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A Review of Particulate Matter Emission Factors for Gas Firing in Combustion Units at Refineries

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A Review of Particulate Matter Emission Factors for Gas Firing in Combustion Units at Refineries

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ABSTRACT

Particulate matter is defined as either filterable (FPM) or condensable (CPM) and by size: FPM2.5 refers to filterable particles with aerodynamic diameters ≤2.5 μm and FPM10 those ≤10 μm. Total filterable PM is referred to as total suspended particulates (TSP), or more commonly as 'dust'. The US EPA assumes that all PM from gas-firing, both filterable and condensable, is less than 1.0 μm in diameter.

A primary use for emission factors (EFs) is the development of PM emission inventories in the absence of measured data. PM emissions from refinery fuel gas (RFG) combustion are estimated, by default, using an EF derived by the US EPA from tests on natural gas (NG) fired industrial combustion units.

A review of published and oil company test data on FPM emissions from RFG-firing has been undertaken. From six tests on five different refinery combustion units, it has been shown that the size profile of total suspended particulates averages 58% FPM2.5 and 99% FPM10. This challenges the widely held assumption that particles from gas-firing are less than 1.0 μm in diameter. However, the tests were all undertaken at one refinery. It is recommended, therefore, that a programme to test different types and sizes of combustion units firing fuel gas at a number of refineries is initiated to establish the validity of the assumption and to compare the average ratios of FPM2.5/TSP and FPM10/TSP with the measurement results above.

The EF for TSP derived from a data set of 42 tests on 28 different RFG-fired units is 0.71 g/GJ. This is of the same order of magnitude as the common EF for FPM2.5, FPM10 and TSP of 0.89 g/GJ for NG-firing in the US EPA AP-42. This is widely replicated for refinery gas firing, for example in the EMEP/EEA *Air Pollutant Emission Inventory Guidebook* (GB). The latter provides guidance to EU Member States on inventory development.

Indicative EFs for FPM10 and FPM2.5 have been derived from the data set of six tests on five RFG-fired units. The EF for FPM10 = 0.7 g/GJ and that for FPM2.5 = 0.41 g/GJ. That for FPM10 is of the same order of magnitude as that in the EMEP/EEA Guidebook. That for FPM2.5, however, is less than 50% of the value of that in the Guidebook.

There were insufficient data for NG-firing in refinery units to establish if the assumption that the size of particles from natural gas combustion is limited to <1.0 μm is valid.

The only published EF for CPM emissions from gas-firing has been shown in an American joint industry/intergovernmental test programme to be conservatively high due to an artefact with the test method used in its derivation. Although the test programme indicated that CPM emissions are negligible relative to FPM from gas-firing, the US EPA has not, as yet, updated the EF for CPM emissions from natural gas fired combustion units.

A series of test campaigns employing ISO standard method 25597 which uses dilution sampling is required to generate robust CPM EFs for both natural gas and RFG-firing.

KEYWORDS

Filterable Particulate Matter (FPM), Condensable Particulate Matter (CPM), Total Suspended Particulates (TSP), Dust, Emission Factor (EF), FPM2.5, FPM10, Gas-Firing, US EPA AP-42, ISO-25597, EN 13284-1:2017, EN ISO 23210:2009

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SUMMARY

Particulate matter (PM) emitted from refinery combustion sources, such as heaters, furnaces and boilers, is composed of filterable and condensable fractions. Filterable PM (FPM) is defined as those particles that are emitted directly from the stack as a solid or liquid at stack conditions and which can be captured on the filter used in standard FPM measurement test methods e.g. EN 13284-1. Condensable PM (CPM) means material that is in the vapour phase at stack conditions, but condenses upon cooling after discharge from the stack to form solid or liquid PM. Particulate matter is divided into size fractions: PM10 and PM2.5 are defined as those particles with an aerodynamic diameter equal to or less than 10 µm and 2.5 µm respectively. Total filterable PM is referred to as total suspended particulates (TSP), or more commonly as ‘dust’.

A primary use of emission factors (EFs) for combustion sources by both competent authorities (CAs) and refineries is the development of 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 emission factors (EFs) for filterable, condensable and total PM emissions from gas-firing. The EFs were derived from tests on natural gas-fired boilers.

Although some critical combustion units at refineries may be fired solely with natural gas (NG), the main gaseous fuel burnt is a mix of process off-gases, known as refinery fuel gas (RFG). The major constituents are typically methane, ethane, propane and hydrogen. Fuel gas may need to be supplemented with natural gas when the volumes of RFG produced are insufficient for site use.

AP-42 does not include PM EFs for RFG-firing. The EPA recommends that the EFs for combustion of NG should be used as the default PM EFs for RFG combustion.

The EPA assumes that all particulate matter, both filterable and condensable, from natural gas-firing is less than 1.0 µm in diameter as NG does not contain ash and the nucleation of PM from combustion products should not yield particles of any larger size. This assumption is widely adopted for both NG and RFG combustion, e.g. in the EMEP/EEA *Air Pollutant Emission Inventory Guidebook* (GB) which provides guidance to EU Member States on inventory development. Because of this supposition a measurement of TSP concentration is assumed to also provide the concentration values for both the FPM2.5 and FPM10 fractions.

Routine measurements of dust emissions from refinery combustion sources are commonly required for emission limit compliance reasons. Measurement of the separate FPM fractions, FPM10 and FPM2.5, requires the use of a standard method (EN ISO 23210:2009) that is more difficult to implement than that for TSP and for gas-firing such test data are considered superfluous. Measurements of the separate FPM fractions from gas-firing, therefore, are not often undertaken.

The common EF for TSP, FPM10 and FPM2.5 for NG-firing in the 2023 edition of the EMEP/EEA Guidebook was reduced from the AP-42 value of 0.89 g/GJ to 0.14 g/GJ. This follows a review of emissions from NG-fired large combustion plants measured with continuous emission monitors (CEMs). The EF value for RFG-firing was left

unchanged at 0.89 g/GJ. This was because the CEMs data base for RFG-firing was considered statistically too small to permit the robust derivation of a revised EF.

Tests have recently been undertaken by the UK National Physical Laboratory (NPL) for Concawe to measure the FPM and CPM emissions from an RFG-fired refinery heater. The tests used EN ISO 23210 to extract all of the FPM from the sample stream before the CPM is formed in the second part of the sampling train. Concentration measurements for both FPM2.5 and FPM10 as well as TSP were obtained. All three measurements were below the minimum detection limit (MDL) of 0.2 mg/Nm^3. The emission factor for FPM derived using the MDL is 0.075 g/GJ. With all data below the detection limit it is not possible to derive a definitive emissions factor. It can only be concluded that in the Concawe/NPL test campaign the FPM emissions were <0.075 g/GJ. This compares to the EF for FPM2.5 in the GB for RFG-firing of 0.89 g/GJ.

In addition, the tests determined that 30% of the measured CPM emissions were in excess of 5.0 µm in size. Not all of the total PM emissions, therefore, were less than 1.0 µm in diameter as assumed by the US EPA.

The tests therefore indicated a significant discrepancy between the measured emissions of FPM2.5 and those that are estimated to occur using the EF in the EPA AP-42. It also challenged the assumption on the size of PM from gas-firing originally used by the EPA in development of the EFs. These have led to a review by Concawe of available FPM and CPM data from emission tests on refinery gas-fired external combustion units. The following summarises that review.

<u>FPM emissions from RFG firing:</u> Measurements of the FPM fractions from RFG-firing are infrequently made. There is, therefore, a sparsity of data in the public domain. The main published sources of data are reports providing the results of tests on different combustion units undertaken as part of an industry/intergovernmental research project in the USA. These provide data on FPM2.5, FPM10, TSP and CPM emissions from gas-fired combustion units at 5 US refineries. Three of these units were RFG-fired, the other two being solely NG-fired.

Concawe, as a result of a questionnaire sent to Member Companies (MCs), received data on the emissions of both TSP and the FPM fractions from 12 tests undertaken on 11 refinery RFG-fired combustion units. Of these only 6 tests, undertaken in 2012/13 on five combustion units at one European refinery, provided FPM2.5 and FPM10 concentration data in excess of their MDLs. The Concawe MC data set also included data from tests in which only TSP was measured. In total there were 39 measurements of TSP on 25 different combustion units at 6 refineries with results in excess of MDL.

TSP data for RFG-firing were therefore available from the 3 units tested in the US as part of the joint industry/government research project and from the 39 tests at Concawe MC refineries.

From these 42 tests the **derived EF for TSP = 0.71 g/GJ**

This EF is of the same order of magnitude as the TSP EF for RFG-firing in the EMEP/EEA GB of 0.89 g/GJ.

Data on the concentrations of FPM2.5 and FPM10 in excess of their MDLs were obtained from six tests undertaken by Concawe MCs.

The average ratios of the mass emission rates of FPM2.5 and FPM10 to the mass emission rates of TSP for these 6 tests were consistent in value between tests, particularly for FPM10/TSP, and are given below:

FPM2.5 / TSP = 0.58 ± 0.05

FPM10 / TSP = 0.99 ± 0.004

These ratios challenge the assumption that all filterable particulates from RFG-firing are less than 1.0 µm in diameter. Almost all TSP from the tests was composed of FPM10; about 60% of the TSP was composed of FPM2.5.

The average of the individual TSP EF for the six tests which provided FPM2.5 and FPM10 data was 0.184 g/GJ. This is just above the first quartile (0.178 g/GJ) of the TSP EFs derived for each of the 39 tests in the Concawe MC TSP data set. EFs derived for FPM2.5 and FPM10 from the six tests data set might, therefore, not be representative of the typical FPM emissions from an RFG-fired refinery combustion unit. EFs for FPM2.5 and FPM10 were therefore calculated using the average values of the ratios shown above and the average TSP EF (0.71 g/GJ) derived from the full (42 tests) data set. The six tests providing the FPM2.5/TSP and FPM10/TSP ratios were all undertaken at the same refinery. It is unknown whether the ratios would be significantly different for other RFG compositions. These EFs, therefore, should be considered as indicative.

Indicative EF for FPM2.5 = 0.41 g/GJ

Indicative EF for FPM10 = 0.7 g/GJ

The indicative EF for FPM10 for RFG-firing is of the same order of magnitude as the common value of the EFs for FPM2.5, FPM10 and TSP of 0.89 g/GJ provided in the EMEP/EEA Guidebook. The indicative EF for FPM2.5 for RFG-firing is less than half of that value in the Guidebook.

The FPM2.5 and FPM10 EFs were derived using data from six tests at one refinery combined with an average TSP EF derived from 42 tests at 9 refineries. It is recommended that further campaigns are undertaken to measure emissions of FPM2.5, FPM10 and TSP from RFG-firing. These would firstly establish the validity of the average ratios of FPM2.5/TSP and FPM10/TSP used in the derivation of the indicative EFs. They would also identify if PM emissions from RFG firing are generally lower, or the ratios of their size fractions are different, from when the six tests were undertaken in 2012/13 due to possible changes in, for example, gas composition and burner technology. The test campaigns should be undertaken on different types and sizes of combustion units firing RFG with a range of gas composition.

FPM emissions from natural gas firing**:** From the published results of the industry/intergovernmental test programme in the USA only two sets of data were available for natural gas firing in refinery combustion units. This very limited data set also indicated differences in the derived EFs for FPM2.5, FPM10 and TSP, but are insufficient to establish if the assumption that all FPM from NG-firing is less than 1.0 µm in diameter is valid.

CPM emissions from gas firing**:** The emission factor for CPM for NG-firing in industrial combustion units published in the EPA AP-42 has been demonstrated to be conservatively high due to an artefact with the test method used in its derivation. There is no other published EF for CPM emissions from gas-firing (either NG or RFG) in industrial combustion units. The results of the US industry/intergovernmental test programme indicated that CPM emissions from gas-firing were negligible relative to total FPM emissions. Concawe has initiated a test programme to measure CPM from RFG combustion in refinery units. The first test, undertaken on a refinery heater, provided results that were the opposite of the US tests in that the total FPM emissions were very low compared to the CPM. It is recommended that further tests to measure CPM are undertaken on both RFG and NG firing.

1. INTRODUCTION

1.1. DEFINITIONS

The term **particulate matter (PM)** is equivalent to "atmospheric aerosol" and defines a suspension of air-borne solid particles and/or droplets of various sizes. The atmospheric aerosol is formed of primary and secondary particulate matter. **Primary PM** means particles that enter the atmosphere as a direct emission from a stack or an open source. It comprises two components: filterable PM (FPM) and condensable PM (CPM). **Secondary PM** refers to particulate formed in the atmosphere, usually as a result of chemical reactions such as the oxidation of SO_2 in the presence of other pollutants.

Filterable PM **(FPM)** means particles that are emitted directly by a source as a solid or liquid at stack or release conditions and captured on the filter used in standard FPM measurement methods e.g. EN 13284-1 [1]. **Condensable PM (CPM)** means material that is in the vapour phase at stack conditions, but condenses upon cooling immediately after discharge from the stack to form solid or liquid PM. **Total PM** is the sum of FPM and CPM.

PM is divided into size fractions; **PM10 and PM2.5** are defined as PM with an aerodynamic diameter equal to or less than 10 µm or 2.5 µm respectively [2]. The latter fraction is also referred to as '**fine**' particulate matter. PM sized between 2.5 and 10 µm is referred to as '**coarse**' particulate matter.

For the purposes of UNECE and EU legislation (e.g. Gothenburg Protocol [3], IED [4]) relating to PM emissions from industrial stacks the terms '**dust**' and '**total suspended particulate matter (TSP)**' have the same meaning, which is the total mass of particles, of any shape, structure or density, dispersed in the gas phase at the sampling point conditions which may be collected by filtration [2]. As the sample is measured at stack conditions the PM measured will be in the filterable phase. In this report, therefore, the terms dust and TSP refer to total FPM emissions.

1.2. LEGISLATIVE BACKGROUND

In recent years there has been an increased focus on 'fine' particulate matter. The EU Ambient Air Quality Directives [5][6] have been revised [7] setting air quality standards for 2030 that are more closely aligned with the World Health Organization (WHO) recommendations. For PM2.5 the original EU air quality annual limit value of 25 $µg/m^3$ has been reduced to 10 $µg/m^3$. The National Emissions Ceiling Directive (NECD) [8] has also been amended and now establishes reduction commitments for EU Member States' emissions of PM2.5. In addition, there is the potential for PM2.5 to be included in the emission reporting requirements in the Industrial Emissions Portal (IEP) Regulation [9], which may have potential implications for the requirements imposed under the revised Industrial Emissions Directive [4].

Guidance to EU Member States on inventory development is provided in the EMEP/EEA *Air Pollutant Emission Inventory Guidebook* (GB) [10]. This, however, is inconsistent in (the sense) that for the majority of sources the emission factors (EFs) for PM are for FPM whereas for automotive emissions the EFs are for total PM, i.e. FPM plus CPM. EFs for CPM have been included in recent editions of the GB for some sources which are known to have significant CPM emissions, e.g. wood burning. To ensure consistency there is the potential for CPM EFs to be provided in the GB for all sources.

With this growing emphasis on fine particles, it is important that the EU national refinery sector FPM2.5 inventories are as robust as possible.

1.3. EMISSION FACTORS

An emissions factor (EF) is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. Conventionally, where the fuel fired has a range of composition, and hence heating value, published emission factors for combustion sources provide an estimate of the mass of pollutant 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 fired.

Particulate emissions from gas-firing, both filterable and condensable, are assumed to be less than 1.0 µm in diameter [11]. This assumption leads to the EF for FPM emissions from gas-firing published in the widely cited US EPA compendium of emission factors AP-42 [12] having the same value for the FPM2.5 and FPM10 fractions and for TSP (dust).

The EF for FPM2.5 in the EMEP/EEA GB is 0.89 g/GJ, replicating its equivalent in imperial units in the EPA AP-42. That for natural gas has been revised downwards in the 2023 edition of the GB [10] from 0.89 g/GJ to 0.14 g/GJ.

The main gaseous fuel burnt in refineries is a mix of process off-gases, known as refinery fuel gas (RFG). The ‘typical’ composition of RFG is shown in a table in Annex B, Section 2.3 of the Refinery BREF [13], with the major constituents, by volume, being methane (25%), ethane (19%), propane (7%) and hydrogen (40.5%). This may need to be supplemented with natural gas (NG) when the volumes of RFG produced are insufficient for site use. NG may also be used as the sole fuel for critical combustion units such as for power generation.

The national inventories of FPM2.5 for the refinery sector can be calculated from emission estimates using EFs, e.g. as given in the EMEP/EEA GB, or from data from continuous emission monitors (CEMs) installed on combustion units with power ratings ≥50 MW and/or from short-term ‘periodic’ FPM concentration measurements.

Both CEMs and periodic tests measure ‘dust’, i.e. total FPM, but as all FPM from gas-firing is assumed to be ‘fine’ then the dust concentration is correspondingly assumed to equal the FPM2.5 concentration.

1.4. ISSUES WITH PUBLISHED EMISSION FACTORS

For refinery particulate emission inventories to be robust there are two requirements:

i) The FPM and CPM EFs need to be representative of emissions from refinery gas-fired units;

ii) The assumption that both CPM and FPM from gas-firing are ≤ 1.0 µm in diameter needs to be correct.

The emission factor for CPM for gas-firing in industrial combustion units published in the EPA AP-42 has been demonstrated to be conservatively high due to an artefact with the test method used in its derivation. Concawe has initiated a test programme to measure CPM from refinery RFG-fired combustion units. The test method used permits the concentrations of FPM2.5, FPM10, TSP and CPM to be measured. The results of the first test campaign [14] (referred to in this report as 'Concawe/NPL test 1') showed that the FPM2.5 concentration was below the minimum detection limit (MDL) for all three tests. The emission factor derived from the value of the MDL is more than an order of magnitude lower than the EF for FPM2.5 for refinery gas firing provided in the EMEP/EEA GB. The derived CPM EF was more than 3 times lower than that provided in the EPA AP-42 publication. The test method also separated the CPM into size fractions above and below 5 µm. The average mass of CPM >5.0 µm from the three tests undertaken during the campaign was determined to be 30% of the total CPM emissions.

The test results, therefore, indicated that the EFs provided in the EMEP/EEA GB and the EPA AP-42 might not be representative for either FPM2.5 or CPM. They also challenged the assumption that all PM from gas-firing is sized ≤ 1.0 µm.

These significant findings, if replicated in other tests, would indicate that the current methodologies to calculate PM inventories are not robust.

This report provides details of the standard methods used to measure both FPM and CPM concentrations. It reviews the EFs for both FPM and CPM from gas-firing published by the US EPA and the EU EEA. It compares these to EFs derived from limited published test data and from FPM test campaigns performed by Concawe member companies (MCs) on RFG-fired combustion units at refineries. Recommendations are made for future testing to improve the knowledge base on particulate emissions from such sources.

2. QUANTIFICATION OF PM CONCENTRATION USING SHORT TERM STACK MEASUREMENTS

The refinery BREF [13] requires continuous monitoring of dust emissions for combustion units rated ≥50 MW. The data from these are used to establish compliance with emission concentration limit values imposed in operating permits. Periodic measurements, which normally are limited to a minimum sampling period of 30 minutes, may also be required. The latter, undertaken in conjunction with stack gas flow measurement, permit the quantification of mass emissions over the test period. This section gives information on ISO and European standards and on test methods developed by the US EPA to measure PM concentration for such purposes.

2.1. FILTERABLE PM

2.1.1. Total FPM – also referred to as Total Suspended Particulate (TSP) or Dust

European standard **EN 13284-1:2017** [1] is used for the measurement of total FPM. The standard applies to concentrations below 50 mg/m^3 at standard conditions. The sampling system consists of an in-stack nozzle and filter holder. Isokinetic sampling is undertaken with the particulates collected on the filter at stack temperature. The filter is weighed prior to and after the test. The minimum detection limit (MDL) is typically between 1 mg/m^3 and 2 mg/m^3 depending on the sensitivity of the weighing system.

In the USA the equivalent standard is **EPA Test Method 5** [15].

2.1.2. FPM10 and FPM2.5

Separation of the particulate matter is achieved using the difference in inertia of the different sized particles. The two techniques using this principle in the measurement of the PM fractions are impactors and cyclones.

European/International standard **EN ISO 23210:2009** [16] is used for the measurement of the 2.5 µm and 10 µm size fractions. This method uses impactors and is thus limited in its application to samples containing FPM concentrations <50 mg/m^3. Above this concentration there is the potential for an impactor to be overloaded [17]. The sampling system comprises an in-stack nozzle, an impactor train comprising two impactors and a back-up filter. Sampling is carried out at a fixed, representative point within the stack. Particles larger in size than 10 µm are deposited on the collecting plate filter of the first impactor, and the 'coarse' PM in the range of 2.5 µm to 10 µm on the plate of the second impactor. The remaining 'fine' particulate, the FPM2.5 fraction, is collected on the back-up filter. The combined particles collected on the second impactor and the back-up filter make up the FPM10 fraction. The mass of particulate on the filters is determined gravimetrically.

The standard specifies limitations on stack gas temperature (≤250°C), pressure (85 – 110 kPa) and humidity (≤110 g/m^3). It is also a requirement that the stack gas dew point is below the stack gas temperature. It is also not applicable to stack gases where the majority of particulates are greater than FPM10.

The standard states that impactors always exhibit losses of mainly coarse particles diffusively on the walls and the nozzle plates of the cascade impactors. There is no rinse, e.g. with acetone, of these surfaces at the conclusion of the test. This artefact results in a negative bias in the measured mass of particles greater in size than 10 µm. The sum of the FPM fractions measured with this standard cannot, therefore, be used to provide an accurate value for the mass of total FPM. If TSP is required in addition to the FPM fractions, a measurement using EN 13284-1 would also need to be undertaken.

In the USA, the standard used for the mass measurement of FPM10 and FPM2.5 is **EPA Method 201A** [18]. The main difference between this and EN ISO 23210 is that in-stack cyclones are used instead of impactors to separate the FPM into size fractions. This method incorporates a post-test acetone rinse as part of sample recovery. The Method 201A states that total FPM can be determined from the sum of the measured mass fractions if sampling is undertaken within 90 to 110 percent of isokinetic flow.

2.2. CONDENSABLE PM

Condensable primary PM measurement requires the flue gas sample stream, after the removal of the filterable fraction, to be cooled to ambient conditions. The latter can be achieved either by the use of condensers and impingers or by mixing the flue gas in a dilution chamber with ambient air. The latter replicates more closely the conditions under which CPM is formed in the atmosphere.

The use of condensers and impingers is described in **US EPA Method 202** [19]. There is no international equivalent. At the front-end of the sample train of Method 202 (M202) the FPM is extracted from the sample and measured using EPA Method 5 or 201A. The gas sample is then cooled in a water-jacketed glass coil condenser with the condensed water vapour from the sample stream 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 a filter which is maintained in the range of 20 to 30 °C. The CPM and condensed water vapour are recovered from the sampling train components up to and including the filter for laboratory analysis via rinsing (with water, acetone and hexane), drying and weighing.

This method has a known artefact where SO_2 in the stack gas reacts chemically in the impinger water to form sulphates [20]. These would not be expected to be formed as CPM in the stack exhaust plume, but are erroneously counted as such in this method. 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 gas-fired sources [21].

The dilution method is described in **ISO 25597:2013** [22]. At the front-end of the sample train is an in-stack cyclone sampling system and filter, equivalent to that used by EPA 201A, to extract and permit measurement of the mass of the filterable fractions. The sample gas stream is mixed with conditioned ambient air at a dilution ratio of at least 20:1 in the mixing zone of the dilution chamber. It then resides for more than 10 seconds in the ageing zone of the chamber to induce the formation of the condensable fraction. A portion of the diluted sample, at ≤42 °C, is then passed to a PM2.5 cyclone to separate the CPM in the ≤2.5 µm size range from any larger diameter particles formed within the dilution chamber. The CPM2.5 sample is then collected on a filter. The CPM is recovered from the dilution chamber and filter via rinsing, drying and weighing.

2.3. TOTAL PM (TPM) - SUM OF FPM AND CPM

US EPA Other Test Method (OTM) 037 [23] is similar to ISO 25597, but with a front-end cyclone system. This can incorporate either PM10 and PM2.5 cyclones or only a

PM10 cyclone depending on the test objectives. To determine TPM2.5 both cyclones are required. The cyclones remove and permit the measurement of FPM sized >10 µm and the 'coarse' FPM sized between 2.5 µm and 10 µm. Unlike ISO 25597 there is no back-up filter to capture the FPM2.5 fraction. This fraction, therefore, is retained in the sample gas which passes into the mixing ('residence') chamber where the CPM is formed. The PM collected within the dilution system and on the final sample filter therefore comprises the sum of the condensable PM and the FPM2.5. As the EPA assumes all condensable PM is sized <1.0 µm, this mass of PM is assumed to be that of total PM2.5 (TPM2.5).

OTM 037 was developed from US EPA Conditional Test Method (CTM) 039 [24]. OTM 037 applies more sensitive gravimetric sampling and analysis methods to the diluted and cooled stack gas samples, achieving better precision than can be achieved with CTM 039 alone. It also includes additional modification of the specifications for CTM 039 equipment to improve accuracy and precision at low concentrations.

3. QUANTIFICATION USING EMISSION FACTORS

This section provides the factors commonly used to estimate PM emissions. Emission factors are used by both competent authorities (CAs) and refineries to develop PM emission inventories. They are used where measurement data, e.g. from continuous emission monitors (CEMs) or periodic testing, are limited or not available. Inventory data are used for example by CAs to meet the reporting requirements of the NECD [8] and by refineries as input to the Industrial Emissions Portal (IEP) [9], formerly known as the E-PRTR.

3.1. FILTERABLE PM

The most widely accepted emission factor for FPM from gas-firing in stationary sources is published by the US EPA in their publication AP-42, Section 1.4 [25].

The factor in **Table 1.4-2** for PM (filterable) from natural gas combustion is 1.9 lb/10^6 scf, equivalent to **0.89 g/GJ**.

The EPA assumes all filterable PM from gas-firing to be less than 1.0 µm in diameter. It believes that these assumptions for PM size are valid "since natural gas does not contain ash and the nucleation of PM from combustion products will not yield particles larger than 1.0 µm" [11]. The published FPM emission factor therefore is used to provide estimates of TSP, FPM10 and FPM2.5.

The EF was developed from 21 tests undertaken on 11 NG-fired utility and industrial boilers in the period 1990 to 1995.

The EPA give EFs a rating providing an overall assessment of how good the factor is based on both the quality of the tests undertaken to derive it and on how well the factor represents the emission source. The rating for the PM (filterable) EF for natural gas-firing is "B" (above average).

AP-42 does not include emission factors for all fuels. For example, for the refining sector it does not provide EFs for the combustion of refinery fuel gas (RFG) or coke. This is recognised in the EPA *Emissions Estimation Protocol for Refineries* [26] which states that the emission factors for filterable and condensable PM in AP-42 for natural gas are also the recommended default emission factors for RFG combustion.

The EF of 0.89 g/GJ is replicated in the EMEP/EEA *Air Pollutant Emission Inventory Guidebook* [10] (the 'Guidebook') to permit the estimation of TSP, FPM10 and FPM2.5 emissions from the combustion of refinery fuel gas in refinery furnaces, process heaters and boilers.

Until the 2023 edition of the Guidebook, the same EF was provided for natural gas combustion. It has been updated with a common EF for FPM2.5, FPM10 and TSP of **<0.14 g/GJ**. This EF was developed by the German Environment Agency (UBA) [27] from continuous emission monitors (CEMs) measuring TSP installed on large combustion plants. The '<' sign indicates that the factor has been derived from measurement data some of which were below the limit of quantification. It is provided solely to give additional information on the data quality. The Guidebook advises that the emission factor of 0.14 g/GJ should be used directly for calculation of TSP for natural gas-fired combustion units.

The Guidebook supports the reporting of air emissions data under the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP) [28]. It must also be used by the EU Member States to fulfil their emissions reporting requirements under the National Emission reduction Commitments Directive (NECD) [8]. This directive establishes reduction commitments for Member States' emissions of fine particulate matter, which is defined as FPM2.5. It also requires annual reporting of FPM2.5 and FPM10 and optional reporting of TSP emissions.

3.2. CONDENSABLE PM

The US EPA also publishes an EF for CPM from gas-firing in stationary sources in their publication AP-42, Section 1.4 [25].

The factor in **Table 1.4-2** for PM (condensable) from natural gas combustion is 5.7 lb/10^6 scf. This equates to **2.67 g/GJ**. The US EPA rating for this EF is "D" (below average).

This EF is now considered unrepresentative as it was based on a very limited data set using an obsolete test method for condensable PM similar to Method 202. The latter is known to be subject to a positive bias because of the partial conversion of non-condensable gases such as SO_2 into residues which are indistinguishable from true CPM. 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 gas-fired sources [21].

Although revisions to M202 have been issued by the EPA to reduce the impact of the known artefacts, no revised EF has, as yet, been proposed by the EPA.

4. DEVELOPMENT OF CPM MEASUREMENT METHODS AND FPM/CPM EMISSION FACTORS

The dilution technique (e.g. method **ISO 25597:2013** [22]) cools the sample to near ambient temperature by mixing with clean ambient air. The conditions for the formation of CPM within the test equipment are therefore similar to those in the exhaust plume from a stack. The test results, therefore, are considered more comparable to ambient air measurement test results than those produced by rapid cooling of the sample, such as in EPA Method 202.

Techniques using dilution have been used for some time for the measurement of total PM (TPM) emissions (i.e. the sum of FPM and CPM) from automotive exhausts, e.g. ISO 8178-1:1996 [29]. These methods, however, are not suitable for measurements on refinery stacks due to the size and weight of the test equipment.

A national ambient air quality standard (NAAQS) was promulgated in the USA in 1997 and implemented by the EPA in 2007. This required consideration of PM2.5 and PM10 emissions, including the condensable fraction, when developing or modifying stationary source air quality permits. As Method 202 was known to have a significant bias for gas-firing, there was a need for an alternative method to provide accurate measurements of industrial stack total PM emissions. There was a focus on PM2.5 as all PM emissions from gas-firing were assumed to be less than 1.0 µm in size.

The need for a dilution system that was small enough to be used on industrial stacks resulted in a series of tests being undertaken. These were initially led by the American Petroleum Institute (API) but evolved into a collaborative industry/government programme [30]. The combined programme is hereafter referred to as the "API/GRI/DOE" (API/Gas Research Institute/US Department of Energy) programme after the main sponsors. The aims of the programme were to develop a) improved dilution sampling technology and test methods and b) emission factors for PM2.5 mass emissions. A series of tests were undertaken between 1998 and 2003 using both dilution and chilled impinger (M202) techniques to permit the comparison of results. As the tests focussed on PM2.5, cyclones were installed in the sampling train to remove any particulates sized >2.5 µm.

Both external and internal combustion units were included in the programme. Six campaigns were undertaken on heaters and boilers firing gaseous fuels, either RFG or NG. Only 5 of these, however, provided comparative data for the dilution method versus Method 202. For the sixth test only the dilution system was used. The results from the API/GRI/DOE programme were summarised in a report by Environ International Corporation for the API [31].

The test programme confirmed that the use of Method 202 to determine condensable PM when burning fuel gas either RFG or NG, even with a low sulphur content, gave positively biased results because of the artificial conversion of SO_2 to sulphate.

The dilution sampling method results for total PM (i.e. condensable + filterable PM) were found to be similar to those for filterable particulate, as measured using a traditional in-stack filter. For the 6 tests reviewed by Environ the average value of the EF for TPM2.5 derived using the dilution method was 0.096 g/GJ. For the 5 tests using M201A/M202, the average value of the EF for FPM2.5 was the same value. The formation of CPM, therefore, was found to be negligible relative to that of FPM from the gas-fired units tested.

The API correspondingly proposed changes to the PM EFs for NG combustion in the EPA publication AP-42, Section 1.4 [25]. These were that the EF for "PM (Condensable)" be changed to "negligible" and that for "PM (Total)" be changed to be the same as that for "PM (Filterable)" i.e. 1.9 lb/10^6 scf (equivalent to 0.89 g/GJ). Those proposed changes have not been implemented by the EPA.

An outcome of the API/GRI/DOE test programme was the development of a compact dilution sampler. The design of this type of sampler was incorporated in EPA Conditional Test Method (CTM) 039 [24] published in 2004. Subsequently CTM 039 was enhanced and further developed into EPA Other Test Method (OTM) 037 [23] published in 2018.

The API has undertaken a series of 111 test campaigns on 58 gas-fired combustion units using OTM 037 at a refinery in the USA [32]. An in-stack PM10 cyclone was used at the front end of the sampling train to ensure any particulate matter sized in excess of 10 µm was excluded from the measurement. The EF for total PM10 developed from those tests was 0.0016 lb/MMBtu (HHV). This equates to 0.76 g/GJ (NCV). As the API considers that CPM emissions are negligible for gas-firing this EF can be deemed to also be representative for FPM10.

In Europe there is also the need for representative EFs for PM2.5 from gas-firing in combustion units in the oil and gas refining sector.

The 2016 NECD [8] establishes reduction commitments on EU Member States for their FPM2.5 emissions. It requests use of the EMEP/EEA Air Pollutant Emission Inventory Guidebook [10] in the development of their inventories. The EF for FPM2.5 from natural gas firing in the most recent edition of the GB has been reduced by over 80% but there has been no revision to the EF for RFG-firing.

A major issue with the GB is that the PM EFs provided are inconsistent on a sector-by-sector basis. Historically, industrial stack PM measurements have been made solely of the filterable fractions and the EFs in the GB for petroleum refining (NFR sector 1.A.1.b) reflect that. Measurements of PM emissions from automobile exhausts, however, have for some time been of total PM (i.e. filterable plus condensable). The EFs in the GB for emissions from this source correspondingly are for total PM.

The GB is regularly updated and part of this exercise in recent years is a review of the published particulate EFs to identify if they represent filterable or total PM. The aim of this partial review is not stated. The implication from the revised text in the GB is that this is the first step in ensuring consistency in PM EFs in a future edition of the GB, with PM EFs for all sectors/sources being either for total PM or separate EFs being provided for both FPM and CPM.

As noted in Section 2.2, the EF for CPM in the EPA AP-42 for gas-firing is now discredited. The API has proposed a revised EF for Total PM from gas-firing, but has not suggested any separate updates of the EFs for FPM2.5 or CPM either from NG-firing or from RFG-firing.

In response to this lack of up-to-date EFs for both FPM and CPM for gas-firing, Concawe has initiated a test programme, undertaken by the UK National Physical Laboratory (NPL, using EPA Method 202 and ISO 25597 to obtain comparative measurements of CPM emissions from gas-fired refinery combustion units. Both of these methods incorporate FPM measurements at the front-end of the sampling train; for TSP with M202 and for FPM fractions FPM2.5 and FPM10 with ISO 25597.

The test programme will therefore also permit the development of FPM EFs for RFG-firing.

One test campaign (Concawe/NPL test 1) on a gas-fired refinery heater has been undertaken to date [14]. The indicative CPM EF derived from the ISO 25597 test data was 0.81 g/GJ.

In all three tests in the campaign the FPM concentration was less than the minimum detection limit (MDL) of 0.2 mg/Nm^3. The EF derived using the MDL concentration value was 0.075 g/GJ. The FPM emissions, therefore, during the test campaign were <0.075 g/GJ. The TPM emissions were correspondingly <0.89 g/GJ.

The results from this preliminary test, therefore, are in agreement with the conclusion from the API/GRI/DOE tests that the TPM for gas-firing is of the same order of magnitude as the EF for FPM in the EPA AP-42 publication (0.89 g/GJ). However, the API/GRI/DOE tests determined CPM emissions to be negligible, whilst the Concawe test indicates that it is the FPM emissions that are negligible.

5. DISCUSSION OF PUBLISHED EMISSION FACTORS AND TEST PROGRAMME RESULTS

There is general universal adoption of the EPA's assumption that the particulate matter produced by gas-firing in industrial stationary combustion units, both filterable and condensable, is all sized with an aerodynamic diameter less than 1.0 µm [11]. The EFs for FPM2.5, FPM10 and TSP all, therefore, have the same value.

Guidance from the EPA states that the PM EFs for NG firing should be used as the defaults for RFG firing.

The EF for FPM in the EMEP/EEA Guidebook for NG-firing has been updated in the 2023 edition, with a reduction from 0.89 g/GJ to 0.14 g/GJ. The original EF was developed from tests undertaken about 30 years ago. The new EF was developed using data from continuous emission monitors (CEMs) installed on NG-fired large combustion plants (LCP) in Germany.

Two series of tests have been undertaken on gas-fired boilers and heaters in the USA. The first, a joint industry/government (API/GRI/DOE) programme, was undertaken primarily to develop a dilution method permitting the derivation of a representative EF for total PM2.5 from gas firing. The tests in that programme were made on a mix of NG and RFG fired units, and the results averaged to provide EFs for 'gas' firing. Comparative tests were undertaken using both EPA Methods 201A/202 and the prototype of CTM 039, the predecessor of OTM 037. The use of Method 201A at the front end of the M202 sampling train also permitted FPM2.5 emissions to be measured. These tests established that Method 202 had a significant positive bias. The EF in AP-42 for CPM for gas-firing, derived using a similar method to 202, is therefore considered not fit for purpose. The API derived an updated FPM EF, assumed applicable to all fractions, of 0.096 g/GJ. The tests established CPM emissions to be negligible.

The second series of tests was undertaken for API on a large number of RFG fired units at a US refinery using dilution method OTM 037 to measure TPM10. The TPM10 EF derived was 0.76 g/GJ.

In Europe a test programme to develop a CPM EF for RFG-firing is being undertaken by Concawe. The test methods used also permit EFs for FPM2.5, FPM10 and TSP to be derived. The first test (Concawe/NPL test 1), in contrast to the API/GRI/DOE results, determined FPM to be negligible and the derived CPM EF to equal 0.81 g/GJ.

The published and/or derived EFs for natural gas firing are summarised in **Table 1**.

Table 1 PM Emission factors for natural gas firing in industrial external combustion units

Reference	Emission Factor g/GJ	
	FPM2.5	CPM[1]
EPA AP-42 [25]	0.89	2.67[2]
API/GRI/DOE[3] [31]	0.096	Negligible
EMEP/EEA GB [10]	<0.14[4]	-

Table notes:

1. CPM assumed to be sized <2.5 µm
2. Known to have significant positive bias and hence EF considered not fit for purpose
3. Average derived from tests on both NG and RFG fired units
4. ‘<’ symbol means some measured data were less than limit of quantification value. Users are advised to use EF value of 0.14 g/GJ

The values of the EFs shown in **Table 1** indicate that the EF for FPM2.5 published in the EPA AP-42 is conservatively high. The API/GRI/DOE EF was developed from tests on a mix of NG and RFG fired units so cannot be considered representative of emissions from solely NG-firing. The EF in the EMEP/EEA Guidebook has been developed recently (published in the 2023 edition of the GB) and is specific to NG-firing. However, the EF was developed from CEMs data, i.e. from TSP (dust) measurements. Its use as the EF for FPM2.5 and FPM10 is based on the assumption that all FPM from NG-firing is sized ≤1.0 µm in diameter.

The API/GRI/DOE test programme used a non-standard dilution method to measure CPM emissions. The tests indicated that CPM emissions from gas-firing are negligible. The API proposed changes to the EPA AP-42 publication, but they were not implemented by the EPA. The initial Concawe test (Concawe/NPL test 1) to develop a CPM EF for RFG-firing confirmed that the CPM EF in the EPA AP-42 publication over-estimates emissions, but contrary to the API/GRI/DOE test findings, it found that the CPM emissions from RFG firing are significantly higher than the FPM emissions.

The published and/or derived EFs for refinery fuel gas firing are summarised in **Table 2**.

Table 2 PM Emission factors for refinery fuel gas firing in external combustion units

Reference	Emission Factor g/GJ		
	FPM2.5	CPM[1]	Total PM[2]
EPA AP-42[3] [25]	0.89	2.67[4]	3.56[4]
EMEP/EEA GB [10]	0.89	-	-
API/GRI/DOE[5] [31]	0.096	negligible	0.096
API/Ramboll [32]	-	-	0.76[6]
Concawe/NPL test 1 [14]	<0.08[7]	0.81	<0.89

Table notes:

1. CPM assumed to be sized <1.0 µm in diameter (for all but Concawe/NPL test 1)
2. Based on assumption that all FPM is sized <2.5 µm in diameter (for all but API/Ramboll and Concawe/NPL test 1)
3. EPA state that AP-42 EFs for NG firing should be used as defaults
4. Known to have significant positive bias for CPM and hence considered not fit for purpose
5. Average derived from tests on both NG and RFG fired units
6. Test method included FPM sized between 2.5 and 10 µm in diameter, hence EF is for total PM10
7. All measured data at less than MDL. If emissions were at value of MDL the EF would = 0.08 g/GJ

6. REVIEW OF DATA FROM FPM MEASUREMENT CAMPAIGNS

6.1. API/GRI/DOE TEST PROGRAMME

The initial test programme undertaken by the API was on three gas-fired refinery combustion units (tests at refineries coded as 'A' [34], 'B' [35] and 'C' [36]). Units 'A' and 'C' were steam raising boilers and unit 'B' was a process heater. These tests evolved into a collaborative joint industry/government programme involving seven tests on both external and internal combustion units and both gas and liquid-fired units. Of these tests two were on gas-fired process heaters (test codes: 'Alpha' [37] and 'Charlie' [38]). The latter was fitted with a selective catalytic reduction (SCR) system to reduce NOx emissions. A final report of all the tests comprising the joint programme was published [30].

The tests were undertaken on a research project basis with sampling being undertaken for six hours on every test run to improve sensitivity. This is in comparison to routine compliance tests which normally require sampling for a minimum of 30 minutes per run.

Where a sample was not detected, i.e. the test value was <MDL, the data were excluded from EF calculations. This treatment of non-detects was acknowledged to differ from the procedure used at that time by the US EPA for development of EFs [33] in which half of the MDL is substituted for the non-detect data point. It was recognised that the EFs calculated using the API/GRI/DOE approach would be higher than those using the EPA methodology.

The tests involved the in-stack separation and measurement of the FPM fractions using cyclones as per EPA Method 201A. These were installed as the front-end of the sampling train for Method 202 used to measure CPM.

Table 3 provides the speciated FPM test results from the tests undertaken under the API/GRI/DOE programme on gas-fired units installed at refineries.

Table 3 FPM Emission factors derived for natural gas and refinery gas-fired combustion units from API/GRI/DOE tests

Test Code	Type of gas fired	TSP Conc. mg/dscm	Emission Factor g/GJ					
			FPM2.5	Uncert. %[1]	FPM10	Uncert. %[1]	TSP	Uncert. %[1]
A	RFG	0.17	0.0126	n/a[2]	0.0755	n/a[2]	0.0793	332
B	RFG	0.85	0.105	62	0.306	82	0.478	51
C	NG	<0.16[3]	0.0335	n/a[2]	0.0368	139	0.0464	196
Alpha	RFG	<0.71[3]	0.208	76	0.282	75	0.425	89
Charlie	NG	0.28	0.0263	170	0.0478	110	0.11	82

Table notes:

1. Uncertainty at 95% confidence level
2. n/a = not applicable. Only one run of the three tests undertaken was within detectable limits
3. Some, but not all, of the constituents of the test results were below MDL

The average FPM EFs for the complete data set and for the different gaseous fuels fired are given in **Table 4**. However, it should be noted that there are high uncertainties associated with the derived EF values. This is despite the efforts to reduce uncertainty by having six-hour sampling periods to collect more PM than would be achieved with the minimum 30 minutes typically used for periodic testing. The ratios of the FPM fraction emission factors relative to TSP emission factors for NG and RFG-firing are shown in **Table 5**.

Table 4 Average FPM EFs for refinery combustion units based on type of gas fired

Data set	Number of data points	Average Emission Factor g/GJ		
		FPM2.5	FPM10	TSP
All	5	0.08	0.15	0.23
RFG fired	3	0.11	0.22	0.33
NG fired	2	0.03	0.04	0.08

Table 5 Ratios of FPM2.5 and FPM10 emission factors to TSP emission factors for refinery combustion units based on type of gas fired

Test Code	Gas fired	EF Ratio %	
		FPM2.5 / TSP	FPM10 / TSP
A	RFG	15.9	95.2
B		22.0	64.0
Alpha		49.0	66.3
Average		**29.0**	**75.1**
C	NG	72.2	79.4
Charlie		23.9	43.5
Average		**48.0**	**61.4**

6.2. PERIODIC TESTS OF TSP AND FPM FRACTIONS UNDERTAKEN AT CONCAWE MEMBER COMPANY REFINERIES

Periodic tests are routinely undertaken at European refineries to confirm compliance with permit conditions relating to dust (TSP) emission concentrations. Tests to measure the emissions of the FPM fractions are undertaken on an infrequent basis.

Concawe has undertaken an exercise to gather data from its Member Companies for both the TSP and the FPM fraction tests. The data sets gathered have been reviewed for the test procedures and methodologies used and data quality. This has resulted in the exclusion of some campaigns from the data set, for example where tests have been undertaken using non-international test methods. In essence this means that only tests using EN 13284-1 for the measurement of TSP emissions and EN ISO 23210 for FPM2.5 and FPM10 emissions have been included for further analysis. In addition, to permit comparison with the results from the API/GRI/DOE programme, all non-detect test results, i.e. those with values <MDL, have been excluded from EF calculations.

As the results for FPM from the first test campaign in the Concawe CPM measurement programme (Concawe/NPL test 1) on an RFG-fired heater were all below the MDL these have also been excluded.

6.2.1. TSP

Results from 46 periodic test campaigns were obtained which were deemed to have been undertaken according to the set criteria outlined above. Of these tests 7 were non-detects. The individual EFs calculated for the 39 tests with measurements in excess of the MDL are provided in Appendix A.

The average TSP EF derived from those 39 tests is 0.74 g/GJ. See **Appendix A, Table A1**.

6.2.2. PM2.5 and PM10

Twelve reports of test campaigns undertaken to measure FPM2.5 and FPM10 using EN ISO 23210, along with tests to measure TSP using EN 13284-1 undertaken during the same campaign, were submitted in response to the Concawe data request.

Six of these 12 tests reported non-detect measurements of FPM2.5 and FPM10. Of those six, two of the corresponding TSP test campaigns also reported measured emissions <MDL.

The other six tests were undertaken at the same refinery for a significantly longer period than the minimum 30 minutes required for routine periodic testing, thus increasing the amount of FPM collected on the filters and decreasing the likelihood of measurements being non-detects.

The EFs derived from the test data from the six campaigns for FPM2.5, FPM10 and TSP are provided in **Table 6**. In addition, the TSP concentration in mg/Nm^3 at 3% O2 on a dry gas basis, is also given for each test.

Table 6 EFs for FPM2.5, FPM10 and TSP from six periodic test campaigns on RFG-fired units

Test campaign number	TSP concentration mg/Nm^3	Emission Factor g/GJ		
		FPM2.5	FPM10	TSP
1	1.1	0.125	0.207	0.208
2	0.4	0.0554	0.0865	0.0867
3	0.3	0.101	0.170	0.171
4	0.2	0.0386	0.0746	0.0756
5	0.3	0.0492	0.0794	0.0804
6	0.5	0.266	0.481	0.485
Average	0.5	**0.106**	**0.183**	**0.184**

The value of the first quartile of the data set of 39 TSP test results tabulated in **Appendix A, Table A1** is 0.178 g/GJ. The TSP EFs for four out of the six tests are in the lower quartile. The EFs for FPM2.5 and FPM10 derived in **Table 6,** therefore, might not be representative of the range of emissions which may be considered typical for refinery combustion units.

The ratios of the FPM2.5 and FPM10 emission factors relative to those of TSP for each of the six test campaigns are shown in **Table 7**.

Table 7 Ratios of FPM2.5 and FPM10 emissions to TSP emissions from six periodic test campaigns on RFG-fired units

Test campaign number	Ratio %	
	FPM2.5 / TSP	FPM10 / TSP
1	60.1	99.5
2	63.9	99.8
3	59.1	99.4
4	51.1	98.7
5	61.2	98.8
6	54.8	99.2
Average	**58.4**	**99.2**
Standard Deviation	**4.7**	**0.4**

The ratios of FPM10 to TSP shown in **Table 7** are consistently close with a standard deviation of 0.4%. The values of the corresponding ratios for FPM2.5 to TSP are less consistent, but with a standard deviation of 4.7%.

These data challenge the general universal adoption of the EPA's assumption that all TSP from gas-firing is sized less than 1.0 µm, i.e. in the FPM2.5 size fraction, in which case all of the ratios should be 100%.

6.3. DISCUSSION

Measuring FPM emissions, particularly the 2.5 µm and 10 µm fractions, using gravimetric methods is considered challenging. This can be seen from the number of tests resulting in non-detects in the data sets reviewed above. A major issue is the low FPM concentration from gas combustion. The API/GRI/DOE test programme was undertaken to a high standard and planned to reduce uncertainty by, for example, running tests for 6-hour periods compared to the 30 minutes typically used for periodic testing. Even so there were a number of tests with values below the MDL. In one of these (code A) the FPM2.5 concentration measured was 0.027 mg/dscm. This was only slightly higher than the PM concentration in the ambient air sampled during the test period of 0.02 mg/dscm.

Filterable PM concentrations determined using EPA M201A are the sum of net filter weights plus one or more acetone rinses to recover particles deposited on the surfaces of the sampling equipment. The API state in [31] that for levels in gas-fired sources, typically net filter weights are less than zero because of unrecovered filter fragments, and the acetone rinse residue weights after drying are indistinguishable from acetone rinse sample train blanks. Thus, the true filterable PM concentration is often biased by these measurement limitations. The issue of the loss of filter micro-fibres has been addressed in the latest (2017) edition of EN 13284-1 which specifies good practice for the pre-conditioning of filters as well as the requirements for the sampling and filter treatment conditions.

Standard EN 13284-1 has been validated in field tests with special emphasis on dust concentrations in the region of 5 mg/m^3. This is in contrast to the TSP concentrations measured in the 39 Concawe MC tests (**Appendix A, Table A1**): these have a median value of 1.6 mg/Nm^3 with a range between 0.1 mg/Nm^3 and 12.9 mg/Nm^3. The CEN standard, therefore, is often being operated at its limits of sensitivity for measurement of dust from gas-firing.

There are significant differences between the determined ratios between the measured TSP emission factors and those of FPM2.5 and FPM10 between both the test programme results and the gases fired. A comparison is shown in **Table 8.**

Table 8 Comparison between the determined ratios of FPM2.5 and FPM10 emission factors to TSP emission factors

Programme	Gas fired	Number of tests	Average Ratio %	
			FPM2.5 / TSP	FPM10 / TSP
API/GRI/DOE	Natural Gas	2	48	61
	Refinery Fuel Gas	3	29	75
Concawe MC	Refinery Fuel Gas	6	58	99

The significant point from these results is that both the API/GRI/DOE and Concawe MC tests indicate that FPM emissions are not limited to particles smaller than 2.5 µm in diameter.

For the six Concawe MC tests the ratios of the FPM10/TSP EFs were very consistent, averaging 0.99 with a standard deviation of 0.004. There was, therefore, very little particulate matter >10 µm in the measured TSP. The ratios of the FPM2.5/TSP EFs were also relatively consistent, averaging 0.58 with a standard deviation of 0.05.

By contrast, the results from the three API/GRI/DOE tests on RFG-fired units showed that the percentage of the TSP formed of particles >10 µm varied from 5% to 36%. TSP was measured by different methods in the two programmes. In the Concawe MC tests it was measured separately using EN 13284-1; the 2.5 µm and 10 µm fractions were measured with EN ISO 23210. The API/GRI/DOE tests used a test equivalent to EPA Method 201A. This uses cyclones to separate the FPM into three fractions (>10 µm, >2.5 µm to ≤10 µm and ≤2.5 µm) which are summed to determine TSP. This methodology increases the uncertainty in the determination of TSP. It should also be noted that the API/GRI/DOE programme was focussed on the determination of total PM2.5, and the measurement of TSP was a peripheral outcome from the use of M201A to measure FPM2.5 emissions.

However, the API/GRI/DOE were undertaken at different refineries with correspondingly different RFG compositions whereas the Concawe MC tests were undertaken at the same refinery with the 6 tests being undertaken within the period of seven months. It is feasible that the composition of the RFG over this period was relatively constant. There is a need, therefore, to undertake further testing to establish the impact of RFG composition on the particle size distribution.

7. CONCLUSIONS

The measurement of PM from gas-firing on refinery stacks is challenging as the concentration of the emissions can be close to ambient, with correspondingly relatively high levels of uncertainty.

Refinery Fuel Gas Combustion - Filterable PM

A review has been undertaken by Concawe of the results from FPM emission measurements reported from a published industry/intergovernmental research project in the USA [30] and from tests undertaken by Concawe Member Companies (MCs) on refinery combustion units firing RFG. The data base of results included 49 tests for TSP (dust) and 9 tests for FPM2.5, FPM10 and TSP.

TSP: The average EF for TSP derived from 42 tests (excluding 7 which were < MDL) = **0.71 g/GJ.**

This EF is of the same order of magnitude as the TSP EF for RFG-firing in the EMEP/EEA GB of 0.89 g/GJ.

FPM2.5 and FPM10: Six of the 12 test results using EN ISO 23210 reported by Concawe MCs provided FPM fraction data in excess of the MDL.

The average ratios of the emissions of FPM2.5 and FPM10 to the TSP emissions for these 6 tests were: FPM2.5 / TSP = 0.58, FPM10 / TSP = 0.99

These results challenge the assumption that all filterable particles from RFG-firing are less than 1.0 µm in diameter. Almost all TSP from the tests was composed of FPM10. About 60% of the TSP was composed of FPM2.5. The 6 tests, on five combustion units, were all undertaken at the same refinery over a 7-month period when the RFG composition may feasibly have been relatively constant. It is not known how RFG composition, which will vary from refinery to refinery, influences the particle size distribution in FPM emissions.

EFs for FPM2.5 and FPM10 for RFG-firing were calculated by multiplying the average ratios of the fractions derived from the six tests with the TSP EF derived from the 42 tests. The TSP EFs from four of the six tests, however, were the first quartile of the Concawe MC 39 tests. The derived EFs, therefore, can only be considered as indicative as it is not known if the average value of the ratios derived from the six tests are representative of the range of typical emissions from RFG-firing.

The derived indicative EFs are: FPM2.5 = 0.41 g/GJ, FPM10 = 0.7 g/GJ.

The indicative EF for FPM10 is of the same order of magnitude as that in the EMEP/EEA Guidebook (0.89 g/GJ). The EF for FPM2.5 in the EMEP/EEA GB is approximately a factor two higher than the derived indicative EF.

Natural Gas Combustion - Filterable PM

Data were available for review from only two tests undertaken on refinery combustion units firing NG. Both tests indicated, as with RFG-firing, that TSP from NG-firing was not composed solely of fine particulates <2.5 µm in size. The averages for the two tests indicated that ~50% and ~60% respectively of the TSP were FPM2.5 and FPM10.

Condensable PM

There is no published EF for CPM from gas-firing which can be considered to provide representative emission estimates.

8. RECOMMENDATIONS

Filterable PM

The indicative EFs for FPM2.5 and FPM10 developed in this report were derived using the average ratios of the derived EFs for FPM2.5 and FPM10 versus that for TSP from each test. For the six campaigns reviewed, the values of both ratios were all relatively constant across the data set. All the tests had relatively low emission levels. They were all undertaken at the same European refinery. A wider test programme should be initiated using EN ISO 23210 in parallel with EN 13284-1 to measure FPM2.5, FPM10 and TSP, allowing the derivation of EFs from a more robust data set. These tests should be undertaken on combustion units with a range of power rating and at different refineries. This would permit the particle size distribution to be determined over a wider range of RFG compositions and FPM concentration values. The measurement of the FPM size fractions is challenging due to the small masses of FPM2.5 and FPM10 collected using EN ISO 23210. The test procedures need to be optimised to ensure where possible that the results are in excess of the MDL.

Periodic TSP test data should also be collected for NG-fired combustion units in refineries to permit the development of an EF for TSP emissions from NG-firing. This would permit comparison with the TSP EF provided in the EMEP/EEA GB developed from data from CEMs installed on large combustion plant.

Condensable PM

CPM EFs need to be developed for both RFG and NG combustion. It is recommended that the current Concawe/NPL programme to measure CPM emissions from a range of refinery sources using ISO 25597 is continued, if possible combined with the FPM test programme outlined above.

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10. APPENDIX A: DATA FROM PERIODIC TESTS TO MEASURE DUST (TSP) UNDERTAKEN BY CONCAWE MEMBER COMPANIES

Table A1 shows the results of TSP measurement campaigns undertaken at 6 refineries on 25 different combustion units firing RFG. Results which were less than the minimum detection limit are excluded. More than one result shown for a particular source (as shown in column 'Comb. Unit code #') indicates periodic tests undertaken at different times.

Table A1 TSP emission factors calculated for each test campaign

Test code #	Refinery	Comb. Unit code #[1]	Concentration mg/Nm^3	Calculated EF g/GJ
1	A	1	0.8	0.224
2	A	2	5.3	1.420
3	A	3	2.5	0.673
4	A	4	1.7	0.448
5	B	5	3.1	0.834
6	C	6	5.8	2.305
7	C	7	0.1	0.027
8	D	8	1.6	0.446
9	D	9	1.9	0.542
10	D	10	4.1	1.107
11	D	11	4.5	1.417
12	E	12	0.5	0.135
13	E	12	1.5	0.480
14	E	13	1.7	0.733
15	E	14	0.2	0.054
16	E	14	2.1	0.702
17 [2]	E	15	1.1	0.208
18 [2]	E	15	0.4	0.087
19	E	16	1.5	0.405
20	E	16	1.4	0.196
21	E	16	0.6	0.185
22 [2]	E	16	0.3	0.171
23	E	17	0.6	0.162
24	E	17	2.3	0.621
25 [2]	E	17	0.2	0.076
26 [2]	E	18	0.3	0.080
27	E	19	12.9	3.482

28	E	19	5.4	2.704
29 [2]	E	19	0.5	0.485
30	E	20	1.4	0.378
31	E	20	0.5	0.052
32	F	21	5.3	1.358
33	F	21	4.9	1.428
34	F	22	3.4	1.560
35	F	22	3.3	1.070
36	F	23	1.7	0.867
37	F	23	2.7	1.247
38	F	24	1.4	0.378
39	F	25	0.5	0.146

Table notes:

1. Code number of combustion unit or common stack tested
2. TSP test campaign undertaken at same time as FPM2.5 / FPM10 test campaigns – see **Table 6**

Properties of Calculated EF data set:

Number in data set	39
Mean	0.741 g/GJ
First quartile	0.178 g/GJ
Median	0.48 g/GJ
Mean to median ratio	1.54

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