

PETRONAS TECHNICAL STANDARDS
HEALTH, SAFETY AND ENVIRONMENT

VOLATILE ORGANIC CARBONS
(GUIDELINE)

PTS 60.1502.03

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PREFACE

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AMENDMENTS RECORD SHEET

Chap.	Sect No.	Description	Issue No.	Date	Rev	Date	App by: (initials)
All	All	PTS 60.190 Volatile Organic Compounds	1	Jan 2005	0	0	IGA

Chap.	Sect No.	Description	Issue No.	Date	Rev	Date	App by: (initials)
All	All	PTS 60.1107 Volatile Organic Compounds	1	June 05	0	0	IGA

Chap.	Sect No.	Description	Issue No.	Date	Rev	Date	App by: (initials)
All	All	PTS 60.1502.03 Volatile Organic Carbons	2	June 06	1	June 06	IGA

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SUMMARY

This document explains the need for addressing VOC emissions and provides an overview and evaluation of the methods available for:

- determining emissions of VOCs
- assessing the health and ecological risks
- emission reduction

The document is aimed primarily at Operations Managers, as well as at HSE staff in OPU/JV

The term 'volatile organic compounds' (VOCs) is used as a generic term for 'non-methane' volatile organic compounds. Specific compounds are identified where relevant for good understanding of the text. Methane is also addressed in this guide because it is often present in conjunction with VOCs.

The hazards of VOCs are primarily:

- (1) Toxicity to man and the environment and
- (2) Deterioration of ambient air quality through formation of photochemical smog (ozone and peroxyacetyl nitrate (PAN) aerosols), in conjunction with oxides of nitrogen (NO_x).

These are harmful to man and to the environment.

Major sources of VOCs in the atmosphere include:

- Motor vehicle exhaust and evaporative emissions from road transport,
- Solvents,
- Emissions from the chemical and oil refining industries.

Natural emissions from vegetation are significant too.

Measurement methods for various sources are described. Remote sensing techniques are suitable for confirmation of the magnitude of emissions and for monitoring air quality. Point sensing is suitable for monitoring ambient air concentrations at ground level.

Emission control techniques are described with some guidance on the application and cost of such techniques to given situations.

This guide provides background information and structured advice; it does not offer specific technical solutions. Technical support and more detailed guidance for implementation of the above principles is provided by the Corporate HSE

1 **INTRODUCTION**

1.1 **PURPOSE, DEFINITION AND SCOPE**

This document explains the need for addressing volatile organic compounds (VOCs) emissions and provides an overview and evaluation of the methods available for:

- determining VOC emissions
- assessing the health and ecological risks
- emission reduction

The term 'volatile organic compounds' can be applied to a wide range of organic chemicals and there is no universally agreed definition, save that they will all evaporate at ambient temperatures¹ and generally contain carbon and hydrogen. VOCs include the group of compounds known as hydrocarbons, which are entirely made of carbon and hydrogen; substituted hydrocarbons, such as mercaptans, and oxygenated compounds such as methyl tertiary butyl ether (MTBE). However, methane is often excluded. The man-made halogenated hydrocarbon solvents are usually also included in the definition of VOCs, but the halogenated hydrocarbons (CFCs, HCFCs and halons), whose use is regulated under the Montreal Protocol for the Protection of the Ozone Layer, form a separate group.

In this report, therefore, the term VOC means 'non-methane' volatile organic compounds. Specific compounds are distinguished where relevant for good understanding of the text. Methane is also addressed in this guide because it is often present in conjunction with VOCs.

The study covers all operations from exploration and production through the delivery of product to third party customers. Flaring and venting field gas in Exploration and Production operations is dealt with in EP documents (ref. 1, 2).

1.2 **HAZARDS AND EFFECTS**

VOC emissions are receiving attention because they have the potential to cause harm to human health and to the environment. The hazards are in the following main categories:

1. Toxicity of certain specific compounds to man and the environment,
2. Formation of ozone and smog from the photochemical reaction of VOCs with oxides of nitrogen (NO_x),
3. Radiative forcing (enhanced greenhouse effect),
4. Ozone depletion in the stratosphere,
5. Fire and explosion hazard following ignition.

This report deals specifically with toxicity and ambient air quality aspects in categories 1 and 2.

Some VOCs cause toxic effects at relatively low concentrations. For example vinyl chloride is a confirmed human carcinogen, and 1,3-butadiene is a suspected human carcinogen. Others such as ethene (ethylene) are toxic to vegetation at low concentration. Mercaptans and MTBE give an unpleasant odour.

The dominant reason for giving attention to VOCs is the photochemical formation of ozone in ambient air in conjunction with oxides of nitrogen (NO_x). Exhaust emissions and evaporative emissions from road transport are the largest single source of VOCs in industrialised countries, immediately followed by solvent use; see section 3. Oxides of nitrogen originate primarily from the combustion of fossil fuels; major sources include road

The Netherlands VOC reduction programme KWS 2000 defines solvents as 'volatile' if vapour pressure is larger than 10 Pa; this is equivalent to liquids with atmospheric boiling point below about 250°C.

Transport and electricity generating plants. Ozone is a powerful oxidant that may cause irritation of the respiratory system. In a number of regions in Europe and in the United States the public may be exposed to ozone concentrations that the World Health Organisation (WHO) has determined to be potentially harmful. Experimental evidence also links high levels of ozone with damage to crops and trees. Consequently, there is mounting legislative pressure to reduce ozone levels through control of VOC emissions.

Unlike the toxic VOCs mentioned above, which are found in the highest concentrations nearest to emission sources, ozone spreads over long distances and, for example, half the ozone recorded in the UK has its origin in Continental Europe.

Methane does not play a significant role in the production of ozone although it does make a contribution to the 'greenhouse effect' which is of global rather than local concern. The concern over CFCs arises from their ability to deplete the protective ozone layer in the stratosphere.

1.3 MONITORING PERFORMANCE

It is recommended that OPU/JV monitor and report their VOC and methane emissions regularly. To that purpose emission performance should be expressed as the quantity in tonnes per annum.

2 AIR CHEMISTRY

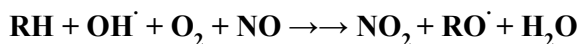
2.1 REACTION MECHANISM

Atmospheric chemistry is complex. Briefly, VOCs that are emitted into the atmosphere can be oxidised through photochemical reactions. The main end products are carbon dioxide, carbon monoxide and water, plus intermediate products such as aldehydes, ketones and acids.

Oxidation

1. Reactive VOCs, represented as RH, react with hydroxyl radicals (OH[•]) to form organic radicals,
2. Organic radicals combine with molecular oxygen to form peroxy radicals,
3. Peroxy radicals react with nitric oxide (NO) to form nitrogen dioxide (NO₂).

The overall reaction equation is simplified as:



The oxide radical (RO[•]) reacts further with hydroxyl radicals, oxygen and nitric oxide to form aldehydes, ketones and acids. These species are very polar and may be precipitated into water or soil at the earth's surface, where generally they are biodegraded. Part of these species remain in the atmosphere and are further mineralised through photochemical reactions to carbon dioxide and water.

Ozone formation

Nitrogen dioxide from the above reaction is photo-dissociated by solar radiation to release oxygen atoms, and reform nitric oxide. Finally, oxygen atoms combine with molecular oxygen to form ozone.

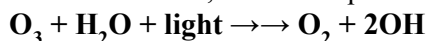
The overall reaction is simplified as:



Certain VOCs have greater photochemical ozone creation potential (POCP) than others; examples of VOCs with a high POCP are propene, octane, xylene and methyl isobutyl ketone.

Ozone depletion and OH radical chain reaction

Ozone disappears from the troposphere due to photo-dissociation by near-ultraviolet solar radiation, and subsequent reaction with water vapour to form two OH radicals:



The resulting OH radicals drive the oxidation process. Furthermore, reactions initiated by the RO[•] radicals can, in the presence of NO, lead to further production of OH. With enough VOCs and NO_x in the atmosphere, the chain reactions represented above can, in the presence of sunlight, lead to concentrations of tropospheric ozone causing adverse health effects.

The rate of VOC transformation depends on concentration and the rate of reaction of the compound with the hydroxyl radicals. Compounds that react only slowly with the hydroxyl radicals will be transported over time into the stratosphere, where they will undergo direct photochemical reactions. These compounds are the halogenated, low