by a sensor to ensure that LNG cistern temperature was maintained, and also stable. After the needle valve the sample was introduced into the vaporizer coil, which was a heat traced (electrical, ATEX-classed) and thermally insulated coiled stainless steel tube. After passing through this coil the LNG was completely vaporized, given that a proper flow rate was maintained. To ensure that the conditions for complete vaporization were met, i.e. a temperature where the vapor pressures of higher hydrocarbons is much higher than the theoretical partial pressures of these compounds at complete evaporation (for concentrations that can be encountered in LNG samples), the temperature, as well as the flow rate, was measured at the coil outlet. The gaseous sample could then be sampled in gas sample bags (for lab determination of composition by gas chromatography), sampled on filter (for particles). Also, online measurements of particles with and OPC (optical particle counter) were performed.

Within this work we have developed an ATEX qualified portable dual line sampler for gas and solid particles $> 0.5 \mu\text{m}$ at LNG/LBG refueling stations and similar. The sampler was successfully tested at a refueling station with an LNG/LBG container. The gas samples demonstrated gas proportions consistent with the latest filling LBG quality of the station tank, with a minor part of LNG from a previous shipment. Regarding the particle sampling results were quantified to $0.2 \text{ mg}/\text{Nm}^3$ gas, with major number of particles being metal, metal oxide and silica.

2 Materials and methods

2.1 SAMPLING STATION

Tests were performed in Gothenburg, Sweden at the refuelling station located at Stigs Center, Hisings Backa. The station was built in 2010 and delivers liquefied natural gas and biomethane (LNG/LBG) to heavy and medium duty trucks and CNG/CBG to gas vehicles. The stationary storage tank volume is 61 m³, which in practice is filled to a maximum of 54 m³. The tank consists of an outer and an inner container. At the bottom of the tank, there is a thermosiphon where LNG/LBG circulates without any mechanical pump. Two pipes are connected to the thermosiphon and allow the circulation of LNG/LBG from the tank to the cryogenic pump whose role is to deliver LNG from the storage tank to the vehicle via a dispenser. The flow of LNG in the two pipes leading to the pump is controlled with cryogenic-control valves. The only places to take samples without modifying the station are at the three-ball valves located nearby the cryogenic control valves (Fig. 3a).



Fig. 2 Picture of the LNG/LBG refuelling station in Hisings Backa, Sweden, where the sampler was tested.

2.2 SAMPLING DEVICE

To remedy the problems with the previous vaporizer, in this project a new vaporizer (based on the previous vaporizer design) has been developed (Figure 3 and 4). To decrease the time of stabilizing the cold side of the vaporizer, and to

lessen the problem of heat transfer from the connecting valve on the LNG-pipe of the station (which cannot be insulated) the LNG flow was increased. This was done by splitting the LNG flow on the cold side. One part was directed into the vaporizer coil, with the same flow as in the previous design. The other part was going to the filter (for sampling of particles). To minimize the risk of particle loss in the sampler, the filter was placed on the cold side, filtering mainly LNG instead of gas. 0.5 μm - Teflon filters were used in the filter holder (Advantec filter holder - Item No. LS-47-HP).



Fig. 3 Picture of the sampling system connected at the Stigs Center station. Parts of the system: a) Connection to the station pipe b) Insulated filter-holder c) Vaporizer for the particle section d) Heated vaporizer for the gas sampling e) Flow meters f) Gas sample outlet g) Boil-off "chimney".

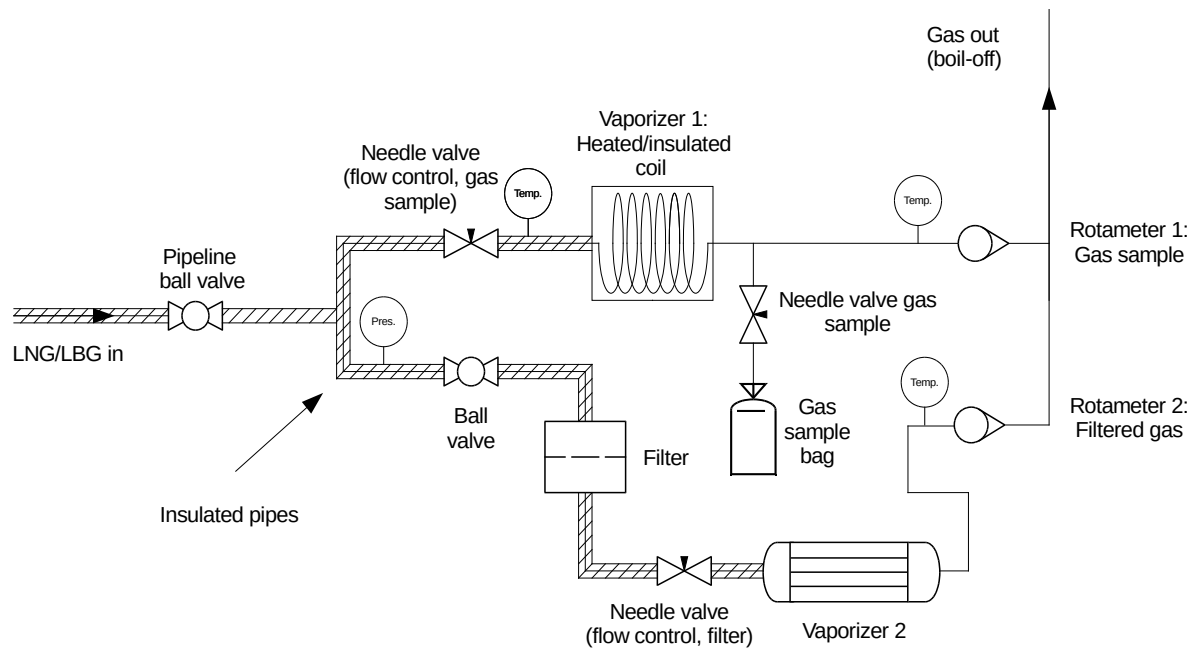


Fig. 4 Schematics of the vaporizer/particle sampler developed in the current project.

Figure 4 shows schematics of the sampler developed in the current project. The vaporizer is connected to the ball valve of the station (LNG pipe/tank, suitable connection point varies between different stations). Through thermally insulated stainless steel tubing, the LNG flow is divided into one part going to a vaporizer coil (“Vaporizer 1” for LNG composition sampling/analysis) and the outer part going to a filter (for sampling of particles). These flows are controlled by valves. For the LNG going to the filter, a needle valve located downstream of the filter is used to control the flow. All valves upstream of the filter are ball valves, which are fully open during sampling to minimize particle loss. All pipes upstream of the vaporizer coil and the filter are thermally insulated. This is the cold side in which pre-evaporation/bubble formation of the LNG must be avoided. To monitor this the temperature and pressure are measured. After the filter, the LNG is introduced into a second vaporizer (“Vaporizer 2”), which purpose is to evaporate the sample to be able to measure the gas flow (“Rotameter 2”), which integrated in time gives the total amount of filtered LNG (for particle content quantification when analyzing the filter). For the flow going through the vaporizer coil (“Vaporizer 1”, electrically heat traced, ATEX-classed), the LNG should be completely vaporized after passing through this coil, without fractionation of the sample. Temperature is measured on the outlet and gas samples are taken in gas sample bags (for lab determination of composition by gas chromatography). The outlets of “Vaporizer 1” and “Vaporizer 2” are let out via a “chimney” to the atmosphere, ~3.5m above ground level (Fig. 3g), but could also be connected to the station boil-off gas system, depending on the station safety regulations.

2.3 ANALYTICAL METHODS

2.3.1 SEM-EDX measurements for morphology and elemental analysis

The instrument used was a Zeiss supra 40VP scanning electron microscope (SEM), provided with a system for energy dispersive X-ray analysis (EDX) with an X-Max 50 mm² X-ray detector from Oxford Instruments. The acceleration voltage during analysis was 2 and 20 kV while the working distance was 3.4 and 8.5 mm for SEM and EDX, respectively. The filter samples were covered with a thin layer of gold/palladium (12 nm) in order to minimize the charging effects of the non-conducting Teflon filter.

2.3.2 Gas analysis

The analyses for the determination of the composition of the gasified LNG and the boil-off gas with regard to methane, ethane, propane and nitrogen were performed on a gas chromatograph 450-GC (Varian) equipped with a FID detector and a TCD-detector. The GC had three columns:

- a CP-Porabond Q (25 m long, 0.53 mm inner diameter, 10 µm film thickness), connected to the FID (for ethane and propane).
- a Hayesep Q, 80–100 MESH, 1 m× 1/8''× 2.0 mm, connected to the TCD (for methane).
- a Molecular Sieve 5A, 60–80 MESH, 1 m× 1/8''× 2.0 mm, the connected to the TCD (for oxygen and nitrogen).

2.3.3 Microscopy

Microscopy imaging was performed on an Olympus BX63 Microscope with an Olympus DP72 color camera. The used light source was an X-cite Series 120PC and the control unit was Olympus BX3-CBH. Some simpler microscopy was performed on an Olympus SZX16 with camera Olympus UC90. Particle analysis for size distributions was performed in open access imaging program ImageJ developed by National Institute of Health (NIH, USA) (13).

3 Results and discussion

3.1 SAMPLINGS AT AN LNG/LBG REFUELING STATION

The first test of the newly developed sampler at the Stigs Center refueling station revealed some problems such as leaking and outlet hoses coming off. This was remedied for the subsequent tests. Overall the first test was promising with good results (see below) and a very quick cooling down of the inlet side of the sampling system (Fig. 5), in about 20 minutes the temperature was down to approximate theoretical LNG pipeline temperature.

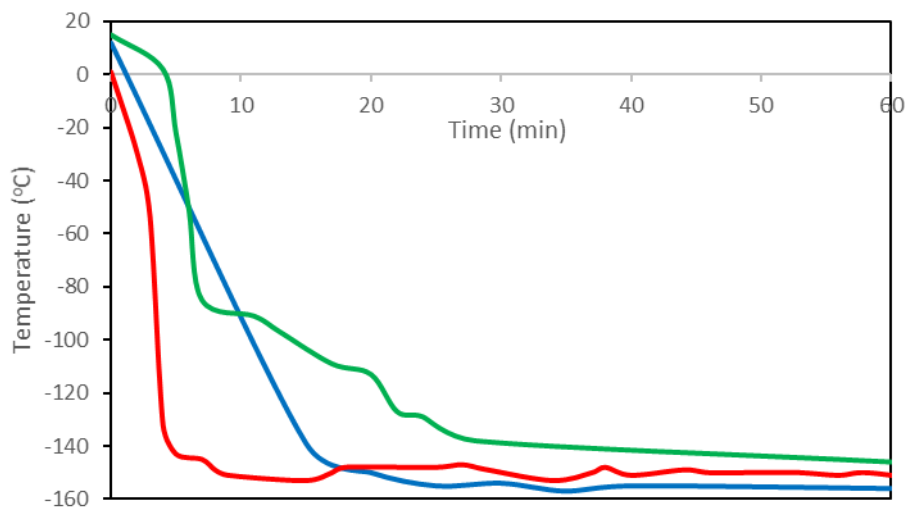


Fig. 5 Temperature curves for the three sampling occasions at Stigs Center refueling station. Blue, green and red dots for the first, second and third sampling occasion, respectively.

Before sampling occasion number two the system was rinsed with methanol to get the last of the particles out on a filter. Unfortunately, there was a methanol residue causing an ice plug of methanol in the filter (which was verified afterwards by a wet methanol smelling filter/filter holder). The freezing of methanol can be observed in the temperature curve (Fig. 5, green line), where the system cooling down rate is slowing down when approaching the freezing point of methanol ($-97\text{ °C @ }1\text{ atm}$). After -freezing the flow in the particle sampling side of the system stopped. Consequently the total flow decreased causing insufficient cooling of the "cold side" of the sampler. This was also evident from the gas composition measurements which showed poor repeatability, especially for higher hydrocarbons than methane (see below, Table 2).

Before the third sampling session at the refueling station, the system was flushed with nitrogen gas (60 L/min, 1 h) after methanol rinsing to ensure that there was no residue methanol that could cause problems. System cooling curve was even faster and already after 10 minutes the temperature was below -150 °C (Fig. 5, red line). System flows were analyzed and integrated for total sampling volumes (Fig. 6).

Initially, before the sampler was cooled by the LNG/LBG and there was a mixture of liquid and gas in the system, the flows were unstable, but after about 40 minutes the flows were stable, which was also when the gas sampling started, the stability was also reflected in small deviations of the gas measurements (Table 3). The flows were integrated to determine the total sampling volumes, which were 9240 and 5640 NL for the particle filter and gas sampling flows, respectively. The volume determination was of course essential for the particle results. A relatively high system flow was needed in order to collect significant amounts of particles in a short time. For the last test in this project, an average total flow of 160 L/min could be used with a stable system flow, 100 and 60 L/min in particle and gas sampling sections, respectively. The total amount of particles found in this last sampling occasion was 0.2 mg/Nm³, within the interval of particle content demonstrated in various qualities in a city network of CNG, 0.12 – 2.2 mg/Nm³ (14).

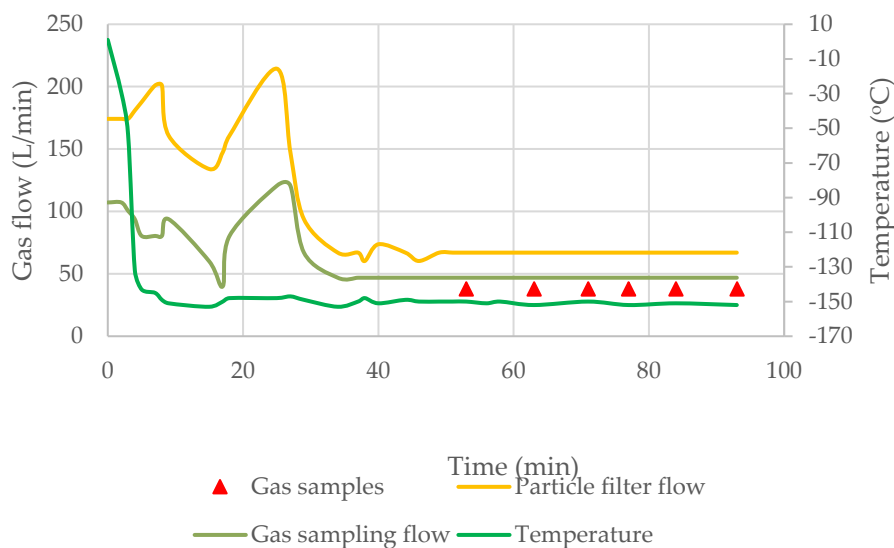


Fig. 6 System flows from sampling occasion 3, including system cold side temperature and indicated gas sample times. Integrated flow volumes were 9240 and 5640 L/min for the particle filter and gas sampling flows, respectively.

3.2 GAS SAMPLING RESULTS

Results from the three gas sampling occasions at Stigs center refueling station are presented in Table 1 – 3. During the first test only three gas sampling bags was collected, as there were several minor problems with missing connectors and discharging gas hoses. Nevertheless, the repeatability of the gas sampled was at an acceptable level (Table 1). For the second sampling occasion things looked promising, however, this time a weakness of the operating procedure was revealed. Residue rinsing methanol froze in the filter part of the system and blocked it. Six gas sampling bags was collected anyway, revealing, very poor repeatability for ethane and higher hydrocarbons (Table 2). This was attributed to left over LNG in the particle sampling section being partially boiled-off to the gas sampling section, which caused fractionated gas samples.

Table 1. Main components measured on sampling occasion 1, including the standard deviations (STD) for each component.

Component	Unit	Sample 1	Sample 2	Sample 3	STD
Methane	Vol-%	99.2	98.4	99.1	0.36
Oxygen	Vol-%	0.2	0.3	0.2	0.05
Nitrogen	Vol-%	0.3	1	0.4	0.31
Hydrogen	Vol-%	< 0.1	< 0.1	< 0.1	-
Carbon dioxide	Vol-%	< 0.1	< 0.1	< 0.1	-
Carbon monoxide	Vol-%	< 0.1	< 0.1	< 0.1	-
Ethane	ppm-vol	2800	2400	2550	165
Propane	ppm-vol	150	100	110	22
Isobutane	ppm-vol	26	16	25	4.5
Butane	ppm-vol	26	18	28	4.3
Isopentane	ppm-vol	< 2	< 2	2	0
Pentane	ppm-vol	< 2	< 2	< 2	-

Table 2. Main components measured on sampling occasion 2, including the standard deviations (STD) for each component.

Component	Unit	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	STD
Methane	vol-%	99	98.8	99.3	99.4	99.1	98.6	0.33
Oxygen	vol-%	0.1	0.2	0.1	< 0.1	0.2	0.1	0.05
Nitrogen	vol-%	0.4	0.5	0.3	0.3	0.5	0.3	0.09
Hydrogen	vol-%	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
Carbon dioxide	vol-%	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
Carbon monoxide	vol-%	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
Ethane	ppm-vol	5300	5100	1700	2100	2300	9500	3442
Propane	ppm-vol	210	120	40	< 5	130	290	80
Isobutane	ppm-vol	15	5	< 5	30	10	25	8.5
Butane	ppm-vol	15	5	< 5	< 5	10	30	10
Isopentane	ppm-vol	< 5	< 5	< 5	< 5	< 5	< 5	-
Pentane	ppm-vol	< 5	< 5	< 5	< 5	< 5	< 5	-
C6	ppm-vol	< 5	< 5	< 5	< 5	< 5	< 5	-

Table 3. Main components measured on sampling occasion 3, including the standard deviations (STD) for each component.

Component	Unit	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	STD
Methane	vol-%	98.9	99.4	99.4	98.6	98.9	98.9	0.14
Oxygen	vol-%	0.3	0.2	0.2	0.4	0.3	0.3	0.05
Nitrogen	vol-%	0.8	0.4	0.4	1.1	0.8	0.8	0.14
Hydrogen	vol-%	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
Carbon dioxide	vol-%	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
Carbon monoxide	vol-%	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
Ethane	ppm-vol	600	620	630	600	610	630	12
Propane	ppm-vol	35	35	35	35	35	35	0
Isobutane	ppm-vol	3	3	3	3	3	3	0
Butane	ppm-vol	3	3	3	3	3	3	0
Isopentane	ppm-vol	< 1	< 1	< 1	< 1	< 1	< 1	-
Pentane	ppm-vol	< 1	< 1	< 1	< 1	< 1	< 1	-
C6	ppm-vol	< 1	< 1	< 1	< 1	< 1	< 1	-

Prior to the third sampling occasion the system was carefully rinsed with nitrogen gas to ensure proper operation. This was also achieved with fast temperature and flow stabilization and consequent good sampling conditions, see figure 6. Repeatability was even better than the first occasion and samplings performed with the previous system (10), see table 3 for the results.

3.3 PARTICLE SAMPLING

3.3.1 Microscopy

Microscopy imaging was performed with an Olympus BX63 microscope. Image analysis and particle size distributions was determined using open source software ImageJ from National institute of health (NIH)(13). Feret's statistical diameter (F_d) was used as a measure of particle size, which in principle approximates the average of all possible diameters for a 2D object in an image (15, 16). Overall, particles tended to accumulate along the edges of the filters, i.e. particles are forced towards the outer regions of the filter as the fine pores of the filter generates a flow through resistance. Figure 7 illustrates accumulated particles and clusters of particles along the edge of the filter collected at sampling occasion 3 at Stigs center refueling station. Particle analysis in ImageJ gave a threshold overlay mask image and particle distribution shown in Fig. 7. The large F_d values, up to above 100 μm , are clearly clusters of particles. This image and particle analysis gave an average particle/cluster size of 9.8 μm (F_d). About 28 % of the particles/clusters had a F_d below 6.5 μm and 85 % below 13 μm .

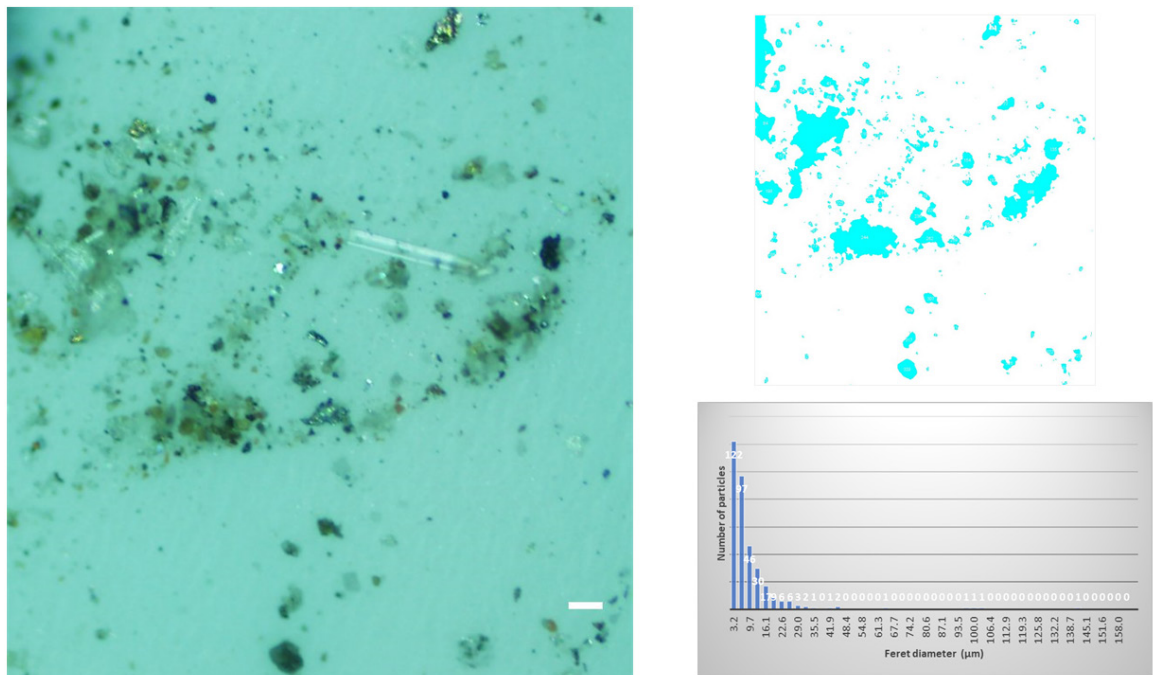


Fig. 7 Microscope image (left) of accumulated particles/particle clusters along the edge of the filter from sampling 3, scalebar is 25x5 μm in size. Top right image is filtered with a threshold and particle analyzed in ImageJ, the image is black and white with colored overlay masks (on found particles). Lower right is the particle size distribution defined as the Feret diameter (15), white numbers indicate particles per size.

For a determination of single particle sizes, center part images from the filter may be more representative values. For this task three images were used (Fig. 8). Image analysis were performed in the same manner, however, overlay mask images are not presented here. Particle size distributions are displayed in figure 8, where for example a maximum particle size of 10.3 μm can be observed. Overall, an average Feret diameter of 0.9 μm was calculated for the in total 1859 particles in the three images. 90 % of the particles had a F_d below 2.5 μm . The larger particle sizes at the edges can be explained by clustering effects as the particles are pressed towards the edge of the filterholder.

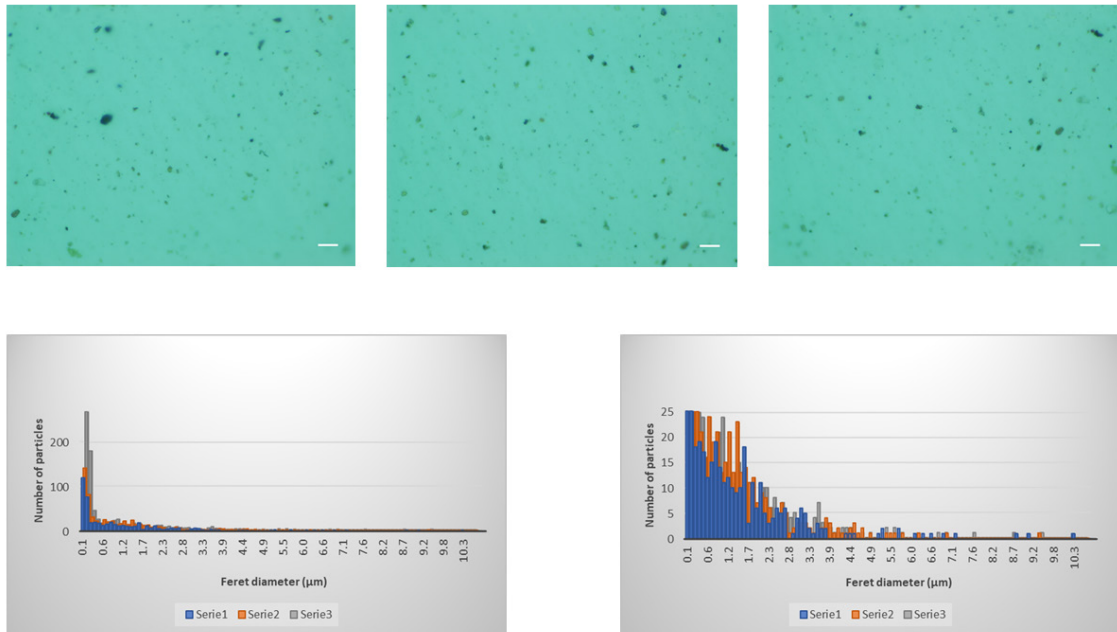


Fig. 8 Microscope images (upper) of sampled particles and corresponding particle size distributions (Feret diameter), the right histogram is zoomed in (y-axis) to better illustrate larger particle frequencies. Scalebars are 10x1 μm in size. Average particle size was 0.9 μm ($n_{\text{Tot}} = 1859$).

A major improvement over the previous particle sampling system was a decreased need for strong solvent (THF) rinsing. Now 1x250 ml methanol was enough to achieve a “clean” system, compared to 6x70 ml or 420 ml THF (9). Images of “rinse” filters can be seen in figure 9, illustrating a relatively clean system, compared with the previous system where in principle all particles were extracted in the rinsing fractions (9).

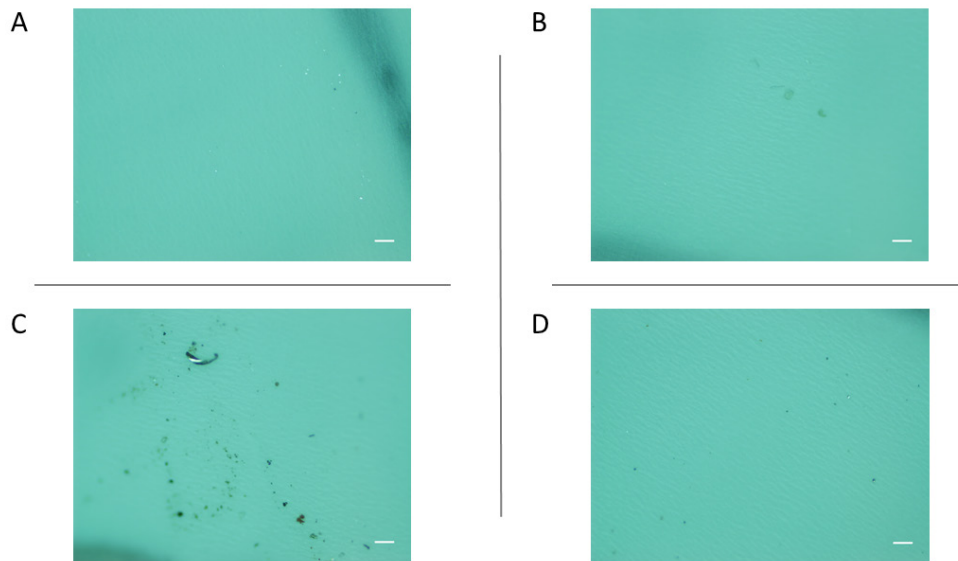


Fig. 9 Microscope images of the rinsed filters, scalebars are 10x1 μm . **A)** Methanol rinsed filter from sampling 1. **B)** Nitrogen gas flow rinsed filter before sampling 3. **C)** Methanol rinsed filter from sampling 3 (image with most particles found). **D)** Methanol rinsed filter from sampling 3 (common number of particles).

3.3.2 Scanning electron microscopy (SEM-EDX)

To further investigate the sampled particles with regards to morphology, fine structure and composition SEM-EDX analysis was performed on the filters from sampling 1 and 3. Figure 10 illustrates SEM and EDX images from sampling occasion 1 at Stigs Center (Filter edge). Most particles in this image were composed of carbon, oxygen and SiO_2 , however, one large particle in the middle is carbon free SiO_2 , with some Al_2O_3 . This sharp rock-like particle is potentially abrasive for various motor parts in engines (12). Figure 11 illustrates another set of images (Sampling 1, edge), which mainly contains carbon/oxygen (organic) particles, but also quite a few metallic and some SiO_2 particles. Figure 12 shows a similar set of images from sampling 3 (filter edge), which to a much lesser extent comprises carbon/organic particles, instead metallic/metal oxide and SiO_2 are dominating. The relatively lower content of carbon-based particles, for sampling 3, was observed in more or less all SEM-EDX analyzes (see below). Figure 13 and 14, demonstrate close-up SEM-EDX measurements on two different particles, where Fig. 13 shows an almost perfectly spherical iron/iron-oxide particle (with small amounts of Co, Si and K), while Fig. 14 display a sharp flake mainly containing SiO_2 , Cr, Co, Fe (also small amounts of other metals, see Appendix I), this quite large flake could be potentially abrasive for engine parts.

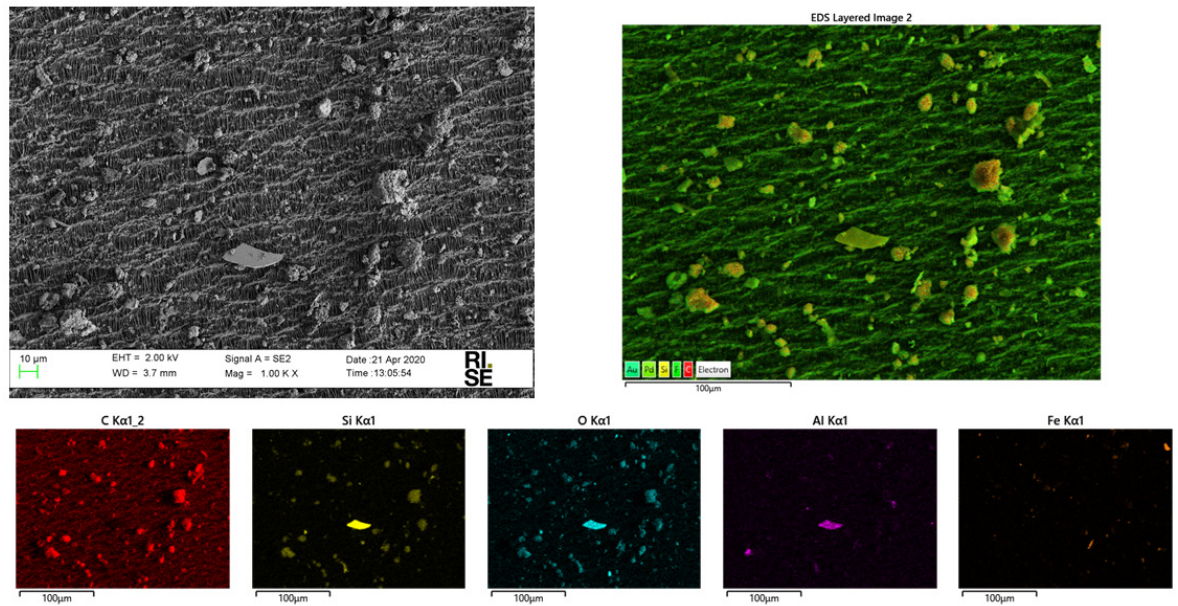


Fig. 10 SEM and EDX images sampling occasion 1 at Stigs Center (Filter edge). Most particles tend to be composed of carbon and SiO_2 , however, one large particle in the middle is carbon free SiO_2 , with some Al_2O_3 . This sharp rock-like particle is potentially abrasive for various motor parts in engines.

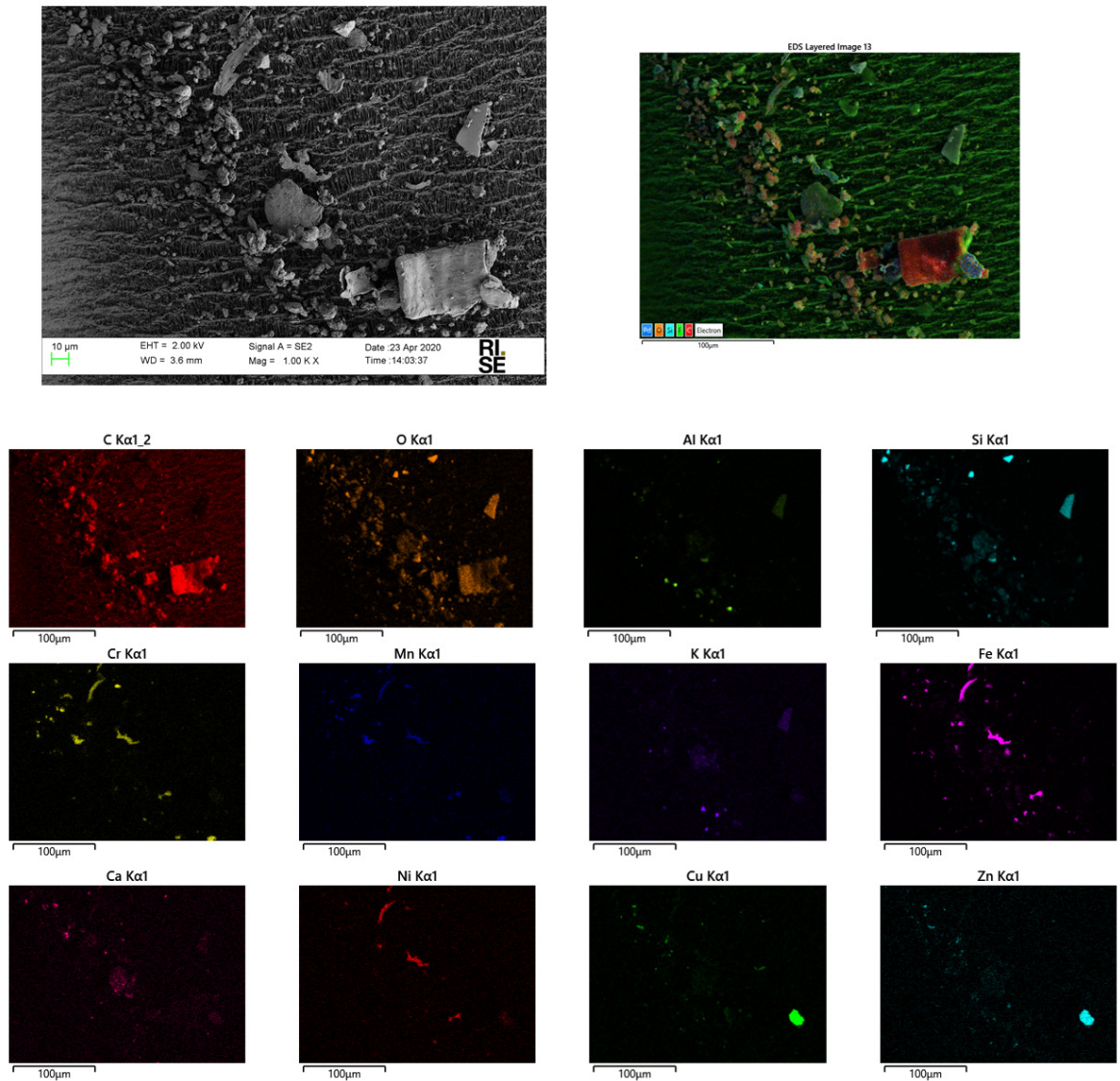


Fig. 11 SEM and EDX images sampling occasion 1 at Stigs Center (Filter edge). Much carbon-based particles are indicated in these images. Quite a few metallic (mainly Cr, Mn, Fe, Ni, Cu, Zn) particles. Also, here some potentially abrasive SiO_2 particles are present in the upper part of the image.

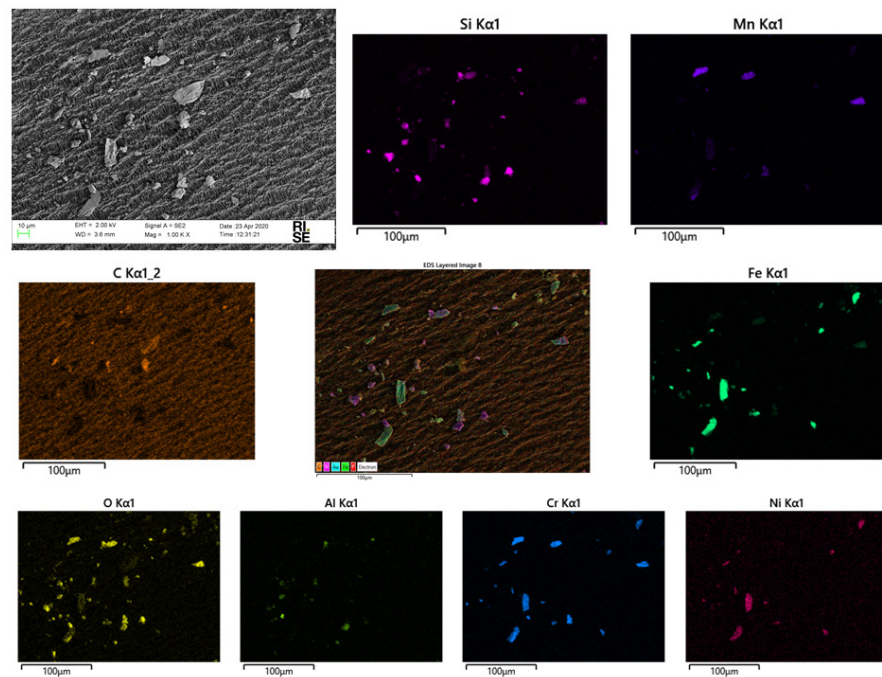


Fig. 12 SEM-EDX images sampling occasion 3 at Stigs Center (filter edge). These demonstrate to a much lesser extent carbon/organic particles, instead metallic/metal oxide and SiO_2 are dominating.

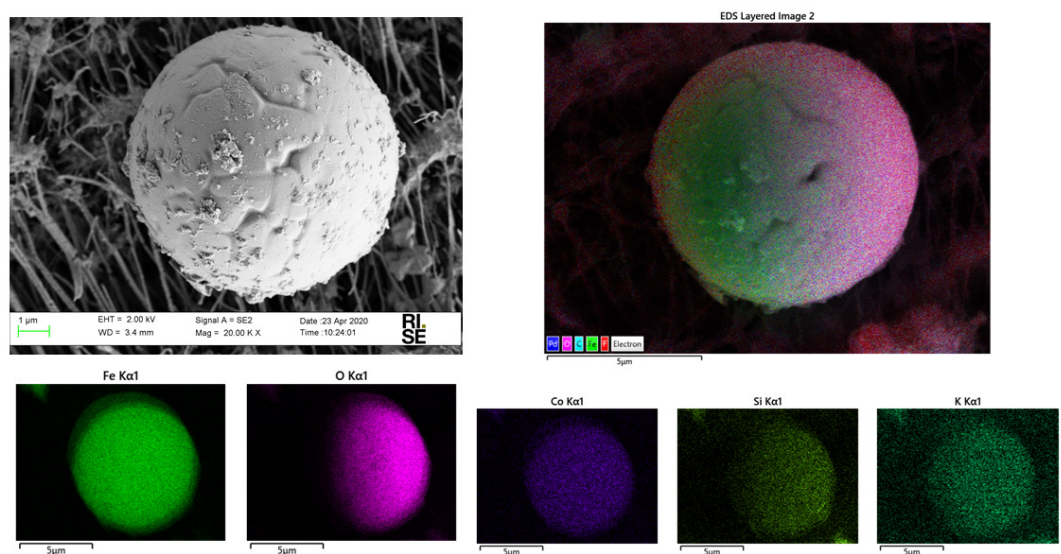


Fig. 13 SEM and EDX images sampling occasion 3 at Stigs Center (filter edge). This spherical particle contains mainly iron, some oxides, and small amounts of Co, Si and K.

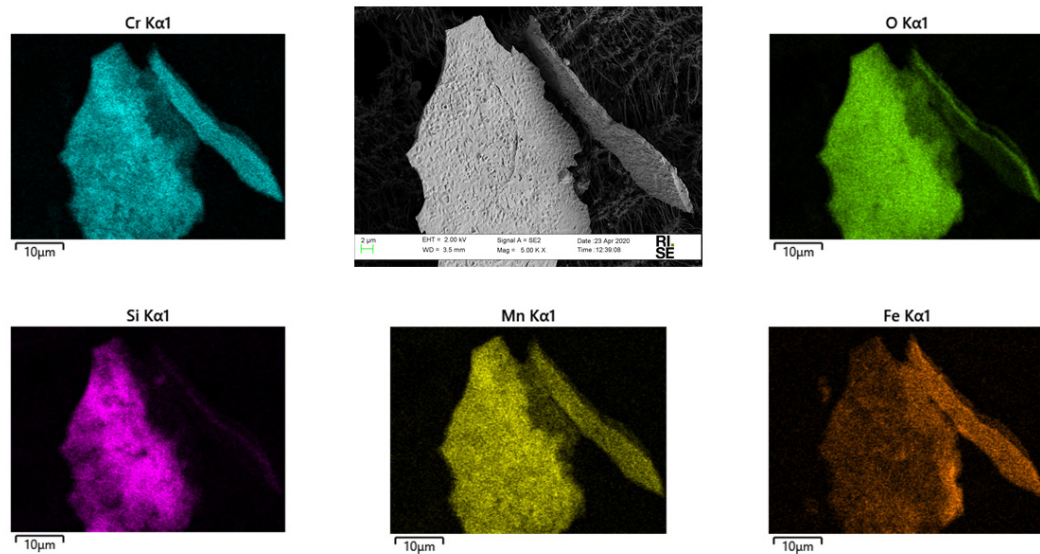


Fig. 14 SEM-EDX images sampling occasion 3 at Stigs Center (filter edge). This sharp flake mainly containing SiO_2 , Cr, Co, Fe (also small amounts of other metals, see Appendix I), can potentially be abrasive for engine parts?

For a summarized content of particles from the different samplings and filter sections see Fig. 15 – 17. Overall, the constant presence of carbon and fluoride (Teflon filter background), plus also the Au/Pd-layer affects the absolute percent of the different components. However, relative to each other different components can be semi-quantified. Figure 15 shows summarized content of trace elements from the center of the filters from the two successful sampling sessions at Stigs Center. The main components are showing similar values in some cases such as Fe, Cu and Al, however, with significantly higher Ni and Cr in the first sampling and more Si and Cl in the second sampling. Surprisingly, a small and spread out content of Uranium was detected at most scanned areas in the center of the filters, but none was found at the edges of the filters. Possible interference?

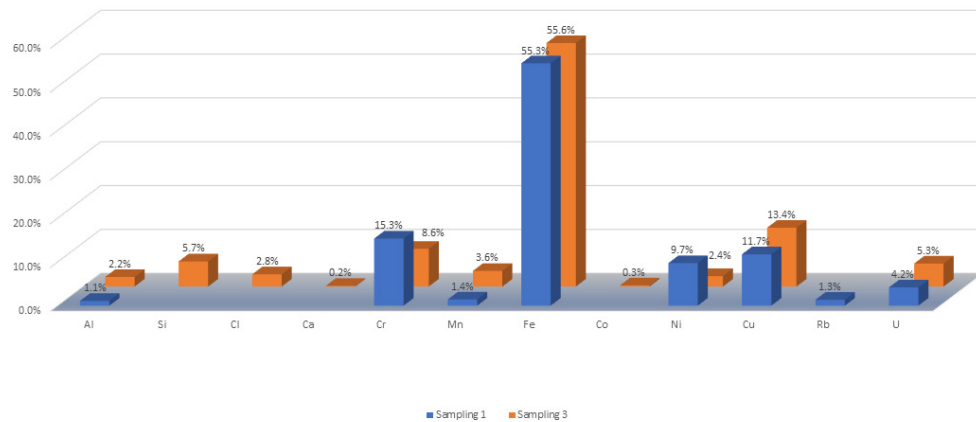


Fig. 15 Summarized content of trace elements (relative to each other) from the center of the filters from the two successful sampling sessions at Stigs Center. The main components are showing similar values in some cases such as Fe, Cu and Al, however, with significantly higher Ni and Cr in the first sampling and more Si and Cl in the second sampling.

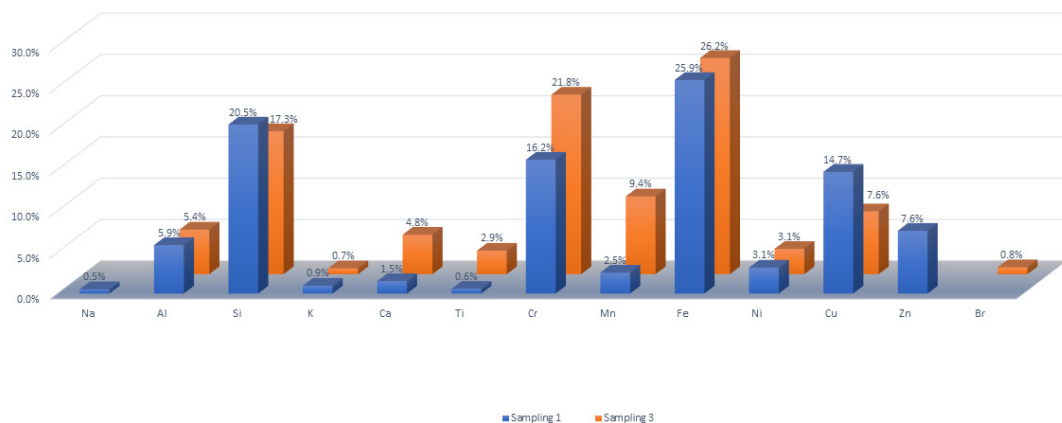


Fig. 16 Summarized content of trace elements (relative to each other) from the edges of the filters from the two successful sampling sessions at Stigs Center. The main components are showing similar values in most cases, however, with significantly higher Cu and Zn in the first sampling and more Ca, Ti and Mn in the second sampling.

Fig. 16 demonstrates the summarized content of trace elements from the edges of the filters from the two successful sampling sessions at Stigs Center. The main components are showing similar values in most cases, however, with significantly higher Cu and Zn (possibly brass particles) in the first sampling and more Ca, Ti and Mn in the second sampling. No Uranium was detected at the edges in contrast to most scanned areas in the center of the filters.

3.1 REMARKS

Overall, the results in this study has been very satisfying and a commercial version of the developed LNG/LBG sampler is well within sight. To further promote the commercialization of this product the manuscript “Utilization of a portable sampler for liquefied natural gas composition and particles at refueling stations” on this research has been submitted to *Journal of Natural Gas Science and Engineering*, and a preprint of this manuscript has been published (17).

4 Outlook and conclusions

4.1 FUTURE WORK

Further tests at a significantly different refueling station (Gasum, Jönköping) are planned. A validation of the method, including intermediate precision and trueness measurements, would be preferable, but would require a reference standard LNG/LBG mixture.

4.2 CONCLUSIONS

For the first time a dual gas composition/liquid phase particle sampler for LNG/LBG has been utilized. The developed sampler was successfully tested at a commercial refueling station. A major improvement over the previously developed system was that close to theoretical LNG pipeline temperature (-160°C) was achieved in the measurement system in about 10 min, leading to minimal pre-vaporization and potential for fast, accurate and repeatable sampling. During the final test LNG/LBG corresponding to approximately 10 and 5 Nm^3 vaporized gas was sampled for particles and gas, respectively. This was also achieved with fast temperature and flow stabilization and precise sampling. Solid particles were quantified to 0.2 mg/Nm^3 gas, with major number of particles being metal, metal oxide and silica. This was also achieved with fast temperature and flow stabilization and consequent samplings at good conditions. Gas sample composition analyses showed repeatable results. The gas composition measurements demonstrated a repeatability, defined as %RSD, of 0.3 % for main component methane (99.0 %), 2.0 % for ethane (615 ppm) and pooled standard deviation for all measurable components were below 1.0 %. Overall, the results show great promise for a continuation of measurements of this type, for further development of the use of LNG/LBG for future heavy-duty transports in line with a sustainable society and the goals of Agenda 2030.

5 References

1. Pan Z, Zhang L, Zhang Z, Shang L, Chen S. Thermodynamic analysis of KCS/ORC integrated power generation system with LNG cold energy exploitation and CO₂ capture. *Journal of Natural Gas Science and Engineering*. 2017;46:188-98.
2. Gowid S, Dixon R, Ghani S. Profitability, reliability and condition based monitoring of LNG floating platforms: A review. *Journal of Natural Gas Science and Engineering*. 2015;27:1495-511.
3. Kumar S, Kwon H-T, Choi K-H, Lim W, Cho JH, Tak K, et al. LNG: An eco-friendly cryogenic fuel for sustainable development. *Applied Energy*. 2011;88(12):4264-73.
4. Pfoser S, Schauer O, Costa Y. Acceptance of LNG as an alternative fuel: Determinants and policy implications. *Energy Policy*. 2018;120:259-67.
5. Zakaria Z, Baslasl MSO, Samsuri A, Ismail I, Supee A, Haladin NB. Rollover Phenomenon in Liquefied Natural Gas Storage Tank. *Journal of Failure Analysis and Prevention*. 2019;19(5):1439-47.
6. Mazyan W, Ahmadi A, Ahmed H, Hoorfar M. Market and technology assessment of natural gas processing: A review. *Journal of Natural Gas Science and Engineering*. 2016;30:487-514.
7. LNG Blue Corridor, Seventh Framework Program (FP7), 2013-2017. 2013.
8. Ribas SJMRPJDX. LNG blue corridors, Gas Quality. 2014.
9. Hakonen A, Karlsson A, Lindman L, B  ker O, Arrhenius K. Particles in fuel-grade Liquefied Natural Gas. *Journal of Natural Gas Science and Engineering*. 2018;55:350-3.
10. Arrhenius K, Karlsson A, Hakonen A, Ohlson L, Yaghooby H, B  ker O. Variations of fuel composition during storage at Liquefied Natural Gas refuelling stations. *Journal of Natural Gas Science and Engineering*. 2018;49:317-23.
11. Oliveira EC, Aguiar PF. Data reconciliation in the natural gas industry: Analytical applications. *Energy and Fuels*. 2009;23(7):3658-64.
12. Parsi M, Najmi K, Najafifard F, Hassani S, McLaury BS, Shirazi SA. A comprehensive review of solid particle erosion modeling for oil and gas wells and pipelines applications. *Journal of Natural Gas Science and Engineering*. 2014;21:850-73.
13. Schneider CA, Rasband WS, Eliceiri KW. NIH Image to ImageJ: 25 years of image analysis. *Nat Meth*. 2012;9(7):671-5.
14. Azadi M, Mohebbi A, Soltaninejad S, Scala F. A case study on suspended particles in a natural gas urban transmission and distribution network. *Fuel Processing Technology*. 2012;93(1):65-72.

15. Walton WH. Feret's Statistical Diameter as a Measure of Particle Size. *Nature*. 1948;162(4113):329-30.
16. Bartley PC, Jackson BE, Fonteno WC, editors. Computerized particle analyzer: the next generation of particle analysis 2019: International Society for Horticultural Science (ISHS), Leuven, Belgium.
17. Aron H, Anders K, Per B, Haleh B, Karine A. Utilization of a Portable Sampler for Liquefied Natural Gas Composition and Particles at Refueling Stations. ChemRxiv (DOI: 10.26434/chemrxiv.13302641.v1), 2020

Keywords

Liquefied natural gas, Liquefied biogas, Trucks refuelling stations, Sampling, Gas analysis, Particle analysis

COMPACT SAMPLER FOR LNG/LBG TRUCKS REFUELING STATIONS

Liquefied natural gas, LNG and liquefied biogas, LBG are very interesting as alternative fuels over conventional fuels used for heavy-duty transports.

However, the roll-out of LNG and LBG as transport fuels requires reliable determination of their composition and physical properties by proper sampling. This has been proven to be highly challenging to provide.

This project has developed and utilized the first dual gas composition/liquid phase particle sampler for LNG/LBG. The sampler was successfully tested at a commercial refueling station.

Energiforsk is the Swedish Energy Research Centre – an industrially owned body dedicated to meeting the common energy challenges faced by industries, authorities and society. Our vision is to be hub of Swedish energy research and our mission is to make the world of energy smarter!



Energiforsk