



Development and validation of methods for test of CNG quality inclusive of oil carryover

(Utveckling och validering av testmetoder för test av fordonsgaskvalitet, inklusive oljeförekomst)

Karine Arrhenius, Haleh Yaghooby, Per Klockar

*"Catalyzing energygas development
for sustainable solutions"*

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Martin Ragnar
Chief Executive Officer



Authors' foreword

The project "Validation of test method for renewable vehicle gas fuel: Development of rig for control of the energy content and the purity of gas fuel inclusive determination of oil and water content" has been conducted from Mars 2012 to October 2013. The project has been carried out by SP technical Research Institute of Sweden and Processkontroll GT in collaboration with the project partners. During the project, telephone meetings have been arranged with the reference group composed of:

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The project report has been written by Karine Arrhenius (main author) and Haleh Yaghooby from SP, and Per Klockar from Processkontroll GT.



Författarnas förord

Detta projekt ” Validering av testmetoder för förnybar fordonsgas: utveckling av rigg för kontroll av energiinnehåll och gasrenhet inklusive bestämning av olja- och vattenhalt” har utförts under perioden mars 2012 till oktober 2013). Huvudutförare har varit SP Sveriges Tekniska Forskningsinstitut och Processkontroll GT, tillsammans med projektpartners nedan. Under projektarbetet har två telefonmöten arrangerats med referensgruppen som bestod av:

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Projektrapporten har författats av Karine Arrhenius (huvudförfattare) och Haleh Yaghooby från SP, och Per Klockar från Processkontroll GT.

Borås, November 2013

Karine Arrhenius, SP Sveriges Tekniska Forskningsinstitut



Summary

In this project, methods for the sampling and analysis of compounds under discussion for regulations or already regulated by SS 15 54 38 have been proposed and evaluated. Methane, carbon dioxide, oxygen, nitrogen, hydrocarbons with 2 to 6 carbon atoms is recommended to be analysed according to standard ISO6974 after sampling on gas bags or gas cylinders, VOC to be sampled on adsorbent tubes and analysed by gas chromatography and mass spectrometry. Ammonia, hydrogen sulfide, water vapour can be analysed by infrared spectroscopy and should be sampled in gas cylinders. Most of these methods are validated.

Two different methods to determine oil carryover from compressors has then been tested. In stations equipped with well-functioning coalescing filters, the oil remaining entrained in the gas after the compressor is almost exclusively dissolved. One way to sample this oil is to drastically reduce the pressure on an adsorbent (which implies that the temperature of the gas also drops) so as to make the oil condense as droplets and deposit on the filter. The most promising method uses two coalescing filters (called here main and backup filters) connected in series. The pressure is reduced just before the filters by forcing the gas to pass through a nozzle spray with a limited hole diameter.

Sampling of gas for oil carryover determination was initially performed after the dispenser. However the safety tests which are performed during the delivery of the first volume of gas (1Nm^3) negatively affect the sampling, the pressure varying as the tests are performed. Moreover, also for safety reasons, the flow from the dispenser cannot be reduced as low as required quantitative absorption.

The sampling was therefore performed between the compressor and the dispenser in order to determine the appropriate flow needed for the oil to be quantitatively adsorbed on the main filter (with the requirement that less than 10% of the oil should be recovered on the backup filter). This flow was determined to be around $10\text{ Nm}^3/\text{h}$ (obtained with a spray nozzle with a 0.3 mm hole diameter), as long as the sampled volume does not exceed 1 Nm^3 .

Finally, a sampler taking gas from the dispenser nozzle was built, taken into account the previous results to sample the gas at the dispenser has been built taken into account the previous results. The sampler has a CNG bottle of 12 liter which is used as a buffer tank. The sampler includes also two filter houses containing a coalescing filter each and the appropriate spray nozzle positioned before the two filter houses. When the bottle has been filled with at least 180 bar of gas, the sampler is taken aside and typically 80 bar (corresponding to 1 Nm^3) of the gas in the bottle is transferred onto the filters. A minimum of three samples are taken for each station.

The sampler was then tested in four different stations using all together three types of oil. In two of these stations, low levels of oil carryover (less than 5 ppmM) have been measured. Unfortunately, a severe contamination of the CNG bottle with oil Rarus SHC 1025 occurred at the first station as the coalescing filters at the station were saturated with oil. This contamination negatively influenced the measurements performed at the two stations using Rarus SHC 1025. Nevertheless, after careful cleaning of the CNG bottle with nitrogen, three new tests were performed at the first station and results showing a carryover of 6.5, 5.0 respectively 7.3 ppmM were obtained. Blank tests were performed by filling the CNG



bottle with nitrogen between each of these tests and contamination of the CNG bottle with oil was found to be negligible.

The oil carryover determined with this method represents oil carryover during defined operational conditions (the average quantity of oil contained in the two first Nm³ delivered and refuelling against an empty tank) and is therefore suitable for comparisons of refuelling stations and compressors with each other. Therefore it is crucial that the sampling is always performed under the same conditions. There is a risk that some oil may deposit in the CNG-bottle of the sampler. This should be studied further in order to guarantee the accuracy of the results.

In a future study, it would be interesting to test if the oil carryover is influenced by the prevailing operational conditions at the station at the time of the sampling (as example the outdoor temperature, the number of vehicles being refuelled at the time of the sampling ...). The next step should be to test the method on a representative number of refuelling stations in order to give recommendations on acceptable oil carryover intervals ensuring a proper functioning of vehicles.



Sammanfattning

I detta projekt har provtagnings- och analysmetoder för ämnen som redan är reglerade i den svenska standard SS 15 54 38 (Motorbränslen - Biogas som bränsle till snabbgående ottomotorer) eller kommer att regleras i den framtida revideringen av standarden, utvärderats. Dessa ämnen är metan, koldioxid, syrgas, kvävgas, kolväten med 2 till 6 kolatomer, svavelväte, ammoniak, vatten och VOC (flyktiga organiska ämnen inklusive bland annat siloxaner, andra kolväten och terpenier) samt oljeförekomst från kompressorer.

Metan, koldioxid, syrgas, kvävgas och kolväten med 2 till 6 kolatomer rekommenderas analyseras enligt ISO-standard 6974 efter provtagning antingen i gaspåsar eller i gascylindrar. Analysmetoden baseras på gaskromatografi med termisk konduktivitetsdetektor och flamjonisationsdetektor. VOC inklusive siloxaner, kväveföreningar och svavelämnar med kokpunkter över 70°C kan provtas genom anrikning på adsorbent vid låga, kända flöden under en kort tid och analyseras med gaskromatografi/masspektrometri. Ammoniak, svavelväte och vattenånga föreslås analyseras med en teknik som kallas OFCEAS (på engelska Optical Feedback Cavity Enhanced Absorption Spectroscopy). Tekniken har som fördel att minimera risken med interferens från andra komponenter och är därmed specifik för ämnena av intresse. För att analysera dessa ämnen bör gasen samlas i gascylindrar. Ammoniakhalten sjunker med tiden om en gas innehållande ammoniak i låga halter förvaras i en gaspåse. Vattenånga från omgivningsluft tränger sig genom påsarnas väggar under transport vilket resulterar i vattenånghalten överskattas.

Två metoder för att bestämma förekomst av olja i fordonsgas har testats. Eftersom de flesta stationer efter kompressorn har filterenheter vars roll är att ta bort kompressorolja som förekommer i form av aerosol, så är resterande olja till stor del löst i gasen. Oljan bör därmed kunna fångas genom drastiskt tryckfall över ett filtermedium. På så sätt kondenserar oljan på filtren. Tryckfallet sker genom att tvinga gasen genom en spraydysa med lämplig håldiameter.

Metoderna använder antingen så kallade coalescingsfilter eller rör packade med en adsorbent benämnd Chromosorb. Coalescingsfilter tillverkas av borosilikatglas mikrofibrer med fluorcarbon som bindemedel. Mikrofibrerna fångar de små vätskedropparna i gasen som förflyttar sig genom filtret så att det bildas stora droppar som rinner ner. Dessa filter används redan idag vid tankstationer i filterenheter placerade efter kompressorn för att effektivt ta bort oljan som aerosol. Chromosorb är en vanlig adsorbent som ofta används i kromatografi som packningsmaterial för kolonner. Chromosorb P används främst för kolväten och måttligt polära föreningar. Samma adsorbent har dessutom använts i studier där oljan i fordonsgas skall kvantifieras. I varje fall kopplas två filter/adsorbent i serie, ett huvudfilter och ett backupfilter. Oljan anses adsorberas kvantitativt om mindre än 10 % av oljan återfinns på backupfiltret. Chromosorb-adsorbent har visat sig vara svår att använda vid högt tryck eftersom själva adsorbenten packar ihop sig hårt under trycket vilket resulterar i att flödet snabbt minskar till noll. Coalescingsfilter har visat sig vara det lämpligaste för bestämning av oljehalten i fordonsgas i tankstationer.

För båda media har först utbytetest utförts. Dessa test har som funktion att visa om en känd mängd olja som sätts på filtren till mer än 90 % kan återfinnas när filtren har behandlats i labbet med en analytisk metod. I metoden ingår provuppar-



betning för att överföra oljan från filtermedia till ett lösningsmedel och analys av den erhållna lösningen med ett analysinstrument (här en gaskromatograf med en masspektrometer) för att bestämma oljemängden. Med båda media har ett utbyte på mer än 90 % uppnåtts.

Provtagningen utfördes först efter dispensern. Vid varje dispenser utförs i början på en tankning (första volymen gas, ca 1 Nm³) olika säkerhetstest som har som mål att kontrollera att det inte finns risk för läckage. Under dessa test varierar parametrarna såsom flöde och tryck. Om testet visar risk för läckage stoppas tankningen.

Olika riggar har byggts och testats under projektet. Med den första riggen reglerades flödet genom filtren manuellt med hjälp av en ventil. Eftersom gasen efter filtren släpptes i omgivningen detekterades elektroniken i dispensern risk för läckage vilket resulterade i att tankningen stoppades nästan omedelbart. Riggen förbättrades därefter genom att tillsätta en CNG-flaska efter de två coalescingfiltren. Men eftersom flödet genom filtren reglerades manuellt spreds resultatet betydligt från test till test. I den tredje riggen ersattes den manuella ventilen med en spraydysa med olika håldiameter (från 0,8 mm respektive 0,68 mm). Med dessa erhållna flöden konstaterades att oljan inte adsorberades kvantitativt eftersom en stor del av olja återfanns på backupfiltren. På grund av säkerhetstestet kunde flödet inte regleras till en tillräckligt låg nivå.

Provtagningen utfördes därför istället mellan dispensern och kompressorn. På så sätt kunde det lämpligaste flödet för att kvantitativt fånga oljan bestämmas. Det lämpligaste flödet uppskattas vara ca 10 Nm³/h så länge den totala volymen inte överskrider 1 Nm³. Det flödet uppnåddes genom att använda en spraydysa med en håldiameter på 0,3 mm.

Slutligen har en provtagare byggts som uppfyller alla förutsättningar som har definieras under de föregående testen. Provtagaren består av en CNG-flaska av 12,5 liter som används som buffertank. Flaskan fylls genom att ansluta dispenserns munstycke till NGV1-kopplingen som finns på provtagaren. När flaskan har fyllts med minst 180 bar fordonsgas körs provtagaren åt sida. Genom att öppna de två ventilerna som befinner sig mellan flaskan och filtren leds en del av gasen i flaskan på filtren. Tre provtagningsvolymmer är lämpliga: 1 Nm³ (vilket innebär att 80 bar gas leds på filtren), 0,75 Nm³ (vilket innebär att 60 bar gas leds på filtren) eller 0,5 Nm³ (vilket innebär att 40 bar gas leds på filtren). Efter filtren släpps gasen i atmosfären genom en skorsten.

Metoden har sedan testats i fyra olika stationer som använde tre olika oljor, Rarus SHC 1025 (i två stationer), Pegasus och Titan Ganymet Ultra.

I de två stationer som inte använder Rarus SHC 1025 har låga nivåer av oljeförekomst uppmätts (mindre än 5 ppmM). Tyvärr inträffade en omfattande kontamination av CNG-flaskan med olja Rarus SHC 1025 vid den första stationen med den oljan. Vid provtagningstillfället var filterenheterna som ansvarar för att ta bort oljan i aerosolform överbelastade på grund av en läckande kompressor, och filtren uppfyllde därmed inte längre sin funktion. Följaktligen har olja även som aerosol kunnat nå dispensern. Denna kontaminering påverkade negativt de mätningar som utfördes vid de två stationerna som använder Rarus SHC 1025 vilket resulterar i en stor spridning i resultat.

Efter omfattande rengöring av CNG-flaskan med kvävgas, togs tre nya prov vid den första stationen. Resultat visar en oljeförekomst på 6,5 - 5,0 respektive 7,3



ppmM (vilket anses vara en acceptabel spridning). Blanktest utfördes mellan varje av dessa försök genom att fylla CNG-flaskan med kvävgas. Den kvävgasen överfördes sedan på provtagningsfiltren med samma metod använd för fordonsgasproverna. Oljehalten på "kvävgas"-filtren visades vara försumbar vilket tyder på att oljan inte fäller ut i CNG-flaskan.

En risk att olja fastnar i CNG-flaskan har identifierats och måste vidare studeras för att garantera resultatens noggrannhet.

Oljeförekomsten som bestäms med denna metod utgör oljeförekomsten under vissa rådande förutsättningar (varierande tryck och flöde (på grund av säkerhetstest som utförs i början på en tankning), medelhalt över de två första Nm³ som levereras) och ska främst användas för att jämföra tankställena och kompressorer med varandra. Därför är det viktigt att provtagningen alltid utförs under samma betingelser.

I en framtida studie är det därmed intressant att testa om oljeförekomsten påverkas av rådande driftsförhållanden vid stationen som till exempel antalet fordon som nyligen har tankat eller gasnivå i gaslagret...).

Nästa steg bör vara att uppskatta ett acceptabelt intervall på oljeförekomst som säkerställer en väl fungerande drift av fordonen. För att uppnå detta mål ska förslagsvis metoden testas på ett representativt antal tankställena.



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1. Background

Vehicle gas, or CNG, is the collective designation used in Sweden for the fuels that can be used for natural gas vehicles (NGV's) such as gas cars powered by gas of natural gas quality under high pressure. Methane is the main component of vehicle gas in form of fossil CNG ("Compressed Natural Gas"), as upgraded bio-gas (also called biomethane), or as a mixture of these.

Today there are three main techniques for the distribution and the refuelling of vehicle gas in Sweden [1]:

1. Natural gas or a mixture of natural gas/biogas from the natural gas grid directly to the CNG refuelling stations.
2. Biogas from the biogas plant directly to the refuelling station.
3. Natural gas/biogas via CNG-cylinder cascade to daughter-stations for CNG

During 2012, 140 million Nm³ vehicle gas were sold in Sweden (compared to 120 Nm³ under 2011) including 83.3 million Nm³ of biogas/biomethane (approximately 57% of the vehicle gas on energy basis) [2,3]. Substituting vehicle gas for gasoline or Diesel fuel prevented 260,000 tons of carbon dioxide from being released. 140 public refueling stations provide gas for 44,000 vehicles.

As an alternative fuel, natural gas has a number of advantages compared to other fossil fuels. Among those can be mentioned lower cost, higher efficiency, lower emissions and lower engine noise level and longer engine lifetime. CNG technology has been developed and applied for decades and is becoming a mature, applicable technology. The biogas used as automotive fuel presents even better environmental characteristics than the natural gas. Some disturbance still appears for the NO_x emissions, but they stay below the EU norms. Concerning carbon dioxide, hydrocarbons and carbon monoxide emissions, the biogas is far better than the NGV's [4].

In order to maintain a positive development of this sector, several conditions must be fulfilled at the same time, among them, financial incentives, increased availability of gas by increased production, easy access to refuelling stations and vehicles, and minimized disturbances for clients.

One of the main problems causing disturbances is the quality of the gas. The primary types of contamination are oil carryover from the compressor system, moisture [5] and other impurities such as siloxanes and sulfur compounds (for biomethane).

Moisture:

Water increases the risk for corrosion as the presence of free water is an essential condition for corrosion to occur. Corrosion is directly linked to the available moisture in the gas which promotes oxidation. Furthermore, water amplifies the effect of a corrosive substance.

Water interacts with other substances such as carbon dioxide and hydrogen sulfide, forming strong acids. In cooler climates, water in the gas can affect the drivability due to the risk of formation of solid hydrocarbon hydrates [6] which in turn can result in temporary plugs/clogs. The formation of hydrates can reduce pipeline flow capacities leading to potential damages to process filters, valves and compressors [7].



Impurities

Among the impurities that are suspected to cause disturbances, ammonia, sulfur species, siloxanes and halogenated hydrocarbons are often mentioned. As an example, siloxanes are suspected of fouling catalysts and lambda sensors as their presence in the fuel may lead to the formation of abrasive silica sand during combustion. The impurities in upgraded biogas produced from different substrates and different upgrading techniques have been studied in SGC report 246 [8]. It was found that the most common impurities are terpenes, mostly D-limonene and p-cymene and a fraction of hydrocarbons of between 9 to 13 carbon atoms' length. Concentrations up to 100 mg/m³ of VOC have been found in the upgraded biogas. The presence of amines in the upgraded gas originating from amine scrubbers has also been observed.

Oil content

Lube oil from gas refuelling stations can be entrained in the gas streams during refuelling. This oil deposits in the gas vehicle tanks and fueling systems.

Oil carryover has a significant negative influence on gas vehicles engines as well as on maintenance and operation of gas refuelling stations [9]:

- Oil aerosol affects the compressor heat exchanger surfaces, resulting in hotter discharge gases that reduce the storage capacity and consume more compressor power.
- Oil carryover increases the vehicle emissions during combustion.
- The maintenance and replacement of oil separators and filters will affect the gas refuelling station's maintenance costs and overall downtime. This will also increase the accumulation of waste oil which is a toxic substance which must be properly disposed.
- Onboard a CNG vehicle, the CNG which is stored at 200 bar, is reduced to 7 bar by a pressure regulator (see Figure 1.1) and then injected into the engine. There are many examples of oil soaking the pressure regulator diaphragm, affecting its accuracy and, in some cases, causing a rupture of the regulator internals if oil clogs the regulator.
- The area most sensitive to oil contamination is the engine itself. The sensors of the engine system are extremely sensitive to any contamination.



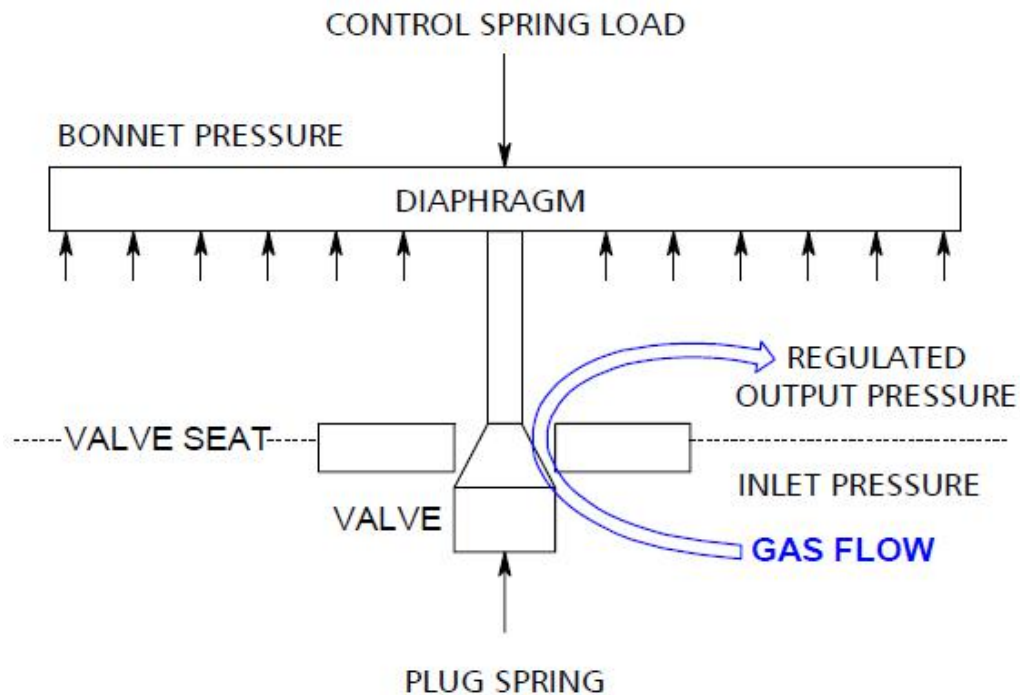


Figure 1.1: schematic of a pressure regulator [10]



Figure 1.2: Example of oil deposition in the regulator [10]

Refuelling station-derived oil carryover depends upon many variables, including compressor design and mechanical conditions, operating parameters (e.g., load, temperature and pressure), the number of compression stages, the presence or absence of filtration devices and the type and amount of oil used [5]. As example,



it has been reported that oil carryover is much less when using polyglycol oil than when using mineral oil [11].

On the other hand, CNG is a very dry fuel, and some oil carryover is necessary to provide lubrication for certain engine parts.

Oil is carried by the compressed gas in two forms: as an aerosol which is formed by the mechanical shearing in the compressor and as a vapour which is formed during oil vapourization and absorption in natural gas.

Oil aerosol particles leaving the compressor generally range from about 0.1 to 8 microns but it is mostly the fine aerosols (from 0.1 to 0.8 microns) that get entrained in the delivered compressed gas.

The use of coalescing filters to remove liquids and aerosols from gases is a well-known, reliable and proven technology for reducing or even practically completely remove oil aerosol carryover. Coalescence is a steady-state process in which larger droplets are created from smaller droplets and aerosols. The gas passes through a fiber media cartridge. Aerosol droplets are forced through the coalescing media from the inside of the cartridge tube to the outside walls. The increased mass of the droplets cause them to fall by gravity from the cartridge into a low velocity area in the bottom of the coalescer housing where oil accumulates until purged.

But compressed gas exiting lubricated compressors also carries oil as a vapor. Depending on their compositions, oils are more or less susceptible to being partly absorbed (dissolved) in natural gas mostly when natural gas is at supercritical state thus acting like a solvent. This oil cannot be filtered by coalescing filters unless pressure and/or temperature decreases, causing the evaporized oil to condense and form a very fine aerosol. Oil vapours can however be removed by adsorption on activated carbon, alumina or similar adsorbents.



2. Objectives

The aim of the project is to develop and validate sampling and measuring devices to determine the gas quality with regard to content of oil, water vapour, hydrogen sulfide, carbon dioxide, oxygen, nitrogen and contaminants (including siloxanes). From the composition of the gas, the gas density, its calorific value and Wobbe index can be calculated as explained in the ISO standard 6976 [12].

One other goal is to provide the biogas industry with standard / recommended methods for the measurement of gas quality and properties. Measured values obtained with validated methods can subsequently be used to set a limit range for e.g. oil content.



3. Literature survey and situation in Sweden

3.1 Analytical methods for water determination

Water is known by different names in different states. It can be measured in many ways [13].

In a gas mixture, the total pressure of the gas is the sum of all the individual pressures of its gas components. The partial pressures also represent the proportion by volume of the various gases:

$$\text{H}_2\text{O \% -vol} = \frac{p_w \text{ H}_2\text{O}}{p_t}$$

The water vapour saturation pressure ($p_{ws} \text{ H}_2\text{O}$) is the maximum partial water pressure ($p_w \text{ H}_2\text{O}$) in a gas which is dictated by temperature.

The relative humidity RH (%) expresses the relation between the amount of water vapour present and the maximum amount that is physically possible at that temperature.

$$\% \text{ RH} = 100\% * \frac{p_w \text{ H}_2\text{O}}{p_{ws} \text{ H}_2\text{O}}$$

Dewpoint temperature is the temperature where condensation begins or where the relative humidity would be 100% if the gas was cooled.

The water vapour saturation pressure is a known variable so the dewpoint can be calculated from the relative humidity and temperature.

If the dewpoint temperature is below the freezing point, the term frostpoint is sometimes used.

Typically, the water content / dewpoint is determined using portable instruments. Mitchell Instruments CERMAX, used for example by the German association for gas and water (DVGW), is equipped with a ceramic humidity sensor. The measurement principle of these sensors is the adsorption / desorption of water molecules on the hygroscopic layer between two conductive plates causes electrical changes in the dielectric constant between the plates, which is a function of the number of water molecules adsorbed. There are other methods, more or less complicated to measure the moisture content as the Karl-Fischer titration (as recommended in SS 15 54 38 [14]) or the use of Dräger detector tubes providing direct impact in mg / L but the last ones are not sensitive enough to measure the level of water that is set in the SS 15 54 38 standard.

3.2 Analytical methods for oil determination

Several methods have been proposed for measuring oil carryover in gas and their complexity often depends on whether it is necessary to measure the dissolved and aerosol oil phases separately or not.

IGT (Institute of Gas Technology) have developed a method [15] comprising a high pressure and a low pressure sample line, each sample line being equipped with a highly efficient coalescing filter. The oil as aerosol will adsorb on the high pressure device while the oil as vapour will pass through. Thereafter, the pressure and temperature are lowered down to atmospheric pressure and -45°C and the oil as vapour will condense and become an aerosol adsorbing on the low pressure device. The oil retained on the filters is then extracted and the samples are analysed by GC / FID (gas chromatography / flame ionization detector). This method



has been evaluated to give reliable results but is not possible to adapt to onsite measurements because of its complexity.

A simpler method has been developed by AGL (Atlanta Gas Light) [15] using a gravimetric collection device for oil in which a tube filled with an adsorbent is connected to a high pressure line. In that case, it is not possible to separately measure oil as aerosol and oil as vapour. Oil content is determined by the flow passing over the device and the weight difference of the tube before and after sampling (after heating to remove water). This method has been compared to the IGT method described above. At low levels of oil carryover (as ex. when polyglycol oil are used), the gravimetric method has been found to overestimate the oil carryover. This is probably due to the fact that a part of the increase of weight is not only due to oil. It may be caused by heavier hydrocarbons naturally occurring in natural gas (also present in biomethane). At higher levels of oil carryover, the gravimetric method has been found to underestimate oil carryover showing that this device is probably less effective in capturing oil vapours than the cryotrap/coalescing filter used in the method of reference (IGT).

For these two methods, it is recommended to perform at least three measurements as some very high readings have been observed indicating a contamination during the sampling process. The observation is considered to occur when a small droplet of oil from the liquid oil film which builds-up on the internal surfaces of piping downstream from the compressor is randomly entrained and enters the sampling device.

DVGW initiated two projects for oil and particles determination in gas refuelling stations. In the first project they developed a gravimetric method to determine oil and particle content [16]. In the second project a number (40) of refuelling stations across Germany were visited in order to determine oil and particle content in CNG (natural gas). Their sampling equipment is modular and includes a gas tank allowing sampling even without having access to a gas vehicle. It consists of a filter system in the high pressure side and gas sampling device on the low pressure side. Temperature, pressure and pressure drop through the filter are measured continuously.

The method to be developed during this project must be practically possible to use in the field, such as the gravimetric method developed by AGL. The drawbacks of the AGL method must be overcome:

- The increase of weight is not only due to oil. A method that is specific for oil could solve this problem.
- A part of the oil vapour phase could pass through the gravimetric device. It is necessary to control that the oil vapour phase is quantitatively adsorbed on the filter during sampling and quantitatively desorbed from the filter prior to analysis.

3.3 Common compressor oils in Sweden

There are today about 140 public refuelling stations in Sweden. They are operated by about 20 operators who have been contacted in order to gather information on which oil they are using.

Four operators are in charge of about 100 stations (more than 10 refuelling stations each) while other operators are in charge of 1 to 3 refuelling stations each.



Operators that responded to our request indicate the following oils to be used in their refuelling stations:

- Mobil Rarus SHC 1025 [17] which according to the product datasheet is produced of wax-free synthetic oils and a system of additives giving resistance to oxidation and thermal degradation
- Mobil Pegasus 1 which is a synthetic base oil with additives.
- Mobil Rarus 427
- Shell Tellus 32, hydraulic oil
- Titan Fuchs

In some stations, two oils are used.

In this study, we have focused on Mobil Rarus SHC 1025, Mobil Rarus 427 and Mobil Pegasus 1 as these oils were used in the refuelling stations where tests were performed. The same analytical procedure which has been developed for these three oils can be used for any other oil.

3.4 Some considerations regarding the refuelling process

The determination of temperature, pressure, flow rate and/or volume, as well as monitoring of the storage cylinder internal temperature, is important information. Knowing the values of the parameters mentioned provides information on the refuelling process as it runs its course. ProcessKontroll GT has some years ago recorded the temperature and pressure during the refuelling process. The gas temperature is cold only in the beginning of the refuelling and drops down to -9°C . This temperature increases then to reach about 23°C as the pressure in the tank increases.

At the beginning of the refuelling at a refuelling station, some tests are performed for safety reasons. Often, two leak tests are performed during the delivery of the first Nm^3 , one after 0.1 to 0.15 Nm^3 and one after 0,8 to $0,9 \text{ Nm}^3$. If the pressure cannot stabilize, the dispenser stops delivering gas and indicates fault E602. Volume of the screen is first shown after 0.4 Nm^3 . At the beginning of the refuelling, the hose is normally under pressure.



4. Sampling and analysis methods

4.1 Determination of oil carryover

Oil carryover [15] is expressed in ppmM (part per million by weight). The principle of the measurement is to determine the amount of oil (in g) in a certain volume of gas (in Nm³). In order to express the oil carryover, it is also necessary to determine the density of the sampled gas. This can be achieved as example from an accurate determination of the gas composition and calculation bases on composition using ISO 6976 [12].

$$\text{Oil carryover in ppmM} = \frac{m_{\text{oil}}(\text{g})}{V_{\text{gas}}(\text{Nm}^3) * \rho(\text{g.Nm}^{-3})} * 10^6$$

4.1.1 Sampling media and procedure in the laboratory

Two different sampling media have been used in the study: an adsorbent, Chromosorb and coalescing filters.

Chromosorb P NAW is a form of silicon dioxide composed of skeletons of prehistoric aquatic plants. It is used for its absorption quality, taking up 1.5-4 times its weight in water. It is a common adsorbent often used in chromatography as a packing material for columns. Chromosorb P is used primarily for hydrocarbons and for moderately polar compounds on both a preparative and analytical chromatography.

Chromosorb adsorbent has been packed in stainless steel tubes (1/4", 20 cm long). Between the main tube and the backup tube as well as after the backup tube, a filter is used to prevent the adsorbent to leave the tubes as seen in Figure 4.1 (on the picture only one tube with Chromosorb is connected)



Figure 4.1: Sample line for Chromosorb



The coalescing filters that have been used are Parker (Balston 100-25-BX) [18] filters made of borosilicate glass microfibers with fluorocarbon resin binders. The microfibers capture the fine liquid droplets suspended in the gas and cause the droplets to run together to form large drops within the depth of the filter cartridge. The large drops driven by the gas flow to the downstream surface of the filter cartridge, from which the liquid drains by gravity. This process is called “coalescing”. Quantitative determination of droplets suspended in a gas may be accomplished if the test is designed so that all the liquid entering the filter cartridge during the test period remains trapped on the fibers, i.e. the sample period is short enough that the filter cartridge does not become saturated and begin to drain liquid. The filters of type 100-25-BX are placed in T-type (37/25) filter housings. See picture in Section 5, Figure 5.2.

Extraction of the oil from the sampling media

Chromosorb

In the lab, the adsorbent is removed from the tubes and extracted with a small volume of dichloromethane in an ultrasonic bath sonicator during 15 minutes. The resulting extract is then analysed by GC/MS.

Coalescing filter

The coalescing filter is introduced in a 500 ml-measuring cylinder which is subsequently filled with dichloromethane covering the whole filter. The oil is extracted by using an ultrasonic bath during 30 minutes. The filter is then turned in the measuring cylinder and undergoes another 30 minutes-extraction in the ultrasonic bath. Two extractions are performed. The two fractions are then mixed into the round bottom flask. The extract is then concentrated by using a rotary evaporator until the volume reaches 10 to 20 ml and then analysed by GC/MS. A last extraction (fraction 3) may be performed in order to control that the oil has quantitatively been extracted in fractions 1+2.

4.1.2 Analysis

In order to quantitate the oil content in vehicle gas, an analytical method needed to be developed. The method must be selective, sensitive and quantitative. In this study, gas chromatography/mass spectrometry has been chosen as it fulfills all these requirements.

Gas chromatography (GC) is used to separate mixtures of chemicals into individual components. The molecules are more or less retained by a capillary column depending on their chemical and physical properties and then elute (come off of) from the column at different times called the retention time. The capillary column is held in an oven that can be programmed to increase the temperature gradually (or in GC terms, ramped), promoting the separation.

The mass spectrometer (MS) creates an electronic signal whenever the presence of a compound is detected. The greater the concentration in the sample is, the greater is the signal. The MS captures, ionizes, accelerates, deflects, and detects the molecules separately. The mass spectrometer “breaks” each molecule into fragments in a characteristic way that can be repeated. The fragments are actually charged ions with a certain mass (further on called ions). The mass spec-



trum generated for each detected molecule can be compared against known library spectra using a matching algorithm.

Mobil Rarus SHC 1025, Mobil Pegasus 1 and Mobil Rarus 427 oils have been analysed by gas chromatography/mass spectrometry after dilution of a small amount of oil in dichloromethane. The obtained chromatograms are shown in Figures 4.3, 4.4 and 4.5.

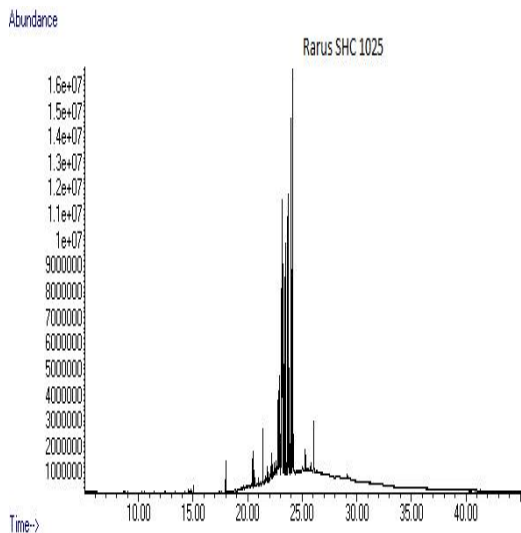


Figure 4.3: Chromatogram of Mobil Rarus SHC 1025:

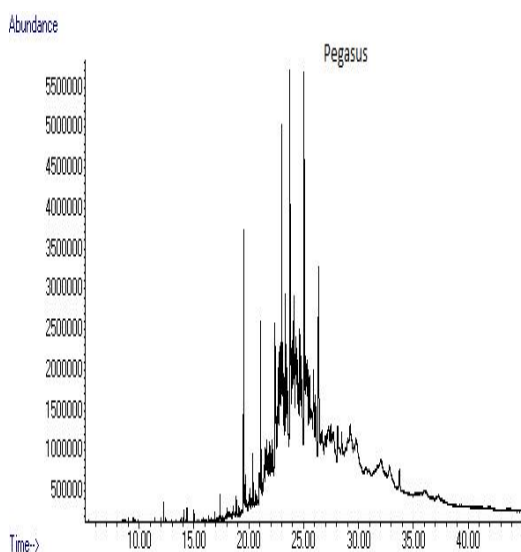


Figure 4.4: Chromatogram of Mobil Pegasus



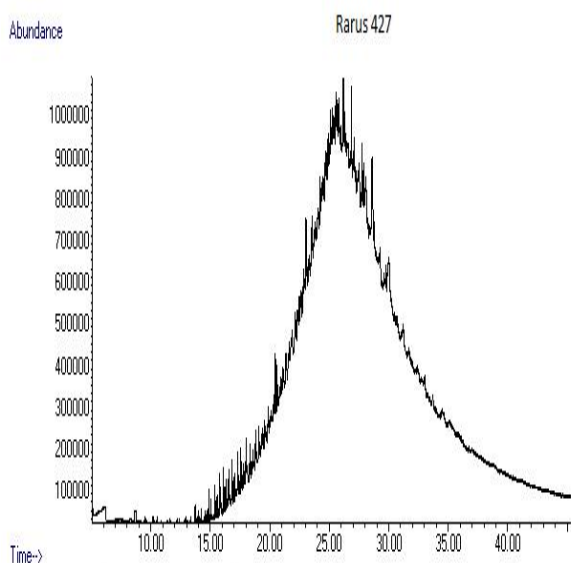


Figure 4.5: Chromatogram of Rarus 427

Oils consist of many compounds that cannot be fully separated from each other (except to some degree for Mobil Rarus SHC 1025). At very low concentrations, it becomes difficult to distinguish between oil and the non-avoidable background level of the instrument. To increase the sensitivity and lower the detection limit, it is possible in some cases to extract one ion that is specific for the targeted oil.

The chromatogram obtained for Rarus SHC 1025 consists of compounds with ion m/z 155, 141.... These compounds cannot be identified by using the MS library. Ion m/z 155 can be extracted. Samples for the calibration curves have been prepared by accurately weighing in known amounts of oil (from 1 to 30 mg) in dichloromethane. The standard curve obtained exhibits a very good linearity ($R^2 = 0.9962$) (Figure 4.6).

Pegasus and Rarus 427 consist of many alkanes that are not separated from each other on the chromatogram. It is therefore difficult to extract a specific ion but ion m/z 57 can be used together with their retention time. Standard curves for Pegasus and Rarus 427 are presented in Figure 4.7 (Pegasus) and 4.8 (Rarus 427).



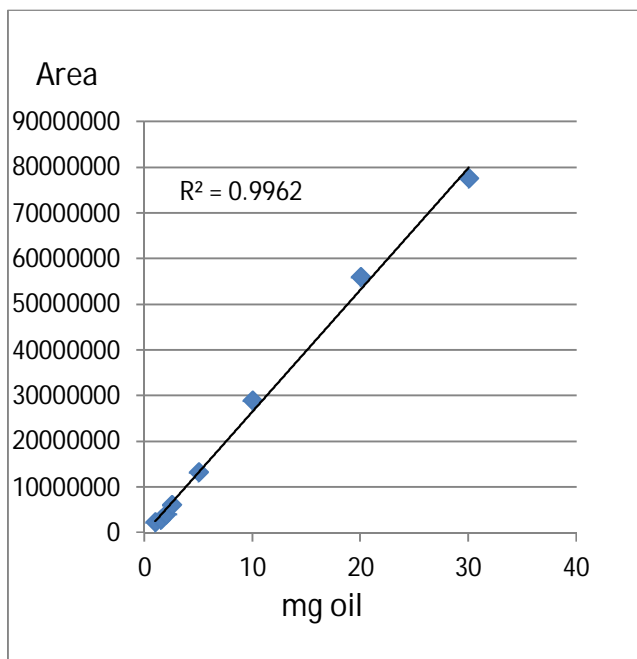


Figure 4.6: Standard curve for Rarus SHC 1025

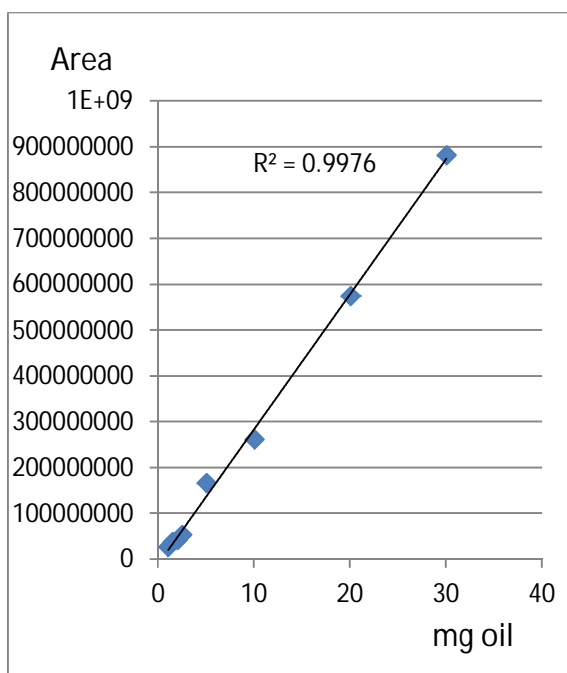


Figure 4.7: Standard curve for Pegasus 1



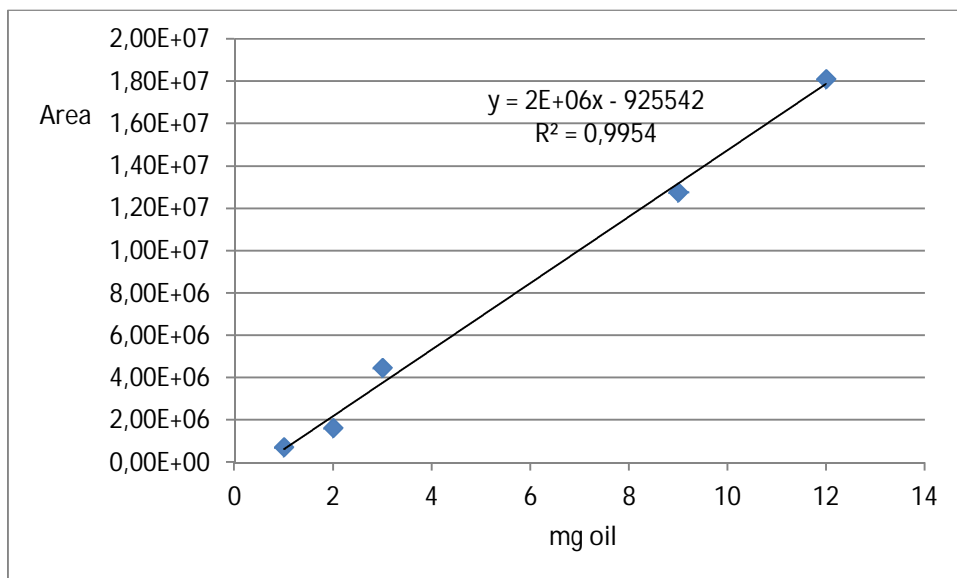


Figure 4.8: Standard curve for Rarus 427

Blank tests

Unused sampling media (chromosorb and coalescing filter) have been extracted according to procedures described in 4.1.1 and the resulting extracts have been analysed by GC/MS and it was verified that the characteristic ions of oils as described above are not present in the background due to the filter itself.

Recovery tests

In order to determine if the sampling media can be used to quantitatively determine oil in vehicle gas, it is necessary to control that a known amount of oil adsorbed on the sampling media can be quantitatively recovered by extraction. These tests are called recovery tests.

The sampling media has been spiked with a known amount of oil (20 mg Pegasus 1 for Chromosorb and 20 mg Mobil Rarus SHC 1025 for coalescing filter). The sampling media is then flushed under nitrogen at a pressure of 10 bar and undergo the extraction procedure as described in 4.1.1. Results are presented in Table 4.1.

Table 4.1: Recovery tests

Media	Oil on main tube/filter	Oil on backup tube/filter	Recovery in %
Chromosorb	20.3	0.7	105
Coalescing filter	18.4	< 1	92

Detection limit

The GC/MS detection limit has been found to be 1 mg oil per device (tube or filter). Based on a density for natural gas of 755 g/m³, the minimum volume of gas to be sampled depending on the detection limit that is required is shown in Table 4.2.

Table 4.2: Detection limits



Min. vol of gas to be sampled, Nm ³	ppmM oil
1.3	1
2.6	0.5
5.3	0.25
13.2	0.1

4.2 Determination of gas composition of vehicle gas with regard to the main and trace components

4.2.1 Sampling at the refuelling station

Two methods have been tested to sample the gas in order to determine its composition. The sampling can be performed by connecting a flow measuring device between the pump nozzle and the filler neck of a gas powered vehicle and filled with the gas to be analysed. This reference measuring device has been developed by NPS [19]. However, this device was found to exhibit a too high background of water. As a consequence, the water content cannot be determined with this device.

A simpler sampler has been built with NGV1/NGV2 connections, an empty filter house (300 ml), a pressure regulator and tubing. The sampler is connected to the dispenser with the adequate connection and a refuelling is started. The filter house is filled with the gas to be analysed and the refuelling is stopped either manually or automatically (security tests performed in the beginning of the refuelling will cause the refuelling to stop as a leak risk is detected).

Both samplers are equipped with a line after a pressure reducing regulator that allows the sampling of the delivered gas in gas tight bags, cylinders and on adsorbent tubes





Figure 4.9: The flowmeter device connected to the pump and the vehicle

4.2.2 Analysis

Main components

The gas collected in gas tight bags is then analysed at the laboratory by gas chromatography with a flame ionization detector with regard to hydrocarbons with 2 to 6 carbon atoms and with a thermal conductivity detector with regard to methane, carbon dioxide, oxygen, nitrogen, hydrogen and carbon monoxide. Analysis is performed according to SS ISO 6974 "Natural gas. Determination of composition with defined uncertainty by gas chromatography" [20]

The gas chromatograph is calibrated using gas standards containing methane, ethane, propane, carbon dioxide, oxygen, nitrogen, hydrogen and carbon monoxide with low uncertainties on the concentrations. The analysis method has been validated and uncertainties calculated according to Handbook for calculation of measurement uncertainty in environmental laboratories [21]

The gas bags have been tested for all the components with regard to the concentration stability over time. Bags have been filled up with gas standards and the content of the gas bag has been analysed every working day during a period of 30 days (see the example of methane in Figure 4.10). The results show that the gas concentrations are stable in bags over at least 2-3 weeks. The analysis should anyway been performed as soon as possible after sampling.



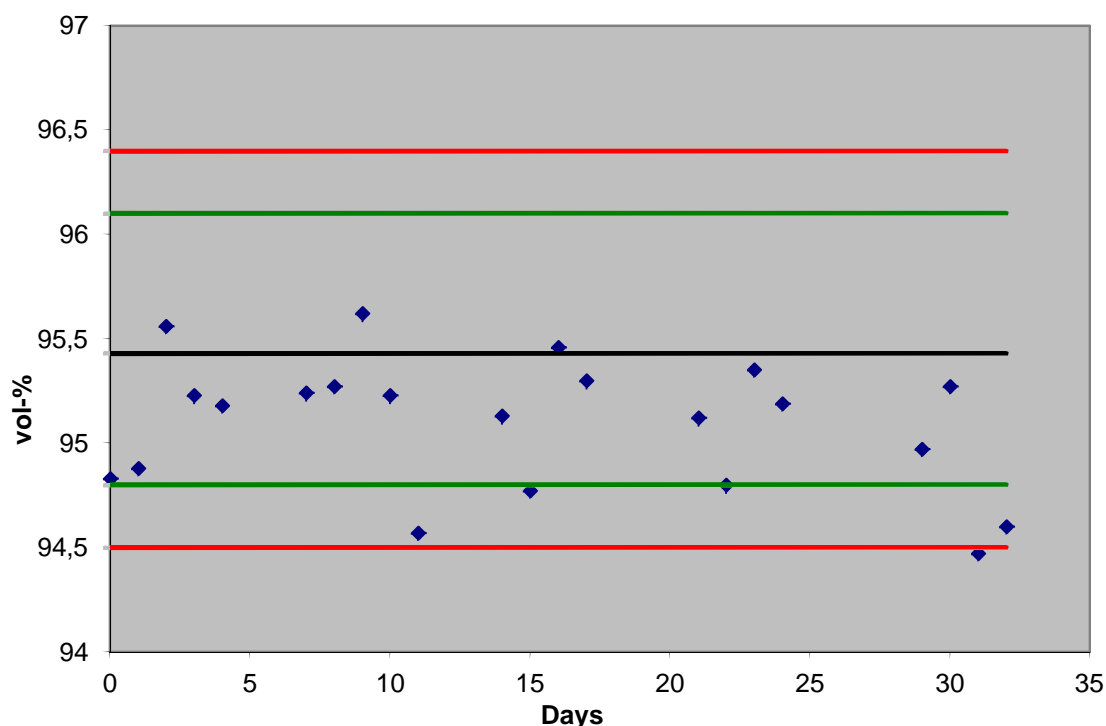


Figure 4.10: Stability of methane (95.43 vol-%) in bags during 30 days

Analysis of trace components:

Ammonia, water and hydrogen sulfide

Ammonia, water and hydrogen sulfide are analysed with an Optical Feedback Cavity Enhanced Absorption Spectrometer (OFCEAS). The analysis principle is based on Infrared spectroscopy. The OFCEAS spectrometer is equipped with a hyper-reflective cavity for the gas cell. A portion of the laser beam is fed back into its source after it has acquired the resonance frequency of the hyper-reflective cavity, enabling the purification of the injected laser beam and improving the signal-to-noise ratio.

The sampling component has a sonic nozzle probe for sample intake, a low pressure (50 mbar) flow circuit, a temperature controlled measurement cell, and a vacuum pump. The lower pressure narrows the absorption wavebands, removing the risk of spectroscopic interference between the absorption wavebands of various chemicals present in the mixture. The analysis instrument is normally drawing ambient air at 25 ml/min. The ambient air contains between 0.3 to 2%-vol water depending on the weather conditions. To analyse vehicle gas with expected water concentrations of less than 30 ppmv, it is therefore necessary to dry the instrument prior to measurements by connecting a drier to the nozzle probe. The drying of the instrument takes at least 10 hours and should therefore be started the evening before a measurement of vehicle gas is planned.

For hydrogen sulfide and ammonia, the analysis instrument has been tested by analysing gas standards containing these gases at known concentrations and stability of the gases in gas bag has been tested by filling gas bags containing stand-



ards and analysing their contents during a period of time. The results for the stability tests are presented below.

Hydrogen sulfide

Tests of stability of hydrogen sulfide in gas bag have been performed at three levels of concentrations: 515 ppmv, 9.95 ppmv and 4.99 ppmv.

Table 4.3: Test of stability of hydrogen sulfide

Days	Measured value for 515 ppmv	Measured value for 9.95 ppmv	Measured value for 4.99 ppmv
0	513	8.4	3.5
1	503	8.4	3.0
2	503	8.1	2.9
3	503	8.1	2.7
4	503	7.9	2.7
7	481	7.8	1.8

Results show good agreements between the concentration of the standard gases and the measured concentrations even if a small amount of hydrogen sulfide is lost probably by adsorption on the walls of the bags. The lowest concentration that can be detected for hydrogen sulfide is estimated to be around 1 ppm but below 5 ppm, the sample should be analysed within one day after the sampling to minimize the loss due to adsorption on the gas bag walls.

Ammonia

Tests of stability of ammonia in conditioned gas bag have been performed at two levels of concentrations: 44 ppmv and 10 ppmv.

Table 4.4: Test of stability of ammonia

Days	Measured value for 44 ppmv	Measured value for 10 ppmv
0	44	9.0
1	44	6.4
2	43	5.7
3	35	5.3
4	35	4.9

Results show that ammonia at low concentrations is not stable in a bag probably because of adsorption of ammonia on the walls of the bags.



The storage of ammonia in small gas cylinders (0.5 to 1 liter) has been shown to be a reliable method to sample gas containing even at low concentrations of ammonia.

The lowest concentration that can be detected for ammonia is estimated to be around 2-3 ppm.

Water

Sampling of water vapour is challenging as a small amount of water vapour from the surrounding air may permeate into the sampling devices. To test the background level of water due to the instrument and/or the sampling media, pure nitrogen with a water concentration of less than 3 ppmv (according to the analysis certificate) has been used.

The measurement of water vapour from samples in gas bags is not recommended as it is difficult to totally eliminate water background in the bag even if it can be reduced to about 50 ppmv by flushing the bags at least 5 times with dry nitrogen. It has also been shown that the level of the water background is varying from bag to bag. Moreover, water vapour permeates into the bag during transport to the laboratory.

Sampling in gas cylinders has been found to be a better alternative as the water background can be reduced to 2-5 ppmv. The concentration of water in dry nitrogen (less than 3 ppmv) stored one day in a small gas cylinder (0.5 liter) has been measured to be less than 5 ppmv showing that permeation of water through the gas cylinder is negligible during the first day of storage.

VOC

VOC are sampled on an adsorbent, Tenax (a porous polymer based on the monomer 2,6-diphenylene oxide).

Analysis of Tenax tubes is carried out by thermal desorption (TD) in which the adsorbed substances are first released with heat and then transferred to a cooling trap for focusing. The cooling trap is reheated quickly and the substances are released and transported to a gas chromatography column for separation. The outflow from the column is divided up into two flows for detection of individual components in a flame ionization detector or mass spectrometer. This technique is known as TD-GC-FID/MS. The quantification limit is at ppb level.

This method has already been used in the project "SGC 246, Characterisation of contaminants in biogas before and after upgrading to vehicle gas" [8a] and has been validated for siloxanes in the project "SGC 243, Contaminants in biogas: validation of an analysis method for siloxanes" [8b].

4.2.3 Calculation of energy content, gas density, Wobbe index

In the SS 15 54 38 standard, it is required that the energy content expressed as Wobbe index (lower) at 273.15 K and 101.325 kPa shall be between 44.7 and 46.4 MJ/m³. The Wobbe index is defined as the calorific value on a volumetric basis at specified reference conditions, divided by the square root of the relative density at the same specified metering reference conditions. In SS 15 54 38 it is recommended to use standard ISO 6976 to calculate the Wobbe-index.

ISO 6976 standard describes method to calculate the superior and inferior calorific value, the density, the relative density and Wobbe index of dry natural gases,



natural gas substitutes and other combustible gaseous fuels from the composition of the gas expressed in mole fraction.

For the calorific value calculated on a volumetric basis, there are some limitations for the composition:

- Nitrogen should not be present in amounts exceeding 0.3 mole fraction (30%-vol)
- Carbon dioxide and ethane should each not exceed 0.15 mole fraction (15 %-vol) and no other compound (except methane) should exceed 0.05 mole fraction (5%-vol).

The method of calculation requires values for various physical properties of the pure compounds. These values are provided in the standard in tables with references to sources.



5. Results for measurement of oil carryover

5.1 Tests with Chromosorb

Test series 1

The following sample line as shown in Figure 5.1 has been tested.



Figure 5.1: First sample line with tubes packed with adsorbent Chromosorb

During the test, the pressure before the two chromosorb tubes is 220 bar thus indicating that the pressure drop occurs directly on the Chromosorb adsorbent. With two tubes, the maximum volume that can be sampled is about 0.1 Nm³. With only one tube, the maximum volume that can be sampled is 0.3-0.4 Nm³. The dispenser then stops delivering gas because of a too high pressure drop across the tube(s). When the tubes were demounted, the Chromosorb powder was found to be hardly packed inside the filter creating a plug that rapidly completely stops the flow of gas.

Test series 2

Another method to pack the tube was used. Chromosorb was packed inside the stainless steel tubes by using a HPLC pump at 10 bar. The two filters are connected by a union.

Three tests were performed. In two cases, it was not possible to read a volume on the dispenser and in the third test, the dispenser could only deliver 0.15 Nm³ before stopping. When the tubes were opened, it could be noticed that the adsorbent was again hardly packed in the end of the first tube. The method has been found to not be appropriate to sample gas at high pressure. The Chromosorb powder is packed together as a result of the high pressure creating a plug that stops the flow of gas across the tubes.



Another series of tests may be performed where the flow and pressure are reduced before reaching the tubes packed with adsorbent as example by using a spray nozzle.

5.2 Tests with coalescing filters

Test series 1

The following sample line has been used for the first tests, from left to right:

LB30, NGV1 receptacle

6-6GOA-SS, male SAE to female NPT

M12A-V8LN-SS, A-LOK, 2-1/2

M12MSC1/2N-316, male connector

EU37/25, filter house (with 100/25BX filter),

M12MSC1/2N-316, male connector

M12MSC1/2N-316, male connector

EU37/25, filter house (with 100/25BX filter),

M12MSC1/2N-316, male connector

The valve allows manual reduction of the flow of gas delivered by the dispenser, a manometer allows reading of the pressure before the sampling devices. Furtheron, a manometer allows reading of the pressure drop after the valve. The gas passes then a first filter house containing a coalescing filter and finally another filter house with a coalescing filter used as a backup (see Figure 5.2), the gas is then released to the atmosphere.



Figure 5.2: First sample line with filter house and coalescing filters



At the beginning of the sampling, the valve is closed. When the refuelling starts, the valve is slightly opened, manually. When the gas delivery stops in order to perform the leakage tests, the valve must be closed. As the refuelling starts again, the valve is manually opened again.

In total, 9 tests were performed with this sample line. Results are presented in Table 5.1.

Table 5.1: Results with sample line 1 with filter houses and coalescing filters

Test		Filter	volym Nm ³	mg	%	sum mg	oil carryover
1	Stora Höga	Only main	4.45	19	-	19	6
2	Stora Höga	Only main	1.94	40	-	40	27
3	Stora Höga	Only main	0.88	79	-	79	119
4	Stora Höga	Only main	0.37	37	-	37	134
5	Stora Höga	Main	5.98	7	48	14.1	3
		Backup		7	52		
6	Stora Höga	Main	2.77	81	68	120	3
		Backup		38	32		
7	Stora Höga	Main	0.47	26	95	27	78
		Backup		1	5		
8	Kallebäck	Main	1.25	32	59	54	57
		backup		22	41		
9	Kallebäck	Main	0.8	11	97	12	19
		backup		0.5	3		

The four first tests were performed without a backup filter house. Four different volumes were tested, 4.45 Nm³, 1.94 Nm³, 0.88 Nm³ and 0.37 Nm³. In many cases, it is necessary to start the refuelling several times in order to reach these volumes. The valve was fully opened for 4.45 Nm³ (high flow) but not for the three other tests (lower flows).

Oil carryover determined from the sample with 0.37 Nm³ and the sample from 0.88 Nm³ are in good agreement which indicates that oil may have been quantitatively retained on these filters.

With a volume of 4.45 Nm³, only 5 mg oil was found on the filter indicating that only a small amount of oil is retained on the filter (oil breakthrough). The same trend was observed with a volume of 1.94 Nm³.

To verify these preliminary results, tests 5, 6 and 7 were performed with a backup coalescing filter. Three different volumes were tested, 5.98 Nm³, 2.77 Nm³ and 0.47 Nm³.

Results with the highest volumes clearly show that oil passes the first filter. However the sampling with 0.47 Nm³ confirmed that at these low sampling volumes, oil is quantitatively retained on the main filter as expected from the tests performed without backup filter.

The sampling is found to be difficult to carry out as it is impossible to control the flow passing through the sampling device. The dispenser stopped at several occasions to deliver gas and the refuelling had to be restarted. As the valve is



controlled manually, it is difficult to reproduce the same sampling conditions from one sampling to the other.

However, some of the results indicate that the oil carryover can quantitatively be determined if volumes of less than 1 Nm³ are sampled.

Test series 2

In the next sample line, an empty tank was added at the end of the sampling device to better simulate a refuelling (see Figure 5.3, here without backup filter).



Figure 5.3: Second sample line with filter house and coalescing filters

In total, 7 tests were performed with this sample line. Results are presented in Table 5.2.



Table 5.2: Results with sample line 2 with filter houses and coalescing filters

Test		Oil	Volume Nm ³	Filter	mg	%	sum mg	oil carryover ppmM
1	Stora Höga	R1025	0.97	Only main	35	-	35	47
2	Stora Höga	R1025	3.1	Only main	14	-	14	6
3	Kallebäck Fordonsgas	R1025	1.12	Main	3	29	9	10
				backup	9	71		
4	Falutorget, Fordonsgas	Pegasus	1.07	Main	4	86	6	6
				backup	1	14		
		R427		Main	18	59	31	38
				backup	12	41		
5	Falutorget, EON	Pegasus	1.12	Main	3	34	8	9
				Backup	5	66		
6	Kruthuset, Fordonsgas	R 1025	1.13	Main	3	33	8	10
				Backup	6	67		
7	Varla, Fordonsgas	R 1025	1.13	Main	8	52	15	15
				Backup	7	48		

The two first tests were carried out without backup filter in order to test if the sampling was eased by the use of an empty tank. The sampling was shown to be easy to carry out and the volume could be sampled at once. A new series of tests were then carried out at 5 different refuelling stations equipped with different compressor models and using different oils (some older models, some newer). Results show that even at low volumes (around 1 Nm³) oil breakthrough is observed in almost all cases. The amount of oil detected on the second filter is even higher than the amount of oil detected on the first filter in 4 cases out of 5. By comparing the results from the first sample line (tests 7, 8, 9, Table 5.1, without tank) and the results obtained with the sample line with tank (tests 3, 4, 5, 6 and 7, Table 5.2 with tank), one could wonder if the presence of the tank negatively influence the absorption of oil on the first filter as oil breakthrough measured on the backup filter was seemingly less important without a tank than with a tank.

As the capacity of the coalescing filter is not an issue, the flow across the filter is suspected to be too high. The contact time with the filter is not long enough for the oil to absorb. As a result, the oil passes onto the next filter and probably also get through to the tank. Moreover, the use of a valve that is manually opened makes the sampling hard to reproduce in term of flow. The flow during these tests was difficult to estimate, probably 200-400 Nm³/hour.

In order to improve the sampling device, a spray nozzle with a hole of 0.8 mm was used instead of the valve.

Test series 3

The valve is replaced by a spray nozzle with a hole of 0.8 mm resp. 0.68 mm (see Figure 5.4). All tests were performed at Stora Höga refuelling station.





Figure 5.4: Third sample line with filter house and coalescing filters

The sampling was found to be easy to reproduce. Three tests were performed, two without backup filter house and one with. This time, the refuelling has to be stopped manually by the operator when the volume to be sampled is reached.

The sampling follows the following pattern: 0.13 Nm³ is first delivered within only some seconds. Then the dispenser stops delivering gas in order to test leak. From 0.13 Nm³ up to about 0.3 Nm³ the refuelling only takes some seconds but from 0.30 Nm³ up to 0.8-0.9 Nm³, the refuelling takes about 20 seconds (the flow is then estimated to be around 90 Nm³/hour). The dispenser stops for a new leak test before the refuelling goes on. From 0.9 Nm³ up to about 1 Nm³ the refuelling only takes some seconds but from 1 Nm³ up to 2 Nm³, the refuelling takes about 30 seconds (the flow is then estimated to be around over 100 Nm³/hour).

In total, 5 tests were performed with this sample line. Results are presented in Table 5.3.

Table 5.3: Results with sample line 3 with filter houses and coalescing filters

Test	Hole diameter mm	Volume Nm ³	Filter	mg	%	sum mg	oil carryover ppmM
1	0.8	0.75	Main	20	-	20	35
2	0.8	2.02	Main	11	-	11	7
3	0.8	2.04	Main	15	52	29	18
			backup	14	48		
4	0.68	0.9	Main	39	46	87	127
			backup	47	54		
5	0.68	2.0	Main	24	43	55	36
			backup	31	57		



Tests performed with backup filters show that even with this sample line it is not possible to avoid oil breakthrough as oil on the second filter is still representing about 50% of oil absorbed. Moreover even if the flow was only estimated by timing the delivery of the gas, it is clear the flow is not constant during the whole period of sampling.

Test series 4

The results from the previous tests suggested that the flow on the coalescing filters must be reduced to less than 100 Nm³/h so the oil can quantitatively adsorb on the first filter. Working at lower flows cannot be achieved at the dispenser which would directly stop delivering gas. Therefore for these tests, gas has been sampled in between the compressor and the dispenser. The connection required to perform these tests is unfortunately not available at most of the refuelling stations. ProcessKontroll GT has installed such a connection in order to perform other tests at Stora Höga refuelling station.



Figure 5.6: Tests performed before the dispenser at Stora Höga

The gas first passed through a flow measuring device, then by a NGV1 receptacle to a spray nozzle, a first filter house with a coalescing filter and finally a second filter house with another coalescing filter. The gas is thereafter released to the atmosphere. Three diameters were tested for the hole of the spray nozzle, 0.28, 0.38 and 0.68 mm. A total of 6 tests were performed. The flow measuring device allows measuring the quantity (expressed in kg) and the flow of gas that passed through the filters. With the 0.28 mm spray nozzle, the flow could not be recorded during test 6 as it was just under the lowest flow that can be measured by the measuring device. In this case, the flow was estimated by divided the delivered quantity with the delivery time.

The flows and sampled volumes for the 6 tests performed at Stora Höga refuelling station are reported in Table 5.4.



Table 5.4: Flows and quantities of gas sampled during tests with different spray nozzles

Test	Hole mm	Total kg	Total Nm ³	Time (min)	Flow in Nm ³ /h
1	0.28	0.41	0.52	2.33	8
2	0.28	0.81	1.01	7.33	8
3	0.68	0.85	1.07	0.67	96
4	0.38	0.81	1.01	2.00	30
5	0.38	2.35	2.93	5.11	34
6	0.28	1.93	2.41	18.15	8*

* estimated

These flows can be compared to the flow during a refuelling which is about 12 to 14 kg/min corresponding to 900-1000 Nm³/h.

Results for the oil carryover measurements are presented in Table 5.5.

Table 5.5: Results with different spray nozzles

Test	Hole diameter mm	Volume Nm ³	Filter	mg	% mg	sum mg	oil carryover ppmM
1	0.28	0.52	Main	17	> 99	17	43
			Backup	< 1	< 1		
2	0.28	1.01	Main	33	90	37	48
			Backup	4	10		
3	0.68	1.07	Main	6	30	19	23
			Backup	13	70		
4	0.38	1.01	Main	3	30	10	12
			Backup	7	70		
5	0.38	2.93	Main	8	46	17	8
			Backup	9	54		
6	0.28	2.41	Main	19	30	65	36
			Backup	46	70		

Oil carryover determined from the samples with the 0.28 mm spray nozzle when 0.52 respective 1.01 Nm³ gas are in good agreement (around 45 ppmM). Moreover oil is quantitatively retained on the main filter as less than 10% of the oil reaches the backup filter. However, a large quantity of oil passed through the main filter when 2.41 Nm³ was sampled (test 6). Results for the other spray nozzles (0.38 mm and 0.68 mm) once again show that at larger flows, oil passes through the main filter even when 1 Nm³ gas is sampled.

The conclusion of these tests is that it is possible to quantitatively determined oil carryover by sampling up to 1 Nm³ at a flow of about 10 Nm³/hour.



Test series 5: Sampler for oil determination after the dispenser

Based on the previous results, a sampler has been designed to sample gas when connected to the dispenser (see Figure 5.7).

The sampler consists of a NGV1 connection, 1/2" tubing, a manometer, 3 ball valves (oasis engineering ltd), a 12.5 liter composite CNG bottle, and two EU37/25 filter houses (with 100/25BX filter) connected in series after a spray nozzle of 0.3 mm hole diameter.



Figure 5.7: Picture of the sampler for oil determination at dispensers

The sampler is connected to the dispenser through the NGV1 connection. A refuelling is started and manually stopped (if necessary) when the pressure in the bottle has reached at least 180 bar (which corresponds to between 2.1 to 2.6 Nm³ gas sampled). The sampler is then disconnected from the dispenser and brought aside.

The gas is released through the chimney by opening a ball valve until the pressure in the bottle reached 180 bar (this pressure has been chosen as it supposedly can be achieved in all stations even the ones working at slightly lower pressures than average). The gas is then led through the coalescing filters by opening the two other ball valves. As the gas passes first through the hole of the nozzle, the pressure drops resulting in a temperature drop and the oil is trapped on the filter. The sampling can then be stopped when the pressure in the bottle reaches 100 bar (equivalent to 1 Nm³ sampled), 120 bar (equivalent to 0.75 Nm³ sampled) or



140 bar (equivalent to 0.5 Nm³). Preferably, the sampler is then refilled with the gas to analyse in the same way to perform several samplings.

Once all samplings are performed, the gas left in the bottle is released through the chimney.

The first tests have been performed at Stora Höga station.

The flow of gas through the coalescing filter is 30 Nm³/h within the first seconds of the sampling and drops to about 5 Nm³/h when 1 Nm³ gas is sampled as shows in Figure 5.8.

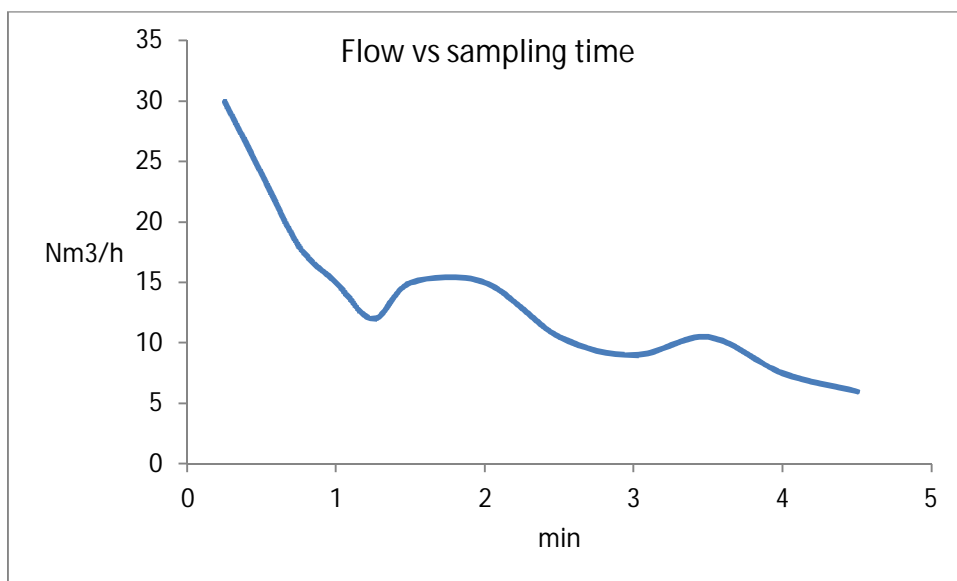


Figure 5.8: flow versus sampling time when sampling 1 Nm³ gas

After several samplings, it is possible to compare the volume read on the dispenser with the volume calculated, expressed as the pressure inside the bottle multiplied by the volume of the CNG bottle. Results are shown in Figure 5.9. They clearly show a good correlation ($R^2 = 0.99$ and $y = 0.9982$) between the volume read on the dispenser and the volume calculated with the pressure readings.



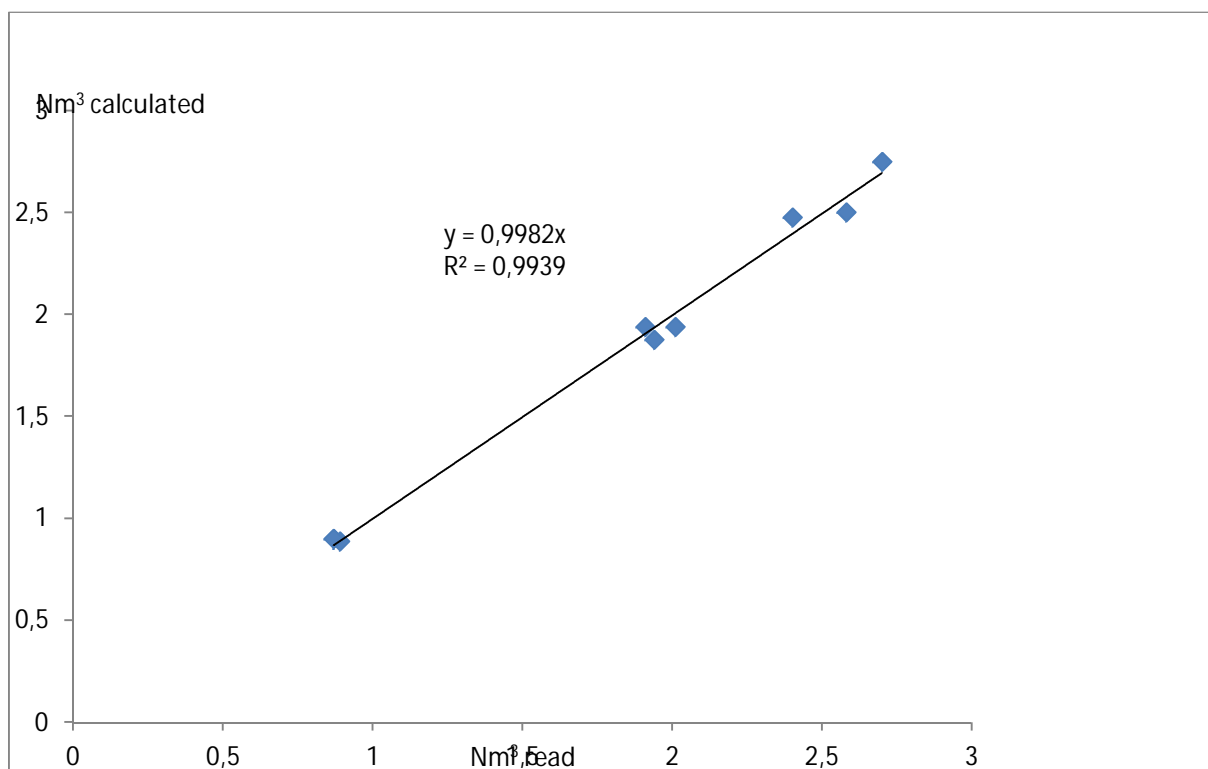


Figure 5.9: Correlation between the volume read on the dispenser and the volume calculated by reading the pressure of the CNG bottle

The results of the tests performed at Stora Höga refuelling station are presented in Table 5.6. For all tests, the amount of oil measured on the backup filter is less than 1% of the amount of oil measured on the first filter showing that the oil is quantitatively retained on the first filter.

Table 5.6: Results of the tests performed at Stora Höga refuelling station

Test	datum	Pressure in the CNG bottle before refuelling (bar)	Sampled "pressure" (bar)	Volume (Equivalents in Nm³)*	ppmM oil
1	13-09-12	0	80	1	16
2	13-09-12	0	80	1	18
3	13-09-12	0	40	0.5	21
4	13-09-12	140	40	0.5	43
5	13-09-12	140	60	0.75	30
6	13-09-18	0	72	0.9	49
7	13-09-18	0	60	0.75	44
8	13-09-18	0	40	0.5	160
9	13-09-18	0	80	1	101

*Calculated assuming the temperature of the gas is at the same temperature during all the tests



Unfortunately, the coalescing filters at this station were overcharged with oil at the time of the testing. The consequence is that oil in the form of droplets was carried out with the gas. Consequently, the results are difficult to interpret.

New tests of the sampler have then been performed at different refuelling stations. Results are presented in Table 5.7. The results of these tests clearly indicate that the bottle was contaminated with oil Rarus 1025.

Table 5.7: Results of the tests performed at different stations using different oils

Stations	Compressor oil	Carryover from oil used at the tested station	Number of tests	Carryover from oil used at the station previously tested	
				ppmM	mg
Stora Höga	Rarus 1025	~100	9	-	-
Karlshamn	Titan Fuchs	< 5	4	From 70 to 10	from 51 to 8
Mölnlycke	Pegasus	< 5	2	From 50 to 30	from 39 to 21
Kungsbacka	Rarus 1025	From 30 to 110	3	< 10	< 1
Mölnlycke	Pegasus	< 5	2	10	10



The results indicate:

- The contamination with Rarus 1025 from the first tested station (Stora Höga) is extensive. Clearly, a significant quantity of oil has deposited in the bottle. During the following tests performed at a station not using Rarus 1025 oil (Karlshamn), the quantity of Rarus 1025 oil recovered on filters decreased from 51 mg during the first test down to 8 mg during test 3 and 4. These results suggested that the oil that has deposited in the bottle was gradually re-dissolved in the gas sampled, thus cleaning the bottle from the contamination.
- Surprisingly, the results of the tests performed later on at another station not using Rarus 1025 (Mölnlycke) exhibits quantities of oil higher than expected (40 mg for the first test, much higher than the 8 mg found during the last test performed at Karlshamn). A possible explanation is that when performing tests in series, the gas sampled in the bottle become colder for each test performed (this has been visually observed). Subsequently, the conditions to re-dissolve the oil present in the bottle become less and less favorable for each test performed.
- The tests performed at stations using Pegasus and Titan Fuchs as compressor oil show that the oil carryover from these stations is low (less than 5 ppmM).

It is important to understand if and under which conditions oil may deposit in the bottle as this information is crucial to interpret the results obtained at any station. Several questions must be answered:

- Does oil deposit in the bottle during the refuelling? If yes, this will affect the results that may be underestimated and cause contamination of next sample (which is mostly problematic if two stations using the same oil are tested one after the other). In that case, it is important to determine under which conditions of pressure and temperature the oil deposits in the bottle. We may assume that the most favourable conditions are when the bottle is empty (which is the case when taking the first sample at any station) as the pressure in the bottle is low. Some of the results confirm this hypothesis indicating also that oil is at least partially redissolved in the gas when taking the second sample by filling the bottle from 100 bar to about 200 bar. If this hypothesis is confirmed, this implies that the first sample may be underestimated and that it will be necessary to take at least two more samples in order to obtain reliable results.
- Does oil deposit in the bottle when emptying the bottle at the end of the sampling? In that case, it will not affect the results but will cause contamination of the next sample. A possible way to solve this problem is to wash-out the bottle between two samplings with nitrogen as oil also dissolves to some extent in nitrogen. This was tested in the following tests.



The CNG-bottle was first cleaned of oil with alcohol and nitrogen to eliminate any rest of Rarus 1025 oil. The following sequence of tests was performed:

- Filling with nitrogen, sampling on coalescing filters from 50 bar to 0 bar.
- Refuelling with vehicle gas, sampling on coalescing filters from 180 to 100 bar.
- Refuelling with vehicle gas, sampling on coalescing filters from 180 to 100 bar, emptying the bottle
- Filling with nitrogen, sampling on coalescing filters from 100 to 20 bar, emptying the bottle
- Refuelling with vehicle gas, sampling on coalescing filters from 180 to 100 bar, emptying the bottle
- Filling with nitrogen, sampling on coalescing filters from 80 to 0 bar

The results are presented in Table 5.8.

Table 5.8: Results of the tests performed at Stora Höga with nitrogen and vehicle gas

Gas	Conditions for sampling	Oil carryover , ppmM
Nitrogen	50 to 0	< 1
Vehicle gas	180 to 100	6.5
Vehicle gas	180 to 100	5.0
Nitrogen	100 to 20	< 1
Vehicle gas	180 to 100	7.3
Nitrogen	80 to 0	< 1

Results for the measurement of oil carryover show an acceptable spreading out. No significant oil carryover was found on the filters when the bottle was filled with nitrogen.



6. Conclusions and recommendations

6.1 Conclusions

Determination of oil carryover

Two different media has been tested in order to determine oil carryover in vehicle gas.

- Chromosorb adsorbent
- Coalescing filters

Both sampling media have been shown to be appropriate to sample oil as they exhibit low oil backgrounds and good recovery yields when spiked with known amount of oils. Chromosorb is easy to work with at the laboratory. But risk of plugging during sampling is high as the adsorbent is hardly packed as soon as a too high pressure is applied to the tubes containing Chromosorb. This method is however effective if the pressure of the gas to test is less than 10 bar.

With coalescing filters, the sampling can be performed under reproducible conditions at all stations. Extracting oil for quantification from coalescing filters is however more time consuming than extracting oil from Chromosorb and the materials needed are more expensive.

Results in all cases show that in order to quantitatively absorb the oil on the coalescing filters, it is necessary to lower the flow of gas to 10 Nm³/h, a level where the dispenser stops delivering gas (flow too low). Moreover, the safety tests which are performed during the delivery of the first Nm³ negatively affect the sampling as the flow varies during the tests.

When possible, sampling can be performed before the dispenser. The sampled volume should not exceed 1 Nm³.

However, the connection required to perform these tests is unfortunately not available at most of the refuelling stations.

Consequently the sampling is recommended to be performed with the sampler developed during this study. Once the CNG bottle is filled with at least 180-200 bar, the sampler is brought to the side and a part of the volume inside the bottle (typically 80 bar) is transferred to coalescing filters. Results obtained during this study show that the oil is quantitatively adsorbed on the first filter as long as the sampled volume doesn't exceed 1 Nm³. Several samplings are needed to evaluate the oil carryover. It is recommended to perform at least 3 tests.

Some more tests are needed to study if oil may deposit in the CNG bottle either during the refuelling of the bottle (which will result in underestimating the oil carryover and causing contamination of the next sample) or when the bottle is emptied at the end of a sampling (which will not affect the results but will cause contamination of the next sample). Theoretically, the conditions for oil to deposit in the CNG bottle are only fulfilled when the pressure in the bottle is low (typically lower than 50 bar).

The results obtained during this study indicate that at low levels of oil carryover, deposition of oil in the bottle is negligible.



Determination of gas composition of vehicle gas with regard to the main components

The determination of vehicle gas with regard to methane, carbon dioxide, oxygen, nitrogen, hydrogen and carbon monoxide can be performed according to standard method ISO 6974. By using high-accuracy primary reference gas mixtures to calibrate the analysis instrument, vehicle gas can be analysed in order to determine if their composition fulfill the requirements as expressed in standards as SS 15 54 38 within the given uncertainty.

Determination of gas composition of vehicle gas with regard to the trace components

Ammonia:

Ammonia is a difficult gas to analyse as it reacts with many surfaces. The analysis method presented in this report is based on infrared spectroscopy, the instrument being an Optical Feedback Cavity Enhanced Absorption Spectrometer (OFCEAS). Small gas cylinders with treated inner surface are the best alternative as sampling media.

Hydrogen sulfide:

The analysis method presented in this report is also based on the infrared spectroscopy, instrument, OFCEAS. Gas bags or small gas cylinders can be used to sample the gas.

Water:

The analysis method presented in this report is also based on the infrared spectroscopy instrument, OFCEAS. Gas bags have been shown to not be adequate to sample the gas as these contain a background of water, which is not possible to fully eliminate. Small gas cylinders are a much better alternative. The sampling line shall be as short as possible otherwise the water content may be overestimated because of surrounding water passing into the sampling line.

VOC:

The quality of the gas with regard to VOC content can be monitored according to methods described in SGC projects 243 and 246 [8a, 8b].

6.2 Recommendations

Table 6.1 presents some recommended methods for the sampling and analysis of compounds under discussion for regulation or already regulated by SS 15 54 38.



Table 6.1: Recommendations for the sampling and analysis of compounds under discussion for regulation in standards for vehicle gas quality

Compounds	Sampling	Sampling media	Analysis	Comments
CH ₄	Through a sampling device having NGV1 and NGV2 connections	Flexfoil bags or small gas Cylinders	GC/TCD	According to ISO 6974 Accredited method
CO ₂ , O ₂ , N ₂ , H ₂ , CO	Through a sampling device having NGV1 and NGV2 connections	Flexfoil bags or small gas Cylinders	GC/TCD	According to ISO 6974 Accredited method
Hydrocarbons with 2 to 6 carbon atoms	Through a sampling device having NGV1 and NGV2 connections	Bags or small gas Cylinders	GC/FID	According to ISO 6974. Accredited method
H ₂ S	Through a sampling device having NGV1 and NGV2 connections	Flexfoil bags or small gas Cylinders	IR	
NH ₃	Through a sampling device having NGV1 and NGV2 connections	Small gas Cylinders	IR	Analysis must be performed shortly after the sampling
Water	Through a sampling device having NGV1 and NGV2 connections	Small gas Cylinders	IR	Short lines in order to avoid contamination with water from surrounding air
VOC inclusive siloxanes	Through a sampling device having NGV1 and NGV2 connections	Tenax tubes	ATD/GC/MS/FID	Method is validated and accredited for siloxanes
Oil	Sampler developed during this project	Coalescing filters	GC/MS	



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