

OPTIMAL OIL CONCENTRATION RANGE IN CNG/BIOMETHANE TO MINIMIZE OPERATIONAL PROBLEMS

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Optimal oil concentration range in CNG/Biomethane to minimize operational problems

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Foreword

The project "Optimal oil concentration range in CNG/biomethane to minimize operational problems" was conducted from May 2014 to December 2014. The project was carried out by SP Technical Research Institute of Sweden in collaboration with the project partners. During the project, two meetings were organised with the reference group composed of:

Energimyndigheten (Swedish Energy Agency)
Staffan Johannesson, E.ON Gas Sverige AB
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Summary

Compressor oil used at CNG/biomethane refuelling stations can be entrained into the final product; these oil slips reach the NGV engines and can cause operational problems with pressure regulators and gas injectors. Therefore, the oil levels need to be monitored and controlled. Oil is carried by the compressed gas in two forms: as an aerosol and as a vapour. The use of coalescing filters to remove liquids and aerosols from gases is a well-known, reliable and proven technology for reducing or even almost completely removing oil aerosol carryover. The oil vapour on the other hand, cannot be filtered by coalescing filters unless the pressure and/or temperature decreases, causing the vapourized oil to condense and form a very fine aerosol.

This is the principle of the method developed by SP together with Prozesskontroll GT in the SGC project 290 "Development and validation of methods for test of CNG quality inclusive of oil carryover" for the measurement of oil carryover at CNG/biogas stations. The pressure reduction is achieved by forcing the high-pressure gas, sampled in a buffer-tank, to pass through a spray nozzle with a small hole. In the project presented below, we have further developed this method. The sampler has been slightly modified so it can now be cleaned between taking two samples. The procedure for extracting the oil absorbed on the filters at the laboratory has also been further developed, with the ambition to be more time-effective and to consume less solvent.

The extract can then be analysed by gas chromatography, coupled to either a mass spectrometer or a flame ionization detector. On average, the results obtained with the FID are 10% higher than the results obtained with the MS. The quantification with FID is more likely to be influenced by the background associated to the filter or to the instrument. It has been shown that you need to perform a careful visual control in order to be able to detect any contamination of the gas by other compounds than the compressor oil.

The method has been validated and the measurement uncertainties have been estimated to be 24% relative uncertainty for the range 4- 45 ppmM and 1 ppmM absolute uncertainty for the range 1-4 ppmM.

A series of measurements was then performed from May 2014 to October 2014 at 16 refuelling stations. The oil carryover measured during these measurements, ranged from a few ppmM (less than 1) to more than 50 ppmM with 69% of the results being less or equal to 12 ppmM. Six stations exhibited relatively high or very high oil carryover, with two measurements, in particular, standing out with oil carryover exceeding 40 ppmM. In several cases either another oil than the one claimed to be used at the station or compounds that could not be identified were found in the gas, clearly showing that the oil/compounds found in the CNG/biomethane may not originate from the station itself. At the stations where oil carryover was found to be high or very high, no evidence was found suggesting that the oil filtration system was not functioning properly. Consequently, it may be of interest to check that the compressor(s) is/are working properly. Adequate construction/maintenance/diagnostics is crucial in order to decrease the risks for oil carryover. Filtration and compressor reliability, including oil properties, are often mentioned as critical aspects for monitoring.

Sammanfattning på svenska

Gasformiga bränslen, inklusive biogas, är accepterade alternativa drivmedel i världen i dag på grund av deras bättre prestanda vad gäller klimatpåverkan och emissioner jämfört med konventionella fossila bränslen som bensin och diesel. Gas som drivmedel används redan i stor utsträckning i många europeiska länder bland annat i Sverige där 54 % av den producerade bi gasen uppgraderas till fordonsgas. För att bibehålla en positiv utveckling av denna sektor, måste flera villkor vara uppfyllda samtidigt, bland annat ekonomiska incitament, ökad gastillgänglighet genom ökad produktion, lätt tillgång till tankstationer och fordon samt minimerade störningar för kunderna.

Kompressorolja vid tankstationer för fordonsgas (CNG/biometan) kan överföras till den slutliga produkten; oljan når fordonsmotorerna och kan orsaka driftproblem i tryckregulatorer och gasinjektorer. Därför måste oljenivån övervakas och kontrolleras. Olja finns i den komprimerade gasen i två former: som aerosol och som en ånga som bildas när oljan förångas och absorberas i gasen. Att använda koalescensfilter för att ta bort aerosolen från gasen är en välkänd, pålitlig och beprövad teknik för att minska eller till och med praktiskt taget helt ta bort olje-aerosol. Olja löst i gasen kan däremot inte filtreras genom dessa filter såvida inte trycket och/eller temperaturen sänks, så att den förångade oljan kondenserar.

Under ett föregående projekt har SP Sveriges Tekniska Forskningsinstitut tillsammans med ProcessKontroll GT utvecklat en provtagare och en mätmetod för att kvantifiera oljeöverföringen från kompressorer till gasen. Metoden är baserad på principen att olja löst i gasen vid högt tryck kondenserar vid kraftigt tryckfall. Provtagaren har en CNG-flaska på 12 liter som används som bufferttank. Provtagaren har även två filterhus innehållande varsitt koalescensfilter och en dysa med ett hål med diameter 0,3 mm placerad före de två filterhusen. När provtagaren kopplas till en dispenser genom en NVG1-koppling, fylls flaskan tills trycket i bufferttanken når minst 180 bar. Då kopplas provtagaren bort och förs åt sidan. 80 bar (motsvarande 1 Nm³) av gasen i bufferttanken överförs till filtren. Trycket reduceras kraftigt när gasen når dysan. Temperaturen sjunker också och oljan kondenserar på det första filtret. Det andra filtret används sompolisfilter för att bekräfta att oljan kvantitativt kondenserat på det första filtret.

I det här projektet har vi vidareutvecklat metoden och provtagaren för att mäta oljeöverföring från kompressorer vid NGV-tankstationer. Provtagaren som utvecklades under det tidigare projektet " Utveckling och validering av testmetoder för test av fordonsgaskvalitet, inklusive oljeförekomst", har ändrats så att det nu är möjligt att rengöra den mellan två provtagningstillfällen.

Förfarandet för extrahering av olja absorberad på filtren på laboratoriet har också utvecklats ytterligare. I synnerhet har vi nu visat att den andra ultraljudsextraktionen kan ersättas med en så kallad gasextraktion där lösningsmedlet som är kvar på filtret i slutet på den första ultraljudsextraktionen avlägsnas med hjälp av en ström av rent kväve. Olika lösningsmedel kan användas; diklormetan, heptan och pentan har visats kunna kvantitativt extrahera oljan från filtren.

Extraktet analyseras därefter genom gaskromatografi, kopplat till antingen en masspektrometer (MS) eller flamjoniseringsdetektor (FID). I genomsnitt är resultat som erhållits med FID 10 % högre än resultat som erhållits med MS. Kvantifieringen med FID påverkas sannolikt mer av bakgrunden som uppstår på grund av själva filtret. Resultat visar också att utredaren behöver utföra en kritisk visuell kontroll i syfte att detektera eventuell kontaminering av gasen med andra ämnen än de härrörande från kompressoroljan som anges användas på den stationen.

Metoden har validerats och mätosäkerheten har beräknats vara 24 % relativt i intervallet 4 till 45 ppmM och 1 ppmM absolut för intervallet 1 till 4 ppmM.

Några frågeställningar som uppstod under den tidigare studien har varit dels om oljeöverföring påverkas av rådande driftförhållanden vid stationen, dels om oljeöverföring mätt med denna metod på första tankadekubikmetern representerar ett bra medelvärde av vad som händer under en hel tankning.

Att utföra praktiska tester för att avgöra om de rådande driftförhållandena vid stationen påverkar mätning av oljeöverföring är inte en lätt uppgift. Rådande driftförhållanden kan inte lätt kontrolleras. Det skulle kräva att man utför ett antal tester vid olika tider under ett dygn, utvalda efter hur många bilar som nyss har tankat, vilket är praktiskt svårt och provtagaren kan behöva rengöras mellan provtagningarna. All oljan som finns i fordonsgas härrör inte nödvändigtvis från själva stationen. Mängden gas som levereras från gaslagret kontra mängden gas som levereras genom kompressorn varierar beroende på antalet fordon som nyligen har tankats eller tankar.

För att rättvist jämföra resultat från olika stationer, bör proverna om möjligt tas när trycket i gaslagret är högt och när inga fordon har tankats på ett tag (vilande anläggning). Om stationen inte har använts på ett tag, levereras de första kubikmetrarna från gaslagret utan att kompressorn arbetar. När trycket i bilen börjar öka kommer kompressorn att börja arbeta, så att tankningen endast tar en kort stund. Emellertid fylls gaslagret med hjälp av kompressorer. De kan ses som stora bufferttankar där eventuell olja är löst i gasen vid högt tryck. Att ta prover från gaslagret kan antas vara ganska representativt för den oljeöverföring som skulle uppmätas under en hel tankning.

Försök att mäta oljeförekomst före och efter dispensern har utförts vid stationen i Stora Höga, men resultaten av testerna var inte avgörande eftersom möjlig kontaminering med olja inträffade när prover togs före dispensern.

En mätkampanj utfördes därefter vid 16 tankställen, bestående av nio tankstationer (snabb tankning) och 7 bussdepåer (6 med långsam tankning och en med snabb tankning), som använder totalt 7 olika oljor. Vissa av dessa oljor var mineraloljor, vissa syntetiska oljor. Analyser av dessa oljor visar att oljorna har antingen alkylerade naftalener eller polyalfaolefiner som basolja. Bland dessa stationer fanns en bra balans mellan stationer som uppgavss ha problem med oljeförekomst och stationer där oljeförekomst inte ansågs orsaka driftproblem.

Oljeförekomst som uppmätts under kampanjen varierar från några ppmM (mindre än 1 ppmM) till mer än 50 ppmM, med 69 % av resultaten lägre än eller lika med 12 ppmM. Sex stationer uppvisar relativt hög eller mycket hög oljeöverföring. Två mätningar av oljeöverföring överstiger 40 ppmM. Vid en station där överföringen uppmätts vara över 40 ppmM, uppskattas oljeöverföringen vara klart större än uppmätt, eftersom en omfattande kontaminering av provtagaren inträffade. Detta tyder på att oljan kondenserades i provtagarens bufferttank och löste sig i gasen vid nästa provtagningstillfälle. Vid flera stationer hittades i gasen antingen en annan olja än den som angavs användas vid stationen eller föreningar som inte kunde identifieras. Detta visar tydligt att olja/föreningar som finns i fordonsgas inte nödvändigtvis härrör från själva stationen. Vissa observationer tyder på att oljor med alkylerade naftalener är mer benägna att följa med gasen och mer benägna att kondensera som oljedroppar när trycket reduceras än oljor med polyalfaolefiner.

Vid de stationer där oljeöverföringen uppmätts vara hög eller mycket hög fanns inga tecken på att oljefiltreringssystemen inte fungerade korrekt. Följaktligen kan det vara intressant att kontrollera att kompressor(erna) fungerar korrekt. Oljegenskaper kan påverkas av en mängd olika smörjningsproblem:

- Översmörjning: kan orsaka avlagringar i ventiler och orsaka oljeöverföring till gasen.
- Utspädning av oljan med gasen: vissa oljor är mer benägna att spädas ut än andra oljor.
- Termisk nedbrytning av olja: eftersom gastemperaturen ökar med ökande tryck kan oljan, om inte kylning sker, utsättas för höga temperaturer och genomgå nedbrytning. Under de rätta termiska betingelserna kan oljan avge flyktig ånga, bestående av vissa ingående komponenter, eller bilda nedbrytningsprodukter.
Oljeabsorption i gasen: som kan inträffa vid högre arbetstryck (>240 bar)
- Accelererad oxidation på grund av sämre oljekvalitet eller höga temperaturer.

Lämpligt underhåll är avgörande för att minska riskerna för oljeöverföring.

Filtreringssystem och oljeegenskaper nämns ofta som kritiska. I litteraturen återfinns ett antal rekommendationer för att förhindra driftproblem på grund av oljeöverföring:

- Bränslekvalitet ska vara kontrollerad (tillhandahållsvid behov av tredje part)
- Minst minimiantalet koalescensfilter installerade på tankningsstation
- Minst minimiantalet koalescensfilter installerade på fordonet.
- För ansvariga för fordonsflotta: regelbundet underhåll och diagnostik, inklusive rutiner för kontroll av filtren, utfört av kvalificerad personal
- För driftansvariga vid tankstationer eller bussdepåer: personal ska utbildas för drift, diagnostik och underhåll, för att säkerställa systemsäkerhet och systems tillförlitlighet.

Vidare bör man studera några av de stationer där hög oljeöverföring uppmäts för att identifiera vad som kan ha orsakat det. För att kunna göra den analysen, så är det nödvändigt att samla in uppgifter som omfattar gaskvalitet, oljeöverföring, hur kompressorer och filtreringsenheter fungerar (volym olja som dräneras och volym olja som fylls på över en viss period, tidsintervall för oljebyte, oljekvalitet mm) och om oljan har hittats i fordonen som tankar vid dessa stationer (volym dränerad olja i fordon per distans). För en sådan studie bör en rad protokoll utvecklas som täcker in de nödvändiga uppgifterna.

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1. Background

Gaseous fuels including biomethane are one of the accepted alternative fuel in the world today because of their positive environmental impact in terms of carbon footprint and emissions compared to conventional fossil fuels such as gasoline and Diesel. The Roadmap developed under the Green Gas Grids Project, within the framework of Intelligent Energy Europe, indicates that if the necessary actions are taken, the level of biomethane production could reach 18-20 million m³, about 3% of the European natural gas consumption by 2030 and biomethane could provide 10% of the total automotive gaseous fuel consumption [1].

Mid 2013, biomethane is produced in 14 European countries and in over 230 upgrading plants with a total capacity of 0.8 billion m³/year. The biomethane produced is mainly fed into the local natural gas grids and is used for power generation. Grid injection is in practice in 11 European states (Austria, Switzerland, Germany, Denmark, Finland, France, Luxembourg, the Netherlands, Norway, Sweden and the United Kingdom). Vehicles are fuelled with biomethane [1] (either pure or blended with natural gas) in 12 European countries (Austria, Switzerland, Germany, Denmark, Finland, France, Hungary, Island, Italy, the Netherlands and the United Kingdom).

Sweden has long experience of using biogas for transport; biomethane is produced in more than 50 upgrading plants [2]. In 2012, 845 GWh, more than half of the total gas produced, was upgraded to natural gas quality.

To maintain a positive growth in this sector, several conditions must be met simultaneously, including, financial incentives, increased gas accessibility by increasing production, easy access to refuelling stations and vehicles, and minimized disturbances for customers.

One of the main problems causing disturbances is the quality of the gas. The primary sources of contamination are oil carryover from the compressor, moisture and other contaminants such as siloxanes and sulphur compounds (for biogas). One way to control the quality of the gas is to develop standards/specifications containing requirements for the quality. Most biomethane standards developed in European countries [3] consist of specifications for injection into the gas network. Only the Swedish SS 155438:1999, which is currently under revision [4] is for the direct utilization of biomethane as vehicle fuel.

The European initiative to harmonize standards across Europe has led so far to a draft standard (prEN 16723) [5,6], Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network. The application of unified European standards for biomethane quality has a double importance for the industry [1]:

- the standards provide the necessary technical guidance for the companies developing the biogas upgrading technologies (biomethane production),
- the standards strengthen the confidence of the biomethane customers.

The draft consists of two parts:

- Part 1: Specifications for biomethane for injection in the natural gas network
- Part 2: Automotive fuel specifications.

In part 1 [5], the oil carryover from compressors is named as one of the parameters to monitor, but without any proposed limit values. Instead, it states that the gas shall be technically free from compressor oil with the following note "To avoid problems with lubricating oil carryover, oil removal filters shall be installed downstream of equipment". In Annex A regarding parameters, it stated for the compressor oil: "It is a

recommended practice to install two coalescing type filters for oil removal, one just after the oil using equipment, and another one just before the gas storage. The distance between them should be such that the temperature of the gas significantly decreases. When using mineral oil as lubricant, a final adsorption filter (e.g. molecular sieve) should also be installed. To enable the estimation of the oil level in the delivered gas, it is recommended to monitor the oil consumption.”

In part 2 [6], the oil carryover from compressors is named as one of the parameters to monitor also without proposed limit values. However, It states in a note that, “to avoid problems with lubricating oil carryover, oil removal filters shall be installed downstream of equipment that may leak oil. An indicative range is from 1 to 20 mg/m³ as calculated by method of subtraction. Presently, there is no standardized test method available for measuring compressor oil”.

Oil carryover [7] is often 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, for example, from an accurate determination of the gas composition and calculation based on composition using ISO 6976 [8].

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

Oil carryover can also be expressed in mg/m³,

$$\text{Oil carryover in mg/m}^3 = \frac{m_{\text{oil}}(\text{mg})}{V_{\text{gas}}(\text{m}^3)}$$

Recently, as part of the SGC project 290 [9], SP Technical Research Institute of Sweden and Process Control GT developed a sampler and a method to quantify oil carryover from compressors. The method is based on the principle that oil dissolved in the gas at high pressure will condense into droplets when the pressure drastically drops (causing a drop in temperature). The condensed oil is then trapped on a coalescing filter. These filters are already used at many refuelling stations to remove oil in the aerosol state after the compressor. To achieve the required pressure drop, it has been shown that it is necessary to reduce the flow to about 10 Nm³/h, by doing so, , the oil can be quantitatively adsorbed on the first filter. This low flow rate cannot be delivered at the dispenser for safety reasons. Therefore, it is necessary to use a “buffer tank”, in this case a 12.5 liters CNG cylinder.

During the SGC290 project, the following observations were made:

- The oil is only recovered on the first filter, indicating that there is no breakthrough onto the second filter
- The calculation of the volume sampled, using the pressure reading and the volume of the buffer tank, is in good agreement with the volume reading on the dispenser
- The tests performed to evaluate the risk of contamination arising from the previous sampling were not conclusive as a severe oil contamination unfortunately occurred during the first test.
- The method for extracting the oils from the filters at the laboratory is time consuming and requires a large volume of solvent.

The results show the oil carryover measured for the first two Nm³ during a refuelling. When delivering the first two Nm³, the flow and pressure vary because of safety tests performed at the start of the refuelling. Anyway, as it is necessary to reduce the pressure and the flow drastically during the sampling procedure, the conditions (pressure, flow, temperature...) cannot be the same as the conditions during a normal refuelling. The sampling should always be performed under the same conditions.

When using a buffer tank, the risk that the oil condenses to some extent in the CNG cylinder needs to be assessed as this leads to contamination of the cylinder. In which case, the next sample may be contaminated to some extent. The contamination risk is at its greatest when the bottle is emptied between two samplings. For this reason, it is necessary to evaluate the need to flush the bottle with nitrogen between two samplings.

A number of issues need to be studied further, for example:

- Improving the method for recovering the oil at the laboratory
- Comparing different detectors for measuring the oil carryover (FID vs MS)
- Validating the method
- Assessing the risk of contamination from previous samples and the need to flush the buffer tank between samples

Answering the following questions:

- Is the amount of oil measured using this methodology (on the first two Nm³) a good average/evaluation of what happens during a refuelling?
- Is the measurement of oil carryover affected by the prevailing operating conditions at the station such as the number of vehicles that have recently fuelled or the gas level in the gas storage?
- Are some oils more likely than others to be entrained in the gas?

The first three points require further developments of the method proposed during the previous project [9]. Once the method has been developed further and validated, the next step should be to perform a series of measurements covering stations where oil carryover from compressors have been pointed out as being a source of operational problems as well as stations where no disturbances attributed to oil carryover has been reported. This step should help in the discussion with the partners involved from both gas and automotive industry regarding the acceptable range of oil carryover to ensure the efficient functioning of vehicles. The measurements should also contribute to answering the questions mentioned above.

2. Experimental/Metodbeskrivning

2.1 IMPROVEMENT OF THE ANALYTICAL METHOD

During SGC project 290 [9], the following procedure was used to extract the oil absorbed on the coalescing filters:

The coalescing filter was introduced into a 500 ml-measuring cylinder which was subsequently filled with dichloromethane covering the whole filter. The oil was extracted in an ultrasonic bath during 30 minutes. The filter was then turned in the measuring cylinder and was subjected to another 30-minute extraction in the ultrasonic bath.

Two extractions in series were performed. The two fractions were then mixed into a round bottom flask. The extract was then concentrated using a rotary evaporator until the volume reached 10 to 20 ml, which was then analysed by GC/MS. A final extraction (fraction 3) was also performed during the early stages of the procedure development which showed that the oil was quantitatively extracted in fractions 1+2, indicating that the third extraction was not necessary to perform.

Since two extractions are needed, the procedure requires a large volume of solvent. The procedure is also time-consuming mainly because of the large volume of solvent to evaporate. In order to improve the analytical methods, some tests have been performed. All of the tests were performed by spiking coalescing filters with 20 mg of Rarus 1025 oil. The following parameters were tested:

- Using different solvents: heptane, pentane, dichloromethane:heptane (1:1 v:v)
- Extending the time of the ultrasonic extraction to avoid the second extraction
- Using a flow of nitrogen to remove the dichloromethane remaining on the filters after the first extraction to avoid the second extraction

The results show that dichloromethane can be replaced by other solvents. For each solvent, two tests were run. The extraction was found to be a recovery yield of 95% with dichloromethane, 103% with a mixture of dichloromethane and heptane (1:1, V/V), 98% with heptane and 86% with pentane. The evaporation time is much longer when using heptane and shorter with pentane.

At the end of the first extraction, some solvent remains absorbed on the filter (approximately 50 ml of the 300 ml introduced into the measuring cylinder), some of the oil to be recovered is probably dissolved in this volume. To recover this oil, a second extraction has been performed up to now. Performing this second extraction is not only time consuming but also requires the use of a large volume of solvent. Another way to recover the oil dissolved in the solvent remaining on the filter is to drain the solvent from the filter under a stream of pure nitrogen in a closed environment (for example inside a filter housing that has a drain in the bottom).

The results of the tests, comparing performing a second extraction and removing the absorbed solvent from the filter, are presented in the Tables 1 and 2:

Table 1: Comparison of different extraction methods to recover the oil remaining on the filter at the end of extraction 1 with dichloromethane as solvent

Tests	Extraction	Method	Recovery Extr. 1 (%)	Recovery Extr. 2 (%)	Recovery Extr. 3 (%)	Recovery [%]
CH ₂ Cl ₂	Extraction 1	Ultrasonic 2x30 min	80			101
	Extraction 2	Ultrasonic 1x30 min		21		
CH ₂ Cl ₂	Extraction 1	Ultrasonic 2x30 min	68			86
	Extraction 2	Ultrasonic 1x30 min		19		
CH ₂ Cl ₂	Extraction 1	Ultrasonic 2x30 min	69			88
	Extraction 2	Gas extraction		19		
CH ₂ Cl ₂	Extraction 1	Ultrasonic 2x30 min	69			90
	Extraction 2	Gas extraction		21		

Table 2: Comparison of different extraction methods to recover the oil remaining on the filter at the end of extraction 1 with pentane as solvent

Tests	Extraction	Method	Recovery Extr. 1 (%)	Recovery Extr. 2 (%)	Recovery [%]
Pentane	Extraction 1	Ultrasonic 2x30 min	67		89
	Extraction 2	Ultrasonic 1x30 min		22	
Pentane	Extraction 1	Ultrasonic 2x30 min	68		86
	Extraction 2	Ultrasonic 1x30 min		18	
Pentane	Extraction 1	Ultrasonic 2x30 min	74		88
	Extraction 2	Gas extraction		14	
pentane	Extraction 1	Ultrasonic 2x30 min	70		85
	Extraction 2	Gas extraction		15	

The preferred extraction method with regard to time and solvent consumption consisted of an ultrasonic extraction followed by the removal of the remaining solvent under a stream of nitrogen.

2.2 STATIONS VISITED AND THE PROPERTIES OF OILS IN THIS STUDY

Oil carryover was measured at 16 stations as part of this study.

There are two main types of stations:

- The fast-fill stations which are suitable for situations where light-duty vehicles arrive randomly and need to fill up quickly. CNG/biomethane at fast-fill stations is often stored in vessels at a high service pressure, so it can deliver fuel to a vehicle faster than fuel that comes directly from the compressor, which delivers fuel at a lower volume flow. Nine fast-fill stations were visited in this study.
- Time-fill stations which are primarily used by fleets of vehicles with large tanks that refuel at a central location at night. Unlike fast-fill stations, vehicles at time-fill stations are generally filled directly from the compressor. Seven time-fill stations were visited as part of this study.

The oils contain a base-oil (synthetic or mineral) and additives (incl. rust inhibitor, anti-oxidant and anti-foam agent). Some results suggest that some of the synthetic oils are formulated with alkylated naphthalenes (AN) as base stocks and/or polyalphaolefins (PAO).

The performance of alkylated naphthalenes has been studied by Hourani *et al.* [10] who concluded that they exhibit outstanding thermo-oxidative stability, have low volatility and excellent thermal stability.

Some of the properties (type of oil, viscosity, viscosity index, gravity) of the oil used are given in Table 3; these data have been taken from the product description or data sheet published by the oil producer online. One of the most important properties of motor oil for maintaining a lubricating film between moving parts (and consequently, reducing wear on moving parts) is its viscosity. The viscosity of a liquid can be thought of as its "thickness" or a measure of its resistance to flow. The viscosity must be high enough to maintain a lubricating film, but low enough for the oil to flow around the engine parts under all conditions. The viscosity index is a measure of how much the oil's viscosity changes as the temperature changes. A higher viscosity index indicates that the viscosity changes less with temperature than with a lower viscosity index. Small changes in viscosity can be magnified at operating temperatures to such an extent that an oil is no longer able to provide adequate lubrication [11].

Table 3: Properties of the oils used at the tested stations

Oils	Units	Rarus 1025	Rarus 427	Pegasus 1	424	629	630	Q8 Schuman 32
Stations		7 stations incl. 2 with another oil	3 stations incl. 1 with another oil	4 incl. 3 stations with another oil	1	1	1	2
Type of oil		synthetic	mineral	synthetic	mineral	synthetic	synthetic	synthetic
Viscosity	cSt* vid 40C cSt vid 100C	44 7.2	104.6 11.6	93.8 13.05	147.3 14.7	150 18.4	220 25.8	32 5.95
Viscosity index		131	100	137	105	144	152	133
Gravity	g/m ³ vid 15C:	0.85	0.88	0.85	0.87	0.86	0.87	0.83

* cSt: centistokes= mm².s⁻¹

The series of measurement was made during the period May 2014 to October 2014 at 16 refuelling stations. The sampler used for these measurements was the one developed during SGC project 290 [9], with some modifications.

The sampler developed under the previous project consisted of a NGV1 connection, 1/2" tubing, a manometer, 3 ball valves (Oasis Engineering ltd), a 12.5 litre composite CNG bottle, and two EU37/25 filter housings (with 100/25BX filter) connected in series downstream a spray nozzle of 0.3 mm diameter hole. The coalescing filters used are Parker (Balston 100-25-BX) [12] filters made of borosilicate glass microfibers with fluorocarbon resin binders.

The sampler is connected to the dispenser via the NGV1 connection. Refuelling is started and stopped manually (if necessary) when the pressure in the bottle has reached at least 180 bar (which corresponds to between 2-2.5 Nm³ sampled gas). The sampler is then disconnected from the dispenser and put aside.

The gas is released through the chimney by opening a ball valve until the pressure in the bottle reaches 180 bar (this pressure has been chosen as it can supposedly be achieved at all stations even those 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 first passes through the hole of the nozzle, the pressure drops resulting in a temperature drop and the oil is trapped on the filter.

The sampling is stopped when the pressure in the bottle reaches 100 bar (equivalent to 1 Nm³ sampled). At least three samples are taken from each station. At the beginning of the test, the buffer bottle is empty. Consequently, the first refuelling is performed from 0 to 180 bar while the other refuelling tests are performed from 100 to 180 bar. In order to have three replicates taken under the same conditions, it was decided to discard the first sample.

During project SGC290, a significant contamination of the sampler occurred at a station where there were disturbances involving the filtration devices (coalescing filters) installed after the compressor. The coalescing filters at this station were overcharged with oil at the time of the test. As a consequence, the oil in the form of droplets was carried over with the gas leading to extensive contamination of the

sampler. This contamination affected the following samples collected since a high amount of the oil used at the station where the contamination occurred was found in the samples taken at the stations tested subsequently. Clearly, a significant quantity of oil had deposited in the buffer tank. The sampler as it was at the time, could not be cleaned easily and two parts of the sampler were identified to be critical for oil deposition in the event of contamination: the buffer bottle and the spray nozzle.

Consequently, a union-tee has been added to the sampler just before the spray nozzle so it can be cleaned of oil by using a solvent.

A special device has also been constructed to flush the buffer bottle between samples. The device consists of a NGV1 nozzle, a filling line and a DIN 477 connector on the other side of the line which can be connected to a bottle of nitrogen allowing the sampler to be flushed with nitrogen. The device also has a valve mounted near the DIN 477 connector to release the pressure in the line after refuelling of the buffer tank has been completed. Using a bottle of nitrogen filled to 250 bar allows the sampler's buffer tank to be filled with 80-100 bar of nitrogen. A sample of nitrogen can be taken in order to determine whether oil from a previous sample is present in the buffer tank.



Figure 1: Modified sampler with a union-tee-connection to rinse the spray nozzle (top) and device to flush the buffer-tank with nitrogen (bottom)

2.3 COMPARISON MS VERSUS FID

Eight samples of oils collected at refuelling stations were analyzed simultaneously by GC/MS and by GC/FID for comparison. The identification methodology included a visual comparison of the chromatograms, and the quantitative comparison of the GC-FID and GC-MS results.

When quantifying with a MS, some ions characteristic for a specific oil were extracted and the peak corresponding to these ions was integrated as a measure of the concentration of the oil in the sample. For oils with AN, the targeted ion was m/z 155 (see figure 2), which gave rise to two distinct peaks and for oils with PAO, the targeted

ion was m/z 57 which gave rise to a “platform” due to the large numbers of co-eluting compounds.

When quantifying with a FID, the peak integration was done in fixed time interval, rather than on individual peaks for both types of oils. The time interval was defined from the chromatograms of the standard solutions (see Figure 3).

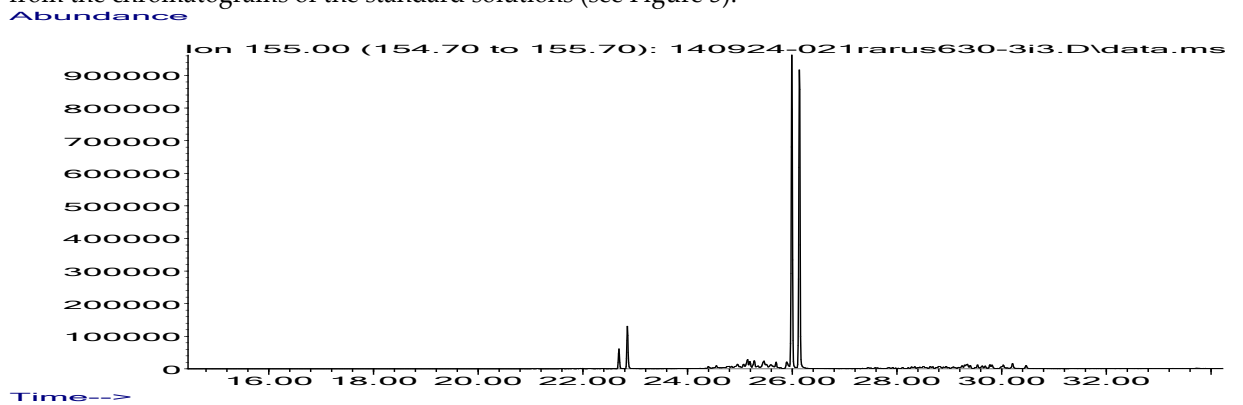


Figure 2: ion m/z 155 in oils with AN as base stock

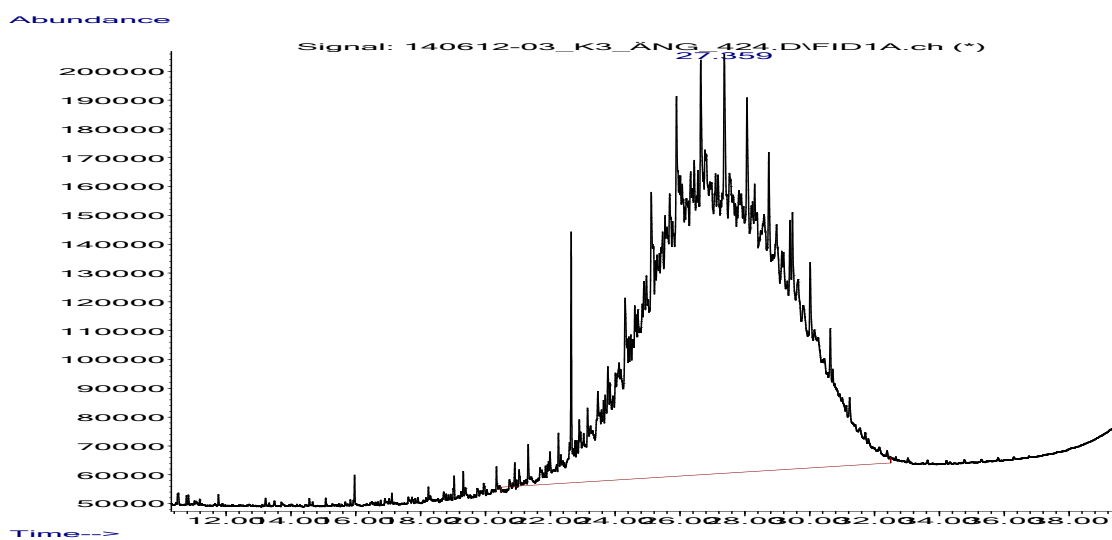


Figure 3: FID signal for oils with PAO as base stock, the signal is integrated from 20 min. to 32 min.

The results, presented in Figure 4, show a good correlation between the results obtained using these two detectors except for one sample that is clearly an outlier.

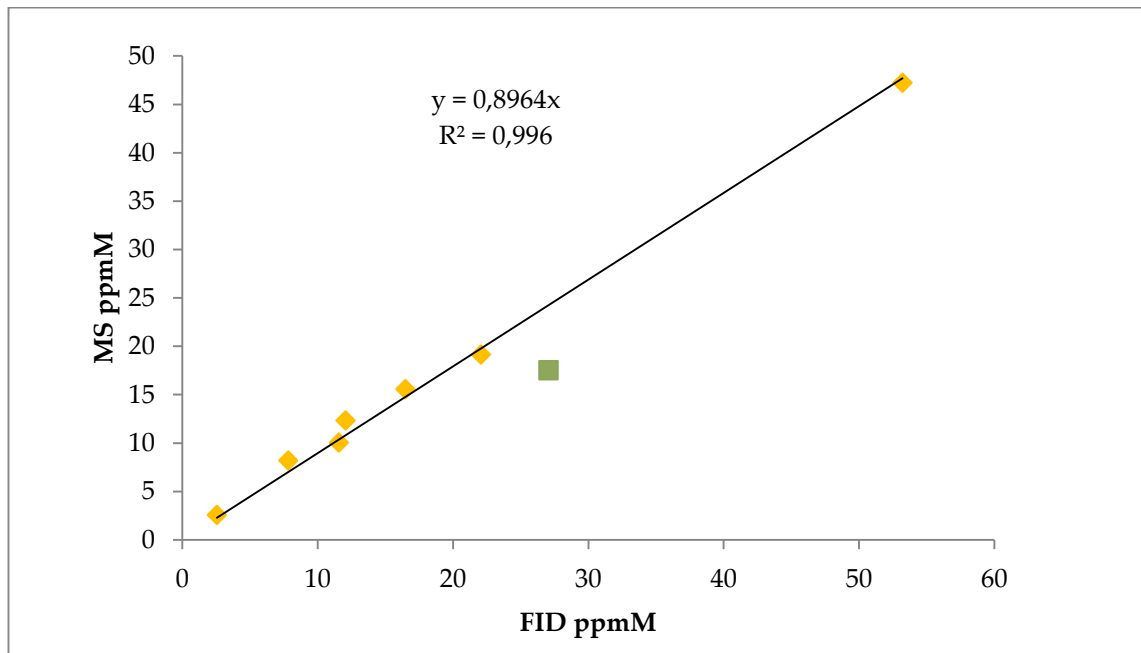


Figure 4: Correlation between the results obtained with FID and results obtained with MS, the green point identified as an outlier

On average, the results obtained with the FID are 10% higher than the results obtained with the MS. Typically, the GC-MS is regarded as an improvement in resolution when compared to GC-FID; the method provides greater selectivity and sensitivity compared to GC-FID. The quantification with FID is more likely to be influenced by the background associated with the filter. Indeed, when the analytical procedure was applied to unused filters, the chromatogram obtained exhibited some peaks eluting at the same time as the target oil. Moreover, the GC-MS method provides the capability to confirm compounds based on both retention time and additional spectral data, as well as an enhanced ability to separate coeluting peaks based on unique ions [13]. The chromatograms from the GC-FID and GC-MS analyses were compared visually for the presence or absence of any compounds. The GC-FID and GC-MS chromatograms for all of the samples were quite similar except for one sample that was distinctly different (the sample is “the outlier” in Figure 4). At one of the stations tested, peaks which did not correspond to the compounds of the target compressor oil eluted at the same time as the target oil. The results from the MS thus gave information on the carryover of the target compressor oil while the results from the FID gave information about the total contamination of the gas (at least regarding compounds eluting in the same time interval). Using GC-FID as the sole detector to measure the carryover of the targeted compressor oil in this particular case, will give rise to erroneous conclusions (overestimation) regarding the evaluation of the carryover due to the oil used at the station and will not permit the detection of another oil or other contaminants in the gas, contamination that probably occurred upstream the compressor. These results also suggest that the investigator needs to perform a critical visual control in order to be able to detect any contamination of the gas by compounds other than the compressor oil.

2.4 VALIDATION OF THE METHOD

The objective of validating [14] an analytical procedure is to demonstrate that it is suitable for its intended purpose. The objective of the analytical procedure governs the validation characteristics that need to be evaluated. Typical validation characteristics, which should be considered are listed below: accuracy, precision (repeatability, intermediate precision and reproducibility), quantification limit, linearity and range. Also, the robustness of the procedure should be considered at an appropriate stage in the development of the analytical procedure

ACCURACY

The accuracy [14] of an analytical procedure expresses the closeness of agreement between the value that is accepted either as a conventional true value or an accepted reference value and the value found. Since the procedure developed for the measurement of oil carryover is a defined sampling procedure, the quantity measured is the true amount. Only the recovery of the oil from the filter needs to be tested. As discussed in the section 2.1 "Improvement of the analytical method", the recovery of the oil has been found to be acceptable.

PRECISION

The precision of an analytical procedure expresses how close the agreement is between a series of measurements obtained from multiple sampling of the same sample. Precision may be considered at three levels: repeatability (under the same operating conditions over a short interval of time.), intermediate precision (within-laboratories variations: different days, different analysts, different equipment, etc.) and reproducibility (between laboratories). In this case, the intermediate precision was estimated not to be larger than the repeatability. The reproducibility cannot be estimated due to the absence of other laboratories performing the procedure.

The repeatability was determined by multiple testing of the each sample taken at different stations. Two to four tests per sample were performed. Results are shown in Table 4:

Table 4: Multiple results obtained at 19 stations (including this study and the previous study [9]) together with average, standard deviations (Sd) and coefficient of variation (CV%)

Stations	P1	P2	P3	P4	Average	Sd	CV%
1		0.5	0.4	0.3	0.4	0.1	25.0
2		0.4	0.4	0.3	0.4	0.1	15.7
3	0.7	0.4	0.3	0.4	0.5	0.2	38.5
4	2.0	2.4		2.1	2.2	0.2	10.6
5			3.2	2.3	2.8	0.6	23.1
6		3.1	3	2.6	2.9	0.3	9.1
7	4.5	4.5	3.5		4.2	0.6	13.9
8	5.8	4.4	6.6		5.6	1.1	19.9
9		6.8	6.2	8.3	7.1	1.1	15.2
10	11.7	8.4			10.1	2.3	23.2
11	13.1	10.2			11.6	2.0	17.6
12			11.4	12.3	11.8	0.6	5.1
13	10.4	10.4	14.7	13.8	12.3	2.3	18.3
14		13.4	13.4	14.8	13.9	0.8	5.8
15	14.9	16.8	18.8	19.6	17.5	2.1	12.0
16			22.5	25.3	23.9	2.0	8.3
17	25.0	24.7	18.9		22.9	3.5	15.1
18			21.7	18.7	20.2	2.1	10.3
19	40.8		43.1	49	44.3	4.2	9.5

From these results, the repeatability is estimated to be 9% relative uncertainty, when measuring oil carryover above 4 ppmM and 0.4 ppmM absolute uncertainty, when measuring oil carryover below 4 ppmM. The data used here have been obtained with a mass spectrometer.

LIMIT OF QUANTIFICATION

The limit of quantification (LOQ) of an analytical procedure is the lowest amount of analyte in a sample that can be quantitatively determined with suitable precision and accuracy. In this project, the LOQ for oil carryover has been expressed as 6 times the standard deviation for the estimation of repeatability at low level. The limit of quantification is estimated to be 1 ppmM.

LINEARITY AND RANGE

The linearity of an analytical procedure is its ability (within a given range) to obtain test results that are directly proportional to the concentration of analyte in the sample.

To determine the linearity, known amounts of the different targeted oils were injected at 6 levels between 0.5 mg (which corresponds to about 1 ppmM oil carryover with the normal conditions for the testing) to 40 mg (which corresponds to about 50 ppmM oil carryover at the normal conditions for the testing). For each level, a weighed amount was dissolved in an appropriate solvent. The response of the detector (FID or MS) shows good linearity in the range 0.5-40 mg (1-50 ppmM).

The range of an analytical procedure is the interval between the upper and lower concentration of analyte in the sample for which it has been demonstrated that the analytical procedure has a suitable level of precision, accuracy and linearity.

It has been observed when oil carryover exceeds 45-50 ppmM, contamination of the sampler may occur (oil may condense in the buffer tank which leads to an underestimation of the oil carryover and a risk for contamination of the next sample). As a consequence, the range of the analytical method is estimated to be from 1 to 45 ppmM.

ROBUSTNESS

The robustness of an analytical procedure is a measure of its capacity to remain unaffected by variations in method parameters and provides an indication of its reliability.

In this case, as there is a choice of peaks to be integrated or fixed time interval to integrate, two different operators may take different decisions which may lead to slightly different estimates of the oil carryover.

Moreover, it has been demonstrated that some memory effects can occur in the sampling device. Even if the sampler has been flushed between taking two samples, some ppmM of oil originating from the station tested just prior to the current station has been found in the samples (more or less depending on the oil, estimated to be <1 to 3 ppmM). The operator needs to decide how to deal with memory effects which may again lead to slightly different reported results.

MEASUREMENT UNCERTAINTIES

The measurement uncertainty has been estimated by combining the various sources of uncertainty described above (repeatability, memory effects and influence of operators on integration) into a single value. Measurement uncertainty [15] is expressed as U, total expanded uncertainty with a coverage factor $k = 2$ which means that the confidence level is about 95%.

The measurement uncertainties are thus estimated to be 24% relative uncertainty for the range 4- 45 ppmM and 1 ppmM absolute uncertainty for the range 1-4 ppmM.

3. Results and discussion

Some questions arising from the previous study [9] need to be discussed and some answers are presented below:

Is the measurement of oil carryover affected by the prevailing operating conditions at the station such as the number of vehicles that have recently fuelled or the gas level in the gas storage ...)?

Performing practical tests to determine whether the prevailing operating conditions at the station affect the measurement of oil carryover is not an easy task. The prevailing conditions are not foreseeable and cannot easily be controlled. The prevailing conditions may affect stations with oil carryover problems and stations without oil carryover problem in different ways. It would require the carrying out of several tests during a single day, which is difficult in practice as the sampler may need to be cleaned between samples, otherwise, the results from the earlier tests may affect the results of the subsequent tests.

Some other considerations must be taken into account. The gas at a fast-fill station can be delivered:

- Directly from the compressor(s)
- From the pre-pressurized vessels
- From a mobile gas storage unit through the compressor or from a pre-pressurized vessel

Oil found in the CNG/biomethane may not originate from the station itself: there are two types of refuelling stations for cars, the mother station; the gas delivered to these stations is from a local or national gas network) and the daughter station; the gas delivered to daughter stations is stored in mobile gas storage vessels. These are filled at a biogas plant where biogas is upgraded to biomethane or at a mother station. In the last case, the gas in the mobile gas storage vessels may contain some oil that is used in compressors in another location.

The amount of gas delivered from the pre-pressurized vessels contra the amount of gas delivered through the compressor depends on the number of vehicles that have recently refuelled or are currently refuelling.

Among the participants who consider that they experience problems due to oil carryover, almost all indicated that they experienced continuous problems with oil, only one answer indicated that the station experienced intermittent problems.

In the station where oil problems were experienced intermittently, three samples were taken at approximately one-week intervals. The results were similar in all three samples. Consequently, no variations of oil carryover with time could be shown.

In order to compare results from different stations fairly, the samples should be taken if possible when the pressure in the vessel storage vessels is high and no vehicle has refuelled for a while.

Is the amount of oil measured with this methodology (on the first Nm³) a good average/evaluation of what happens during a complete refuelling event?

If the station has not been used for a while (no vehicle has refuelled), the first Nm³ at the dispenser will be delivered from the pre-pressurized storage vessels and will be delivered without the compressor working. When the pressure in the car starts increasing the compressor will work to deliver the pressure to ensure that the refuelling only takes a short period of time. However, the pre-pressurized vessels are filled using the compressors. So they can be considered to be large volume buffer tanks where the oil, if present, is dissolved in the gas since the pressure is high. So taking samples from these pre-pressurized vessels is assumed to be reasonably representative of the average oil carryover.

At the station located in Stora Höga, a filling line with a NGV1 connection at the end has been installed upstream the compressor for research purposes. This is a prerequisite to perform tests prior to the dispenser. Tests have been carried out to measure the oil carryover before and after the dispenser in order to evaluate whether the oil carryover measured in the first Nm³s delivered at the dispenser are comparable to the average oil carryover. On the same day, samples were taken after the dispenser and, using the aforementioned tubing, before the dispenser. The oil carryover after the dispenser was evaluated to be 10 ppmM (average of three measurements: 11.2, 8.4, 10.4) while the oil carryover before the dispenser was found to be 55 (sample 1), 55 (sample 2) resp. 23 ppmM (sample 3), considerably higher than the oil carryover measured after the dispenser. One possible explanation for this large discrepancy is that some oil may have deposited inside the filling line (since it is not often used). The filling line should have been flushed with gas for some time before taking the samples.

3.1 RESULTS FROM THE SERIES OF MEASUREMENT

The results obtained from the series of measurements are presented in Figures 5 and 6.

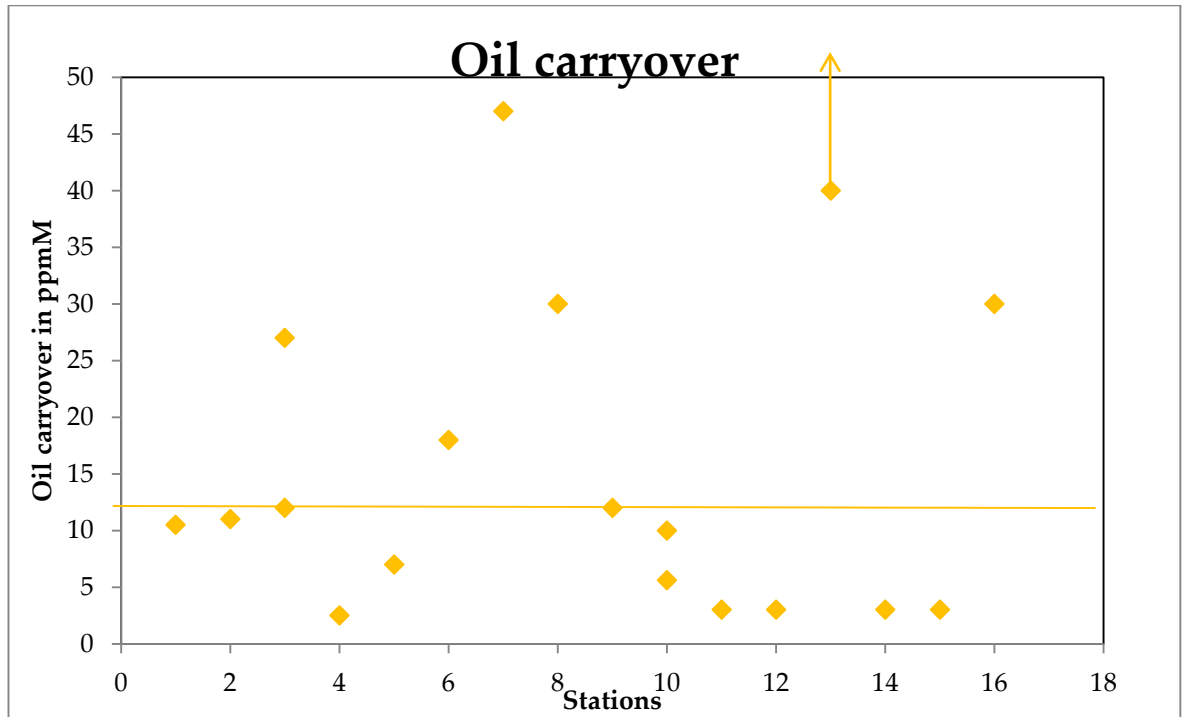


Figure 5: results of oil carryover in ppmM at 16 tested stations

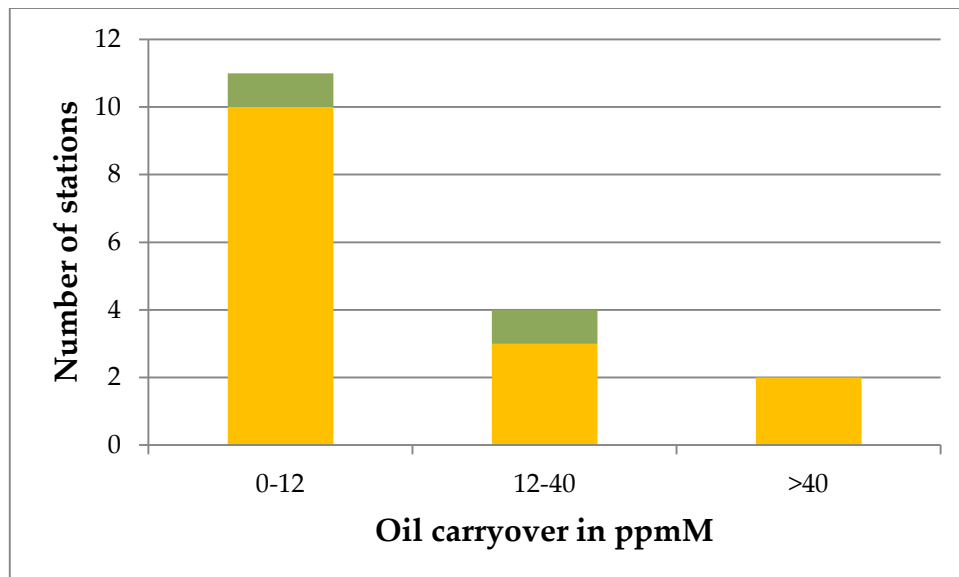


Figure 6: Results of oil carryover in ppmM grouped in different intervals (0-12 ppmM, 12-40 ppmM and >40 ppmM)

In green: a station where contamination by compounds other than the oil used at the station was found. The two green areas thus represent the same station; the oil carryover from the oil used at the station was determined to be 12 ppmM, while the total oil carryover, including the one from unknown compounds, push up the total oil carryover to 27 ppmM.

Oil carryover measured during the measurements ranges from a few ppmM (less than 1) to more than 50 ppmM, with 69% of the results being less than or equal to 12 ppmM. Two measurements stand out with an oil carryover exceeding 40 ppmM.

Six stations exhibit relatively high or very high oil carryover. Moreover, at one of the stations where the oil carryover was found to be 12 ppmM or less, it was observed that the gas was contaminated by other compounds, (see Figure 7). The compounds presenting ion m/z 91,129,207 (see Figure 8) in their mass spectra could not be identified by using a mass spectra library. At the same station, lighter contaminants were also found in the gas (styrene, trimethylbenzenes, tetramethylbenzenes, C12-alkanes...).

At one station, the oil carryover was so high that the sampler was severely contaminated by the oil even after flushing the buffer tank with nitrogen several times.

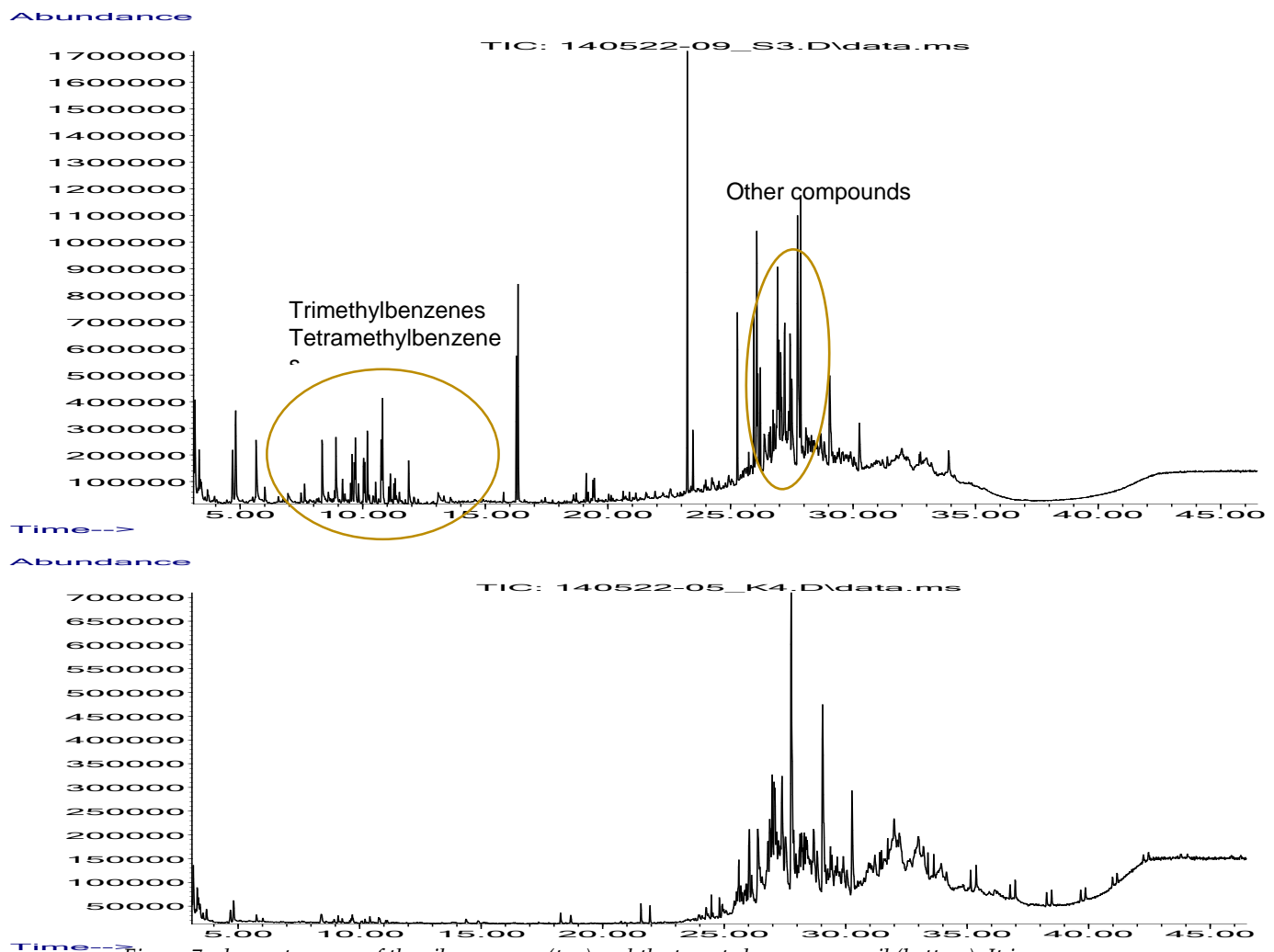


Figure 7: chromatograms of the oil carryover (top) and the targeted compressor oil (bottom). It is clear that some oil is present in the gas but at the same elution time, a group of other compounds can be seen.

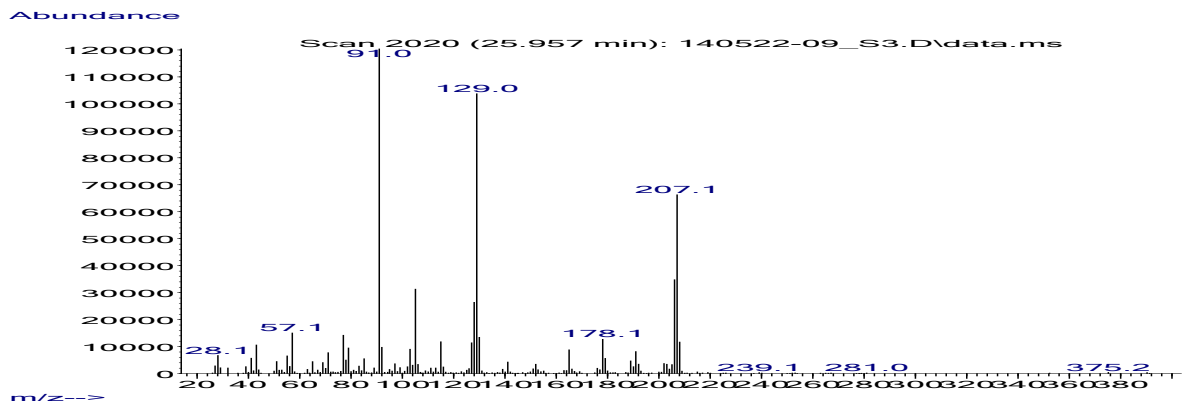


Figure 8: Mass spectrum of one of the unknown compounds found at a station where the gas was contaminated by other compounds than the target compressor oil.

At the stations where oil carryover was found to be high or very high, no evidence was found suggesting that the oil filtration system was not functioning properly. Consequently, it may be interesting to check that the compressor(s) is/are working properly. This has not been done during the course of this study.

Adequate maintenance is also crucial in order to decrease the risks for oil carryover. Filtration and oil properties are often mentioned as critical. The choice of a compressor lubricant depends on the type and construction of the compressor, the gas being compressed, the degree of compression and the final outlet temperature. The lubrication system (lubricator pump, filtration etc) in a compressor has to be designed and maintained properly since poor design will cause operational and maintenance problems. Oil coolers should work properly to maintain a correct operating temperature.

3.2 FILTRATION

Several recommendations can be found in the literature regarding the number of coalescing filters that need to be installed, their location and the maintenance of the filtration system. For example, in the draft prEN 16723 [5,6], the recommended practice is to install two coalescing type filters for oil removal, one just after the oil using equipment, and another one just before the gas storage. The distance between them should be such that the temperature of the gas significantly decreases. When using mineral oil as lubricant, a final adsorption filter (e.g. molecular sieve) should also be installed.

In the same way, the natural gas vehicle institute (NGVi) [16] states that a refuelling station should have no less than two coalescing filters between the discharge from the compressor and the inlet to the high-pressure storage system. These filters should be located as close to the storage unit as possible because this gives the gas more time to cool and for the oil to drop out and be captured in the filter element. The filters should be inspected and drained periodically. If upon inspection there is oil in the coalescing filter bowl, the filters should be drained daily until there is no more oil.

3.3 OIL PROPERTY

Oil property may be affected by a variety of lubrication problems:

- Over-lubrication: can cause deposits in valves and gas passages and lead to carryover into the gas stream.
- Dilution of the oil by the process gas: Some oils are more prone to dilution than other oils. Higher discharge gas pressure will cause greater oil dilution; higher discharge gas temperature will cause less oil dilution.
- Thermal degradation of oil: Because the gas temperature increases with increasing pressure, if the heat is not removed, the lubricant may be exposed to high temperatures and decompose. Under the right thermal conditions lubricating oil may give off a volatile vapor from one of its original constituent components or form new pyrolytic vapour degradation products
- Lubricant absorption into the gas stream: usually occurs at higher operating pressures (>240 bar)
- Accelerated oxidation due to poor oil quality or high temperatures

Adequate maintenance of the vehicle is also mentioned as one of the ways to prevent oil carryover problems [15].

NGVi give 5 recommendations in total to prevent oil carryover:

- Fuel quality shall be contracted if provided by a third party
- At least the minimum number of coalescing filters at the refuelling station
- At least the minimum number of coalescing filters on the vehicle
- Comprehensive maintenance practices, including routine filter inspection for vehicles for CNG vehicle operators/maintenance
- Specific training for the refuelling equipment at the station including operation, diagnostic and maintenance practices to ensure clean fuel, system safety and reliability

Are some oils more likely than others to be entrained in the gas?

Among the four stations where oil carryover was high, only one uses two types of oil (one accounting for 20 ppmM of the total oil carryover and one accounting for 10 ppmM of the total oil carryover). Three other stations use two types of oil. The oil carryover at these stations was found to be less than 12 ppmM. Consequently, using several oils does not seem to increase the risks of oil carryover.

The three other stations where oil carryover was found to be high use compressor oils with the same type of base stock (suggested in this case to be alkylated naphthalenes, AN). However, other stations using the same type of oil have low oil carryover suggesting that the station (design or maintenance) has an essential role in oil carryover.

The contamination of a sample by the previous sample was evaluated to be 3-5 ppmM at stations using compressor oil with AN as the base stock while the contamination from other types of oil (those with polyalphaolefins, PAO, as base stock) was found to be much less (maximum 1-2 ppmM) even when the oil carryover at the station was relatively high.

These observations indicate that oils formulated with AN have a tendency to condense in the buffer tank (probably while emptying the buffer tank at the end of the sampling process) and dissolve in the gas when then next sample is taken.

Consequently, these two observations suggest that oils formulated with AN are more likely to follow along with the gas, and more likely to condense as oil droplets when the pressure is reduced, than oils formulated with PAO.

4. Conclusions

In this project, we have further developed a method measuring oil carryover from compressors at NGV refuelling stations. The sampler has a CNG bottle of 12.5-litre which is used as a buffer tank. The sampler also includes two filter housings each containing a coalescing filter and the appropriate spray nozzle positioned before the two filter housings. Once the bottle has been filled with at least 180 bar, the sampler is taken aside and typically 80 bar (corresponding to 1 Nm³) of the gas in the bottle is transferred onto the filters. A minimum of three samples are taken for each station.

The sampler developed during the previous project "Development and validation of methods for test of CNG quality inclusive of oil carryover" has been modified slightly so it can now be cleaned between taking two samples.

The procedure for extracting the oil absorbed on the filters at the laboratory has also been developed further. In particular, we have now shown that the second ultrasonic extraction can be replaced by a gas extraction where the solvent remaining on the filter at the end of the first ultrasonic extraction is removed by a stream of pure nitrogen. Different solvents can be used: dichloromethane, heptane, pentane have all been proven to extract oil quantitatively from the filters.

The extract is then analysed by gas chromatography coupled to either a mass spectrometer or flame ionization detector. On average, the results obtained with the FID are 10% higher than the results obtained with the MS. The quantification with FID is more likely to be influenced by the background due to the filter or the instrument. These results also suggest that the investigator needs to perform a careful visual control in order to be able to detect any contamination of the gas by compounds other than the compressor oil.

The method has been validated and the measurement uncertainties have been estimated to 24% relative uncertainty in the range of 4- 45 ppmM and 1 ppmM absolute uncertainty in the range of 1-4 ppmM.

Some questions that arose in the previous study have to be discussed and some answers have been presented regarding whether the measurement of the oil carryover is affected by the prevailing operating conditions at the station and if the amount of oil measured with this methodology on the first Nm³, represents a good average/evaluation of what happens during a full refuelling.

Performing practical tests to determine whether the prevailing operating conditions at the station affect the measurement of oil carryover is not an easy task. It would require carrying out several tests during a single day, which is challenging practically as the sampler might need to be cleaned between samples. Oil found in the CNG/biomethane may not originate from the station itself. The amount of gas delivered from the pre-pressurized vessels contra the amount of gas delivered through the compressor varies depending on the number of vehicles that have recently refuelled or are currently refuelling.

In order to compare results from different stations fairly, the samples should be taken if possible when the pressure in the vessel storage vessels is high and no vehicle has refuelled for a while.

If the station has not been used for a while (no car has refuelled), then the first Nm³ at the dispenser are delivered from the pre-pressurized storage vessels and will be delivered without the compressor working. When the pressure in the car starts increasing the compressor will work to deliver the pressure so the refuelling only takes a short time. However, the pre-pressurized vessels are filled using the compressors. So they can be considered to be large volume buffer tanks where the oil, if present, is dissolved in the gas since the pressure is high. For this reason, taking samples from

these pre-pressurized vessels is assumed to be reasonably representative of the average oil carryover.

Oil carryover has been measured at the station of Stora Höga before and after the dispenser but the results of the tests were not conclusive as there was a possible contamination with oil when taking the samples upstream the dispenser.

A series of measurements was then made at 16 refuelling stations. The oil carryover measured during the series of measurements ranged from a few ppmM (less than 1) to more than 50 ppmM with 69% of results being less or equal to 12 ppmM. Six stations exhibit relatively high or very high oil carryover. Two measurements stand out, in particular, with oil carryover exceeding 40 ppmM. At one of these stations, the oil carryover was clearly higher than measured as there was an extensive contamination of the sampler. At several stations, either another oil than the one claimed to be used at the station, or compounds that could not be identified, were found in the gas, clearly showing that the oil/compounds found in the CNG/biomethane may not always originate from the station itself.

At the stations where oil carryover was found to be high or very high, no evidence was found suggesting that the oil filtration system was not functioning properly. Consequently, it may be interesting to check that the compressor(s) is/are working properly.

Adequate maintenance is crucial in order to decrease the risks of oil carryover. Filtration and oil properties are often mentioned as critical.

Some observations suggest that oils formulated with alkylated naphthalenes are more likely to be entrained in the gas and more likely to condense as oil droplets when the pressure is reduced than oils formulated with polyalphaolefins.

It would be interesting to study some of the stations where high oil carryover was measured further, in order to identify what may be causing the elevated levels of oil carryover. For this, it will be necessary to have a proper set of data evaluating the gas quality, the oil carryover, how the compressors and the filtering devices are working (volume of oil drained, volume of oil filled, interval of oil change, oil quality) and whether oil is found in the vehicles refuelling at these stations (volume of oil collected in the vehicles per distance covered). This study would require the development of a series of protocols to be followed and filled in, in order to collect the necessary data.

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6. Literature

- [1] Proposal for a European Biomethane Roadmap, http://european-biogas.eu/wp-content/uploads/2014/02/GGG_European-Biomethane-Roadmap-final.pdf, dec. 2013
- [2] Biogasportalen, section "Svenska Anläggningar" (Swedish biogas plants), <http://www.biogasportalen.se/>
- [3] Marcogaz report "Injection of gases from non-conventional sources into gas networks", 2006, ([http://www.marcogaz.org/membernet/show.asp?wat=WG-Biogas-06-18_D497_Final Recommendation.pdf](http://www.marcogaz.org/membernet/show.asp?wat=WG-Biogas-06-18_D497_Final%20Recommendation.pdf))
- [4] SIS (1999). "SS 15 54 38 Motorbränslen - Biogas som bränsle till snabbgående ottomotorer (Motor fuels - Biogas as fuel for high-speed otto engines)"
- [5] European Organization for Standardization, "prEN 16723-1 -- Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network -- Part 1: Specifications for biomethane for injection in the natural gas network", 2014
- [6] European Organization for Standardization, "prEN 16723-2 -- Natural gas and biomethane for use in transport and biomethane for
- [7] Gas Research Institute (GRI)- report GRI-98/0228 "validation Testing of a gravimetric method to measure CNG Compressor Oil Carryover", Gas Research Institute, 1998
- [8] ISO 6976:1995, "Natural gas - Calculation of calorific values, density, relative density and Wobbe index from composition"
- [9] "Development and validation of methods for test of CNG quality inclusive of oil carryover", K. Arrhenius, H. Yaghooby, P. Klockar, report SGC290, 2013
- [10] "Alkylated naphthalenes as high-performance synthetic lubricating fluids", M.J. Hourani, E.T. Hessell, R.A. Abramshe, J. Liang, Tribology Transactions, 50 (2007) 82-87
- [11] "Oil viscosity - how it's measured and reported", Machinery Lubrication, <http://www.machinerylubrication.com/Read/411/oil-viscosity>
- [12] Parker Application Notes, Information om Balston Filters, parker Hannifin
- [13] "Gas chromatographic quantification of fatty acid methyl esters: Flame ionization detection vs. electron impact mass spectrometry", E.D. Dodds, M.R. McCoy, L.D. Rea, J.M. Kennish, lipids, 40(2005) 419-428.
- [14] "Validation of analytical procedures: text and methodology", European Medicines Agency, 1995
- [15] "Handbook for calculation of measurement uncertainty in environmental laboratories", B. Magnusson, T. Näykki, H. Hovind, M. Krysell, I NORDTEST Technical report 537
- [16] "The Achilles heel of natural gas vehicles: the symptoms, diagnosis and prevention of oil carryover", L. Thomason, Natural Gas Vehicle Institute (NGVi)

Optimal concentration range in CNG/Biomethane to minimize operational problems

En nyhet på gasfordonsmarknaden är den testmetod för olja som SP Sveriges Tekniska Forskningsinstitut tog fram i samband med ett annat forskningsprojekt (SGC-rapport 290). Testmetoden är lättanvänd och stabil, vilket underlättar tankstationernas kvalitetsarbete, som säkerställer prestanda och körglädje för alla som använder gasdrivna fordon. Metoden gör det möjligt att mycket noggrant bestämma oljehalten. Man kan till och med skilja på olika slags motoroljor.

I och med den här rapporten har man vidareutvecklat testmetoden, och validerat den genom att analysera oljehalten i fordonsgas på 16 olika gastankställen i Sverige. Resultatet har gjort det möjligt att bestämma en rimlig kravnivå för olja i standardiseringen av fordonsgaskvalitet, till exempel i den kommande svenska standarden för fordonsgas (SS155438). Metoden kommer också att ha betydelse internationellt, eftersom det tidigare inte funnits någon validerad testmetod för provtagning och bestämning av oljehalt i fordonsgas.

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