Concawe
Environmental Science for
European Fuel Manufacturing

Report

Report no. 1/25

Measurements of emissions of Particulate Matter (PM) and Semi-Volatile and Intermediate-Volatility Organic Compounds (S/IVOC) from refinery sources

Phase 1: A refinery fuel gas-fired heater

ISBN 978-2-87567-196-7

Measurements of emissions of Particulate Matter (PM) and Semi-Volatile and Intermediate-Volatility Organic Compounds (S/IVOC) from refinery sources

Phase 1: A refinery fuel gas-fired heater

G. Valastro (Concawe Science Executive)

This report was prepared by: B. Smithers (Consultant)

Under the supervision of: T. Megaritis (Concawe Science Associate)

At the request of:

Concawe Special Task Force on Refining Emissions Determination and Reporting (STF-69)

Thanks for their contribution to:

Members of STF-69: A. Bakker, J. Keesom, F. Leotoing, D. Steinert
Members of AQMG: C. Dupre, A. L. H. Vågenes
Members of American Petroleum Institute (API): B. Coleman

Brussels
January 2025

ABSTRACT

This report provides the results from two measurement campaigns carried out on a gas-fired heater at a refinery in north-west Europe. The main purposes of the campaigns were i) to measure the emissions of primary particulate matter (PM) and also the volatile organic compounds (VOCs) which act as precursors to the formation of secondary PM and ii) to derive emission factors (EFs) for comparison with those published by the US EPA. In this report the EFs are expressed as g/GJ, with energy based on the net calorific value (NCV) of the fuel.

First campaign. In this campaign measurements were made of both filterable particulate matter (FPM) and condensable particulate matter (CPM).

Condensable particulate matter (CPM). Two different test methods to measure CPM were used simultaneously. Those methods were US EPA M202 (2017 version) which uses chilled impingers and ISO 25597:2013 which uses dilution to cool the sample.

In these tests, M202 provided CPM concentration values about six times higher than the ISO method. However, the measurement uncertainty of the ISO method was significantly greater than that of M202 due to the effect of sample dilution. The CPM emission factors derived using the two test methods were:

- Dilution (ISO 25597): 0.81 g/GJ
- Chilled impinger (EPA M202): 4.79 g/GJ

For comparison the factor published by the EPA, derived from tests using M202, is 2.67 g/GJ.

CPM speciation analysis was only undertaken on the samples from the M202 tests. Insufficient sample was collected from the ISO 25597 tests. The average composition comprised 14% organics and 86% inorganics by weight. The main inorganic constituents were 30% sulphate and 19% nickel. Further testing established that the nickel and majority of the sulphate were due to contamination. The main organic constituent was diethylene glycol dibenzoate. This was unexpected and contamination is also suspected, but it has not been possible to identify the source.

Filterable particulate matter (FPM). In all tests the FPM concentration was less than the limit of detection value (LDV) of 0.2 mg/Nm^3. The FPM emissions, related to energy consumption, were therefore <0.075 g/GJ. For comparison the FPM EF factor published by the EPA is 0.89 g/GJ.

Second campaign. This campaign measured the emissions of VOCs classified as semi- and intermediate-volatility organic compounds (S/IVOCs). No tests to measure total S/IVOCs have been previously reported for gas-fired sources in European refineries. This initial test was used to provide a preliminary estimate of emissions rather than an accurate quantification.

Samples were collected on sorbent tubes. Analyses were carried out using automated thermal desorption (ATD) systems, one linked to a gas chromatograph (GC) with a flame ionisation detector (FID) for quantification, with the other linked to a GC fitted with a mass spectrometer (MS) for compound identification. The protocol used for VOC classification was that a compound with the same retention time as an n-alkane had the same classification as the latter. The indicative

emission factors derived were 0.95 g/GJ (LHV) for IVOCs and 1.2 g/GJ (LHV) for SVOCs.

KEYWORDS & ABBREVIATIONS

US Environmental Protection Agency (EPA) M202, ISO 25597:2013, Condensable Particulate Matter (CPM), Filterable Particulate Matter (FPM), Semi-Volatile Organic Compounds (SVOC), Intermediate-Volatility Organic Compounds (IVOC), Non-Methane Volatile Organic Compounds (NMVOCs), Emission Factor (EF), Refinery Fuel Gas (RFG), Lower Heating Value (LHV), Gas-fired Heater, Limit of Detection Value (LDV), Flame Ionisation Detector (FID), Convention on Long-Range Transboundary Air Pollution (CLRTAP), National Emissions Ceiling Directive (NECD), Secondary Organic Aerosol (SOA), Total Suspended Particulates (TSP)

INTERNET

This report is available as an Adobe pdf file on the Concawe website (www.concawe.eu).

CONTENTS

SUMMARY

Particulate matter (PM) is formed of so-called 'primary' and 'secondary' fractions. The main purposes of the test programme were to measure the emissions of primary particulate matter (PM), in particular the condensable PM (CPM) fraction, and the volatile organic compounds (VOCs) which act as precursors to the formation of secondary PM from refinery fuel gas combustion and to derive emission factors for these pollutants.

PM primary fraction

The primary fraction is composed of filterable PM (FPM) and condensable PM (CPM). The primary PM sectorial emission inventories developed by European Union Member States under the Convention on Long-Range Transboundary Air Pollution (CLRTAP) and for the National Emissions Ceiling Directive (NECD) are inconsistent. Some sectors (e.g., automotive) include estimates of both FPM and CPM, whereas others, including combustion in oil and gas refining, are limited to FPM. The emission factors for CPM from refinery sources published by the US EPA are known to have a positive bias due to issues with the EPA method (M202) as originally published used for their derivation.

Concawe is undertaking a test programme to measure CPM emissions from refinery stationary combustion sources. In the test reported here two different methods were used to measure CPM simultaneously. These methods were an improved version (2017) of the US EPA M202 which uses chilled impingers and ISO 25597:2013 which uses dilution to cool the sample and promote the formation of CPM. These two test methods provide different conditions for the formation of CPM. The dilution method is designed to more closely represent the actual conditions under which CPM is formed in the atmosphere. Differences in emission measurements between M202 and other dilution methods have been reported previously. There are a number of other CPM measurement test methods using dilution techniques, e.g. EPA OTM-37. However, both ISO 25597 (unlike OTM-37) and M202 extract the FPM from the sample gas in the first stage of their sample trains permitting direct comparison of the values of CPM concentration measured.

PM secondary fraction

The secondary fraction is formed in the atmosphere from gaseous precursors via gas- and aqueous chemistry. This fraction is made up of both inorganic and organic material.

The secondary organic aerosol (SOA) is formed in the atmosphere from volatile organic compounds (VOCs) after one or more generations of oxidation. The VOCs that can contribute the most to the SOA concentration are classified as non-methane volatile organic compounds (NMVOC), intermediate-volatility organic compounds (IVOC) and semi-volatile organic compounds (SVOC).

Currently sectorial emission inventories of NMVOCs exist for European sources, including oil refineries, but there are no S/IVOC inventories.

Emission factors (EFs)

A primary use of EFs for combustion sources by both competent authorities (CAs) and refineries is the development of particulate emission inventories. To permit comparison between sources firing different fuels, EFs conventionally provide a measure of the mass emitted per unit of energy consumed. In this report the

particulate EFs are expressed as g/GJ, with energy based on the net calorific value (NCV) of the fuel.

The most widely cited compendium of emission factors is the US EPA publication AP-42 *Compilation of Air Pollutant Emission Factors from Stationary Sources*. This includes EFs for filterable, condensable and total PM emissions from gas-firing. The EFs were derived from tests on natural gas-fired boilers. AP-42 does not include PM EFs for refinery fuel gas (RFG) firing. The EPA recommends that the EFs for combustion of NG should be used as the default PM EFs for RFG combustion.

Objectives of test programme

There are two methodologies for the determination of CPM concentration. These involve either rapid cooling by passing the stack gas sample through a chilled impinger or a more gradual cooling by diluting the sample with clean ambient air. The first method is used in the USA EPA Method 202 (M202). ISO 25597 uses the dilution method and is suitable for use on industrial stacks. The latter is considered to more closely represent the conditions in which CPM is formed in the atmosphere close to a stack. Moreover, Method 202 is known to have a positive bias due to an artefact where non-condensable sulphate is formed in the impinger. The method has undergone revision in 2010 and again in 2017 to reduce the artefact. The programme was developed to provide simultaneous measurements using ISO 25597 and M202, but with the focus on the use of ISO 25997 on refinery stacks.

Intermediate volatility organic compounds (IVOC) and semi-volatile organic compounds (SVOC), together referred to as S/IVOCs, are precursors to the formation of the organic fraction of the secondary organic aerosol. The magnitude of S/IVOC emissions from refinery sources is unknown. Measurements of S/IVOCs were therefore undertaken in conjunction with the FPM/CPM test programme.

The objectives of the programme were:

- To undertake primary PM emission measurements with ISO 25597 and derive emission factors for both the CPM and FPM fractions;
- To undertake comparative measurements with M202 to determine if the positive bias identified in previous tests has been resolved following the 2017 revision;
- To identify any issues with the application of ISO 25597 to refinery CPM sources
- To undertake measurements of the IVOC and SVOC emissions from refinery fuel gas-firing and derive emission factors.

Measurement campaigns

The first phase of the programme involved campaigns to measure FPM, CPM and S/IVOC emissions from a process heater firing refinery fuel gas at a north-west European oil and gas refinery. This report provides the results from those campaigns. The PM campaign comprised three test runs with both M202 and ISO 25597 being used simultaneously. The S/IVOC measurements were undertaken as a separate campaign.

CPM measurements

The average CPM concentration measured with ISO 25597 was 2.2 mg/Nm^3. By comparison, the average measured with EPA M202 was 12.9 mg/Nm^3. It is known that the original version of M202 suffered from a high bias for gas-fired sources mainly because of a measurement artefact where sulphate is formed in the chilled impinger due to aqueous chemistry and not due to condensation. The method has been improved since first publication to minimise this artefact and these measurements were undertaken using the latest (2017) version.

The average emission factors for CPM derived from the results from the two measurement techniques were:

- Dilution (ISO 25597): 0.81 g/GJ
- Chilled impinger (EPA M202): 4.79 g/GJ

For comparison the factor published by the EPA in AP-42, derived from tests using M202, is 2.67 g/GJ.

There was a much higher uncertainty associated with method ISO 25597, with the 95% confidence interval in excess of 100% of the measured CPM concentration value for all three test runs. This increased uncertainty was due to the low total volume of stack gas (in the range 0.1 to 0.2 m^3 per run) collected due to the dilution effect. This resulted in a low mass of CPM collected on the filter and in the rinses. For comparison, the 95% confidence intervals for the M202 concentration values were, for all three runs, of the order of 4%.

The CPM samples gathered from the M202 tests were accumulated to provide sufficient sample for speciation analysis. There was insufficient sample from the ISO test to permit speciation.

With M202 the organic fraction averaged 14% of the total CPM by weight. Diethylene glycol dibenzoate (DEGDB) was identified with the highest probability (72.6%) as being the major component of the organic fraction. This was unexpected as particulate matter in gas combustion is usually comprised of larger molecular weight hydrocarbons that have not been fully combusted. The main usage of this compound is as a plasticiser raising uncertainty as to whether its presence was due to contamination during the sampling or analysis processes. Review of these were undertaken but it was not possible to draw any conclusions as to the source of the DEGDB.

The sulphate content of the inorganic fraction accounted for 30% of the total CPM. Nickel accounted for 18.7% of the total CPM. As only trace levels of metals were expected, an investigation was carried out to identify the possible source of the nickel. This established that the container in which the aqueous fraction of the CPM samples were evaporated down was made principally of nickel (+98%) instead of stainless steel. The use of an incorrect type of container was due to a procurement error by the test contractor. Tests were subsequently carried out in a stack simulator using a gas composition as close as possible to that in the actual test campaign. These tests established that the main source of the nickel was contamination due to leaching from the container into the CPM sample. The determination of the CPM mass is gravimetric with the container weighed before and after the introduction of the CPM sample. The nickel contamination did not, therefore, affect the measured mass of CPM emissions.

The stack simulator test also identified both sulphate artefact and additional sulphate formation in the CPM sample evaporated and dried in the nickel container. The most probable cause of the additional contaminant was $NiSO_4$. This would increase the measured mass of CPM leading to a positive bias in the emission factor derived from the M202 test results.

There is significant uncertainty in the value of CPM sulphate concentration determined with the stack simulator test and hence no attempt has been made to correct the campaign test results. The expanded uncertainty value for the measured CPM concentration has, however, taken account of the stack simulator results.

In order to identify possible reasons for the differences in measured CPM concentration between M202 and ISO 25597, comparative speciation data for the two methods, particularly for anions, are needed. For example, the measured sulphate concentration in the M202 sample, even if fully due to a measurement artefact/contamination, do not account for the differences in CPM concentration measured by the two methods. In this respect, it has been postulated that the rapid cooling of the sample gas in the M202 sample chain results in higher saturation ratios for the condensable constituents, with consequently greater condensation. The ISO method, which cools the sample using dilution air, is considered to more closely represent the conditions in which CPM is formed in the atmosphere close to a stack.

The ISO method specifies the use of a cyclone after the dilution chamber to separate the CPM into size fractions. CPM is traditionally assumed to comprise particles with an aerodynamic diameter of less than 1 µm. However, the tests using ISO 25597 indicated that CPM with diameter >5 µm comprised ≥16% of the total CPM emissions.

FPM measurements

In addition to CPM, the FPM phase was collected in-stack at the front-end of the sampling trains of both M202 and ISO 25597 during the test campaign. Upstream of the M202 sample train FPM was measured using an in-stack filter. With the ISO method an in-stack impactor chain was used. For all three test runs, with both M202 and ISO 25597, the FPM concentrations were below the limit of detection value (LDV) of 0.2 mg/Nm3.

The emission factor for FPM derived using the LDV is 0.075 g/GJ. With all data below the detection limit it is not possible to derive a definitive emissions factor. However, to aid comparison with published EFs and to determine EFs for total PM, in this report a so-called ‘indicative’ EF for FPM is derived using 50% of the FPM LDV. The average ‘indicative’ FPM EF derived from these tests is 0.037 g/GJ. This compares to the EPA emission factor for FPM from gas-firing of 0.89 g/GJ.

Total PM (CPM + FPM) emission factors

The EF for CPM derived from the ISO test data was 0.81g/GJ. Using the ‘indicative’ FPM EF of 0.037 g/GJ provides a total PM EF of 0.85 g/GJ.

For comparison the EF published by the EPA solely for FPM from gas-firing is 0.89 g/GJ. The total PM emissions from gas-firing where a dilution method was used to measure the CPM fraction were therefore of the same order of magnitude as the estimate provided using the EPA’s EF for FPM.

This finding has also been obtained from tests in the USA where the API has proposed that the EPA emissions factor for filterable $PM_{2.5}$ for gas-firing (0.89 g/GJ) in reality should be used to estimate total primary PM i.e., FPM plus CPM.

The dilution method (OTM-37) being used by the API to develop PM emission factors for refinery gas-fired units only provides concentration data for total PM. However, it is likely in Europe that emission factors for both FPM and CPM will be required for inclusion in the EMEP/EEA[1] guidelines to Member States to assist in their estimation of PM emissions for submission to both the Convention on Long-range Transboundary

---

[1] Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) / European Environment Agency

Air Pollution (CLRTAP) and National Emissions Ceiling Directive (NECD) inventories. It is recommended that further test data on FPM emissions from refinery gas-fired combustion units are obtained to permit the development of robust and representative particulate emission factors for this source type.

A constraint with the use of the ISO 25597 sampling system

In the test campaign a Dekati modified Deed-300 Dilution Sampling System was used. The physical length of this system will be a constraint to its use on some refinery stacks as the sampling platform needs to have a width of at least 2m in front of the sampling ports. This is the minimum distance required to safely manipulate the sampling system into the stack.

S/IVOC measurement campaign

A further campaign, comprising three test runs, was undertaken on the same refinery heater to measure intermediate volatility and semi-volatile organic compounds (IVOCs and SVOCs). Although these pollutants are precursors to secondary atmospheric organic aerosol (OA) formation, measurements of these compounds have not been reported previously from European refinery combustion sources. This initial test was used to provide a preliminary indication rather than accurate quantification of the S/IVOC emissions from refinery fuel gas-firing. It also permitted the contractor (UK National Physical Laboratory) to identify possible refinements to the analytical techniques to improve the accuracy in determining total IVOC and total SVOC concentrations in future tests.

Sampling was undertaken by adsorption on sorbent tubes. Two linked tubes were used containing Carbopack-X and Tenax, ensuring capture of VOCs within a carbon number range from C7 to C32. Analysis was carried out on an automated thermal desorption system linked to a gas chromatograph (GC). The peaks were quantified using a flame ionisation detector (FID) and identification was undertaken by mass spectrometry (MS).

There are a number of conventions for the classification of VOCs, e.g., boiling point, vapour pressure. In this report, the definitions of NMVOC, IVOC and SVOC provided in Concawe report 01/21 are used. These definitions are based on ranges of saturation vapour concentration (C*). In this first campaign a simple convention was adopted based on the saturation vapour concentration (C*) values of n-alkane. The retention times of n-alkanes on the GC column were determined using an n-alkane standard run alongside the sample. VOCs with the same retention time on the GC column as an n-alkane were assumed to have the same volatility classification as that n-alkane. So, compounds with retention times corresponding to n-alkanes with carbon numbers from C12 to C19 were classified as IVOCs and from C20 to C27 as SVOCs. The concentration values derived from the FID measurements by retention time were allocated to the associated VOC class. Those compounds with the greatest concentration were identified, but none were quantified individually. Many of the VOCs which could be identified with reasonable certainty were oxygenated compounds. The higher molecular weight compounds were difficult to identify accurately. For some of the more complex compounds the use of the classification scheme chosen may therefore not be appropriate. This adds to the uncertainties in the accurate allocation of the mass of emitted VOCs into volatility classes.

There were significant unexplained variations in the measured concentration of VOCs, classified as either IVOC or SVOC, between runs. This was not expected as the heater, particularly during runs 2 and 3 was operating under relatively stable conditions and firing gas in a narrow range of calorific value.

In particular, the average concentration of SVOCs ranged from 0.25 mg/Nm^3 to 9.0 mg/Nm^3 between the three test runs, with a corresponding range of derived EFs of 0.08 g/GJ to 2.92 g/GJ. The average SVOC concentration was 3.70 mg/Nm^3 with a median value of 1.84 mg/Nm^3. The derived emission factor using the average concentration value was 1.2 g/GJ.

The average concentration of IVOCs measured over the three test runs was 2.97 mg/Nm^3 with a median value of 2.71 mg/Nm^3. The former equated to an emission factor of 0.95 g/GJ.

1. INTRODUCTION

1.1. PARTICULATE MATTER (PM)

Particulate matter (PM) (also known as atmospheric aerosol) comprises a mixture of solid particles and liquid droplets suspended in the air. It is made up of a number of components, including organic and inorganic compounds (e.g., nitrates, sulphates, metals, etc.) [1] from both man-made and natural sources. PM emissions are reported by size fractions, based on the nominal aerodynamic diameter. For example, $PM_{2.5}$ refers to particulates within the size range up to 2.5 μm.

The atmospheric aerosol is formed of so-called primary and secondary fractions.

1.1.1. The PM primary fraction

The primary fraction comprises filterable PM (FPM) and condensable PM (CPM). The former is defined [2] as particles which are directly emitted by a source as a solid or liquid at stack or release conditions and captured on the filter of a stack test sampling train. CPM is defined as material that is in its vapour phase at stack conditions, but which condenses and/or reacts upon cooling and dilution in the ambient air immediately after discharge from the stack to form solid or liquid PM. All CPM is assumed to be in the $PM_{2.5}$ fraction.

1.1.2. The PM secondary fraction

The secondary fraction is formed in the atmosphere from gaseous precursors far from their original source via gas- and aqueous chemistry (the latter in atmospheric waters such as cloud droplets). This fraction is made up of both inorganic and organic material. NO_x, SO_x and ammonia in the atmosphere, for example, can result in the secondary aerosol constituents of nitrates and sulphates. The organic fraction of secondary PM (called the secondary organic aerosol (SOA)) is formed in the atmosphere from volatile organic compounds (VOC) after one or more generations of oxidation. VOCs are commonly classified by their volatility. One naming convention [3] is based on the saturation vapour concentration, C^*, of the organic compound. The VOCs that can contribute significantly to the SOA concentration are classified as non-methane volatile organic compounds (NMVOC), intermediate volatility organic compounds (IVOC) and semi-volatile organic compounds (SVOC), where these VOCs lie in ranges with decreasing values of C^* [1]. Modelling of the formation of SOA using inventory data for NMVOCs, IVOCs and SVOCs would provide a robust representation.

1.2. EMISSION INVENTORIES

Currently, sectorial emission inventories of FPM and NMVOCs exist for European sources, including oil refineries, derived for example from the data submitted by industry under the terms of the European Pollutant Release and Transfer Register (E-PRTR) Regulation [4] or by Member States under the terms of the Convention on Long-Range Transboundary Air Pollution (CLRTAP) [5] and the EU National Emission Ceilings Directive (NECD) [6]. There are inconsistencies in the latter inventories as the PM database for automotive sources has for some time reported total primary PM, i.e., FPM plus CPM. More recently some of the inventories for small combustion sources (e.g., residential wood combustion), which are known to be significant emitters of CPM, have similarly reported total PM. The inventories for industry, including refining, on the other hand only report FPM.

1.2.1. Condensable particulate matter (CPM)

There are no emission factors for CPM from industrial sources provided in the guidance document published by EMEP/EEA [7] to assist European Member States in the compilation of national sectorial emission inventories. Factors have been published by the US EPA [8] but these are now discredited, particularly for CPM emissions from gas-firing. The EPA Method (M202) [9] as originally published in 1991 was used to derive the factors. This version was found to have a positive bias when sampling stack gases containing, for example, sulphur dioxide which formed sulphates via aqueous chemistry, rather than condensation, in the wet sampling train. While the amount of bias is small for many types of sources, test results show it is very large relative to the low PM concentrations found in the emissions from gas-fired sources. Although the method has now been revised and improved [14], no updated CPM emission factors have been published by the EPA. The E-PRTR Regulation[1] [11] requires facilities to submit data on PM_{10} emissions, with the Implementation Guidance [12] providing the reference standard measurement method as ISO 23210 [13] i.e. for filterable PM. CPM is consequently not included in the E-PRTR database. The magnitude of the CPM emission inventory for the European refining sector is therefore unknown.

1.2.2. Semi-volatile and intermediate volatility VOCs (S/IVOCs)

Concawe has undertaken a literature review of S/IVOC emissions [1] which established that there are no European sectorial emission inventories for these pollutants and indeed no published results of S/IVOC emissions measurements at refineries in Europe.

1.3. STRUCTURE OF REPORT

The lack of information on the emissions of both CPM and S/IVOCs from the European refining sector, pollutants that are known to contribute to the atmospheric aerosol, is a significant knowledge gap. Concawe has therefore initiated a project to measure these pollutants from a range of refinery combustion sources. This report provides the results and conclusions from the first series of measurement campaigns on a refinery gas-fired heater. Section 3 of this report provides the results from the campaign to determine CPM emissions. Section 4 provides the results from the measurements of FPM which are an integral part of the CPM test methods used. Section 5 provides the results of the S/IVOC measurements.

---

[1] The E-PRTR has been replaced by the Industrial Emissions Portal (IEP) [10]

2. DETAILS OF HEATER TESTED

The measurement campaigns were undertaken on the dedicated stack connected to a catalytic reformer unit charge heater installed at a north-west European refinery. The heater is a large vertical, cylindrical unit with a steam raising convection section. The unit is fitted with 12 low-NO_x, forced draught, dual-fuel burners firing vertically upwards.

The heater is fired with refinery fuel gas (RFG). Compositional analyses of the gas were undertaken of the RFG fired during the CPM tests (see **Table 1**). The average net calorific value (NCV) of the gas fired during the tests was:

- CPM test campaign: 48.4 MJ/kg
- S/IVOC test campaign: 46.9 MJ/kg

Table 1 Average RFG composition during CPM tests.

Component	% Vol
H_2	24.0
N_2	0.79
CH_4	27.1
C2	30.0
C3	11.6
C4	4.2
C5	0.5
C6+	0.8
H_2S	0.008
CO_2	1.0

The heater has a thermal rating of 63 MW. During the tests it was operating at about 60% capacity.

- CPM test campaign: average 35.8 MW
- S/IVOC test campaign: average 40 MW

The average stack flows during the two campaigns were 13.3 Nm^3/s and 12.7 Nm^3/s respectively. The stack temperature during both campaigns was 188°C.

The stack is vertical and positioned above the convection section of the heater. It has a circular cross section with a diameter of 2.3 m. A total of four 8 inch flanged sample ports are installed equidistantly around the stack at the upper platform. These were used for the particulate sampling. A fifth sampling point, located near the stack damper, was used for gaseous sampling.

The upper platform is permanently installed on the heater roof – see **Figures A1.2** and A1.3 in Appendix 1. Access is from staircases and fixed ladders.

3. CONDENSABLE PARTICULATE MATTER (CPM)

CPM is formed of material which is in a vapour state in the stack and forms solid or liquid PM as it cools after discharge from the stack. The material either condenses as new liquid aerosols or onto the surface of existing particles, or reacts with other substances in the plume close to the stack. Particle condensation mechanisms in the atmosphere are dependent on the time over which reaction/formation can occur as well as temperature.

3.1. CPM MEASUREMENT TECHNIQUES

Two test techniques were chosen for the measurement of CPM from refinery processes; US EPA Method 202 (M202) [9] and ISO 25597 [15]. The former uses chilling and the latter uses dilution with ambient air to cool the sample and promote CPM formation. The former was used, in its original version, to derive the CPM emission factors for refinery sources published by the US EPA. The dilution technique is a more recent development, designed to more closely represent the conditions under which CPM is formed in the atmosphere.

There are a number of CPM measurement test methods using dilution techniques. Some of these are specific to certain source types, e.g. ASTM E2515-11 [17] for solid-fuel-burning appliances (e.g. woodstoves, fireplaces, etc.) and ISO 8178-1: 2020 [18] for automotive exhaust emissions. For industrial stack measurements the US EPA have developed 2 test methods using dilution techniques: Conditional Test Method (CTM) 39 (2004) [19] and, for low concentration emissions, Other Test Method (OTM) 37 (2018) [20]. Both of these methods, however, are designed for the measurement of total PM i.e., FPM plus CPM.

As an aim of the Concawe test programme is to compare the results of CPM measurements made using a dilution method versus M202, the internationally recognised ISO 25597 was chosen as the dilution technique test method for these test campaigns. Both M202 and ISO 25597 extract the FPM from the sample gas in the first stage of their sample trains, permitting a direct comparison of just the CPM concentrations. As there is separate measurement of FPM, this provides the additional opportunity to check the emission factor for FPM from gas-firing currently used [6] to develop European inventories.

During the campaign both M202 and ISO 25597 were used simultaneously to permit direct comparison of the results between the two test techniques. It also enabled any practical issues with their use on refinery stack sampling platforms to be identified.

It was also planned to undertake speciation analyses of the CPM collected from both methods, particularly to determine sulphate concentrations. It is known that the original version of EPA M202 exhibited a significant artefact due to sulphate formation when used to measure CPM emissions from gas-fired combustion units where SO_2 is present in the stack gas – see Section 3.1.1. Revisions to the test method have been introduced to reduce the artefact and the method used for this test campaign was the latest version introduced in 2017 [9]. It was planned to compare the sulphate concentrations in the CPM measured with M202 (v2017) versus the ISO method to provide some indication of whether the artefact is still significant.

3.1.1. US EPA Method 202:2017

This method was originally promulgated by the US EPA in 1991. In that first version the stack gas sample, following removal of the FPM by an in-stack filter, was bubbled through water in iced impingers and then drawn through a filter. Following issues with the method the EPA subsequently identified two factors which could lead to inconsistent results. The first was that it was possible to use different combinations of the optional procedures permitted in the original 1991 version of M202 which could result in large variations in the CPM measured. The second was due to an artefact where SO_2 in the stack gas reacts chemically in the impinger water to form sulphates [14]. These would not be expected to be formed as CPM in the plume, but were erroneously counted as such in the method.

The emission factors for CPM published in the US EPA AP-42 [8] were derived from tests undertaken using this original version of M202.

The EPA subsequently made major revisions to the method in 2010 with further refinements in 2017 [9]. In the latest version (**Figure 1**) the stack gas sample, after removal of the FPM, is cooled in a water-jacketed glass coil condenser with the condensed water collected in a knock-out bottle. The gas then flows into a dry glass impinger mounted in a water bath maintained at ≤ 30 °C. Finally, the gas passes through the so-called “CPM” filter (90 mm PTFE), which is maintained in the range of 20°C to 30°C, before being dried and metered. The CPM and condensed water vapour are recovered from the sampling train components up to and including the CPM filter for laboratory analysis via quantitative rinsing with water, acetone and hexane. The water rinses are referred to in this report as the “aqueous fraction”. The rinses using acetone and hexane are called the “organic fraction”. The CPM concentrations determined from these fractions are reported separately in this report.

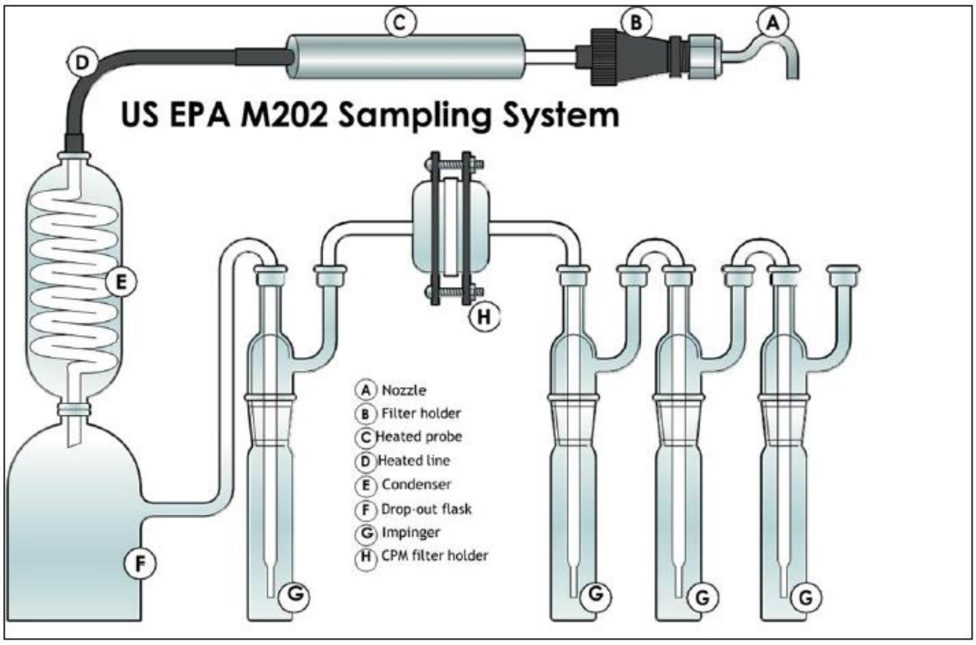

Figure 1 *Schematic of US EPA M202 sampling train*.

The EPA state [14] that in laboratory and field tests, the 2010 revisions reduced the SO_2 oxidation bias by 90 percent over the best results obtained using the original 1991 version of Method 202.

In the test campaign reported here, the 2017 version of Method 202 was used to measure CPM. The in-stack measurement of FPM, prior to the sample gas passing to the M202 test chain, was undertaken according to EN 13284-1:2017 [16] – see Section 4.1.1. The FPM measurement system consisted of an in-stack filter holder and nozzle attached to a heated probe. In this campaign 47mm quartz fibre filters were used to capture the FPM.

3.1.2. ISO 25597:2013

The ISO method specifies procedures for the measurement of both FPM and CPM.

The first stage of the sampling train described in the standard uses in-stack PM_{10} and $PM_{2.5}$ cyclones and filters to collect FPM in the two size ranges. An alternative system was used in this test campaign comprising a Johnas Cascade Impactor with impaction stages for $PM_{2.5}$ and PM_{10} and with back-up filtration.

The impactor was connected by means of a heated sampling probe to the second stage dilution train (**Figure 2**). This comprises “mixing” and “ageing” sections. In the diluter the stack sample gas is thoroughly mixed with conditioned ambient air to dilute and cool the sample. The method specifies that the dilution ratio shall be at least 20:1. The second section acts as an ageing zone where CPM formation through condensation and reaction can be completed. This section comprises the residence time chamber which is designed to be of sufficient volume to provide a minimum residence time of 10 seconds.

The method also specifies that the relative humidity of the diluted sample should not exceed 70%, as higher levels can significantly affect particle mass and size distribution within the residence time chamber and therefore change the nucleation, condensation and accumulation processes.

A slip-stream of the diluted sample in the chamber is drawn off to a cyclone and associated back-up filter for CPM collection. In this campaign a 47 mm Teflon filter was used. The ISO 25597 method specifies a cyclone with a cut point of 2.5 µm. However, in these tests the cut point, at the sampling system flow rate set to ensure limits of detection were met, was 5 µm. This resulted in CPM categorisation being split into fractions above and below 5 µm.

The ISO method specifies that the filter temperature should be 42 °C or less. As M202 stipulates a filter temperature between 20 °C and 30 °C, the temperature of the residence time chamber during this campaign was controlled to ensure that the ISO 25597 filter was maintained, as far as possible, in the same range. This was done in an attempt to eliminate one possible cause for a potential difference in the results between the two methods.

Because the ISO 25597 method is intended to cool the sample without condensing the water vapour present in the sample, there is no liquid phase in contact with the gas sample and thus no opportunity for the water chemistry measurement artefacts that are sometimes significant in Method 202.

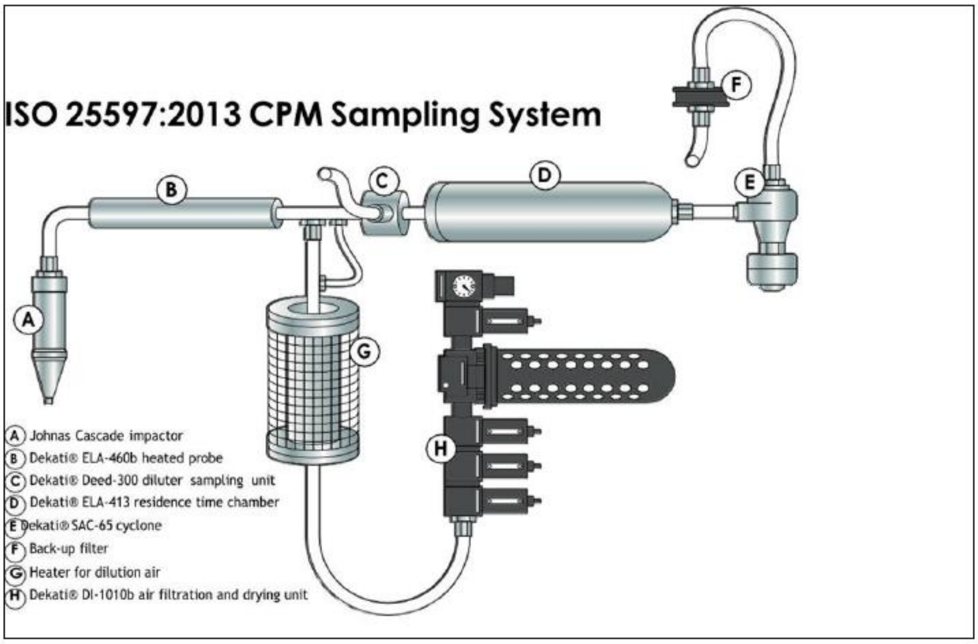

Figure 2 *Schematic of ISO 25597 sampling train*.

In the test campaign a Dekati modified Deed-300 Dilution Sampling System was used. Photographs of the system used are presented in Appendix 1. The system comprises a Dekati ELA-460b heated probe, a Deed-300 diluter sampling unit, a Dekati ELA-413 residence time chamber with a residence time of 11.3 secs at 20 l/min flow rate and a Dekati SAC-65 cyclone and associated back-up filter holder. The dilution air was generated using an oil-free air compressor and supplied at between 4 and 4.5 bar through the Dekati DI-1010b pressurised air filtration and drying unit, resulting in a dilution factor of between 21 and 23.5.

The dilution ratio was determined by measuring directly the nitrogen monoxide contents of the stack gas and the outlet of the Dekati system in accordance with EN 14792:2017 [21].

For both test methods, oxygen measurements according to EN 14789:2017 [22] were taken in order to correct results to reference conditions.

3.2. EXPERIENCE WITH MEASUREMENT EQUIPMENT

The measurement campaigns were undertaken by the UK National Physical Laboratory (NPL), Teddington, England. They reported that the ISO 25597 method is a lot more labour intensive than EPA M202, especially if an air supply is not available on the platform and the sampling location is at an elevated height.

Due to the length of the Deed-300 dilution sampling train, the sampling platform needs to have a width of at least 2m in front of the sampling ports – see **Figure A1.2** in Appendix 1. This is the minimum distance required to safely manipulate the sampling system into the stack. This constraint will limit the applicability of the use of the Dekati system as some sampling platforms on refinery stacks would not meet this criterion.

The dilution system uses specially designed equipment, unlike the EPA M202 sampling train which uses more traditional laboratory equipment. The ISO method, however, requires less complex post-sampling analysis. Due to the dilution effect used, the ISO method requires much longer sampling times than the EPA M202 to achieve similar CPM sample sizes.

The temperature and humidity requirements (i.e. particle filter temperature at 42°C or lower and humidity of the diluted sample below 70%) of the ISO method were found to be easily achieved.

3.3. TEST RESULTS

A test campaign to determine the CPM emissions from a refinery heater (Section 2) was undertaken by the NPL over a two day period in May 2021. Speciation analyses of the samples collected were also undertaken. The organic fraction was analysed by NPL, but their laboratory specialises in VOC analysis so it was unable to analyse the inorganic fraction and this was undertaken by Intertek, Sunbury, England.

3.3.1. Test dates and periods

Table 2 provides details of test dates and duration of test runs. The second and third test runs were shortened after experience gained with the first run. Both US EPA Method 202 and the ISO 25597 test method were used simultaneously during the three runs.

Table 2 Dates and duration of test runs and stack conditions

Test Runs	Date	Period mins	Stack gas flow m^3/s [1]	Stack gas flow 95% CI [2] m^3/s	Stack Temperature °C
1	12-05-2021	310	13.1	0.8	188.2
2	13-05-2021	215	13.4	0.8	188.4
3	13-05-2021	214	13.4	0.8	187.8

Table Notes:

1. Stack flow at reference conditions - 273°K, 101.3 kPa, 3% Oxygen on a dry gas basis
2. Confidence Interval

3.3.2. Test results – EPA Method 202

Table 3 provides the concentration data, with associated 95% confidence interval (CI) values, from the tests using the EPA Method 202. It also gives the average temperature of the CPM filter, which is specified in the method to be in the range of 20°C to 30°C.

Table 3 CPM Concentration - Results of M202 tests.

Test Run	CPM Aqueous Fraction		CPM Organic Fraction		CPM Total		Filter Temp °C
	Conc. mg/Nm^3	95% CI mg/Nm^3	Conc. mg/Nm^3	95% CI mg/Nm^3	Conc. mg/Nm^3	95% CI mg/Nm^3	
1	10.3	0.4	2.1	0.1	12.4	0.5	22.5
2	10.7	0.4	2.6	0.2	13.3	0.5	18.6

3	12.2	0.5	0.8	0.1	13.0	0.5	20.9

The Table shows a deviation from the method for test run 2 with the average filter temperature being 1.4°C below the specified range (20-30°C). The formation of CPM depends upon the temperature that the sample gas is exposed to. In these tests the range of the filter temperatures was less than 4°C over the duration of the three test runs and therefore the impact of this deviation was considered minimal. In addition, the temperatures of the filters in the M202 and ISO sampling chains were within 4°C of each other (see **Table 4**) ensuring comparable CPM collection conditions.

3.3.3. Test results - ISO Method 25597

Table 4 provides the concentration data, with associated 95% confidence interval (CI) values, from the tests using ISO 25597. To ensure limit of detection requirements were met the ISO 25597 sampling system flow rate was set at 20 l/min. However, the Dekati SAC-65 cyclone in the sample line after the residence time chamber has a cut point of 10 µm at 10 l/min and about 5 µm at 20 l/min flow. Therefore the CPM samples were collected in fractions above and below 5 µm and not 2.5 µm as specified in ISO 25597.

Table 4 also gives the average values of the parameters for which values are specified in the method. These are: the dilution ratio ≥ 20:1, diluted gas temperature at the filter ≤ 42 °C, diluted gas relative humidity (RH) ≤ 70 %.

Table 4 CPM Concentration - Results of ISO 25597 tests.

Test Run	CPM Fraction			95% CI mg/Nm³	Dilution Ratio	Filter Temp [1] °C	Sample RH %
	$< PM_5$	$\geq PM_5$	Total				
	Concentration mg/Nm³						
1	1.6	0.9	2.5	2.8	23.4	18.6	29.1
2	1.5	0.3	1.8	2.9	23.2	19.2	29.3
3	1.4	0.8	2.2	2.5	21.8	20.5	29.0

Table Note 1: Temperature measured at exit of residence time chamber.

3.3.4. Derivation of emission factors

Data were provided by the refinery on the amount of refinery fuel gas (RFG) fired during the test runs and the average net calorific value (NCV) of the gas. Stack gas flow measurements (**Table 2**) were undertaken by NPL according to EN ISO 16911-1:2013 [23]. The calculated average mass emissions (g/h) for each test run are shown in **Table 5**. CPM emission factors were derived from these data and are also shown in **Table 5**.

The emission factor (EF) was calculated from:

EF (g/GJ) = Mass emission rate (g/h) / [Fuel firing rate (t/h)] x Fuel NCV (GJ/t)]

Table 5 CPM Emission Factors derived from results of tests using EPA M202 and ISO 25597.

Test Run	Fuel Fired t/h	Fuel NCV MJ/kg	Total CPM Emissions g/h		Emission Factor g/GJ	
			M202	ISO 25597	M202	ISO 25597
1	2.6	48.16	584	118	4.69	0.94
2	2.7	48.53	642	87	4.90	0.66
3	2.69	48.49	627	106	4.81	0.81
Average					*4.79*	*0.81*

3.4. CPM SPECIATION

Differences in CPM concentration levels from fuel gas firing measured by EPA M202 and dilution techniques have been reported previously [24]. Speciation of the organic and inorganic fractions of the CPM collected by both M202 and ISO 25597 were planned, with the aim of identifying any potential reasons for such differences. Unfortunately, analyses were only undertaken on the sample from the tests using M202. The ISO 25597 CPM samples were not analysed due to concerns over meeting the analysis limit of detection (LOD), since less mass of CPM was collected relative to the M202 tests due to the dilution effect.

The preparation process for the M202 samples consisted of combining the aqueous (inorganic) samples from the three field tests into one. The organic fraction samples were similarly combined. This was to ensure that there was enough sample to analyse and the analysis LOD could be met. The inorganic samples were then re-dissolved into a minimum volume of water and the organic extracts into hexane.

3.4.1. Organic fraction analysis

The resulting solution from the CPM tests was evaporated to dryness. The resulting residue was a colourless gel. This residue was dissolved into dichloromethane to ensure any high molecular weight alkanes were dissolved prior to analysis. 30 µl of the residue solution was injected onto a thermal desorption tube containing Tenax TA and purged with scrubbed air. The analyses were carried out using an automated thermal desorption (ATD) system linked to a gas chromatograph (GC) fitted with a mass spectrometer (MS). Each tube was purged with an inert gas and then heated, whilst a stream of inert carrier gas was passed through the tube to desorb the trapped compounds. These were then passed through a cold trap and cryo-focused before being injected onto a 30 m x 0.25 mm x 0.25 µm capillary column for individual species separation. For comparison and quantification purposes several standards were run alongside this sample. These standards included two QA/QC standards for quantification purposes, retention time standard for a series of n-alkanes in the range nC10 to nC26 and a polycyclic aromatic hydrocarbon (PAH) retention time standard.

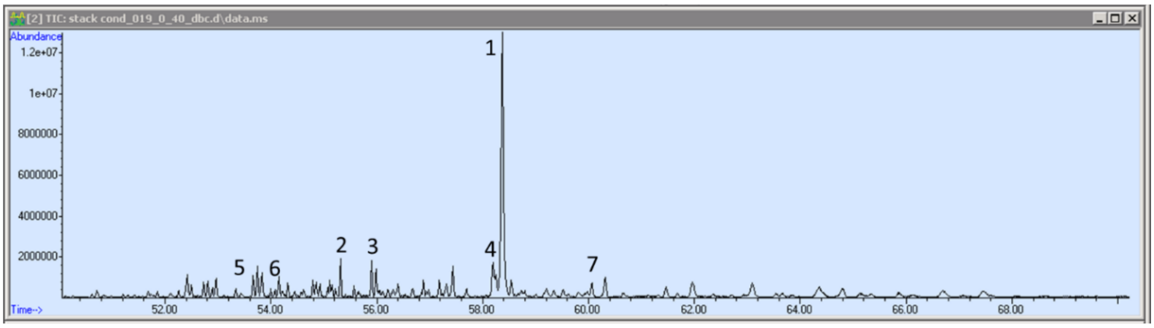

Figure 3 Chromatograph of the CPM organic residue showing identified peaks.

The chromatograph of the residue (**Figure 3**) shows one predominate peak (1) which was identified as diethylene glycol dibenzoate (DEGDB) with the identification given a 72.6% probability. Other potential compounds had probabilities less than 9%. The concentration of this component was 0.18 mg/Nm^3 with an uncertainty (90% confidence interval) of 0.04 mg/Nm^3. This represents 9.8 % of the organic residue. The presence of DEGDB was unexpected as particulate matter in gas combustion is usually comprised of larger molecular weight hydrocarbons that have not been fully combusted. The main usage of this compound is as a plasticiser raising uncertainty as to whether its presence is due to contamination during the sampling or analysis processes. Review of these were undertaken but it was not possible to draw any conclusions as to the source of the DEGDB.

Other peaks identified were mainly branched alkanes and oxygenated hydrocarbons. These were: peak 2 - C21 branched alkane, peak 3 - C19 branched alkane, peak 4 - n-propyl benzamide, peak 5 - C16 branched alkane, peak 6 - isobutyl butyl ester terephthalic acid and peak 7 - nC26. These were more difficult to identify as the probabilities were much lower with numerous other similar configurations also being possible.

PAHs were looked for but not found, although they may have been present below their limits of detection.

3.4.2. Inorganic fraction analysis

Analysis of the inorganic fraction of the aqueous samples was carried out using ICP-MS, with determination of anions by Ion Exclusion Chromatography.

Table 6 shows the elemental analysis of the combined CPM aqueous fraction sample from the M202 tests. The elements shown are those with concentrations in excess of 1.0 µg/Nm^3. **Table 7** shows the anion analysis from the same sample.

Table 6 Concentration of elements - combined CPM sample.

Element	Concentration µg/Nm^3	Uncertainty (95% CI) µg/Nm^3
Nickel	2415.0	700.3
Sodium	56.7	16.4
Calcium	37.9	11.0
Iron	26.7	7.7

Potassium	8.0	2.3
Magnesium	5.6	1.6
Copper	5.3	1.5
Zinc	4.9	1.4
Manganese	4.5	1.3
Aluminium	2.9	0.8
Lanthanum	1.6	0.5
Total	*2569.1*	

Table 7 Concentration of anions - combined CPM sample.

Substance	Concentration µg/Nm^3	Uncertainty (95% CI) µg/Nm^3
Sulphate	3860.3	1119.5
Nitrate	131.5	38.1
Chloride	19.9	5.8
Fluoride	3.1	0.9
Bromide	0.4	0.1
Phosphate	<0.7	0.2
Nitrite	<0.4	0.1
Total	*4015.8*	

The nickel concentration (2.4 mg/Nm^3) is much higher than expected. A nickel oxide catalyst is used in steam reforming so it was postulated that carryover may have occurred from the hydrogen plant into the refinery fuel gas supply main. However, the nickel emissions are of the same order of magnitude as the total CPM measured with ISO 25597 (2.2 mg/Nm^3). A more feasible possibility is that the nickel is due to sample contamination. The CPM samples were evaporated down in containers, the use of stainless steel being the standard practice for EN 13284 [16]. The stainless steel alloy contains approximately 12% nickel. It was suggested that if the liquid sample was strongly acidic, possibly because of the presence of sulphates, material may have leached from the container. However, NPL advise that these containers have proven inert when used for evaporation of washings from normal particulate analyses, even those from stacks with high sulphur dioxide concentrations, although these are usually in the containers for a much shorter period. An investigation was therefore carried out to identify the possible source of the nickel. This established that the container in which the aqueous fractions of the CPM samples were evaporated down was made principally of nickel (+98%) instead of stainless steel. The use of an incorrect type of container was due to a procurement error by the test contractor.

To establish if the nickel container was the source of the contamination, and to what extent, a test was subsequently carried out in a stack simulator (see Appendix 2) at the NPL facilities in Teddington, England. This used a circulating ‘flue’ gas stream with a composition as close as possible to that in the original heater test campaign (see **Table A2.1**, Appendix 2). Two simultaneous identical tests using M202 were undertaken for the same duration as the tests undertaken on the heater. For one of the M202 tests an inert, glass container was used to hold the aqueous solution for evaporation and drying whilst for the other test a nickel container of the same type used in the heater test was employed.

The 'flue' gas circulated through the stack simulator was generated using pure gases (NO_2, SO_2, CO_2, CO and O_2). There were no combustion processes involved with the stack simulator and hence theoretically there should be no CPM formation. The residues from the evaporation and drying of the M202 aqueous fractions from the two M202 tests (trains 1 and 2) were analysed for nickel and sulphate content. Any sulphate content in the residues from drying the aqueous fractions was, therefore, due to the sulphate artefact known to exist with M202 where SO_2 is present in the stack gas [14] and possibly any sulphate formed by contact between the container used and sulphurous acidic compounds in the aqueous fraction. The results of the simulator tests are shown in **Table A2.2**, Appendix 2.

The result of the analysis for nickel in the train 2 residue (evaporated to dryness in the inert, glass container) indicated a negligible concentration (0.001 mg/Nm^3). By comparison, the train 1 sample, using the nickel container, showed a value of 1.1 mg/Nm^3. This test proved that the vast majority of the nickel content of the CPM measured in the original heater test was due to contamination from the nickel container. It should be noted, however, that in M202 the determination of the CPM mass is gravimetric. The container in which the CPM fractions is dried is weighed before and after the introduction of the CPM sample. Even though some nickel leached into the CPM sample, the mass of elemental nickel would have been the same before and after weighing of the container. The nickel contamination, therefore, did not affect the measured mass of CPM emissions.

The measured concentration of 'CPM' in sampling train 2 using the glass container was 0.7 (±0.2) mg/Nm^3. The result of the sulphate analysis for this train was 0.8 (±0.2) mg/Nm^3. As the container was inert it can be considered that the sulphate in the 'CPM' residue was due solely to the known M202 artefact. The SO_2 concentration in the 'flue' gas in the simulator tests was 11 mg/m^3 (4.2 ppm). This demonstrates that the revisions made to M202 by the EPA in 2010 and 2017 have not eliminated the sulphate artefact, even where the stack SO_2 concentration is low.

The result of the analysis for sulphate in the train 1 residue (evaporated to dryness in the nickel container) showed a value of 2.6 (±0.6) mg/Nm^3. Assuming a value of the M202 sulphate artefact of 0.8 mg/Nm^3, this indicates an additional 1.8 (±0.6) mg/Nm^3 of sulphate in the 'CPM' sample in the nickel container. The most likely reason for this is contamination by the formation of $NiSO_4$. In the original heater tests this contamination would have increased the measured value of the CPM emissions.

A much less likely scenario is that the M202 post-test purge process to reduce the concentration of dissolved SO_2 in the liquid in the chilled impingers is not repeatable under the same test conditions. In this scenario the increased sulphate concentration in train 1 is also due to the known M202 sulphate artefact. To confirm this scenario further testing would be required using the simulator. However, in this report, as the two tests (using sampling trains 1 and 2) were undertaken at the same time and under the same conditions and it has been proven that nickel leached from the container into the 'CPM' residue in train 1, it is assumed that the increase in sulphate concentration between train 1 and 2 is due to $NiSO_4$ contamination.

There is an anomaly in the simulator test results in that the 'CPM' concentration in train 1 was 4.2 (±0.2) mg/Nm^3. There is a larger difference between this and the result for train 2 of 0.7 (±0.2) mg/Nm^3 than can be accounted for by sulphate alone, even allowing for the uncertainty in the analyses. It is unclear whether any other complex chemical reactions may have occurred due to the Ni contamination which resulted in a further increase of the mass of 'CPM' in the container.

Due to the above, the expanded uncertainty of the US EPA M202 CPM measurement results has been calculated based on a worst-case scenario in which all the 'CPM' identified during the Train 1 stack simulator tests (4.2 mg/m3) was in the form of additional sulphate (as NiSO4) deducting any 'CPM' identified in Train 2 (0.7 mg/m3) assuming this was from the M202 sulphate artefact bias and also assuming that the latter was identical for both trains.

The concentration of the elements (minus nickel) plus the anions in the combined CPM aqueous samples from the original heater M202 tests was 4.2 mg/Nm^3. The average CPM concentration for the aqueous samples from the tests was 11.1 mg/Nm^3. Further testing with more comprehensive analysis is required to identify the balance of the composition of the M202 aqueous samples.

Ammonia also exacerbates a condensable PM measurement artefact caused by reactions with SO_2 in Method 202 [24]. Ammonia was not reported by the refinery to be a constituent of the fuel gas fired (see **Table 1**).

3.5. DISCUSSION OF RESULTS OF CPM TESTS

3.5.1. Comparison of measured CPM concentrations

The average CPM concentration in the stack measured with EPA M202 was six times higher than measured by test method ISO 25597.

There is, however, a much higher uncertainty associated with method ISO 25597, with the 95% confidence interval in excess of 100% of the measured CPM concentration value for all three test runs. This increased uncertainty is due firstly to the low total volume of stack gas (in the range 0.1 to 0.2 m^3 per run) collected due to the dilution effect, and secondly to the low mass of CPM collected on the filter and in the rinses. For comparison, the 95% confidence intervals for the M202 concentration values were, for all three runs, of the order of 4%.

3.5.2. Size of condensable particulates

The US EPA [8] assumes that all PM emissions from gas-firing, both filterable and condensable, are less than 1.0 µm in diameter.

In the test programme described in this report, the tests using ISO 25597 provided CPM fractions above and below 5 µm. The results indicate that the CPM fraction >5 µm was in the range of 16% to 36% of the total CPM emissions over the three test runs. These results question the assumption that CPM from RFG-firing is formed of particles less than 1.0 µm in diameter. Further testing is required to confirm these measurements. If correct, this implies the need for the derivation of emission factors for CPM fractions from RFG combustion both above and below 2.5 µm.

3.5.3. CPM emission factor

The CPM emission factor for natural gas combustion in the US EPA publication AP-42 of 2.67 g/GJ was derived using the original 1991 version of M202. This has been shown to be biased high due to measurement artefacts. Although the test method has been revised twice since the factor was originally published to reduce the artefacts, no amendments to the CPM emission factor in the AP-42 have been made.

The ISO method provides measurement conditions designed to simulate those atmospheric conditions immediately downstream of a refinery stack. The CPM EF derived from these tests using ISO 25597 was 0.81 g/GJ, i.e. 30% of the value of the CPM EF provided in the EPA AP42 publication. This factor is considered to provide more representative estimates of condensable PM emissions from gas-fired combustion units at refineries than that published in the EPA AP-42.

4. FILTERABLE PARTICULATE MATTER (FPM)

The sampling trains in both methods used in this test programme incorporate in-stack devices to collect the filterable particulate fraction: a filter in M202 and an impactor train in ISO 25597. Consequently, FPM concentrations were able to be measured for all three test runs by both methods.

Previous measurements in the USA [24] had identified that the measured FPM fraction for gas-fired combustion systems was, on average, an order of magnitude lower than would be estimated using the emission factor published by the US EPA in their publication AP-42 [8]. That emission factor is replicated in the EEA/EMEP Guidebook [7] which is used by European Member States to assist in the compilation of sectorial emission inventories. The concentration measurements from this test programme have been used to derive an FPM emission factor for comparison with the published factor.

4.1. MEASUREMENT TECHNIQUES

4.1.1. US EPA M202:2017

EPA M202 only specifies the sample chain after the separation of the filterable fraction. Method 202 suggests the use of one of a number of other EPA test methods (Methods 5, 17 or 201A) to collect the FPM fraction. As this test campaign was undertaken in Europe, the in-stack measurement of FPM, prior to the sample gas passing to the M202 test chain, was undertaken according to EN 13284-1:2017 [16]. The FPM measurement system consisted of an in-stack nozzle and filter holder attached to the heated probe leading to the dilution system. 47mm quartz fibre filters were used.

4.1.2. ISO 25597:2013

This standard specifies the methodologies for both the collection of the FPM and CPM fractions. The use of in-stack PM_{10} and $PM_{2.5}$ cyclones is specified prior to the dilution sampling train, although the PM_{10} cyclone is optional for gas-fired units. In practice a Johnas Cascade Impactor, designed in accordance with ISO 23210:2009 [13], with impaction stages for $PM_{2.5}$ and PM_{10} and with back-up filtration, was used. This was installed in-stack upstream of the heated dilution system probe. As with the M202 train, 47mm quartz fibre filters were used.

4.2. TEST RESULTS

Table 8 provides the measured FPM concentration data from the three test runs for both EPA M202 and ISO 25597 sampling systems, along with the associated 95% confidence intervals (CI).

Table 8 FPM concentrations measured by EPA M202 and ISO 25597.

Test run	EPA M202		ISO 25597			
	FPM	95% CI [1]	FPM fraction			95% CI
			$\leq$ PM$_{2.5}$	> PM$_{2.5}$ and < PM$_{10}$	$\geq$ PM$_{10}$	
	mg/Nm^3	mg/Nm^3	mg/Nm^3	mg/Nm^3	mg/Nm^3	mg/Nm^3
1	< 0.2	0.1	< 0.2	< 0.2	< 0.2	0.1
2	< 0.2	0.1	< 0.2	< 0.2	< 0.2	0.1
3	< 0.2	0.1	< 0.2	< 0.2	< 0.2	0.1

Table Note 1: Confidence Interval

For all runs, and for the FPM collection systems used by the two test methods, the FPM concentrations were very low and below the limit of detection.

4.3. DERIVATION OF EMISSION FACTORS

Data on the amount of fuel gas fired during the test runs, the average net calorific value (NCV) of the gas and the average stack gas flowrate for the period of the tests are provided in Section 3.3.4. The calculated average FPM mass emissions (g/h) for each test run are shown in **Table 9**. As the FPM concentrations were below the limit of detection (0.2 mg/Nm^3) for all tests it is not possible, according to the EPA procedures for the derivation of emission factors [25], to determine a 'definitive' EF, but the EPA state that it should be reported as being below LDV. The factors derived for emissions at the limit of detection value are shown in **Table 9**. These show that the FPM emissions related to energy consumption were <0.075 g/GJ. To aid comparison with published EFs and to determine EFs for total PM, in this report a so-called 'indicative' EF for FPM is derived using 50% of the FPM LDV. **Table 9** shows that the average FPM 'indicative' EF was 0.037 g/GJ. For comparison the FPM EF in the EPA AP-42 for gas-firing is 0.89 g/GJ.

Table 9 FPM Emission factors derived from test results.

Test Run	Fuel Fired t/h	Fuel NCV MJ/kg	FPM Emissions g/h	Emission Factor for FPM at LDV g/GJ	FPM 'indicative' Emission Factor g/GJ
1	2.6	48.16	<9.4	0.075	0.038
2	2.7	48.53	<9.6	0.074	0.037
3	2.69	48.49	<9.6	0.074	0.037
Average				0.075	0.037

4.4. COMPARISON OF DERIVED AND PUBLISHED EMISSION FACTORS

Table 10 provides a comparison of the emission factors derived for CPM, FPM and total primary PM from the tests with those published in the US EPA publication AP-42 [8]. The emission factor for FPM published in the AP-42 is replicated in the EMEP/EEA 2019 Air pollutant emission inventory guidebook [7].

Table 10 Derived and published emission factors for gas-firing.

		CPM g/GJ	FPM g/GJ	Total Primary PM (CPM + FPM) g/GJ
Derived	M202	4.83 [1]	0.037 [2]	4.87 [3]
	ISO	0.81	0.037 [2]	0.85 [3]
Published in AP-42		2.67	0.89	3.56

Table Notes:

1. EF includes positive bias due to $NiSO_4$ contamination
2. ‘Indicative’ EF derived from 50% FPM LDV
3. Total PM EF = CPM EF + ‘Indicative’ FPM EF

4.5. DISCUSSION OF TEST RESULTS FOR FPM AND TOTAL PM

The emissions of FPM measured by both methods in all tests were less than the limit of detection value of 0.2 mg/Nm^3. It is not feasible to derive a ‘definitive’ EF but in this report ‘indicative’ FPM EFs have been derived using 50% of the FPM LDV. The FPM emissions from the heater tested are significantly lower than would be calculated using the FPM EF published in the EPA AP-42 (and the EMEP/EEA Guidebook). This is in agreement with test results from the USA undertaken on gas-fired combustion units [24].

The EF for FPM published by the US EPA is of the same order of magnitude as the EF for total primary PM (i.e. ‘indicative’ FPM plus CPM) derived for the emissions from the heater using the ISO 25597 system. The API has suggested that the FPM emission factor for gas-firing published by the EPA should be for total PM instead of solely for FPM. The results of these tests confirm that proposal i.e. the current separate EFs for gas-firing in the EPA AP-42 for FPM, CPM and total PM should be replaced by a single factor for total PM of 0.89 g/GJ. This, however, poses an issue for emission reporting in Europe where estimates of both FPM_{10} and $FPM_{2.5}$ emissions are required. Further work is therefore required to develop robust EFs for the FPM fractions for gas-firing.

5. SEMI-VOLATILE AND INTERMEDIATE VOLATILITY ORGANIC COMPOUNDS (S/IVOCS)

Semi-volatile and intermediate volatility organic compounds, designated together as S/IVOCs, can play a significant role in the formation of the secondary organic aerosol (SOA) in the atmosphere. The lack of knowledge of the refining sector's contribution to the S/IVOC emissions inventory resulted in a literature review being undertaken by TNO [1] in 2020 on behalf of Concawe. That literature review has shown that there are no published S/IVOC emissions measurements from refineries in Europe. The CPM test programme has, therefore, been enhanced with the addition of S/IVOC concentration measurements alongside those of CPM. A test campaign has been undertaken on the heater described in Section 2. In this first phase of testing, the S/IVOC measurement campaign was undertaken separately to the CPM campaign reported in Section 3.

5.1. DEFINITIONS OF NMVOC, IVOC AND SVOC

The vast majority of volatile organic compounds (VOCs) are photo-chemically reactive. Estimates of VOC emissions, excluding those of methane, are required for use in atmospheric chemical and transport models. VOCs (minus methane) can be classified into volatility ranges for use in such studies. The three more volatile ranges are classified as non-methane volatile organic compounds (NMVOC), intermediate volatility organic compounds (IVOC) and semi-volatile organic compounds (SVOC). Less volatile organic compounds are classified as being low volatility (LVOCs) or extremely low volatility (ELVOCs) organic compounds. There are a number of definitions of these classes based on, for example, boiling point, vapour pressure and Henry's Law Constant. In this report, the definitions of NMVOC, IVOC and SVOC originally suggested by Murphy et al [3] and provided in Concawe report 01/21 [1], are used. These definitions are based on ranges of saturation vapour concentration (C*). These are:

NMVOC: C*(at 298°K) is > 3,200,000 µg/m^3

IVOC: C*(at 298°K) is in the range 320 µg/m^3 to 3,200,000 µg/m^3

SVOC: C*(at 298°K) is in the range 0.32 µg/m^3 to 320 µg/m^3

The value of C* for a compound can be calculated from its vapour pressure, molecular weight and the gas constant. To establish the carbon number ranges for the NMVOCs, IVOCs and SVOCs which were likely to be present in the stack samples, the C* values of straight chain alkanes from nonane (C_9H_{20}) through triacontane ($C_{30}H_{62}$) were calculated – see Appendix 3, **Table A3.1**. Aakko-Saksa [27] had suggested that, for n-alkanes, the carbon number for the IVOCs ranged from C12 to C22, and for SVOCs from C23 to C32. The C* values calculated and shown in **Table A3.1** indicate similar ranges: IVOCs from C12 to C19 and SVOCs from C22 to C27, but with an anomaly as icosane (C20) according to the calculated C* value is classified as an SVOC whereas heneicosane (C21) is identified as an IVOC. The vapour pressure value for heneicosane in the data library used [28] is deemed less reliable than that for icosane, as the former had been extrapolated. For the purposes of this report, therefore, heneicosane is considered an SVOC. For straight chain alkanes with carbon numbers C28 to C30 the C* values indicate a classification of LVOC.

Emissions data for IVOCs and SVOCs are not routinely reported in national inventories, the exception being some polycyclic aromatic hydrocarbons (PAHs). In

Concawe report 01/21 [1] TNO have used PAHs as indicator compounds to estimate total S/IVOC emissions. This is based on an assumption in Wu et al [29] that most, if not all, PAHs are S/IVOCs. C* values for those PAHs for which refinery emissions data have to be reported under the E-PRTR Regulation [30] (anthracene, naphthalene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene) have been calculated and shown in **Table A3.1**. This shows that naphthalene is classified as an IVOC, anthracene and benzo(b)fluoranthene are SVOCs and the other 3 PAHs are LVOCs.

5.2. S/IVOC MEASUREMENT METHODS

5.2.1. Sampling

Stack gas sampling was carried out by NPL according to PD CEN/TS 13649:2014 [26]. Sampling involved the adsorption of VOCs on sorbent tubes, which had been prepared by thermo-desorption.

The concentration of water vapour within the heater stack gas was determined from the CPM measurement campaign on the same stack to be approximately 17%. This is high enough to cause condensation in the sampling system. Therefore, as per TS 13649, a dynamic dilution sampling system was used to avoid the formation of any condensation throughout the system.

The system used an aspirator driven by nitrogen which extracted the sample from the stack. The sample gas was passed consecutively through particulate filters and a glass critical orifice. The sample was then diluted with the nitrogen from the aspirator creating positive pressure in the sample line that allowed the transportation of the diluted gas to the gas analyser used to measure the dilution ratio. The dilution ratio was determined by measuring the nitrogen monoxide content of the stack gas and at the outlet of the unheated dilution probe sampling line. The selected critical orifice determined the flow rate at which the sample was extracted from the stack to avoid the formation of any condensation.

A set of linked Perkin-Elmer ATD-type thermal desorption tubes which contained Tenax and Carbopack-X material were installed in a sampling side stream, off the dilution sampling system. The use of two linked tubes provided a carbon number range from C5 to C32, with Tenax being suitable for the range C7 to C32 and Carbopack-X covering C5 to C10. Known volumes of diluted sample gas were drawn into these tubes using low constant-flow sampling pumps at approximately 50 ml/min.

5.2.2. Analysis

Analysis was undertaken in the NPL VOC Diff laboratories based on EN ISO 16017-1 [31]. The analyses were carried out using automated thermal desorption (ATD) systems, one linked to a gas chromatograph (GC) with a flame ionisation detector (FID) for quantification, with the other linked to a GC fitted with a mass spectrometer (MS) for compound identification.

Each tube was first purged with an inert gas. They were then heated whilst a stream of inert carrier gas was passed through the tube to desorb the trapped compounds. These were then passed through a cold trap and cryo-focused before being injected onto a capillary column for individual species separation. For comparison and quantification purposes several standards were run alongside the sample. These standards included two QA/QC standards for quantification purposes, a retention time standard for a series of n-alkanes (C10 to C26) and a PAH retention time standard. As the elution time for compounds in excess of C32 is very long, and these compounds would most likely be LVOCs, the analysis was limited to compounds that were retained for the same period on the GC column as dotriacontane ($C_{32}H_{66}$).

This initial S/IVOC measurement campaign was considered, from an analytical point of view, to be a learning experience permitting future analyses to be refined to allow more accurate quantification. It was not known, for example, what range of VOCs would need to be analysed. Experience from the speciation of the CPM samples had shown that, even where components had been identified, it had been difficult for some compounds to find accurate values for the physical properties needed to calculate their C* values.

Even if the major compounds could be identified accurately, review of **Table A3.1** in Appendix 3 shows that the use of carbon numbers as an indicator of VOC classification can result in some erroneous volatility classifications. For example, naphthalene is an IVOC according to the value of its C*, but with a carbon number of 10 would be classified as an NMVOC. Similarly, benzo(a)pyrene is an LVOC according to its C* value, but with a carbon number of C20 would be classified as an SVOC.

In this first campaign a simple convention was adopted based on the saturation vapour concentration (C*) values of n-alkanes: VOCs with the same retention time on the GC column as an n-alkane were assumed to have the same volatility classification as the n-alkane. A review of the C* values listed in **Table A.3.1** resulted in the following VOC volatility classifications:

- NMVOCs: Compounds retained on the GC column up to the same period as undecane ($C_{11}H_{24}$).
- IVOCs: Compounds retained on the GC column for the same period as dodecane ($C_{12}H_{26}$) through and including nonadecane ($C_{19}H_{40}$).
- SVOCs: Compounds retained on the GC column for the same period as isocane ($C_{20}H_{42}$) through and including hexacosane ($C_{27}H_{56}$).
- LVOCs: Compounds retained on the GC column for the same period as octacosane ($C_{28}H_{58}$) or longer.

It was decided to limit speciation reporting to the sum of the concentration data for compounds retained on the GC column for the same period as n-alkane carbon number pairs, i.e. C8 plus C9 (hexane + nonane) through to C30 plus C31 (triacontane + hentriacontane). The retention times for these n-alkane pairs are shown in Appendix 4, **Table A4.1**.

The compounds with the greatest probability of association with the main chromatograph peaks were individually identified but not quantified. The 11 highest peaks on the chromatograph for one of the Tenax tubes are reviewed in Appendix A4. For the peaks associated with compounds classified as NMVOC or IVOC the probability of correct identification is reasonable. However, there was high uncertainty in peak identification for compounds classified as SVOC or LVOC.

5.3. TEST RESULTS

A test campaign to determine the IVOC and SVOC emissions from the same refinery heater as earlier tested for CPM emissions (Section 3) was undertaken by the National Physical Laboratory (NPL) over a three day period in January 2022. Speciation analyses of the samples collected were also undertaken by NPL.

5.3.1. Test dates and periods

Table 11 provides details of the test dates and duration of the three test runs. An earlier start for the second and third test runs enabled longer sampling times than with the first run. The stack temperature over the three runs was in the range 186°C to 191°C.

Table 11 Dates of campaign and duration of test runs.

Test Runs	Date	Period (mins)
1	25-01-2022	270
2	26-01-2022	360
3	27-01-2022	360

5.3.2. Test Results

Many of the identified hydrocarbons were oxygenated compounds (see Appendix A4). The higher molecular weight compounds were difficult to identify accurately due to the fragility of the parent ion, which tended to break down at high temperature. This resulted in identifications with very low probabilities. PAHs had been used in Concawe report 01/21 [1] as indicators of S/IVOC emissions. However, no PAHs were identified in the test samples, although they may have been present at concentrations below their limits of detection.

The results from the speciation analyses, by carbon number pairing based on n-alkane retention times, are shown in **Table 12**.

The analysis uncertainty is higher than NPL would normally expect. It was not possible for NPL to use bespoke calibration standards due to the unknown nature of the species to be analysed. NPL’s existing standards (for n-alkanes and aromatic compounds) were therefore used to quantify the species found, resulting in higher uncertainties.

There are some anomalies in the results. Firstly, the measured concentrations for run 1 (except for C18/19) are lower than for runs 2 and 3. The fuel gas fired during run 1 had a 9% lower NCV than during the other two runs, with a corresponding 16% increase in the mass of fuel burnt – see **Table 14**. The RFG compositional changes between tests 1 and 2 (and 3) are not known.

Secondly, the sample concentration values for C20/21 during runs 1 and 2, and for C30/31 during run 1, are below the limit of detection. This is in sharp contrast to the values in neighbouring C number bands and to the values for this C number pair for run 3. No reason for these differences can be identified which are due to the analytical processes.

The sample concentration values by VOC classification, using the convention described in section 5.2.2, are shown in **Table 13**. The two linked sorption tubes provided a carbon number range from C5 to C32, so NMVOCs (classified as C2 to C11) are only partially represented. Similarly, the range of LVOCs reported in these tests is very limited.

Table 12 Concentration values for compounds retained on GC column for same periods as n-alkane carbon number ranges.

Carbon Number Range	VOC Class	Run 1		Run 2		Run 3	
		Conc.[1] mg/Nm^3	CI [2] mg/Nm^3	Conc. mg/Nm^3	CI mg/Nm^3	Conc. mg/Nm^3	CI mg/Nm^3
< C8	NMVOC	1.9	0.9	5.5	2.3	5.7	2.4
C8 + C9	NMVOC	6.8	3.2	15.3	6.6	9.8	4.2
C10 + C11	NMVOC	3.1	1.4	9.8	4.2	8.3	3.6
C12 + C13	IVOC	0.6	0.31	2.1	0.9	1.5	0.6
C14 + C15	IVOC	0.08	0.04	0.24	0.1	0.24	0.1
C16 + C17	IVOC	0.65	0.31	0.98	0.42	0.73	0.31
C18 + C19	IVOC	0.88	0.13	0.68	0.29	0.24	0.1
C20 + C21	SVOC	< 0.002	0.0009	< 0.002	0.0009	0.11	0.05
C22 + C23	SVOC	0.05	0.02	1.5	0.6	0.05	0.02
C24 + C25	SVOC	0.11	0.05	4.4	1.9	0.48	0.2
C26 + C27	SVOC	0.09	0.04	3.1	1.3	1.2	0.5
C28 + C29	LVOC	0.1	0.05	1.2	0.5	0.8	0.34
C30 + C31	LVOC	< 0.002	0.0009	0.42	0.18	0.34	0.14

Table Notes:

1. Concentration
2. Confidence Interval

Table 13 Concentration values by VOC classification.

VOC Classification	Concentration mg/Nm^3			
	Run 1	Run 2	Run 3	Average
NMVOC (partial)	11.8	30.6	23.8	22.1
IVOC	2.21	4.0	2.71	2.97
SVOC	0.25	9.0	1.84	3.70
LVOC (partial)	0.1	1.62	1.14	0.95

5.4. DERIVATION OF EMISSION FACTORS

Data on the amount of refinery fuel gas fired during the test runs and the average net calorific value of the gas were provided by the refinery. These data are shown in **Table 14**. The average stack gas flowrate determined by NPL was 12.7 m^3/s, with a 95% CI of 0.8 m^3/s.

Table 14 Details of fuel gas fired.

Refinery Fuel Gas	Test Run		
	1	2	3
Mass fired t/h	3.38	2.92	2.9
NCV MJ/kg	44.07	48.19	48.37

From the stack gas flowrate and concentration data in **Table 13**, mass emission rates for the NMVOCs (limited to higher carbon number compounds), IVOCs and SVOCs have been calculated and shown in **Table 15**. From these and the fuel data in **Table 14**, emission factors in units of g/GJ have been derived and are also shown in **Table 15**.

Table 15 Emission rates and derived emission factors.

Test run	Emissions g/h			Emission factor g/GJ		
	NMVOC (partial)	IVOC	SVOC	NMVOC (partial)	IVOC	SVOC
1	539	101	11.4	3.62	0.68	0.08
2	1399	183	411	9.93	1.30	2.92
3	1088	124	84.1	7.75	0.88	0.60
Average				*7.10*	*0.95*	*1.20*

The sorbent tubes used in these tests were suitable for the range C5 to C32. The emission factor for NMVOCs shown in **Table 15** therefore only represents the portion of total NMVOCs with lower volatility.

For comparison the emission factor for NMVOCs from natural gas firing (derived from difference between EFs for VOCs and methane) given in EPA publication AP-42 [8] and duplicated in the EMEP/EEA Guidebook [7] is 2.58 g/GJ. That EF is for VOCs with carbon number from C2 upwards.

Run 2 significantly influences the EF for SVOCs. The range in emission rates for SVOCs is unexpectedly high as the heater was considered to be running under relatively stable conditions, particularly for runs 2 and 3.

5.5. DISCUSSION ON RESULTS OF S/IVOC TESTS

To accurately determine mass emissions of total IVOCs and SVOCs requires two steps. Firstly, the VOCs need to be sampled and then analysed by a method that permits the accurate identification and quantification of the individual significant compounds, in particular those which are heavier and less volatile. Secondly, the values of the physical and chemical parameters of those compounds need to be determined from data libraries to permit the value of their saturation vapour concentrations (C*) to be calculated, thereby providing their VOC classifications.

As this was the first time that NPL had undertaken measurements of S/IVOCs, and no published data on emissions of these compounds from gas-firing at refineries had been identified, the nature of the species to be analysed was not known. It was not possible, therefore, to use bespoke calibration standards. For this initial test it was agreed to gain preliminary indications rather than accurate quantifications of emissions.

In this campaign a simple convention was adopted based on the saturation vapour concentration (C*) values of n-alkanes. The concentration values derived from the GC FID measurements for retention periods based on those of n-alkanes were allocated to the associated VOC class. The use of this convention is adequate if simple compounds form the majority of emissions. However, where identified (see **Table A4.2**), many of the VOCs were oxygenated compounds. Moreover, the higher molecular weight compounds were difficult to identify accurately. For each of the 5 highest GC peaks classified as SVOC using the retention time convention there were a number of compounds identified by NPL as potential matches. **Table A4.2** shows the most likely 4 or 5 compounds for each of these peaks, each having a low probability. Of the 24 candidate VOCs classified to be SVOCs using the retention time convention, 14 were so classified using their values of C* but 10 were classified as IVOCs. All 5 candidate VOCs classified as LVOCs using the retention time convention were deemed to be SVOCs from their values of C*. There is, therefore, significant uncertainty in allocating concentration values against a classification of NMVOC, IVOC or SVOC when applying the convention based on the retention time of n-alkanes used in this report.

A lesson learnt from the CPM measurement campaign and its associated speciation analyses was that, even where compounds could be identified, for some it was difficult to find accurate values of the parameters which are required to calculate C*. For example, the major constituent of the CPM sample was diethylene glycol dibenzoate. Although the data library used [28] contained a value for the vapour pressure of this compound there was no corresponding reference temperature given. For the 11 highest peaks in the GC analysis of the compounds adsorbed on the test 2 Tenax tubes, NPL identified 39 compounds as potential matches. Values of C* could be determined for all of these, but this required searches of 5 different data bases and information systems.

The results of the tests showed variations in mass emission rates for all classifications of VOCs between runs, with significantly higher emissions of SVOCs in run 2. The NCVs of the fuel fired in runs 2 and 3 were similar and the heater was considered to be operating under stable conditions. Without further information on heater operation or fuel gas composition it is not possible to identify the reasons for these significant differences in SVOC emission rates. However, run 2 significantly influences the average emission factor for SVOCs.

Indicative emission factors were derived from the test data: that for IVOCs was 0.95 g/GJ and for SVOCs was 1.2 g/GJ. For comparison that published by the US EPA for non-methane VOCs (NMVOCs), deemed to have carbon numbers from C2 to C11 in the convention used, is 2.58 g/GJ. The indicative value of S/IVOC emissions derived from these tests, therefore, is of the same order of magnitude as the NMVOC estimated emissions using this factor.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1. CONDENSABLE PARTICULATE MATTER (CPM)

A campaign to measure stack gas CPM concentration has been undertaken on a refinery fuel gas fired heater at a refinery in north-west Europe.

Two test methods were used simultaneously. These were the ISO Method 25597 which dilutes the sample gas with conditioned ambient air to simulate cooling in the atmosphere close to the stack exit and the US EPA Method 202 which uses chilled impingers to reduce the stack gas sample temperature.

The average CPM concentration in the stack measured with ISO 25597 was 2.2 mg/Nm^3. The average CPM concentration measured with EPA M202 was 12.9 mg/Nm^3.

The average emission factors for CPM derived from the measurement results are:

- Dilution technique (ISO 25597): 0.81 g/GJ
- Chilled impinger technique (EPA M202): 4.79 g/GJ.

For comparison the factor published by the EPA, derived from tests using M202, is 2.67 g/GJ.

A difference in emission measurements between M202 and dilution methods has been reported previously. It is known that M202 suffers from a positive bias due to a measurement artefact where residues such as sulphates, are formed in the chilled impinger due to aqueous chemistry and not condensation. The method has been improved since first publication (in 2010 and 2017) to minimise this artefact and also to eliminate some test procedural issues. For this test campaign the 2017 version of M202 was used. In addition, it has been postulated that the rapid cooling of the sample gas in the M202 sample chain results in higher saturation ratios and consequently greater condensation of the condensable constituents. The ISO method, which cools the sample using dilution air, is considered to more closely represent the conditions in which CPM is formed in the atmosphere close to a stack.

There was, however, a much higher uncertainty associated with method ISO 25597, with the 95% confidence interval in excess of 100% of the measured CPM concentration value for all three test runs. This was mainly due to the significantly lower stack gas sample flow rate with the dilution method compared to M202 as well as the lower mass of CPM collected over the test period. For comparison, the 95% confidence intervals for the M202 concentration values were, for all three runs, of the order of 4%.

The CPM samples gathered from the M202 tests were accumulated to provide sufficient sample for speciation analysis. There was insufficient sample from the ISO test to permit speciation.

The organic fraction averaged 14% of the total CPM. Diethylene glycol dibenzoate was identified as the major component of the organic fraction. The presence of this compound was unexpected and investigations were carried out to identify its source but without success. It is probable that it is due to contamination during testing or analysis.

Analyses of the residue following evaporation and drying of the aqueous fraction from the M202 tests identified that the sulphate content of the inorganic fraction accounted for 30% of the total CPM. Nickel accounted for 18.7% of the total CPM. The high concentration of nickel was also unexpected. Subsequent tests have shown that the vast majority of the nickel in the CPM sample was due to contamination from the container used for the drying of the CPM residue. Due to a procurement error the container used was almost pure nickel instead of stainless steel. Although the nickel contamination was significant, it had no impact on the measured mass of CPM which is determined gravimetrically. However, subsequent testing using a stack simulator under the same conditions as the original heater tests identified both the known M202 sulphate artefact (0.8±0.2 mg/Nm^3) and additional contamination from $NiSO_4$ (1.8±0.6 mg/Nm^3) in the CPM sample evaporated and dried in the nickel container. Where M202 is used to determine CPM concentration it is therefore recommended that the test contractor ensures that the container used for the drying of the CPM residue is suitable for acidic solutions. The stack simulator tests also demonstrated that the revisions made to M202 by the EPA in 2010 and 2017 have not eliminated the sulphate artefact, even where the stack SO_2 concentration is low.

It was not possible to undertake speciation analyses of the CPM collected in the ISO 25597 tests due to lack of sample. Without comparative speciation data for the two methods, particularly for anions, it is not possible to put the results into context. However, the measurement artefact plus the sulphate contamination does not account for the differences in CPM concentration measured by the two methods.

It is recommended that further test campaigns are undertaken on other refinery gas-fired combustion units to derive a representative emission factor. ISO 25597, however, in this first test had a much higher uncertainty than M202 due to the lower mass of CPM collected over the test period. One reason for this was the dilution method used resulted in a significantly lower stack gas sample flow rate. In further tests using ISO 25597, therefore, longer sampling periods will be required. Collection of more CPM sample from the ISO 25597 method will permit speciation analysis to be undertaken, which was not possible in this first test campaign. Comparison with the results from the analysis of M202 CPM samples will allow a better understanding of the results from using different techniques to promote CPM formation.

Tests using ISO 25597 provided CPM fractions above and below 5 µm. The results indicate that the CPM fraction >5 µm was in the range of 16% to 36% of the total CPM emissions over the three test runs. These results question the assumption that CPM from gas-firing is formed of particles less than 1.0 µm in diameter. Further testing is required to confirm these measurements. If correct, this implies the need for the derivation of emission factors for CPM fractions above and below 2.5 µm.

6.2. FILTERABLE PARTICULATE MATTER (FPM)

The FPM phase was collected in-stack at the front-end of the sampling trains used with both M202 and ISO 25597 during the test campaign.

For all three test runs with both M202 and ISO 25597 the FPM concentrations were below the limit of detection value (LDV) of 0.2 mg/Nm^3.

Assuming an ‘indicative’ FPM concentrations equal to 50% of the LDV, i.e. 0.1 mg/Nm^3, the FPM contribution to total PM (i.e. FPM plus CPM) ranged from 0.8 % to 4.8 %, depending on the CPM measurement technique. This difference between FPM and CPM emissions is similar to the results from tests using dilution methods undertaken in the USA.

An ‘indicative’ FPM emission factor for RFG-firing of 0.037 g/GJ has been derived using a concentration of 50% of FPM LDV. For comparison the EF for FPM from gas-firing in US EPA AP-42 is 0.89 g/GJ.

That EF for FPM published by the US EPA is of the same order of magnitude as the EF for total primary PM (i.e. ‘indicative’ FPM plus CPM) derived for the emissions from the heater using the ISO 25597 system. The API has suggested that the FPM emission factor for gas-firing published by the EPA should be for total PM instead of solely for FPM. The results of these tests confirm that proposal i.e. the current separate EFs for gas-firing in the EPA AP-42 for FPM, CPM and total PM should be replaced by a single factor for total PM of 0.89 g/GJ.

The API are recommending the use of EPA test method OTM-37, which uses dilution without front end capture of FPM, for the reporting of total PM for gas-firing. In Europe it is anticipated that separate reporting of FPM and CPM will be required. It is recommended, therefore, that further test data on FPM emissions from refinery gas-fired combustion units are obtained to permit the development of a robust and representative EFs for the FPM fractions for this source type.

To ensure that the mass of FPM samples in further testing is above the limit of detection value it is recommended that either longer sampling times to gather more FPM sampling are employed or a more sensitive method is used to quantify FPM mass.

6.3. S/IVOCS

A further campaign, comprising three test runs, has been undertaken on the same refinery heater to measure intermediate volatility and semi-volatile organic compounds (IVOCs and SVOCs). Measurements of these compounds have not been reported previously from refinery combustion sources. This initial test, therefore, was used to provide a preliminary indication rather than accurate quantification of the S/IVOC emissions from the refinery gas-fired heater. It also permitted the contractor (UK National Physical Laboratory) to identify possible refinements to the analytical techniques for future tests.

Samples were collected on sorbent tubes and analysed using GC/MS. Concentrations were determined based on the retention times for pairs of n-alkanes. VOC classifications for the latter were derived using values of saturation vapour concentration, C*. It was assumed that a VOC with the same retention time as an n-alkane had the same VOC classification as that compound. The most likely candidates matching the highest peaks from the GC analysis were identified. For the compounds classified as SVOCs the probability of correct identification was poor. No individual compounds were quantified. This classification method is adequate if the VOCs emitted are simple components, such as n-alkanes. In reality, many of those hydrocarbons that were identified were either branched alkanes or oxygenated compounds. This resulted in significant uncertainty in allocating concentration values against a classification of IVOC or SVOC.

In addition, due to the fragility of the parent ion of the higher molecular weight compounds the use of thermal desorption may have resulted in some breakdown of these.

There were significant variations in the measured concentration of VOCs, classified as either IVOC or SVOC, between runs. This was not expected as the heater, particularly during runs 2 and 3 was considered to be operating under relatively stable conditions and firing gas in a narrow range of calorific value, and hence assumed to be of relatively constant composition. In particular, the average concentration of SVOCs ranged from 0.25 mg/Nm^3 to 9.0 mg/Nm^3 between the three test runs, with a corresponding range of derived EFs of 0.08 g/GJ to 2.92 g/GJ. The average concentration of SVOCs measured over the three test runs was 3.70 mg/Nm^3. This equated to an average emission factor of 1.2 g/GJ.

The average concentration of IVOCs measured over the three test runs was 2.97 mg/Nm^3. This equated to an average emission factor of 0.95 g/GJ.

Due to the uncertainty in the derivation of these emission factors it is recommended that further testing is undertaken. To permit the determination of robust factors, it is further recommended that analytical methods are used, if possible, which provide both identification and quantification of the emitted VOCs with lower uncertainty than achieved during the campaign reported here.

In addition, it is recommended that other sampling techniques are investigated to overcome the problems of degradation of the sample due to thermal desorption, for example the use hydrophobic polyaromatic resin (XAD) adsorbers in conjunction with EPA Test Method 8270D [32].

These tests were the first step taken in the development of the inventory of S/IVOC emissions from European refinery sources. It is recommended that tests are undertaken on other combustion sources e.g. FCCU catalyst regeneration. A review, potentially including analytical testing, should also be undertaken of the composition of VOCs emitted due to vaporisation from potential refinery sources of S/IVOCs, e.g., heated fuel oil storage tanks.

7. REFERENCES

1. Concawe (2021) Literature review on emissions of semi- and intermediate volatile organic compounds and formation of organic aerosols with focus on the refinery sector. Report 01/21. Brussels: Concawe

2. US Office of the Federal Register (2008) U.S. Code of Federal Regulations, Title 40, CFR 51, §51.50

3. Murphy, B. N., Donahue, N. M., Robinson, A. L. and Pandis, S. N.: A naming convention for atmospheric organic aerosol, Atmospheric Chemistry and Physics, 14(11), 5825–5839, https://doi.org/10.5194/acp-14-5825-2014, 2014

4. EEA (2022) European industrial emissions portal. Copenhagen: EEA, https://industry.eea.europa.eu

5. EEA. The UNECE Convention on Long-range Transboundary Air Pollution (LRTAP Convention) database, https://www.eea.europa.eu/data-and-maps

6. EU (2001) Directive 2001/81/EC of the European Parliament and of the Council of 23 October 2001 on national emission ceilings for certain atmospheric pollutants. Official Journal of the European Communities No. L309, 27.11.2001

7. EEA (2019) EMEP/EEA air pollutant emission inventory guidebook. Copenhagen: European Environment Agency

8. EPA (1998) AP 42, fifth edition: Compilation of air pollutant emission factors. Vol. 1: Stationary point and area sources. Chapter 1: External combustion sources. Section 4, Natural gas combustion. Research Triangle Park, NC: US Environmental Protection Agency

9. EPA (2017) Method 202 - Condensable Particulate Matter. Research Triangle Park, NC: US Environmental Protection Agency, www.epa.gov/emc/method-202-condensable-particulate-matter

10. EU (2024) Regulation of the European Parliament and of the Council on reporting of environmental data from industrial installations and establishing an Industrial Emissions Portal and repealing Regulation (EC) No. 166/2006. Official Journal of the European Union, No. L, 2024/1244, 02.05.2024

11. EC (2006) Regulation (EC) 1/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a European Release and Transfer Register and amending Council Directives 91/698/EEC and 9/61/EC. Official Journal of the European Communities No. L33/1, 4.2.2066

12. EC (2006) Guidance Document for the Implementation of the European PRTR. Brussels: European Commission

13. ISO (2009) Stationary source emissions – Determination of $PM_{10}/PM_{2.5}$ mass concentration in flue gas – measurement at low concentrations by use of impactors. International Standard ISO 23210:2009. Geneva: International Organization for Standardization

14. EPA (2016) EPA Method 202 Best Practices Handbook. Research Triangle Park, NC: US Environmental Protection Agency

15. ISO (2013) Stationary source emissions – Test method for determining $PM_{2.5}$ and PM_{10} mass in stack gases using cyclone samplers and sample dilution. International Standard ISO 25597:2013. Geneva: International Organization for Standardization

16. CEN (2017) Stationary source emissions - Determination of low range mass concentration of dust - Part 1: Manual gravimetric method. European Standard EN 13284-1:2017. Brussels: Comité Européen de Normalisation

17. ASTM International (2017) Standard Test Method for Determination of Particulate Matter Emissions Collected by a Dilution Tunnel. Test Method ASTM E2515-11. West Conshohocken, PA: ASTM International

18. ISO (2020) Reciprocating internal combustion engines – Exhaust emission measurement – Part 1: Test-bed measurement systems of gaseous and particulate emissions. International Standard ISO 8128-1:2020. Geneva: International Organization for Standardization

19. EPA (2004) Measurement of $PM_{2.5}$ and PM_{10} emissions by Dilution Sampling. Conditional Test Method (CTM) 039. Research Triangle Park, NC: US Environmental Protection Agency

20. EPA (2018) Measurement of Direct $PM_{2.5}$ and PM_{10} Emissions at Low Concentrations by Dilution Sampling. Other Test Method 37 (OTM-37). Research Triangle Park, NC: US Environmental Protection Agency

21. CEN (2017) Stationary source emissions - Determination of mass concentration of nitrogen oxides - Standard reference method: chemiluminescence. European Standard EN 14792:2017. Brussels: Comité Européen de Normalisation

22. CEN (2017) Stationary source emissions - Determination of volume concentration of oxygen - Standard reference method: Paramagnetism. European Standard EN 14789:2017. Brussels: Comité Européen de Normalisation

23. ISO (2013) Stationary source emissions – Manual and automatic determination of velocity and volume flow rate in ducts – Part 1: Manual reference method. International Standard ISO 16911-1:2013. Geneva: International Organization for Standardization

24. Environ (2012) Development of fine particulate emission factors and speciation profiles for oil- and gas-fired combustion systems. Guide to $PM_{2.5}$ mass emission factors. Stack test support data. Project Number: 04-24298F. Prepared for: American Petroleum Institute, Washington, D.C. Irvine: Environ International Corporation

25. EPA (2023) Recommended Procedures for Development of Emissions Factors and Use of the WebFIRE Database, EPA-453/R-23-001. Research Triangle Park, NC: US Environmental Protection Agency

26. CEN (2014) Stationary source emissions - Determination of the mass concentration of individual gaseous organic compounds - Sorptive sampling method followed by solvent extraction or thermal desorption. European Technical Specification CEN/TS 13649:2014. Brussels: Comité Européen de Normalisation

27. Aakko-Saksa, P. Experiences in semivolatile (SVOC) emission measurements at VTT. Presentation given at Task Force on Emission Inventories and Projections, May 13-15th, Thessaloniki, 2019

28. National Institutes of Health (NIH), PubChem database, https://pubchem.ncbi.nlm.nih.gov

29. Wu, L., Wang, X., Lu, S., Shao, M., and Ling, Z. Emission inventory of semi-volatile and intermediate-volatility organic compounds and their effects on secondary organic aerosol over the Pearl River Delta region, Atmospheric Chemistry and Physics, 19, 8141–8161

30. EU (2006) Regulation (EC) No. 166/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register and amending Council Directives 91/689/EEC and 96/61/EC. Official Journal of the European Union No. L33, 04.02.2006

31. ISO (2000) Indoor, Ambient and Workplace Air - Sampling and Analysis of Volatile Organic Compounds by Sorbent Tube/Thermal Desorption/Capillary Gas Chromatography - Part 1: Pumped Sampling. International Standard ISO 16017-1:2000. Geneva: International Organization for Standardization

32. EPA (2014) Test Method 8270D: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry. Research Triangle Park, NC: US Environmental Protection Agency

APPENDIX 1 PHOTOGRAPHS OF EQUIPMENT USED

Figure A1.1 The Dekati modified Deed-300 Dilution sampling system installed on stack simulator at NPL's laboratory.

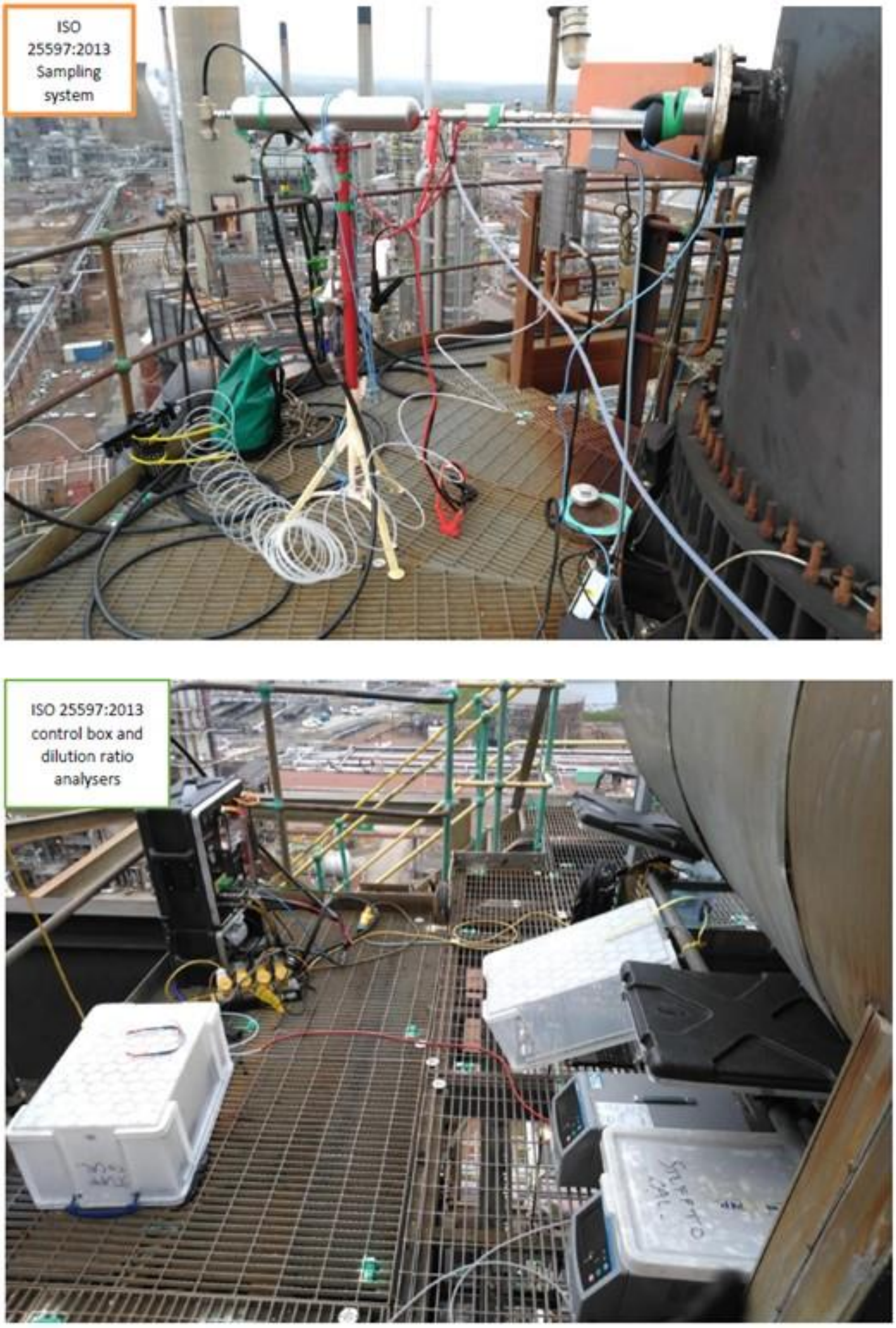

Figure A1.2 The Dekati modified Deed-300 Dilution sampling system installed on heater stack.

Figure A1.3 The US EPA M202 sampling system installed on heater stack.

APPENDIX 2 NPL STACK SIMULATOR TESTS

EPA M202 requires the aqueous fraction from the extraction of the CPM sample to be evaporated at 105°C in an oven and then allowed to dry at room temperature. During the tests a nickel container was used to hold the aqueous fraction instead of a stainless steel one due to a procurement error. Analysis of the residue after drying indicated very high concentrations of nickel. It was postulated that a possible cause for this was that nickel leached from the container into the sample if it was strongly acidic and reacted to produce $NiSO_4$. To verify this, a test was undertaken by NPL on their stack simulator facility at Teddington, England.

A2.1 Description of stack simulator

The NPL stack simulator facility is able to reproduce a wide range of simulated stack gases under controlled operation conditions. It has a rectangular shape with cross-stack path length of 1.5m. It is equipped with two ports at either end of the path length to allow two cross-stack instruments to be installed or the attachments of gas analysers or manual extractive systems.

The facility is a recirculating system which allows flows of air, nitrogen and a selection of 'pollutant' gases into the stack simulator chamber at controlled rates to create predictable mixture concentrations. Complex gas mixtures are generated by blending the test gases from source gas cylinders with nitrogen and air from reservoirs. The stack simulator also incorporates a water injector to provide a controlled water vapour concentration. The gases are recirculated to create a high vertical stack velocity with low gas consumption and low release to the atmosphere. The velocity profile is approximately constant along the length of the test paths. Internal electric heaters allow the 'stack temperature' to be set above the dew point of the recirculating gas mixture.

A2.2 Test undertaken

The test undertaken was designed to replicate as far as possible the original CPM measurement using EPA M202 on the heater stack. The stack simulator gas matrix was generated to be as close to the original heater stack gas composition as possible (see **Table A2.1**). To establish the impact of the use of the nickel container, two M202 tests were undertaken simultaneously for the same duration (3 h 30 mins) as the original tests. The aqueous sample from one M202 system (train 1) was evaporated in the same type of nickel container as used in the original tests. The sample from the second system (train 2) was evaporated in an inert, glass container.

Table A2.1 Composition[1] and temperature of gas used in stack simulator test

Compound	Value	Unit
NO	96.0	mg/m3
SO2	11.0	mg/m3
CO	1.0	mg/m3
CO2	9.4	%vol
O2	10.7	%vol
Water vapour	14.5	%vol
Temperature	175	°C

Table note 1: Concentration data expressed at reference conditions - 273.15K, 101.3 kPa on a dry gas basis

A2.3 Test results

The aqueous fractions from the extraction of the ‘CPM’ samples from trains 1 and 2 were placed on the pre-weighed nickel and glass containers respectively. Following evaporation and drying the containers were re-weighed to determine the mass of the ‘CPM’ samples. The residues were then analysed for nickel and sulphates. **Table A2.2** shows the derived concentrations of the ‘CPM’ and the nickel and sulphate.

Table A2.2 Results of stack simulator test

	Train 1[1]	Train 2[2]	Units
‘Particulate’ concentration[3]	4.2	0.7	mg/m^3
‘Particulate’ expanded uncertainty	0.2	0.2	mg/m^3
Nickel concentration[3]	1.1	0.001	mg/m^3
Nickel expanded uncertainty	0.2	0.0003	mg/m^3
Sulphate concentration[3]	2.6	0.8	mg/m^3
Sulphate expanded uncertainty	0.6	0.2	mg/m^3

Table notes:
1- Sample evaporated and dried in nickel container
2- Sample evaporated and dried in glass container
3- Concentration data expressed at reference conditions - 273.15K, 101.3 kPa on a dry gas basis

A2.4 Conclusions

The gas circulating in the stack simulator was composed of pure compounds; there were no products of combustion and therefore no CPM was present.

The container in train 2 was inert, so no contamination of the sample should occur. The concentrations of ‘particulates’ and sulphates were within their uncertainty ranges, and can be considered the same. The ‘particulate’ measured in train 2, therefore, comprised the known M202 artefact due to SO_2 in the stack gas reacting chemically within the chilled impinger to form sulphate.

The nickel concentration in the ‘particulate’ sample in train 1 is 3 orders of magnitude higher than that measured in train 2. The vast majority of the nickel in the CPM samples in the original tests was, therefore, contamination.

As the ‘particulate’ mass is determined gravimetrically, (i.e. equals mass of container including CPM sample minus mass of container), any nickel leached into the sample from the container does not affect the measured weight of the sample.

However, the sulphate concentration in the train 1 sample is more than three times higher than that from train 2. In addition to the artefact observed in train 2, the most probable explanation for the additional sulphate in train 1 is the formation of $NiSO_4$. This contaminate would have increased the measured CPM mass in the original heater stack tests.

The difference between the measured ‘particulate’ concentrations in train 1 and train 2 is 1.6±0.63 mg/m^3. This cannot be accounted for solely by uncertainty in the determination of the ‘particulate’ and sulphate concentrations. In the anion analysis of the original heater CPM, sulphates comprised the great majority (96.1%)

of the sample, with nitrates forming 3.3% and chlorides 0.5%. Neither of the latter, therefore, can be considered to account for the difference. It is not known whether any other complex chemical reactions may have occurred resulting in the increase in the mass of sample in the train 1 nickel container.

APPENDIX 3 VALUES OF SATURATION VAPOUR CONCENTRATION (C*) FOR SELECTED VOCS

Table A3.1 Values of saturation vapour concentration (C*) for selected VOCs

Compound	Formula	Saturation Vapour Concentration, C* µg/m^3	VOC Classification based on C* [3]
Straight chain alkanes			
Nonane	C_9H_{20}	3.07E+07	NMVOC
Decane	$C_{10}H_{22}$	1.09E+07	NMVOC
Undecane	$C_{11}H_{24}$	3.47E+06	NMVOC
Dodecane	$C_{12}H_{26}$	1.24E+06	IVOC
Tridecane	$C_{13}H_{28}$	3.72E+05	IVOC
Tetradecane	$C_{14}H_{30}$	1.60E+05	IVOC
Pentadecane	$C_{15}H_{32}$	5.62E+04	IVOC
Hexadecane	$C_{16}H_{34}$	1.82E+04	IVOC
Heptadecane	$C_{17}H_{36}$	2.95E+03	IVOC
Octadecane	$C_{18}H_{38}$	4.67E+03	IVOC
Nonadecane	$C_{19}H_{40}$	7.08E+02	IVOC
Icosane	$C_{20}H_{42}$	7.02E+01	SVOC
Heneicosane	$C_{21}H_{44}$	1.39E+03	IVOC
Docosane	$C_{22}H_{46}$	2.14E+01	SVOC
Tricosane	$C_{23}H_{48}$	3.04E+02	SVOC
Tetracosane	$C_{24}H_{50}$	7.42E+01	SVOC
Pentacosane	$C_{25}H_{52}$	2.87E+01	SVOC
Hexacosane	$C_{26}H_{54}$	9.25E+00	SVOC
Heptacosane	$C_{27}H_{56}$	5.74E+00	SVOC
Octacosane	$C_{28}H_{58}$	3.40E-02	LVOC
Nonacosane	$C_{29}H_{60}$	9.46E-03	LVOC
Triacontane	$C_{30}H_{62}$	6.21E-04	LVOC
PAHs			
Naphthalene	$C_{10}H_8$	5.86E+05	IVOC
Anthracene	$C_{14}H_{10}$	6.29E+01	SVOC
Benzo(b)fluoranthene	$C_{20}H_{12}$	6.79E+00	SVOC
Benzo(a)pyrene	$C_{20}H_{12}$	7.45E-02	LVOC
Benzo(k)fluoranthene	$C_{20}H_{12}$	1.31E-02	LVOC
Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	1.86E-03	LVOC

The value of saturation vapour mass concentration (C*) is based on values of saturation vapour pressure, molecular weight and the Ideal Gas Constant.

$$C^* = (P * MW * 1.0\text{E-}09) / (GC * 298)$$

Where:

C* is saturation vapour concentration (µg/m^3)

P is vapour pressure at 25°C (atm)

MW is molecular weight (g/mol)

GC is gas constant = 0.082059 litres.atm/K/mol

To calculate C*, the values of P and MW for each compound were obtained from the National Institutes of Health (NIH), PubChem open chemistry database [28].

The VOC classification was determined by the naming convention described in Section 5.1, based on Murphy et al [3].

There is an anomaly as the calculated value of C* for heneicosane (C21H44) indicates that it is an IVOC whereas icosane ($C_{20}H_{42}$) is indicated as an SVOC. The value of vapour pressure for heneicosane in reference [28] was reported to be extrapolated whereas that for icosane was reported to be measured. The value of C* for heneicosane, therefore, was deemed less reliable. Other naming conventions using values of boiling point and vapour pressure indicate heneicosane as an SVOC. For the purposes of this report, therefore, heneicosane is considered an SVOC.

APPENDIX 4 SPECIATION AND CLASSIFICATION OF VOLATILE ORGANIC COMPOUND EMISSIONS

Two Perkin-Elmer ATD-type thermal desorption tubes containing Tenax and Carbopack-X material were used in series to capture a range of VOCs in the stack gas sample. The use of two linked tubes provided a carbon number range from C5 to C32, with Tenax being suitable for the range C7 to C32 and Carbopack-X covering C5 to C10. The convention used in this report (Section 5.1) is that VOCs with the same GC retention time as n-alkanes with carbon numbers from C12 to C19 are deemed to be IVOCs and from C20 to C27 to be SVOCs. As this report focuses on the emissions of S/IVOCs, the GC analyses of the compounds absorbed on the Tenax tube have been used to provide VOC speciation and classification.

The chromatogram from the Tenax tube used for test run 2 on 26th January is shown in **Figure A4.1**. This sample was chosen for detailed analysis as the measured concentrations of IVOCs and SVOCs emitted during this run were significantly greater than those determined for the other two runs.

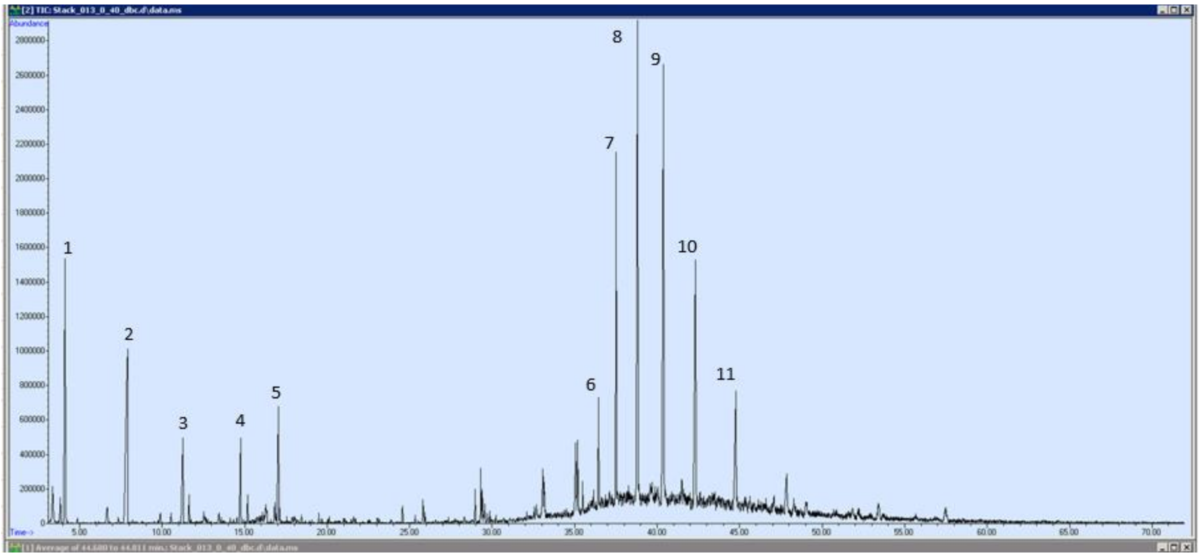

Figure A4.1 Chromatograph of the Tenax tube used for the S/IVOC measurement campaign test run 2

A retention time standard was run for a series of n-alkanes with the results shown in **Table A4.1**.

Identification of those compounds having the greatest probabilities of matching the 11 highest peaks are provided in **Table A4.2**. The probability of positively identifying the relevant compound for peaks 1 through 5 is above 50%. The compound which has the next highest probability is also listed for these peaks. Peaks 6 through 11 are mainly aliphatics, but the probability of correct identification is low. For these peaks the four or five most likely compounds have been listed in descending order of probability.

Table A4.1 Retention times for n-alkane carbon number pairs

Carbon Number	VOC classification	Retention time on GC column	
		Start time - minutes	End time - minutes
<C8	NMVOC	0.00	3.91
C8 - C9		3.92	11.35
C10 - C11		11.36	18.10
C12 - C13	IVOC	18.11	23.94
C14 - C15		23.95	24.89
C16 - C17		24.90	31.05
C18 - C19		31.06	33.34
C20 - C21	SVOC	33.35	35.35
C22 - C23		35.36	37.34
C24 - C25		37.35	40.12
C26 - C27		40.13	44.47
C28 - C29	LVOC	44.48	51.63
C30 - C31		51.64	63.50

Table A4.2 Speciation and classification of VOCs with the highest concentrations absorbed on the Tenax tube used for test run 2 of the S/IVOC measurement campaign

Peak No.	Retention Time Mins	Compound	Formula	Probability of correct peak identity %	Saturation Vapour Conc. C* $\mu g/m^3$	VOC Category		Ref[1]
						From Value of C*	**From GC Retention Time**	
1	4.13	Hexanal	$C_6H_{12}O$	60.2	6.09E+07	NMVOC	NMVOC	1
1	4.13	2-Methyl-Cyclopentanol	$C_6H_{12}O$	10.1	3.13E+07	NMVOC	NMVOC	2
2	7.91	Heptanal	$C_7H_{14}O$	88.0	2.16E+07	NMVOC	NMVOC	1
2	7.91	3-Methyl-Haxanal	$C_7H_{14}O$	3.7	3.64E+07	NMVOC	NMVOC	3
3	11.29	2-Octanone	$C_8H_{16}O$	77.7	9.31E+06	NMVOC	NMVOC	1
3	11.29	6-Methyl-Heptanone	$C_8H_{16}O$	11.5	1.20E+07	NMVOC	NMVOC	4
4	14.77	2-Hexyl-Furan	$C_{10}H_{16}O$	58.6	5.74E+06	NMVOC	IVOC	4
4	14.77	2,4-Decadienal	$C_{10}H_{16}O$	10.6	2.46E+05	IVOC	IVOC	4
5	17.08	2-Nonenal (Z)	$C_9H_{16}O$	64.4	2.26E+06	IVOC	NMVOC	2
5	17.08	2-Nonenal (Z)	$C_9H_{16}O$	19.7	1.93E+06	IVOC	NMVOC	4
6	36.46	9-Hexyl-Heptadecane	$C_{23}H_{48}$	8.2	6.34E+01	SVOC	SVOC	5
6	36.46	3-Ethyl-5-(2-ethylbutyl)-Octadecane	$C_{26}H_{54}$	6.0	3.20E+00	SVOC	SVOC	5

6	36.46	2,6,10-Trimethyl-Tetradecane	$C_{17}H_{36}$	5.3	7.62E+04	IVOC	SVOC	3
6	36.46	Eicosane	$C_{20}H_{42}$	4.9	7.02E+01	SVOC	SVOC	1
6	36.46	7-Hexyl-Eicosane	$C_{26}H_{54}$	4.1	3.20E+00	SVOC	SVOC	5
7	37.54	Eicosane	$C_{20}H_{42}$	8.5	7.02E+01	SVOC	SVOC	1
7	37.54	Tetracosane	$C_{24}H_{50}$	5.1	1.04E+02	SVOC	SVOC	5
7	37.54	10-Methyl-Eicosane	$C_{21}H_{44}$	4.7	4.52E+02	IVOC	SVOC	5
7	37.54	9-Hexyl-Heptadecane	$C_{23}H_{48}$	4.0	6.34E+01	SVOC	SVOC	5
8	38.84	Eicosane	$C_{20}H_{42}$	18.6	7.02E+01	SVOC	SVOC	1
8	38.84	10-Methyl-Eicosane	$C_{21}H_{44}$	5.0	4.52E+02	IVOC	SVOC	5
8	38.84	9-Octyl-Heptadecane	$C_{25}H_{52}$	3.6	8.71E+00	SVOC	SVOC	5
8	38.84	2,6,10,15 Tetramethyl-Heptadecane	$C_{21}H_{44}$	3.3	9.27E+02	IVOC	SVOC	5
8	38.84	Heneicosane	$C_{21}H_{44}$	3.2	9.74E+02	IVOC	SVOC	4
9	40.41	Eicosane	$C_{20}H_{42}$	10.4	7.02E+01	SVOC	SVOC	1
9	40.41	10-Methyl-Eicosane	$C_{21}H_{44}$	5.1	4.52E+02	IVOC	SVOC	5
9	40.41	Heneicosane	$C_{21}H_{44}$	4.7	9.74E+02	IVOC	SVOC	4
9	40.41	11-Butyl-Docosane	$C_{26}H_{54}$	4.1	3.20E+00	SVOC	SVOC	3
9	40.41	Tetracosane	$C_{24}H_{50}$	4.0	7.42E+01	SVOC	SVOC	1
10	42.36	Eicosane	$C_{20}H_{42}$	7.8	7.02E+01	SVOC	SVOC	1
10	42.36	Tetracosane	$C_{24}H_{50}$	7.0	7.42E+01	SVOC	SVOC	1
10	42.36	Heneicosane	$C_{21}H_{44}$	5.2	9.74E+02	IVOC	SVOC	4
10	42.36	2-Methyl-Icosane	$C_{24}H_{50}$	4.6	4.28E+02	IVOC	SVOC	4
10	42.36	10-Methyl-Eicosane	$C_{21}H_{44}$	3.9	4.52E+02	IVOC	SVOC	5
11	44.78	3-Ethyl-5-(2-ethylbutyl)-Octadecane	$C_{26}H_{54}$	7.3	3.20E+00	SVOC	LVOC	5
11	44.78	9-Hexyl-Heptadecane	$C_{23}H_{48}$	6.5	6.34E+01	SVOC	LVOC	5
11	44.78	1-Chloro-Heptacosane	$C_{27}H_{55}Cl$	6.0	1.32E+01	SVOC	LVOC	3
11	44.78	11-Decyl-Tetracosane	$C_{34}H_{70}$	4.7	3.84E+00	SVOC	LVOC	3
11	44.78	11-(1-ethylpropyl)-Heneicosane	$C_{26}H_{54}$	3.7	4.12E+00	SVOC	LVOC	5

Table Note 1. Websites used to obtain vapour pressure data for compounds in order to derive values of saturation vapour concentration C*:

1 - National Institutes of Health (NIH), PubChem database: https://pubchem.ncbi.nlm.nih.gov
2 – ChemSpider database of chemicals: https://chemspider.com
3 – ChemSrc database: https://www.chemsrc.com/en/
4 – The Good Scents Company Information System: https://www.thegoodscentscompany.com
5 – LookChem Company: https://lookchem.com

For each compound its VOC classification has been determined in two ways. Firstly using the VOC classification of the n-alkane with the same retention time as the compound and secondly using the value of the saturation vapour concentration C* of the compound itself. The values of vapour pressure at 25°C required to derive the latter for the compounds listed were not freely available from a single source. The websites used are given in **Table A4.2**.

Review of the Table indicates that for the 11 largest GC peaks there are 39 potential compounds identified. A comparison of the conventions used to determine their VOC classification is shown in **Table A4.3**.

Table A4.3 Comparison of numbers of VOC classifications by naming convention

VOC Classification	Naming Convention	
	Sat. Vapour Conc. C*	GC Retention Time
NMVOC	7	8
IVOC	13	2
SVOC	19	24
LVOC	0	5

This shows that the use of GC retention time instead of the value of C* as the naming convention, as used in this report to derive the concentration of IVOCs and SVOCs, under-estimates the emissions of IVOCs and over-estimates those of SVOCs.

Concawe

Environmental Science for
European Fuel Manufacturing

Concawe
Boulevard du Souverain 165
B-1160 Brussels
Belgium

Tel: +32-2-566 91 60
Fax: +32-2-566 91 81
e-mail: info@concawe.eu
http://www.concawe.eu

ISBN 978-2-87567-196-7
9 782875 671967