



**National Pollutant Inventory**

# **Emission Estimation Technique Manual**

**for**

**Non-Petroleum  
Industrial Gases**

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**EMISSION ESTIMATION TECHNIQUES  
FOR  
NON-PETROLEUM INDUSTRIAL GASES**

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## 1.0 Introduction

The purpose of all Emission Estimation Technique (EET) Manuals in this series is to assist Australian manufacturing, industrial and service facilities to report emissions of listed substances to the National Pollutant Inventory (NPI). This Manual describes the procedures and recommended approaches for estimating emissions from facilities engaged in the manufacture of non-petroleum industrial gases.

The non-petroleum industrial gases manufacturing activities covered in this Manual apply to facilities primarily engaged in the manufacture of hydrogen, oxygen, acetylene, carbon dioxide, nitrogen, argon, nitrous oxide or other industrial gases (except when produced as a by-product of oil refining or directly from coal). At the time of development of this Manual, carbon monoxide was not manufactured in facilities (other than as a part of petroleum refining processes) in Australia and, hence, is not covered in this Manual.

EET MANUAL:            Non-Petroleum Industrial Gases

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## 1.1 Manual Structure

- **Section 2** discusses the NPI reporting issues associated with the non-petroleum industrial gases manufacturing industry. The issue of transfers is discussed in **Section 2.1**. Relevant emissions for each of the NPI threshold categories are discussed in **Sections 2.2, 2.3 and 2.4**. Emissions to air water and land are then discussed in **Sections 2.5, 2.6 and 2.7** respectively.
- **Section 3** examines each of the processes covered in this Manual and identifies the NPI-listed substances for which reporting is required and, where necessary, provides emission estimation techniques which can be used for the characterisation of emissions for the purposes of NPI reporting.
- **Section 4** provides a glossary of technical terms and abbreviations used in this Manual.
- **Section 5** provides a list of references used in the development of this Manual.
- **Appendix A** provides an overview of the four general types of emission estimation techniques: sampling or direct measurement; mass balance; engineering calculations and emission factors, as well as example calculations to illustrate their use. Reference to relevant sections of this appendix is recommended in understanding the application of these techniques with particular respect to the non-petroleum industrial gases manufacturing industry.
- **Appendix B** provides a discussion of the reliability and uncertainty involved with each of the techniques presented in **Appendix A**.
- **Appendix C** provides a list of variables and symbols used in this Manual.

## 1.2 Manual Application

### *Context and use of this Manual*

This NPI Manual provides a ‘how to’ guide for the application of various methods to estimate emissions as required by the NPI. It is recognised that the data that is generated in this process will have varying degrees of accuracy with respect to the actual emissions from non-petroleum industrial gas manufacturing facilities. In some cases, there will necessarily be a large potential error due to inherent assumptions in the various emission estimation techniques (EETs) and/or a lack of available information regarding chemical processes.

### *EETs should be considered as ‘points of reference’*

The EETs and generic emission factors presented in this Manual should be seen as ‘points of reference’ for guidance purposes only. Each has associated error bands that are potentially quite large. **Appendix B** discusses the general reliability associated with the various methods. The potential errors associated with the different EET options should be considered on a case-by-case basis as to their suitability for a particular facility. Facilities

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may use EETs that are not outlined in this document. They must, however, seek the consent of their relevant environmental authority to determine whether any 'in house' EETs are suitable for meeting their NPI reporting requirements.

*Hierarchical approach recommended in applying EETs*

This Manual presents a number of different EETs, each of which could be applied to the estimation of NPI substances. The range of available methods should be viewed as a hierarchy of available techniques in terms of the error associated with the estimate. Each substance needs to be considered in terms of the level of error that is acceptable or appropriate with the use of the various estimation techniques. Also the availability of pre-existing data and the effort required to decrease the error associated with the estimate will need to be considered. For example, if emissions of a substance are clearly very small no matter which EET is applied, then there would be little to be gained by applying an EET which required significant additional sampling.

The steps in meeting the reporting requirements of the NPI can be summarised as follows:

- For Category 1 substances, identify which reportable NPI substances are used or produced. For Category 1a substances (Total Volatile Organic Compounds), identify which reportable NPI substances are used or stored. Determine whether the amounts used or handled are above the 'threshold' values and therefore trigger reporting requirements. Please note that substances in transit in unopened containers are not reportable under the NPI;
- For Category 2a and 2b substances, determine the amount and rate of fuel (or waste) burnt each year, the annual power consumption and the maximum potential power consumption, and assess whether the threshold limits are exceeded;
- For Category 3 substances, determine the annual emissions to water and assess whether the threshold limits are exceeded; and
- For those substances above the threshold values, examine the available range of EETs and determine emission estimates using the most appropriate EET.

Generally, it will be appropriate to consider various EETs as alternative options whose suitability should be evaluated in terms of:

- The associated reliability or error bands; and
- The cost/benefit of using a more reliable method.

The accuracy of particular EETs is discussed in **Appendix B**.

*NPI emissions in the environmental context*

It should be noted that the NPI reporting process generates emission estimates only. It does not attempt to relate emissions to potential environmental impacts, bioavailability of emissions or natural background levels.

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## 2.0 Reporting Thresholds and Emissions

### 2.1 Transfers

Under the NPI, the following are classed as transfers and are not required to be reported:

- Discharges of substances to sewer or tailings dam;
- Deposit of substances to landfill; and
- Removal of substances from a facility for destruction, treatment, recycling, reprocessing, recovery, or purification.

The definition of transfer has been clarified by the NPI Implementation Working Group as:

“All emissions of listed substances, except those which are directed to, and contained by, purpose built facilities, are to be reported to the NPI. This applies irrespective of whether the substances’ fate is within or outside a reporting facility boundary. With respect to receipt of NPI-listed substances, such receiving facilities are to be operating in accordance with any applicable State or Territory government requirements.”

A number of emissions from the non-petroleum industrial gas manufacturing industry are classed as transfers. These are discussed below in Sections 2.6 and 2.7.

### 2.2 Category 1

The Category 1 threshold is triggered if a facility handles, manufactures, imports, processes, co-incidentally produces, or otherwise uses 10 tonnes or more of a Category 1 substance. The transfer or handling of unopened containers containing Category 1 substances does not trigger the Category 1 threshold. A facility need only report on the Category 1 substances for which reporting thresholds have been triggered. If a reporting threshold is exceeded, then emissions of these substances must be reported for all operations/processes relating to the facility, even if actual emissions are very low or zero.

It is unlikely that any non-petroleum industrial gas manufacturing facilities will trigger the Category 1 threshold for any substance. One possible exception is the use of acetone in acetylene cylinder filling (Section 3.2). Other potential issues are:

- (a) the coincidental production of nitric acid as part of the manufacture of nitrous oxide; and
- (b) the use of sulfuric acid for the removal of impurities in the nitrous oxide manufacturing process.

Each individual facility should, however, examine their use of Category 1 substances, if any, to determine whether any Category 1 thresholds are triggered.

It should be noted that, at the time of preparing this draft Manual (August 1999), there was no production of carbon monoxide in stand alone (non-petroleum refining) facilities in Australia. The pure carbon monoxide (less than 10 tonnes per annum) presently used in Australia is imported.



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## 2.3 Category 2

The Category 2 threshold is based on energy consumption or fuel use. The Category 2a threshold for fuel usage is triggered if:

- A facility burns 400 tonnes or more of fuel or waste per year; or
- A facility burns 1 tonne or more of fuel or waste per hour.

The Category 2b threshold is triggered if:

- A facility burns 2000 tonnes or more of fuel or waste per year; or
- A facility uses 60 000 megawatt hours (MWh) or more of energy in a year; or
- A facility's maximum potential power consumption is rated at 20 megawatts (MW) or more at any time during the year.

Based on these thresholds, the amount of fuel usage required to trigger these thresholds may be calculated (as shown in Table 1). It should be noted that Category 2 threshold calculations should be performed for total fuel usage. If a number of different fuels are used at one facility, the sum of each individual fuel use needs to be calculated to determine whether or not the Category 2 threshold is triggered.

From discussions with the industry, it is likely that a number of facilities will trigger the Category 2a and 2b reporting thresholds. In the specific context of the non-petroleum industrial gases manufacturing industry, it is important to recognise that the potential power consumption does not apply to facilities who simply consume large quantities of electricity (but where that electricity is generated elsewhere).

**Table 1 - Approximate Fuel Usage Required to Trigger Category 2 Thresholds**

Fuel Type	Category 2a	Category 2b
Natural Gas <sup>a</sup>	2.06 * 10 <sup>7</sup> MJ per reporting year, or at least 5.14 * 10 <sup>4</sup> MJ in any one hour in the reporting year	1.03 * 10 <sup>8</sup> MJ per reporting year
Liquefied Petroleum Gas (LPG) <sup>b</sup>	7.87 * 10 <sup>5</sup> L per reporting year, or at least 1.97 * 10 <sup>3</sup> L in any one hour in the reporting year	3.94 * 10 <sup>6</sup> L per reporting year
Diesel <sup>c</sup>	4.44 * 10 <sup>5</sup> L per reporting year, or at least 1.11 * 10 <sup>3</sup> L in any one hour in the reporting year	2.22 * 10 <sup>6</sup> L per reporting year
Propane <sup>d</sup>	2.02 * 10 <sup>7</sup> MJ per reporting year, or at least 5.04 * 10 <sup>4</sup> MJ in any one hour in the reporting year	1.01 * 10 <sup>8</sup> MJ per reporting year
Butane <sup>e</sup>	1.98 * 10 <sup>7</sup> MJ per reporting year, or at least 4.96 * 10 <sup>4</sup> MJ in any one hour in the reporting year	9.92 * 10 <sup>7</sup> MJ per reporting year

<sup>a</sup> Assuming natural gas with a gross heating value of 51.4 MJ/kg. Natural gas (NSW) data from the *Natural Gas Technical Data Handbook* (AGL Gas Company (NSW) Limited, 1995).

<sup>b</sup> Assuming ideal gas with a density of 508 kg/m<sup>3</sup> at 15°C under pressure from the *Natural Gas Technical Data Handbook* (AGL Gas Company (NSW) Limited, 1995)

<sup>c</sup> Assuming a density of 900 kg/m<sup>3</sup> at 15°C for fuel oil for commercial use (Perry, et al., 1997)

<sup>d</sup> Assuming a gross heating value of 50.4 MJ/kg at 25°C and 101.325 kPa (Lide, 1994).

<sup>e</sup> Assuming a gross heating value of 49.6 MJ/kg at 25°C and 101.325 kPa (Lide, 1994).

If a facility triggers the Category 2a threshold, all Category 2a pollutants need to be reported. If a facility triggers the Category 2b threshold, all Category 2a and Category 2b pollutants need to be reported. The NPI-listed Category 2 substances are listed in Table 2.

**Table 2 - NPI-listed Category 2 Substances**

Category 2a Substances	Category 2b Substances
Carbon Monoxide	Arsenic & compounds
Fluoride Compounds	Beryllium & compounds
Hydrochloric Acid	Cadmium & compounds
Oxides of Nitrogen	Chromium (III) compounds
Particulate Matter (PM <sub>10</sub> )	Chromium (VI) compounds
Polycyclic Aromatic Hydrocarbons	Copper & compounds
Sulfur Dioxide	Lead & compounds
Total Volatile Organic Compounds	Magnesium Oxide Fume
	Manganese & compounds
	Mercury & compounds
	Nickel & compounds
	Nickel Carbonyl
	Nickel Subsulfide
	Polychlorinated Dioxins & Furans
	PLUS all Category 2a substances

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## 2.4 Category 3

Under Clause 13 of the *NPI NEPM*, the reporting threshold for a Category 3 substance is exceeded in a reporting period if the activities of the facility involve the emission to water (excluding emissions to groundwater and sewer) of:

- 15 tonnes or more per year of Total Nitrogen; or
- 3 tonnes per year or more of Total Phosphorus.

For non-petroleum industrial gas manufacturing facilities, it is extremely unlikely that the Category 3 threshold will be triggered.

## 2.5 Emissions to Air

The emissions to air from specific processes are described in Section 3.0 of this Manual. For facilities with combustion sources, there is a need to explicitly consider emissions from those sources.

For guidance on the estimation of emissions from combustion processes, please refer to Table 3. It is recognised that facilities burn other fuel types that do not fit the exact description of the fuels/combustion systems presented in Table 3. In these situations, site-specific data should be used for emissions estimation. If such data are not available, the emission factors for combustion of natural gas may be used as a starting point for emissions estimation.

**Table 3 - Sources of Information for Combustion Processes**

Combustion Type	Sources of Information
<b>Boilers</b> Coal Fuel oil (eg. diesel) Natural gas Liquefied petroleum gas (LPG)	<i>Emission Estimation Technique Manual for Combustion in Boilers (Section 3.4)</i>
<b>Gas Flaring</b>	<i>Emission Estimation Technique Manual for Petroleum Refining (Section 4.2.1)</i>
<b>Combustion Engines</b> Petrol and diesel industrial engines Petrol and diesel motor vehicles, commercial vehicles and trucks Large stationery diesel and dual fuel engines	<i>Emission Estimation Technique Manual for Combustion Engines (Section 3.4)</i>

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Fugitive emissions may also be an issue within the non-petroleum industrial gases manufacturing industry. All sources (including non-combustion sources) of Category 2a and Category 2b substances need to be reported if these thresholds are triggered. Category 2 substances are emitted from operations such as:

- Vehicle movement and exhaust;
- Arc welding;
- Maintenance operations;
- Equipment leaks;
- Liquid spills; and
- Storage tanks.

Fugitive emissions are a highly site-specific issue and will not be covered further in this Manual. For guidance on the estimation of emissions from fugitive sources, please refer to the *Emission Estimation Technique Manual for Fugitive Emissions*.

## **2.6 Emissions to Water**

The liquid releases from non-petroleum industrial gas manufacturing facilities are likely to be routed to sewer or sent for off-site treatment, recycling or disposal. These releases are classed as transfers under the National Pollutant Inventory and, hence, is not required to be reported.

Due to the nature of the processes and activities involved in the manufacture of non-petroleum industrial gases, it is extremely unlikely that the industry will have any reportable releases to water.

## **2.7 Emissions to Land**

Due to the nature of the processes and activities involved in the manufacture of non-petroleum industrial gases, it is extremely unlikely that the industry will have any reportable releases to land.

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## 3.0 Process Descriptions

### 3.1 Introduction

In this section, the following processes are described:

- Acetylene manufacture;
- Carbon dioxide manufacture;
- Hydrogen manufacture;
- Nitrogen, oxygen and argon manufacture; and
- Nitrous oxide manufacture.

Each of the processes is considered with regard to the NPI reporting issues associated with them. You should note that the emphasis of this section is on releases to air from the process operations (reflecting the likely reporting requirements for the industry). The following specific sources may also need to be considered:

- On-site combustion (see Section 3.7)
- Releases to water (see Section 2.6); and
- Releases to land (see Section 2.7).

### 3.2 Acetylene Manufacture

Acetylene is manufactured from calcium carbide. A stoichiometric excess of water ( $\text{H}_2\text{O}$ ) is added to calcium carbide ( $\text{CaC}_2$ ), to produce acetylene ( $\text{C}_2\text{H}_2$ ) gas and a sludge containing calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and water. The acetylene gas is then compressed and dissolved in acetone, which is held absorbed on a porous mass in cylinders.

#### 3.2.1 Reporting Issues

Table 4 summarises the NPI reporting issues associated with acetylene manufacture.

**Table 4 - Reporting Issues for the Acetylene Manufacturing Industry**

Source	Issues	Sources of Information
Storage	In the customer use of acetylene cylinders, some loss (typically 0.1 - 0.2 kg) of acetone occurs. This requires replacing prior to refilling of the cylinder. This topping up activity may trigger Category 1 thresholds at some facilities.	An estimate of emissions for the purposes of NPI reporting can be obtained by assuming that emissions are equal to the difference between the amount of acetone purchased by a facility and the amount of ammonia added to acetylene cylinders. (This assumed that the difference is an actual release to the environment and does not take account of measurement error or inaccuracy).
Waste Streams	All solid and liquid waste streams are likely to be considered transfers and, hence, are not required to be reported.	Refer to Section 2.1 for a discussion of transfers.
Acetylene Manufacture	There may be some emissions of acetylene from the manufacturing process. Acetylene is classed as a VOC and therefore any emissions would need to be considered when estimating total VOC emissions from a facility.	There are, at present no emission factors for emissions of acetylene from the acetylene manufacturing process.

### 3.3 Carbon Dioxide Manufacture

In Australia, carbon dioxide (CO<sub>2</sub>) is manufactured by the recovery of low CO<sub>2</sub> concentrations from flue gases, the recovery of high CO<sub>2</sub> concentrations from ammonia or ethylene oxide plants or from fermentation processes (Winterbottom, 1999).

Flue gas carbon dioxide is usually recovered by absorption in liquid monoethanolamine (MEA) from which it is recovered in a reboiler and stripper column. The small quantities of hydrocarbons in the ethylene oxide waste stream are catalytically burnt out with oxygen to less than 10 ppm hydrocarbons as methane. Ammonia plant CO<sub>2</sub> waste streams contain negligible hydrocarbons (Winterbottom, 1999).

Carbon dioxide is also obtained from ground wells, which also contain some hydrocarbons. The hydrocarbons are separated after liquefaction and the waste streams containing hydrocarbons are used to provide power or heat via gas engines or burners (Winterbottom, 1999).

#### 3.3.1 Reporting Issues

The NPI reporting issues associated with carbon dioxide manufacture are summarised in Table 5.

**Table 5 - NPI Reporting Issues for Carbon Dioxide Manufacture**

Source	Issues	Sources of Information
Combustion Processes	<p>Some combustion of hydrocarbons over a catalyst may occur for ethylene oxide streams. This may trigger Category 2a or 2b reporting thresholds.</p> <p>The methane component of the gases from CO<sub>2</sub> wells may be collected and burnt for energy recovery.</p>	<p>The emissions of NPI-listed substances from this process are expected to be negligible, in particular in those situations where all of the gas is collected (ie. no releases to atmosphere). However, depending on the system configuration, there may be releases of various combustion products.</p> <p>Guidance on the estimation of emissions from combustion sources may be provided in <b>Section 3.7</b> of this Manual.</p> <p>In the absence of site-specific data, the gas combustion emission factors in <b>Section 3.4.2</b> of the <i>Emission Estimation Technique Manual for Combustion in Boilers</i> may be used as a starting point for calculations.</p>
Waste Streams	<p>All solid and liquid waste streams are likely to be considered transfers and, hence, are not required to be reported.</p>	<p>Refer to <b>Section 2.1</b> of this Manual for a discussion of transfers.</p>

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### 3.4 Hydrogen Manufacture

The two methods of hydrogen manufacture in Australia are electrolysis and pressure swing adsorption of streams from either reformers or other chemical processes.

Electrolysis involves the use of two oppositely charged electrodes in water to split the water to obtain hydrogen and oxygen gases. The electrical energy from the electrodes is used to recombine the hydrogen ( $H^+$ ) and hydroxide ( $OH^-$ ) ions to hydrogen ( $H_2$ ) and oxygen ( $O_2$ ) (UWA, 1999).

The pressure swing adsorption (PSA) process operates on a repeated cycle with fundamental steps of adsorption, purge and regeneration. Feed gas containing hydrogen (and hydrocarbons) is passed over one or more adsorbent beds, which selectively adsorb the impurities, leaving a high purity hydrogen product. Feed flow continues through the bed until the bed is short of being fully saturated with impurities. The feed gas is then automatically switched to a clean adsorber. The loaded adsorber is taken off line for regeneration (Axsia, 1999).

Regeneration is the process of desorbing the impurities, which were adsorbed during the adsorption step, followed by repressurisation to adsorption pressure so that the cycle can be repeated. At the end of the adsorption step, the adsorber vessel contains a significant amount of high purity hydrogen in the void volume of the adsorbent bed. Much of this hydrogen is saved by pressure equalisation with other vessels, after which the adsorber is blown down to low pressure in preparation for the next step (Axsia, 1999). The impurities remaining after blow down are removed by passing purified hydrogen from on-line adsorber at low pressure through the contaminated bed which has just been blown down. The adsorber is then repressurised to adsorption pressures ready for a new run step. This is achieved by a combination of pressure equalisation with other vessels and repressurisation with a slip-stream of pure hydrogen (Axsia, 1999). The bed regeneration stream containing the contaminants is either burnt in the reformer unit or returned to the chemical process plant source.

### 3.4.1 Reporting Issues

The NPI reporting issues associated with hydrogen manufacture are summarised in Table 6.

**Table 6 - NPI Reporting Issues for Hydrogen Manufacture**

Source	Issues	Sources of Information
Hydrocarbon in feedstocks	Feedstocks contain hydrocarbons, which may be NPI-listed. Hydrocarbons are reformed to mainly hydrogen and carbon dioxide. These are separated in PSA beds, which are reactivated with a pure hydrogen stream. This produces a waste stream, which is fed back to the reformer and burnt or sent to the source chemical process plant.	Emissions from the reformer are expected to be negligible. Emissions for heating may be treated as combustion processes (see below).  Fugitive emissions of NPI-listed substances may be an issue. For further guidance, please refer to the <i>Emission Estimation Technique Manual for Fugitive Emissions</i> .
Combustion Processes	Natural gas is often burnt to heat the reformer.	If site-specific information is not available, refer to the emission factors for natural gas combustion in the <i>Emission Estimation Technique Manual for Combustion in Boilers</i> (Section 3.4.2) as a starting point for calculations.
Waste Streams	All liquid and solid waste are likely to be considered transfers and, hence, are not required to be reported.	Refer to Section 2.1 of this Manual for a discussion of transfers.

### 3.5 Nitrogen, Oxygen and Argon Manufacture

In Australia, nitrogen and oxygen are primarily manufactured by cryogenic air separation (distillation). Plants producing argon will have an additional column designed to make the separation between argon and oxygen.

Smaller, lower purity plants may employ pressure swing adsorption (PSA) units.

#### 3.5.1 Reporting Issues

The NPI reporting issues associated with nitrogen, oxygen and argon manufacture are summarised in Table 7.

**Table 7 - Reporting Issues for Nitrogen, Oxygen and Argon Manufacture**

Source	Issues	Sources of Information
Combustion Processes	Natural gas burners may be used as an alternative to electrical heaters for the heating reactivation streams in the cryogenic distillation process.	If site-specific monitoring information is not available, refer to the emission factors for natural gas combustion in the <i>Emission Estimation Technique Manual for Combustion in Boilers</i> (Section 3.4.2) as a starting point for calculations.



### 3.6 Nitrous Oxide Manufacture

Nitrous oxide ( $\text{N}_2\text{O}$ ) is produced by the dissociation of high purity (>97%) ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) in an aqueous solution containing chlorides and nitric acid (Ullmann, 1985).

#### 3.6.1 Reporting Issues

The NPI reporting issues associated with nitrous oxide manufacture are summarised in Table 8.

**Table 8 - NPI Reporting Issues for Nitrous Oxide Manufacture**

Source	Issues	Sources of Information
Product	Nitrous oxide is considered an oxide of nitrogen (ie. a Category 2a substance), for the purposes of NPI reporting and all sources need to be reported if the Category 2a threshold is triggered. At the time of preparing this Manual (September, 1999), there were no nitrous oxide manufacturing processes on the same site as combustion facilities which trigger either Category 2a 2b reporting thresholds.	At present, no emission estimation techniques are available which apply specifically to nitrous oxide releases. A facility may perform a mass balance to estimate its emissions (see Appendix A.2)
Nitric Acid Sulfuric Acid	Nitric acid is an initial side product but on cooling it recombines with ammonia to reform $\text{NH}_4\text{NO}_3$ which is washed back to the base of the decomposition vessel for re- decomposition. In addition wash towers of caustic, $\text{H}_2\text{SO}_4$ and water remove any trace carried over from the initial decomposition vessel (Winterbottom, 1999).	Waste streams from wash towers will be considered transfers (see Section 2.1) and will not require reporting. It is unlikely that there will be emissions of nitric acid. However, where Category 1 reporting is triggered because of the formation of nitric acid, facilities will be required to report zero emissions (where there are no emissions).
Waste Streams	All liquid and solid waste streams are likely to be considered transfers and, hence, are not required to be reported.	Refer to Section 2.1 of this Manual for a discussion of transfers.

### 3.7 Combustion Processes

If a facility has on-site power/heat/steam generation and it triggers either of the Category 2 thresholds, the emissions from these combustion processes need to be estimated.

For guidance on the estimation of emissions from combustion processes, please refer to the *Emission Estimation Technique Manual for Combustion in Boilers*. If facilities burn gas in a process that is similar to the flaring of off-gases at petroleum refineries, please refer to the *Emission Estimation Technique Manual for Petroleum Refining*. The *Emission Estimation Technique Manual for Fossil Fuel Electric Power Generation* (Section 5.2.5) provides emission factors for industrial boilers of LPG that can be used as a starting point for estimations in the absence of site-specific information.

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## 4.0 Glossary of Technical Terms and Abbreviations

AIGMA	Australian Industrial Gases Manufacturing Association
ANZSIC	Australian and New Zealand Standard Industrial Classification
CEMS	Continuous Emission Monitoring System
CO	Carbon Monoxide
EEA	European Environment Agency
EET	Emission Estimation Technique
EFR	Emission Factor Rating
NEPM	National Environment Protection Measure
NO <sub>x</sub>	Oxides of Nitrogen
NPI	National Pollutant Inventory
PM	Particulate Matter
PM <sub>10</sub>	Particulate matter with an equivalent aerodynamic diameter of 10 micrometres or less (ie. ≤10µm)
PSA	Pressure Swing Adsorption
SO <sub>2</sub>	Sulfur Dioxide
STP	Standard Temperature and Pressure (0°C and 101.3 * 10 <sup>3</sup> Pa)
Transfer	Transfers consist of a deposit of a substance into landfill, or discharge of a substance to a sewer or tailings dam, or removal of a substance from a facility for destruction, treatment, recycling, reprocessing, recovery or purification. Emissions classed as transfers are not required to be reported under the NPI.
TSP	Total Suspended Particulate
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Compounds. Defined by the USEPA (USEPA, 1999) as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.

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The following Emission Estimation Technique Manuals referred to in this Manual are available at the NPI Homepage ([www.npi.gov.au](http://www.npi.gov.au)), and from your local environmental protection agency or authority:

*Emission Estimation Technique Manual for Combustion in Boilers;*  
*Emission Estimation Technique Manual for Fugitive Emissions;*  
*Emission Estimation Technique Manual for Organic Chemical Processing Industries;*  
*Emission Estimation Technique Manual for Petroleum Refining; and*  
*Emission Estimation Technique Manual for Sewage and Wastewater Treatment.*

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## Appendix A - Emission Estimation Techniques

Estimates of emissions of NPI-listed substances to air, water and land should be reported for each substance that triggers a threshold. The reporting list and detailed information on thresholds are contained in the *NPI Guide*.

In general, there are four types of emission estimation techniques (EETs) that may be used to estimate emissions from your facility.

The four types described in the *NPI Guide* are:

- Sampling or direct measurement;
- Mass balance;
- Fuel analysis or other engineering calculations; and
- Emission factors.

Select the EETs (or mix of EETs) that is most appropriate for your purposes. For example, you might choose to use a mass balance to best estimate fugitive losses from pumps and vents, direct measurement for stack and pipe emissions, and emission factors when estimating losses from storage tanks and stockpiles.

If you estimate your emission by using any of these EETs, your data will be displayed on the NPI database as being of 'acceptable reliability'. Similarly, if your relevant environmental authority has approved the use of EETs that are not outlined in this handbook, your data will also be displayed as being of 'acceptable reliability'.

This Manual seeks to provide the most effective emission estimation techniques for the NPI substances relevant to this industry. However, the absence of an EET for a substance in this handbook does not necessarily imply that an emission should not be reported to the NPI. The obligation to report on all relevant emissions remains if reporting thresholds have been exceeded.

<p><b>You are able to use emission estimation techniques that are not outlined in this document. You must, however, seek the consent of your relevant environmental authority. For example, if your company has developed site-specific emission factors, you may use these if approved by your relevant environmental authority.</b></p>
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You should note that the EETs presented or referenced in this Manual relate principally to average process emissions. Emissions resulting from non-routine events are rarely discussed in the literature, and there is a general lack of EETs for such events. However, it is important to recognise that emissions resulting from significant operating excursions and/or accidental situations (eg. spills) will also need to be estimated. Emissions to land, air and water from spills must be estimated and added to process emissions when calculating total emissions for reporting purposes. The emission resulting from a spill is the net emission, ie. the quantity of the NPI reportable substance spilled, less the quantity recovered or consumed during clean up operations.

The **usage**<sup>a</sup> of each of the substances listed as Category 1 and 1a under the NPI must be estimated to determine whether the 10 tonnes (or 25 tonnes for VOCs) reporting threshold is exceeded. If the threshold is exceeded, **emissions** of these Category 1 and 1a substances must be reported for all operations/processes relating to the facility, even if the actual emissions of the substances are very low or zero.

<sup>a</sup> Usage is defined as meaning the handling, manufacture, import, processing, coincidental production or other uses of the substances.

A list of the variables and symbols used in this Manual may be found in **Appendix C**.

## A.1 Direct Measurement

You may wish to undertake direct measurement in order to report to the NPI, particularly if you already do so in order to meet other regulatory requirements. However, the NPI does not require you to undertake additional sampling and measurement. For the sampling data to be adequate and able to be used for NPI reporting purposes, it would need to be collected over a period of time, and to be representative of operations for the whole year.

### A.1.1 Sampling Data

Stack sampling test reports often provide emissions data in terms of kg per hour or grams per cubic metre (dry). Annual emissions for NPI reporting can be calculated from this data. Stack tests for NPI reporting should be performed under representative (ie. normal) operating conditions. You should be aware that some tests undertaken for a State or Territory license condition may require the test be taken under maximum emissions rating, where emissions are likely to be higher than when operating under normal operating conditions.

An example of test results is summarised in Table 9. The table shows the results of three different sampling runs conducted during one test event. The source parameters measured as part of the test run include gas velocity and moisture content, which are used to determine exhaust gas flow rates in m<sup>3</sup>/s. The filter weight gain is determined gravimetrically and divided by the volume of gas sampled, as shown in Equation 1 to determine the PM concentration in grams per m<sup>3</sup>. Note that this example does not present the condensable PM emissions.

Pollutant concentration is then multiplied by the volumetric flow rate to determine the emission rate in kilograms per hour, as shown in Equation 2 and Example 1.

#### Equation 1

$$C_{PM} = C_f / V_{m,STP}$$

where:

$$\begin{aligned} C_{PM} &= \text{concentration of PM or gram loading, g/m}^3 \\ C_f &= \text{filter catch, g} \\ V_{m,STP} &= \text{metered volume of sample at STP, m}^3 \end{aligned}$$

## Equation 2

$$E_{PM} = C_{PM} * Q_d * 3.6 * [273 / (273 + T)]$$

where:

$$\begin{aligned} E_{PM} &= \text{hourly emissions of PM, kg/hr} \\ C_{PM} &= \text{concentration of PM or gram loading, g/m}^3 \\ Q_d &= \text{stack gas volumetric flow rate at actual conditions, m}^3/\text{s, dry} \\ 3.6 &= 3600 \text{ seconds per hour multiplied by 0.001 kilograms per gram} \\ T &= \text{temperature of the gas sample, } ^\circ\text{C} \end{aligned}$$

**Table 9 - Stack Sample Test Results**

Parameter	Symbol	Test 1	Test 2	Test 3
Total sampling time (sec)		7200	7200	7200
Moisture collected (g)	$g_{MOIST}$	395.6	372.6	341.4
Filter catch (g)	$C_f$	0.0851	0.0449	0.0625
Average sampling rate (m <sup>3</sup> /s)		$1.67 * 10^{-4}$	$1.67 * 10^{-4}$	$1.67 * 10^{-4}$
Standard metered volume (m <sup>3</sup> )	$V_{m, STP}$	1.185	1.160	1.163
Volumetric flow rate (m <sup>3</sup> /s), dry	$Q_d$	8.48	8.43	8.45
Concentration of particulate (g/m <sup>3</sup> )	$C_{PM}$	0.0718	0.0387	0.0537

### Example 1 - Using Stack Sampling Data

PM emissions calculated using Equations 1 and 2 (above) and the stack sampling data for Test 1 (presented in Table 9, and an exhaust gas temperature of 150°C (423 K)).

$$\begin{aligned} C_{PM} &= C_f / V_{m, STP} \\ &= 0.0851 / 1.185 \\ &= 0.072 \text{ g/m}^3 \\ E_{PM} &= C_{PM} * Q_d * 3.6 * [273 / (273 + T)] \\ &= 0.072 * 8.48 * 3.6 * (273 / 423 \text{ K}) \\ &= 1.42 \text{ kg/hr} \end{aligned}$$

The information from some stack tests may be reported in grams of particulate per cubic metre of exhaust gas (wet). Use Equation 3 below to calculate the dry particulate emissions in kg/hr.

### Equation 3

$$E_{PM} = Q_a * C_{PM} * 3.6 * (1 - \text{moist}_R / 100) * [273 / (273 + T)]$$

where:

$E_{PM}$	=	hourly emissions of PM in kilograms per hour, kg/hr
$Q_a$	=	actual (ie. wet) cubic metres of exhaust gas per second, m <sup>3</sup> /s
$C_{PM}$	=	concentration of PM or gram loading, g/m <sup>3</sup>
3.6	=	3600 seconds per hour multiplied by 0.001 kilograms per gram
$\text{moist}_R$	=	moisture content, %
273	=	273 K (0°C)
T	=	stack gas temperature, °C

Total suspended particulates (TSP) are also referred to as total particulate matter (total PM). To determine PM<sub>10</sub> from total PM emissions, a size analysis may need to be undertaken. The weight PM<sub>10</sub> fraction can then be multiplied by the total PM emission rate to produce PM<sub>10</sub> emissions. Alternatively, it can be assumed that 100% of PM emissions are PM<sub>10</sub>; ie assume that all particulate matter emitted to air has an equivalent aerodynamic diameter of 10 micrometres or less ie. ≤10µm. In most situations, this is likely to be a conservative assumption, but it may be a suitable technique to obtain a reasonable characterisation of emissions for the purposes of NPI reporting.

To calculate moisture content use Equation 4

### Equation 4

Moisture percentage =  $\frac{100 * \text{weight of water vapour per specific volume of stack gas}}{\text{total weight of the stack gas in that volume}}$

$$\text{moist}_R = \frac{100 * \left( \frac{g_{\text{moist}}}{(1000 * V_{m,STP})} \right)}{\left( \frac{g_{\text{moist}}}{(1000 * V_{m,STP})} \right) + \rho_{STP}}$$

where:

$\text{moist}_R$	=	moisture content, %
$g_{\text{moist}}$	=	moisture collected, g
$V_{m,STP}$	=	metered volume of sample at STP, m <sup>3</sup>
$\rho_{STP}$	=	dry density of stack gas sample, kg/m <sup>3</sup> at STP {if the density is not known a default value of 1.62 kg/m <sup>3</sup> may be used. This assumes a dry gas composition of 50% air, 50% CO <sub>2</sub> }

### Example 2 - Calculating Moisture Percentage

A 1.2m<sup>3</sup> sample (at STP) of gas contains 410g of water. To calculate the moisture percentage use Equation 4.

$$\text{moist}_R = \frac{100 * \left( \frac{g_{\text{moist}}}{1000 * V_{m,STP}} \right)}{\left( \frac{g_{\text{moist}}}{1000 * V_{m,STP}} \right) + \rho_{STP}}$$

$g_{\text{MOIST}} / 1000 * V_{m,STP}$	=	410 / (1000 * 1.2)
	=	0.342
moist <sub>R</sub>	=	100 * 0.342 / (0.342 + 1.62)
	=	17.4%

#### A.1.2 Continuous Emission Monitoring System (CEMS) Data

A continuous emission monitoring system (CEMS) provides a continuous record of emissions over time, usually by reporting pollutant concentration. Once the pollutant concentration is known, emission rates are obtained by multiplying the pollutant concentration by the volumetric gas or liquid flow rate of that pollutant.

Although CEMS can report real-time hourly emissions automatically, it may be necessary to estimate annual emissions from hourly concentration data manually. This Section describes how to calculate emissions for the NPI from CEMS concentration data. The selected CEMS data should be representative of operating conditions. When possible, data collected over longer periods should be used.

It is important to note that, prior to using CEMS to estimate emissions, you should develop a protocol for collecting and averaging the data in order that the estimate satisfies the local environmental authority's requirement for NPI emission estimations.

To monitor SO<sub>2</sub>, NO<sub>x</sub>, VOC, and CO emissions using a CEMS, you use a pollutant concentration monitor that measures the concentration in parts per million by volume dry air (ppm<sub>vd</sub> = volume of pollutant gas/10<sup>6</sup> volumes of dry air). Flow rates should be measured using a volumetric flow rate monitor. Flow rates estimated based on heat input using fuel factors may be inaccurate because these systems typically run with high excess air to remove the moisture out of the kiln. Emission rates (kg/hr) are then calculated by multiplying the stack gas concentrations by the stack gas flow rates.

Table 10 presents example CEMS data output for three periods for a hypothetical furnace. The output includes pollutant concentrations in parts per million dry basis (ppm<sub>vd</sub>), diluent (O<sub>2</sub> or CO<sub>2</sub>) concentrations in percent by volume dry basis (%v, d) and gas flow rates, and may include emission rates in kilograms per hour (kg/hr). This data represents a snapshot of a hypothetical boiler operation. While it is possible to determine total emissions of an individual pollutant over a given time period from this data, assuming the CEMS operates properly all year long, an accurate emission estimate can be made by adding the hourly emission estimates if the CEMS data is representative of typical operating conditions.



**Table 10 - Example of CEMS Output for a Hypothetical Furnace Firing Waste Fuel Oil**

Time	O <sub>2</sub> content	Concentration				Gas Flow Rate (Q)	Production Rate of Product (A)
	% by volume	SO <sub>2</sub> (ppm <sub>vd</sub> )	NO <sub>x</sub> (ppm <sub>vd</sub> )	CO (ppm <sub>vd</sub> )	VOC (ppm <sub>vd</sub> )	m <sup>3</sup> /s	tonnes/hour
1	10.3	150.9	142.9	42.9	554.2	8.52	290
2	10.1	144.0	145.7	41.8	582.9	8.48	293
3	11.8	123.0	112.7	128.4	515.1	8.85	270

Hourly emissions can be based on concentration measurements as shown in Equation 5.

**Equation 5**

$$E_i = (C_i * MW_i * Q_{st} * 3600) / [22.4 * ((T + 273)/273) * 10^6]$$

where:

E <sub>i</sub>	=	emissions of pollutant i, kg/hr
C <sub>i</sub>	=	pollutant concentration, ppm <sub>vd</sub>
MW <sub>i</sub>	=	molecular weight of the pollutant i, kg/kg-mole
Q <sub>st</sub>	=	stack gas volumetric flow rate at actual conditions, m <sup>3</sup> /s
3600	=	conversion factor, s/hr
22.4	=	volume occupied by one mole of gas at standard temperature and pressure (0°C and 101.3 kPa), m <sup>3</sup> /kg-mole
T	=	temperature of gas sample, °C
10 <sup>6</sup>	=	conversion factor, ppm.kg/kg

Actual annual emissions can be calculated by multiplying the emission rate in kg/hr by the number of actual operating hours per year (OpHrs) as shown in Equation 6 for each typical time period and summing the results.

**Equation 6**

$$E_{kpy,i} = \sum (E_i * OpHrs)$$

where:

E <sub>kpy,i</sub>	=	annual emissions of pollutant i, kg/yr
E <sub>i</sub>	=	emissions of pollutant i, kg/hr (from Equation 5)
OpHrs	=	operating hours, hr/yr

Emissions in kilograms of pollutant per tonne of product produced can be calculated by dividing the emission rate in kg/hr by the activity rate (production rate (tonnes/hr)) during the same period. This is shown in Equation 7 below.

It should be noted that the emission factor calculated below assumes that the selected time period (ie. hourly) is representative of annual operating conditions and longer time periods should be used for NPI reporting where they are available. Use of the calculation is shown in Example 3.

### Equation 7

$$E_{\text{kpt},i} = E_i / A$$

where:

$$\begin{aligned} E_{\text{kpt},i} &= \text{emissions of pollutant } i \text{ per tonne of product} \\ &\quad \text{produced, kg/t} \\ E_i &= \text{hourly emissions of pollutant } i, \text{ kg/hr} \\ A &= \text{production, t/hr} \end{aligned}$$

Example 3 illustrates the application of Equation 5, Equation 6 and Equation 7.

### Example 3 - Using CEMS Data

This example shows how SO<sub>2</sub> emissions can be calculated using Equation 5 based on the CEMS data for Time Period 1 shown in Table 10, and an exhaust gas temperature of 150°C (423 K).

$$\begin{aligned} E_{\text{SO}_2,1} &= (C * MW * Q * 3600) / [(22.4 * (T + 273/273) * 10^6)] \\ &= (150.9 * 64 * 8.52 * 3600) / [22.4 * (423/273) * 10^6] \\ &= 296\,217\,907 / 34\,707\,692 \\ &= 8.53 \text{ kg/hr} \end{aligned}$$

For Time Period 2, also at 150°C

$$E_{\text{SO}_2,2} = 8.11 \text{ kg/hr}$$

For Time Period 3, also at 150°C

$$E_{\text{SO}_2,3} = 7.23 \text{ kg/hr}$$

Say representative operating conditions for the year are:

$$\begin{aligned} \text{Period 1} &= 1500 \text{ hr} \\ \text{Period 2} &= 2000 \text{ hr} \\ \text{Period 3} &= 1800 \text{ hr} \end{aligned}$$

Total emissions for the year are calculated by adding the results of the three Time Periods using Equation 6:

$$\begin{aligned} E_{\text{kpy},\text{SO}_2} &= E_{\text{SO}_2,1} * \text{OpHrs} + E_{\text{SO}_2,2} * \text{OpHrs} + E_{\text{SO}_2,3} * \text{OpHrs} \\ &= (8.53 * 1500) + (8.11 * 2000) + (7.23 * 1800) \text{ kg} \\ &= 42\,021 \text{ kg/yr} \end{aligned}$$

Emissions, in terms of kg/tonne of product produced when operating in the same mode as time period 1, can be calculated using Equation 7

$$\begin{aligned} E_{\text{kpt},\text{SO}_2} &= E_{\text{SO}_2} / A \\ &= 8.53 / 290 \\ &= 2.94 * 10^{-2} \text{ kg SO}_2 \text{ emitted per tonne of product produced} \end{aligned}$$

When the furnace is operating as in time periods 2 or 3, similar calculations can be undertaken for emissions per tonne.

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## A.2 Mass Balance

Mass balances involve examining a process to determine whether emissions can be characterised based on an analysis of operating parameters, material composition, and total material usage. Mass balance involves the quantification of total materials into and out of a process, with the difference between inputs and outputs being accounted for as a release to the environment (to air, water, land) or as part of the facility's waste. Mass balance is particularly useful when the input and output streams can be readily characterised and this is most often the case for small processes and operations.

Mass balance can be applied across individual unit operations (see Section A.2.2) or across an entire facility (see Sections A.2.1). Mass balance techniques and engineering estimates are best used where there is a system with prescribed inputs, defined internal conditions, and known outputs.

It is essential to recognise that the emission values produced when using mass balance are only as good as the values used in performing the calculations. For example, small errors in data or calculation parameters (eg. pressure, temperature, stream concentration, flow, or control efficiencies) can result in potentially large errors in the final estimates. In addition, when sampling of input and/or output materials is conducted, the failure to use representative samples will also contribute to uncertainty. In some cases, the combined uncertainty is quantifiable and this is useful in determining if the values are suitable for their intended use.

### A.2.1 Overall Facility Mass Balance

Mass balances can be used to characterise emissions from a facility providing that sufficient data is available pertaining to the process and relevant input and output streams. Mass balances can be applied to an entire facility (see Example 4). This involves the consideration of material inputs to the facility (purchases) and materials exported from the facility in products and wastes, where the remainder is considered as a 'loss' (or a release to the environment).

The mass balance calculation can be summarised by:

Total mass into process = Total mass out of process

In the context of the NPI, this equation could be written as:

Inputs = Products + Transfers + Emissions

where:

Inputs = All incoming material used in the process.

Emissions = Releases to air, water, and land (as defined under the NPI). Emissions include both routine and accidental releases as well as spills.

Transfers = As defined under the *NPI NEPM*, transfers include substances discharged to sewer, substances deposited into landfill and substances removed from a facility for destruction, treatment, recycling, reprocessing, recovery, or purification.

Products = Products and materials (eg. by-products) exported from the facility.

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Applying this to an individual NPI substance (substance 'i'), the equation may be written as:

Input of substance 'i' = amount of substance 'i' in product  
+ amounts of substance 'i' in waste  
+ amount of substance 'i' transformed or consumed in process  
+ emissions of substance 'i'.

The mass balance approach can be used for each NPI-listed substance for which the facility has a responsibility to report. Emissions can then be allocated to air, water, and land.

Example 4 provides an example of a mass balance.

#### **Example 4 - Overall Facility Mass Balance**

A chemical facility receives 1000 tonnes of an NPI-listed solvent product per annum. The solvent is stored on-site. It is known that this solvent product contains 2 percent water that settles during storage, and is drained to sewer. The solubility of the solvent in water is 100 g/kg (ie. 0.1 weight fraction). It is known that 975 tonnes of solvent per annum is utilised in the process, based on actual addition rate data. During the year, it was recorded that 1 tonne of solvent was lost due to spillage, of which 500 kg was recovered and sent for appropriate disposal, with the rest washed to sewer.

Considering the water content of the solvent and the solubility of solvent in water the following data can be derived:

Quantity of water received in the solvent annually:

$$\text{Water} = 1000 \text{ tonnes} * (2/100) = 20 \text{ tonnes of water (containing 100 g/kg solvent)}$$

The solubility of solvent in this water is 100 g/kg:

$$\text{Therefore, solvent in water} = 20 * (0.1) = 2 \text{ tonnes of solvent}$$

Excluding the water component, the quantity of solvent received annually is:

$$\text{Total solvent (excluding water)} = 1000 * 0.98 = 980 \text{ tonnes}$$

#### Example 4 - Overall Facility Mass Balance cont'

Incorporating the solvent contained within the water component:

Total solvent received at facility (including solvent in water) =  $980 + 2 = 982$  tonnes solvent

Once the above quantities have been ascertained, the quantity of solvent released to the environment can be determined as follows:

Solvent to sewer = drainage from solvent tank + uncaptured spillage  
=  $2000 \text{ kg} + 500 \text{ kg}$   
=  $2500 \text{ kg}$

Captured spillage =  $500 \text{ kg}$

As no solvent was spilled on unsealed ground, there are no emissions to land. Therefore, the emission of solvent to air is derived as follows:

Air Emission = Total solvent received – sewer release - captured spillage  
- solvent utilised in the process  
=  $982 - 2.5 - 0.5 - 975$   
=  $4 \text{ tonnes}$

Therefore, 4 tonnes of solvent is lost to the atmosphere each year from storage and handling operations. For NPI reporting, it would then be necessary to determine the quantity of NPI substances present in the solvent and to determine the quantities of each of these substances emitted to atmosphere. It is important to note that any emission controls must be taken into account when determining your emissions (eg. the solvent released to air may be routed through an incinerator before being released to the atmosphere).

#### A.2.2 Individual Unit Process Mass Balance

The general mass balance approach described above can also be applied to individual unit processes. This requires that information is available on the inputs (ie. flow rates, concentrations, densities) and outputs of the unit process.

The following general equation can be used:

##### Equation 8

$$E_i = \sum Q_i W_{fi} \rho_i - \sum Q_o W_{oi} \rho_o$$

where:

$E_i$  = flow rate of component i in unknown stream (kg/hr)  
 $Q_i$  = volumetric flow rate of inlet stream, i ( $\text{m}^3/\text{hr}$ )  
 $Q_o$  = volumetric flow rate of outlet stream, o ( $\text{m}^3/\text{hr}$ )  
 $W_{fi}$  = weight fraction of component i in inlet stream i  
 $W_{oi}$  = weight fraction of component i in outlet stream o  
 $\rho_i, \rho_o$  = density of streams i and o respectively ( $\text{kg}/\text{m}^3$ )

Information on process stream input and output concentrations is generally known as this information is required for process control. The loss  $E_x$  will be determined through analysis of the process. It should be noted that it is then necessary to identify the environmental medium (or media) to which releases occur.

### A.3 Engineering Calculations

An engineering calculation is an estimation method based on physical/chemical properties (eg. vapour pressure) of the substance and mathematical relationships (eg. ideal gas law).

#### A.3.1 Fuel Analysis

Fuel analysis is an example of an engineering calculation and can be used to predict  $SO_2$ , metals, and other emissions based on application of conservation laws, if fuel rate is measured. The presence of certain elements in fuels may be used to predict their presence in emission streams. This includes elements such as sulfur that may be converted into other compounds during the combustion process.

The basic equation used in fuel analysis emission calculations is the following:

#### Equation 9

$$E_{kpy,i} = Q_f * (C_i/100) * (MW_p / EW_f) * OpHrs$$

where:

$E_{kpy,i}$	=	annual emissions of pollutant i, kg/yr
$Q_f$	=	fuel use, kg/hr
$OpHr$	=	operating hours, hr/yr
$MW_p$	=	molecular weight of pollutant emitted, kg/kg-mole
$EW_f$	=	elemental weight of pollutant in fuel, kg/kg-mole
$C_i$	=	concentration of pollutant i in fuel, weight percent, %

For instance,  $SO_2$  emissions from fuel oil combustion can be calculated based on the concentration of sulfur in the fuel oil. This approach assumes complete conversion of sulfur to  $SO_2$ . Therefore, for every kilogram of sulfur ( $EW = 32$ ) burned, two kilograms of  $SO_2$  ( $MW = 64$ ) are emitted. The application of this EET is shown in Example 5.

#### Example 5 - Using Fuel Analysis Data

This example shows how  $SO_2$  emissions can be calculated from fuel combustion based on fuel analysis results, and the known fuel flow of the engine.  $E_{kpy,SO_2}$  may be calculated using Equation 9 and given the following:

Fuel flow ( $Q_f$ )	=	20 900 kg/hr
Weight percent sulfur in fuel	=	1.17 %
Operating hours	=	1500 hr/yr

$$\begin{aligned}
 E_{kpy,SO_2} &= Q_f * (C_i/100) * (MW_p / EW_f) * OpHrs \\
 &= (20\,900) * (1.17/100) * (64 / 32) * 1500 \\
 &= 733\,590 \text{ kg/yr}
 \end{aligned}$$

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## A.4 Emission Factors

In the absence of other information, default emission factors can be used to provide an estimate of emissions. Emission factors are generally derived through the testing of a general source population (eg. boilers using a particular fuel type). This information is used to relate the quantity of material emitted to some general measure of the scale of activity (eg. for boilers, emission factors are generally based on the quantity of fuel consumed or the heat output of the boiler).

Emission factors require 'activity data', that is combined with the factor to generate the emission estimates. The generic formula is:

$$\text{Emission Factor} \left( \frac{\text{mass}}{\text{unit of activity}} \right) * \text{Activity Data} \left( \frac{\text{unit of activity}}{\text{time}} \right) = \text{Emission Rate} \left( \frac{\text{mass}}{\text{time}} \right)$$

For example, if the emission factor has units of '*kg pollutant/m<sup>3</sup> of fuel burned*', then the activity data required would be in terms of '*m<sup>3</sup> fuel burned/hr*', thereby generating an emission estimate of '*kg pollutant/hr*'.

An emission factor is a tool used to estimate emissions to the environment. In this Manual, it relates the quantity of substances emitted from a source, to some common activity associated with those emissions. Emission factors are obtained from US, European, and Australian sources and are usually expressed as the weight of a substance emitted, divided by the unit weight, volume, distance, or duration of the activity emitting the substance (eg. kilograms of sulfur dioxide emitted per tonne of fuel burned).

Emission factors are used to estimate a facility's emissions by the general equation:

### Equation 10

$$E_{\text{kpy},i} = [A * \text{OpHrs}] * EF_i * [1 - (CE_i/100)]$$

where :

- $E_{\text{kpy},i}$  = emission rate of pollutant i, kg/yr
- $A$  = activity rate, t/hr
- $\text{OpHrs}$  = operating hours, hr/yr
- $EF_i$  = uncontrolled emission factor of pollutant i, kg/t
- $CE_i$  = overall control efficiency of pollutant i, %.

Emission factors developed from measurements for a specific process may sometimes be used to estimate emissions at other sites. Should a company have several processes of similar operation and size, and emissions are measured from one process source, an emission factor can be developed and applied to similar sources. It is necessary to have the emission factor reviewed and approved by State or Territory environment agencies prior to its use for NPI estimations.

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## **Appendix B - Emission Estimation Techniques: Acceptable Reliability and Uncertainty**

This section is intended to give a general overview of some of the inaccuracies associated with each of the techniques. Although the National Pollutant Inventory does not favour one emission estimation technique over another, this section does attempt to evaluate the available emission estimation techniques with regards to accuracy.

Several techniques are available for calculating emissions from non-petroleum industrial gas manufacturing facilities. The technique chosen is dependent on available data, and available resources, and the degree of accuracy sought by the facility in undertaking the estimate. In general, site-specific data that is representative of normal operations is more accurate than industry-averaged data, such as emission factors.

### **B.1 Direct Measurement**

Use of stack and/or workplace health and safety sampling data is likely to be a relatively accurate method of estimating air emissions from non-petroleum industrial gas manufacturing facilities. However, collection and analysis of samples from facilities can be very expensive and especially complicated where a variety of NPI-listed substances are emitted, and where most of these emissions are fugitive in nature. Sampling data from a specific process may not be representative of the entire manufacturing operation, and may provide only one example of the facility's emissions.

To be representative, sampling data used for NPI reporting purposes needs to be collected over a period of time, and to cover all aspects of production.

In the case of CEMS, instrument calibration drift can be problematic and uncaptured data can create long-term incomplete data sets. However, it may be misleading to assert that a snapshot (stack sampling) can better predict long-term emission characteristics. It is the responsibility of the facility operator to properly calibrate and maintain monitoring equipment and the corresponding emissions data.

### **B.2 Mass Balance**

Calculating emissions from non-petroleum industrial gas manufacturing facilities using mass balance appears to be a straightforward approach to emission estimation. However, it is likely that few Australian facilities consistently track material usage and waste generation with the overall accuracy needed for application of this method. Inaccuracies associated with individual material tracking, or other activities inherent in each material handling stage, can result in large deviations for total facility emissions. Because emissions from specific materials are typically below 2 percent of gross consumption, an error of only  $\pm 5$  percent in any one step of the operation can significantly skew emission estimations.



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### B.3 Engineering Calculations

Theoretical and complex equations, or models, can be used for estimating emissions from non-petroleum industrial gas manufacturing production processes. EET equations are available for the following types of emissions common to non-petroleum industrial gas manufacturing facilities.

Use of emission equations to estimate emissions from non-petroleum industrial gas manufacturing facilities is a more complex and time-consuming process than the use of emission factors. Emission equations require more detailed inputs than the use of emission factors but they do provide an emission estimate that is based on facility-specific conditions.

### B.4 Emission Factors

Every emission factor has an associated emission factor rating (EFR) code. This rating system is common to EETs for all industries and sectors and therefore, to all Industry Handbooks. They are based on rating systems developed by the United States Environmental Protection Agency (USEPA), and by the European Environment Agency (EEA). Consequently, the ratings may not be directly relevant to Australian industry. Sources for all emission factors cited can be found in the reference section of this document. The emission factor ratings will not form part of the public NPI database.

When using emission factors, you should be aware of the associated EFR code and what that rating implies. An A or B rating indicates a greater degree of certainty than a D or E rating. The less certainty, the more likely that a given emission factor for a specific source or Category is not representative of the source type. These ratings notwithstanding, the main criterion affecting the uncertainty of an emission factor remains the degree of similarity between the equipment/process selected in applying the factor, and the target equipment/process from which the factor was derived.

The EFR system is as follows:

A	-	Excellent
B	-	Above Average
C	-	Average
D	-	Below Average
E	-	Poor
U	-	Unrated

## Appendix C - List of Variables and Symbols

Variable	Symbol	Units
Annual emissions of pollutant i	$E_{kpy,i}$	kg/yr
Total emissions of pollutant i per hour	$E_i$	kg/hr
Uncontrolled emission factor for pollutant i	$EF_i$	kg of pollutant/tonne
Emissions per tonne	$E_{kpt,i}$	kg of pollutant i per tonne of fuel consumed
Overall control efficiency, (ie. Emission reduction control factor)	$CE_i$	% reduction in emissions of pollutant i
Material entering the process	$Q_i$	kg/hr
Fuel used	$Q_f$	kg/hr
Material leaving the process	$Q_o$	kg/hr
Volumetric flow rate of stack gas	$Q_a$	actual (ie. wet) cubic metres per second ( $m^3/s$ )
Concentration of pollutant i	$C_i$	kg/L
Concentration of PM	$C_{PM}$	$g/m^3$
Elemental weight of pollutant i in fuel	$EW_f$	kg/kg-mole
Molecular weight of pollutant i	$MW_i$	kg/kg-mole
Operating hours	OpHrs	hr/yr
Activity rate	A	units/hr, eg t/hr
Temperature	T	°Celsius (°C) or Kelvin (K)
Standard Temperature & Pressure	STP	0°C (273 K) and 1 atmosphere 101.3 kPa
Filter Catch	$C_f$	g
Metered volume of sample at STP	$V_{mSTP}$	$m^3$
Dry density of stack gas sample at STP	$\rho_{STP}$	$kg/m^3$
Weight fraction of component i in inlet stream	$W_{fi}$	
Weight fraction of component i in outlet stream o	$W_{oi}$	
Density of stream i	$\rho_i$	$kg/m^3$
Density of stream o	$\rho_o$	$kg/m^3$
Hourly emissions of PM	$E_{PM}$	kg/hr
Moisture collected	$g_{moist}$	g
Moisture content	$moist_R$	%
Stack gas volumetric flowrate	$Q_{st}$	$m^3/s$