ENGINEERING STANDARD

FOR

AIR POLLUTION CONTROL

FIRST EDITION

OCTOBER 2007

This standard specification is reviewed and updated by the relevant technical committee on Sep. 2013. The approved modifications are included in the present issue of IPS.

FOREWORD

The Iranian Petroleum Standards (IPS) reflect the views of the Iranian Ministry of Petroleum and are intended for use in the oil and gas production facilities, oil refineries, chemical and petrochemical plants, gas handling and processing installations and other such facilities.

IPS is based on internationally acceptable standards and includes selections from the items stipulated in the referenced standards. They are also supplemented by additional requirements and/or modifications based on the experience acquired by the Iranian Petroleum Industry and the local market availability. The options which are not specified in the text of the standards are itemized in data sheet/s, so that, the user can select his appropriate preferences therein

The IPS standards are therefore expected to be sufficiently flexible so that the users can adapt these standards to their requirements. However, they may not cover every requirement of each project. For such cases, an addendum to IPS Standard shall be prepared by the user which elaborates the particular requirements of the user. This addendum together with the relevant IPS shall form the job specification for the specific project or work.

The IPS is reviewed and up-dated approximately every five years. Each standards are subject to amendment or withdrawal, if required, thus the latest edition of IPS shall be applicable

The users of IPS are therefore requested to send their views and comments, including any addendum prepared for particular cases to the following address. These comments and recommendations will be reviewed by the relevant technical committee and in case of approval will be incorporated in the next revision of the standard.

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GENERAL DEFINITIONS:

Throughout this Standard the following definitions shall apply.

COMPANY:

Refers to one of the related and/or affiliated companies of the Iranian Ministry of Petroleum such as National Iranian Oil Company, National Iranian Gas Company, National Petrochemical Company and National Iranian Oil Refinery And Distribution Company.

PURCHASER:

Means the “Company” where this standard is a part of direct purchaser order by the “Company”, and the “Contractor” where this Standard is a part of contract documents.

VENDOR AND SUPPLIER:

Refers to firm or person who will supply and/or fabricate the equipment or material.

CONTRACTOR:

Refers to the persons, firm or company whose tender has been accepted by the company.

EXECUTOR:

Executor is the party which carries out all or part of construction and/or commissioning for the project.

INSPECTOR:

The Inspector referred to in this Standard is a person/persons or a body appointed in writing by the company for the inspection of fabrication and installation work.

SHALL:

Is used where a provision is mandatory.

SHOULD:

Is used where a provision is advisory only.

WILL:

Is normally used in connection with the action by the “Company” rather than by a contractor, supplier or vendor.

MAY:

Is used where a provision is completely discretionary.

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0. INTRODUCTION

Air pollution is waste remaining from the many ways as production of goods, process of hydrocarbon and petrochemicals, use of transport and generation of energy to heat and light.

The major cause of all air pollution is combustion. When perfect or theoretical combustion occurs, the hydrogen and carbon in the fuel combine with oxygen from the air to produce heat, light, carbon dioxide, and water vapor. Impurities in the fuel, poor fuel-to-air ratio, or too high or too low combustion temperatures cause the formation of such side products as carbon monoxide, sulfur oxides, nitrogen oxides, fly ash and unburned hydrocarbons.

There can be different approach for controlling air pollution. Design approach of air pollution control one of the best ideas for controlling air pollution especially oil, natural gas, petrochemical and refining industry.

In this Standard, methods of reducing air pollution and means to decrease the pollution of the environment is discussed.

1. SCOPE

This Standard represents the minimum requirements for air pollution control and covers the following main topics:

- Pollution sources
- Types of emission
- Standard levels
- Measurement of air pollution
- Consideration in the selection of the pollution control equipment
- Process control
- Threshold limit values (TLV)

Note 1:

This is a revised version of this standard, which is issued as revision (1)-2007. Revision (0)-1994 of the said standard specification is withdrawn.

Note 2:

This standard specification is reviewed and updated by the relevant technical committee on Sep. 2013. The approved modifications by T.C. were sent to IPS users as amendment No. 1 by circular No. 391 on Sep. 2013. These modifications are included in the present issue of IPS.

Note 3:

If there is some non-conformity through legislative requirement which has been approved by Iranian governmental organization such as Department of Environment and Health Ministry, the performance criteria shall be consider base on the above legislative mentioned.

2. REFERENCES

Throughout this Standard the following dated and undated standards/codes are referred to. These referenced documents shall, to the extent specified herein, form a part of this standard. For dated references, the edition cited applies. The applicability of changes in dated references that occur after the cited date shall be mutually agreed upon by the Company and the Vendor. For undated references, the latest edition of the referenced documents (including any supplements and amendments) applies.

EPA (U.S. Environmental Protection Agency)

Compilation of air pollutant emission factors, Volume I (AP-42, 5th,1995)

EPA-650/9-75-001a

“The World Air Quality Management Standards Volume I” (Oct. 1974)

EPA-650/9-75-001b

“The World Air Quality Management Standards Volume II” (Oct. 1974)

Human Environmental Laws, Regulation Criteria and Standards

By Department of Environment of Iran (1st ed. Nov. 2012)

IPS (IRANIAN PETROLEUM STANDARDS)

IPS-G-SF-860	"General Standard for Air Pollution Control"
IPS-E-PR-460	"Engineering Standard for Process Design of Flare and Blowdown System"
IPS-G-ME-210	"General Standard for Flare and Flare Stacks"
IPS-E-PR-810	"Engineering Standard for Process Design of Furnaces"

ISO (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION)

ISO 6584: 1981	"Cleaning Equipment for Air and other Gases-Classification of Dust Separator"

3. DEFINITIONS AND TERMINOLOGY

ABSORPTION

A physico-chemical process in which a substance associates with another to form a homogeneous mixture presenting the characteristics of a solution.

ACCESS HOLE

A hole in the duct, at the extremity of a sampling line, through which sampling is undertaken.

ACGIH

American Conference of Governmental industrial Hygienists, Inc (ACGIH) is an organization open to all practitioners in industrial hygiene, occupational health, environmental health, or safety.

ADSORPTION

A physical process in which the molecules of a gas, of dissolved substances or of liquids, adhere in extremely thin layers to the exposed surface of solid substances with which they come into contact.

AEROSOL

A suspension, in a gaseous medium, of solid particles, liquid particles, or solid particles and liquid particles, having a negligible falling velocity.

Note:

In physics, an upper value is arbitrarily assigned to the dimensions of particles capable of constituing an aerosol, adopting for the place being considered a maximum limit for the falling velocity. It is defined as being that of a spherical particle of density equal to 10^3 kg/m^3 and of diameter 100 µm, falling under the effect of its own weight in an immobile gas at a temperature of 20°C and at a pressure of 101.3 kPa. In air, under a gravitational acceleration of 9.81 m/s^2, this speed is 0.25 m/s.

AGGLOMERATE

A collection of solid particles adhering to each other.

AGGLOMERATION

The action leading to the formation of agglomerates.

AGGLUTINATION

The action of joining, by impact, solid particles coated with a thin adhesive layer or of trapping solid particles by impact on a surface coated with adhesive.

AGGREGATE

A relatively stable assembly of dry particles, formed under the influence of physical forces.

ANTHROPOGENIC

Referring to environmental alterations resulting from the presence or activities of humans.

(Dictionary of Environmental Science, McGraw-HILL pub, inc. 2003)

ASH

The solid residue of effectively complete combustion.

CAPTURE

The extraction of solid particles, liquid particles or gases close to their sources.

CLEANING (after clogging)

The removal of the deposit of solid or liquid particles which has produced clogging.

CLEANING FACTOR

The ratio of the quantity of pollutants entering a separator to the quantity leaving it.

CLOGGING

The deposition, progressive or otherwise, of solid or liquid particles on or within a filter medium, causing the flow to be obstructed.

CLOGGING CAPACITY; HOLDING CAPACITY

The particle mass that can be retained by equipment up to the point at which one of the specified operational limits is reached.

COALESCENCE

The action by which liquid particles in suspension unit to form larger particles.

COLLECTION EFFICIENCY

With regard to filters, dust separators and droplet separators, the ratio of the quantity of particles retained by a separator to the quantity entering it (generally expressed as a percentage).

CONCENTRATION; CONTENT

The quantity of a solid, liquid or gaseous material expressed as a proportion of another material in which it is contained in the form of a mixture, a suspension or a solution.

CONTAMINANT

See pollutant.

CONTAMINATION

See pollution.

CONTENT

See concentration.

CYCLONE

A dust separator or droplet separator utilizing essentially the centrifugal force derived from the motion of the gas.

DISPERSION

An operation as a result of which solid particles or liquid particles are distributed in a fluid. Also applied to a two-phase system in which one phase, known as the "dispersed medium", is distributed throughout the other, known as the "dispersion medium".

DROPLET

A liquid particle of small mass, capable of remaining in suspension in a gas. In some turbulent systems, for example clouds, its diameter can reach 200 µm.

DROPLET SEPARATOR

An apparatus for separating liquid particles from a gas stream in which they are suspended.

DUST

Small solid particles conventionally taken as those particles below 75 µm in diameter which settle out under their own weight but which may remain suspended for some time....(see dust, and, grit): A general term applied to solid particles of different dimensions and origin generally remaining suspended in a gas for a certain time.

DUCT

An enclosed structure through which gases travel from one point to another.

DUST CONTROL

The whole of the processes for the separation of solid particles from a gas stream in which they are suspended. (By extension, also the activities involved in the construction and commissioning of a dust separator.)

DUST SEPARATOR

An apparatus for separating solid particles from a gas stream in which they are suspended.

Note:

Dust separators working on the following principles are given as examples:

- **gravity;**

- **inertia;**
- **centrifugal force;**
- **electricity;**
- **fibrous layer;**
- **packed tower;**
- **bubble washer;**
- **spray washer;**
- **venturi-scrubber.**

ELUTRIATION

A method of separating particles using the difference in apparent weight which may exist between the particles when they are suspended in a fluid.

Emission

A natural or anthropogenic discharge of particulate, gaseous, or soluble waste material or pollution into the air.

Emission Factor

An emission factor 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. These factors are usually expressed as the weight of pollutant divided by a unit weight, volume, distance, or duration of the activity emitting the pollutant (e.g., kilograms of particulate emitted per mega gram of coal burned).

EQUIVALENT DIAMETER

The diameter of a spherical particle the size of which will give identical geometric, or optical, or electrical or aerodynamic behavior to that of the particle being examined.

For sieves, the equivalent diameter is the diameter of the holes in a round hole sieve which will pass the same proportion of material as will a specified square mesh sieve. It is dependent upon the shape and size of the particles under examination.

FILTER

An apparatus for separating solid or liquid particles from a gas stream in which they are suspended. This apparatus is generally formed of a porous or fibrous layer or of an assembly of porous and/or fibrous layers. (By extension, applied also to some oil-bath devices and some electrical devices.)

FILTER MEDIUM

The part of a filter on or within which the particles are retained.

FILTRATION

The separation by a filter of solid particles or liquid particles from a gas stream in which they are suspended. (By extension, also the whole of the activities involved in the construction and commissioning of a filter installation.)

FLY ASH

Ash entrained by combustion gases.

FUME

An aerosol of solid particles, usually from metallurgical processes, generated by condensation from the gaseous state generally after volatilization from melted substances and often accompanied by chemical reactions such as oxidation.

FUMES

In popular usage, gaseous effluents, often unpleasant and malodorous; which might arise from chemical processes.

GAS

A mixture of gaseous compounds or elements flowing in a duct, carrying particulate matter.

GAS-PURIFIER

An apparatus for totally or partially removing one or more constituents from a gas mixture.

GRIT

Airborne solid particles in the atmosphere or flues in the United Kingdom

HOOD

An inlet device for an extraction system.

IMPACT

A collision of two particles with each other or of a particle with a solid or liquid surface.

IMPACTION

The action of particles entering into contact with a surface.

ISOKINETIC SAMPLING

Sampling at such a rate that the average velocity of the gas entering the sample nozzle is the same as that of the gas in the duct at the sampling point.

LD50

Lethal Dose 50 is Standard measure of the toxicity of a material that will kill half of the sample population of a specific test animal in a specified period through exposure via ingestion, skin contact, or injection.

MIST

A suspension of droplets in a gas.

NORMAL TEMPERATURE AND PRESSURE (NTP)

15°C and 101325 N/m^2.

OSHA

Occupational Safety and Health Administration

PARTICLE

A small discrete mass of solid or liquid matter.

PARTICLE SIZE ANALYSIS

The science which deals with the measurement of the dimensions and determination of the shape of particles.

PARTICLE SIZE ANALYSIS; GRANULOMETRIC ANALYSIS

The whole of the operations by which a particle size (granulometric) distribution may be obtained.

PARTICLE SIZE DISTRIBUTION; GRANULOMETRIC DISTRIBUTION

A presentation, in the form of tables of numbers or of graphs, of the experimental results obtained using a method or an apparatus capable of measuring the equivalent diameter of particles in a sample or capable of giving the proportion of particles for which the equivalent diameter lies between defined limits.

PARTICULATES

Solid matter, in a gas stream, that is solid at normal temperature and pressure.

PENETRATION; TRANSMISSION

The ratio of the quantity of particles leaving a filter, dust separator or a droplet separator, to the quantity entering it.

POLLUTANT; CONTAMINANT

Any undesirable solid, liquid or gaseous matter in a gaseous or liquid medium.

POLLUTION; CONTAMINATION

The introduction of pollutants into a liquid or gaseous medium, the presence of pollutants in a liquid or gaseous medium, or any undesirable modification of the composition of a liquid or gaseous medium.

POROUS LAYER

A permeable layer of solid material in any form having interstices of small size, generally known as "pores".

PRECIPITATION

An operation in which particles are separated from a gas stream in which they are suspended, by the action of an electrical field or a thermal gradient.

PURIFICATION

The total or partial removal of unwanted constituents from a gaseous medium.

RATED FLOW

The gas flow rate through a separator either as stated by the manufacturer for defined conditions of use or as agreed between the interested parties for a particular installation.

SAMPLING LINE

The line across the sampling plane on which the sampling points are located.

SAMPLING PLANE

The cross section of the duct in which all sampling is carried out.

SAMPLING POINT

A specific location on a sampling line at which an individual sample is extracted.

SAMPLING POSITION

A place in a duct where sampling is carried out.

SEDIMENTATION

Separation under the action of gravity of particles from the fluid in which they are suspended.

SEPARATOR

An apparatus for separating, from a gaseous stream in which they are suspended or mixed, solid particles (filter and dust separator), liquid particles (filter and droplet separator) or gases (gas-purifier).

SERVICE FLOW

The gas flow rate through a separator under given service conditions.

SITE

Works or plant where sampling is to be carried out.

SMOKE

A visible aerosol resulting from combustion.

Note:

In some literature, smoke is referred to quantitatively in terms of a Ringelmann Number, a smoke shade, a darkness of stain or a mass of deposit collected.(see fume, fumes, and especially smoke, for approximate terms)

The whole of the combustion gases and the particles entrained by them. (By extension, also the gases charged by particles resulting from a chemical process or from a metallurgical operation.)

SOOT

Agglomerates of carbonaceous particles formed by incomplete combustion and deposited before emission.

SUSPENSION

A two-phase system in which one phase, known as the "dispersed medium", is distributed throughout the other, known as the " dispersion medium".

THRESHOLD LIMIT VALUES (TLVs)

Refer to air borne concentration of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects.

TEST FLOW

The gas flow rate through a separator during a rig test or a site test. This flow, which can differ from the rated flow, shall be specified or, failing this, agreed between the interested parties.

WASHER

Any dust separator, droplet separator or gas purifier that depends for its operation on a liquid acting as a collecting medium.

4. UNITS

This standard is based on international system of units (SI), as per IPS-E-GN-100 except where otherwise specified.

5. GENERAL

Serious damage can be caused by polluting material discharged into environment from various sources. Such emission can adversely affect agricultural land and crops and can spoil clothing and buildings, as well as corrode metal installations and can have harmful effect on the health of community.

6. AIR POLLUTION

Air pollution is defined as the addition to our atmosphere of any material which will have a deleterious effect to life upon our planet. The material might be a toxic gaseous hydrocarbon with some long-lasting effect on an organism ingesting it or perhaps a particulate irritant which could cause similar problems. It might be atomic radiation in a form that we cannot see which would be damaging to animal or plant cells. A pollutant can be anything which when put into the atmosphere either purposely or through some act of nature reduces the oxygen content or significantly changes the composition of the air.

An air pollutant does not have to be inhaled. It becomes a pollutant merely by being in the air. Smog, made up of gases and particulate matter in large quantities, and seen over many of our major cities in the last fifteen years, forms a blanket which shields some of the sun’s radiation so necessary to life on earth. This blanket changes heat absorption patterns on the surface of the earth and can prohibit reradiation of the earth’s heat to the sky, resulting in the "greenhouse effect" which ultimately changes weather and temperature patterns across the entire surface of the planet.

6.1 Clean Air

The earth is surrounded by approximately 500 billion tons of air, of which 20.9 percent is oxygen, 78.0 percent is nitrogen, and 0.9 percent is argon. Excluding water vapor, these gases make up all but 0.04 percent of the atmosphere and three-quarters of the remainder is carbon dioxide. The last 0.01 percent contains the other noble gases, hydrogen, nitrogen oxides, ozone, and traces of many other gases. Table 1 summarizes the major gases, and their concentrations on a dry basis. These figures remain essentially constant as long as water vapor is not included, since it varies in a range from as high as 3 percent by volume to less than 1 percent. In ambient air measurements this variation is normally within the reproducibility limits of the determinations and can be ignored.

Despite this, samples are often dried before testing.

Water vapor normally cannot be considered as an air pollutant even though it is produced in great quantities in combustion processes. Natural evaporation and precipitation move far greater amounts of water than any man-made process. One exception to this may occur in the near future with the advent of the supersonic transport. This plane may release large amounts of water vapor into the stratosphere causing increased cloudiness and a temperature rise.

Water vapor has a synergistic effect upon air pollutants, increasing many deleterious effects. For example, sulfur dioxide, which itself is an irritating and corrosive pollutant, can combine with water vapor and atmospheric oxygen to form highly corrosive sulfuric acid mist. Smog also depends upon water vapor for its formation. Monitoring of pollution in urban areas must consider the humidity and predict its effect on pollutants.

TABLE 1 – APPROXIMATE CONCENTRATION (VOLUME %)

CONSTITUENT	APPROXIMATE CONCENTRATION
NITROGEN (N_2)	78.03
OXYGEN (O_2)	20.99
CARBON DIOXIDE (CO_2)	0.03
ARGON (A)	0.94
NEON (Ne)	0.00123
HELIUM (He)	0.0004
KRYPTON (Kr)	0.00005
XENON (Xe)	0.000006
HYDROGEN (H_2)	0.01
METHANE (CH_4)	0.0002
NITROUS OXIDE (N_2O)	0.0005
WATER VAPOR (H_2O)	Variable
PARTICULATE MATTER	a)Variable type and quantity
OZON (O_3)	b)Variable
FORMALDEHYDE (HCHO)	c)Uncertain

a) The types and concentrations of these substances may vary substantially from one region to another and within any period of time from natural conditions.

b) From ultraviolet radiation and probably thunderstorms, concentrations will vary from 0 to 0.07 ppm.

c) From biological sources or oxidation of CH_4; possible concentrations not determined.

d) To observe chemical composition of dry atmospheric air, see Air Pollution, Its origin and control (Third Edition 1998, Sec.1-4, Table1-2) By: Kenneth Wark.

6.2 Pollution Sources

Major categories of air pollution is considered to be caused by:

1) Transportation

2) Domestic heating

3) Electric power generation

4) Industrial fuel burning and process emission.

Major industrial polluters have been classified relative to the type of industry. Generally they can be catergorized as follows:

a) Petroleum refineries; particulate, sulfur oxide hydrocarbons, and carbon monoxide.

b) Petrochemical industries; hydrocarbon, carbon mono oxide particulate.

c) Fertilizer industries particulates, Nox, gaseous floride compounds.

6.3 Types of Emissions in Petroleum Industries

6.3.1 Refinery

Potential sources of refinery emissions are given in Table 2.

TABLE 2 - POTENTIAL SOURCES OF SPECIFIC EMISSIONS FROM REFINERIES

TYPES OF EMISSION	POTENTIAL SOURCES
Oxides of sulfur	Boilers, process heaters, catalytic cracking unit regenerators, treating units, H_2S flares, decoking operations, etc.
Hydrocarbons	Loading facilities, turnarounds, sampling, storage tanks, waste water separators, blowdown systems, catalyst regenerators, pump, valves, blind changing, cooling towers, vacuum jets, barometric condensers, air blowing, high pressure equipment handling volatile hydrocarbons, process heaters, boilers, compressor engines, etc.
Oxides of nitrogen	Process heaters, boilers, compressor engines, catalyst regenerators, flares, etc.
Particulate matter	Catalyst regenerators, Boilers, process heater Decoking operations, Incinerators, Sulfur Granulation Process, etc.
Aldehydes	Catalyst regenerators
Ammonia	Catalyst regenerators
Odors	Treating units (air blowing, steam blowing) drains, tank vents, barometric condenser sumps, waste water separators.
Carbon monoxide	Catalyst regeneration, decoking, compressor engines, incinerators.
Arsene	Regeneration hydro de sulfurize
Phosgene	Regeneration hydro de sulfurize
Cyanides	Regeneration hydro de sulfurize
HCl	Platformers is omerization
HF	HF alkylation
H_2SO_4	Alkylation acid plant

6.3.1.1 Emission factors in refinery

Emission factors and emission inventories have long been fundamental tools for air quality management. Emission estimates are important for developing emission control strategies, determining applicability of permitting and control programs, ascertaining the effects of sources and appropriate mitigation strategies, and a number of other related applications by an array of users, state, and local agencies, consultants, and industry.

The general equation for emission estimation is:

$$E=A\times EF\times (1-ER/100)$$

Where:

- E= emission,
- A= activity rate,
- EF= emission factor, and
- ER= overall emission reduction efficiency, %.

ER is further defined as the product of the control device destruction or removal efficiency and the capture efficiency of the control system. When estimating emissions for a long time period (e.g., one year), both the device and the capture efficiency terms should account for upset periods as well as routine operations.

Emission factor for major atmospheric pollution in refinery are given in Table 3.

TABLE 3 - EMISSION FACTORS FOR REFINERY

PROCESSES	UNITS OF EMISSION FACTORS	EMISSION FACTOR
a. boiler and process heater	gram Hydrocarbon/m^3 oil burned	399
	gram Hydrocarbon/m^3 gas burned	0.416
	gram Particulate/m^3 oil burned	2280
	gram Particulate/m^3 gas burned	0.32
	gram NO_2/m^3 oil burned	8265
	gram NO_2/m^3 gas burned	3.68
	gram CO/m^3 gas burned	negligible
	gram CO/m^3 gas burned	negligible
	gram $HCHO/m^3$ oil burned	400
	gram $HCHO/m^3$ gas burned	0.0496
b. fluid catalytic unit	gram Hydrocarbon/m^3 of fresh feed	627
	gram Particulate/ton of catalyst circulation	783
	gram NO_2/m^3 of fresh feed	179.5
	gram CO/m^3 of fresh feed	39045
	gram $HCHO/m^3$ of fresh feed	54.15
	gram NH_3/m^3 of fresh feed	153.9
	gram SO_2/m^3 of fresh feed	1411.3
c. moving bed catalytic cracking units	gram Hydrocarbon/m^3 of fresh feed	248
	gram Particulate/ton of catalyst circulation	1740
	gram NO_2/m^3 of fresh feed	14.25
	gram CO/m^3 of fresh feed	10830
	gram $HCHO/m^3$ of fresh feed	34.2
	gram NH_3/m^3 of fresh feed	17
d. Compressor internal combustion engines	gram Hydrocarbon/m^3 of fuel gas burned	19.2
	gram NO_2/m^3 of fuel gas burned	13.76
	gram CO/m^3 of fuel gas burned	negligible
	gram $HCHO/m^3$ of fuel gas burned	1.76
	gram NH_3/m^3 of fuel gas burned	3.2
e. Miscellaneous process equipment:		
1. Blow down system	gram Hydrocarbon/m^3 refinery	
a. with capacity control		14.25
b. without control		855
2. Process drains	gram Hydrocarbon/m^3 waste water	
a. with control		22.8
b. without control		598.5

(to be continued)

TABLE 3 - (continued)

PROCESSES	UNITS OF EMISSION FACTORS	EMISSION FACTOR
3. Vacuum Jets	gram Hydrocarbon/m^3 vacuum distillation capacity	
a. with control		negligible
b. without control		370.5
4. Cooling tower	gram Hydrocarbon/3,785,000 liters cooling water	2616
5. Pipeline valves and flanges	gram Hydrocarbon/m^3 refinery capacity	79.8
6. Vessel relief valves	gram Hydrocarbon/m^3 refinery capacity	31.35
7. Pump seal	gram Hydrocarbon/m^3 refinery capacity	48.45
8. Compressor seal	gram Hydrocarbon/m^3 refinery capacity	14.25
9. Others (air blowing)	gram Hydrocarbon/m^3 refinery capacity	28.5

Note:

Table 3 is compiled from IRVIN SAX. N.

Industrial pollution, vannos trand reinhold company.

6.3.1.2 Odors in refineries

Some Typical Refinery Smells, their possible source, and the most probable compounds contributing to the odors are summarized as follows:

"REFINERY ODORS AND SOURCES"

TYPE OF SMELL	SOURCE	ODORS COMPOUNDS
BAD EGGS	CRUDE STORAGE DISTILLATION OF GASES SULPHUR REMOVAL, FLARE STACKS (COLD FLARE)	H_2S + TRACE OF DISULPHIDES
SEWER SMELL	EFFLUENT WATER, BIOLOGICAL TREATMENT PLANTS LPG ODOR-IZING SPENT CAUSTIC LOADING AND TRANSFER	DIMETHYL SULPHIDE, ETHYL AND METHYL MERCAPTANS
BURNT OIL	CATALYTIC CRACKING UNIT COKING ASPHALT BLOWING ASPHALT STORAGE	UNSATURATED HYDROCARBONS
GASOLINE	PRODUCT STORAGE, CPI & API SEPARATORS	HYDROCARBONS
AROMATICS (BENZENE)	AROMATIC PLANTS, NAPHTHA REFORMERS	BENZENE, TOLUENE
HOT TAR	ASPHALT STORAGE	HYDROCARBONS MERCAPTANS, H_2S

A table of the most common odor-causing compounds found in the refinery emission is given hereunder:

ODORS OF COMPOUNDS WHICH MAY BE FOUND IN REFINERY EMISSIONS

Chemical	Odor Threshold (ppb)*	Odor Description
Acetic acid	1,000	Sour
Acetone	100,000	Chemical, sweet
Amine, monomethyl	21	Fishy, pungent
Amine, dimethyl	47	Fishy
Amine, trimethyl	0.2	Fishy, pungent
Ammonia	46,800	Pungent
Benzene	4,700	Solvent
Benzyl sulphide	2	Sulphidy
Carbon disulphide	210	Vegetable-like, sulphidy
Chlorine	314	Bleach, pungent
Chlorophenol	0.03	Medicinal
Dimenthyl sulphide	1-2	Vegetable-like, sulphidy
Diethyl sulphide	6	Garlic-like, foul
Diphenyl sulphide	5	Burnt, rubbery
Hydrogen sulphide	5	Rotten eggs
Methyl ethyl ketone	10,000	Sweet
Mercaptan, methyl	1-2	Sulphidy, decayed cabbage
Mercaptan, ethyl	0.4-1	Sulphidy, decayed cabbage
Mercaptan, n-propyl	0.7	Sulphidy
Mercaptan, n-butyl	0.7	Strong, sulphidy
Paracresol	1	Tarry, pungent
Paraxylene	470	Sweet
Phenol	47	Medicinal
Phosphine	21	Oniony, mustard
Sulphur Dioxide	470	Sharp, Pungent
Toluene	2,000 - 4,700	Solvent, moth balls
Butane	6,000	
Heptane	18,000	
Amylenes and pentenes	170 - 2,100	

***Units in parts per billion by volume.**

6.3.2 Petrochemicals

Pollutant from petrochemical plant is given in Table 4.

TABLE 4 - POLLUTANT FROM PETROCHEMICAL PLANT

Combustion	o SO_x, NO_x and other pollutants in waste gas from boiler for power generation, heating furnace (fractionator reboiler) and cracking furnaces (naphtha, EDC, steam reforming)
Evaporation and Drying	o Drying of synthetic rubber, plastics - Emission of dry air containing solvent and monomer o Vaporization from storage tanks (mostly when charging) - Emission of hydrocarbons o Opening of vessel manholes - Emission of hydrocarbons
Off-gas, Vent Gas, Flare Stack Gas	o Air used for oxidation, oxichlorination and ammooxidation changes into a waste gas consisting of nitrogen, carbon dioxide and a bit of byproducts o Non-condensing gas from distillation tower and reactor is accompanied with hydrocarbons and byproducts o Pollutants in combustion gas from flare stack
Powder Handling	o Dispension of plastics during transportation and storage o Dispersion of catalysts used for fluidized-bed
Leakage (Loss)	o Leakage from pump and compressor shafts and flanges and storage tank - Emission of hydrocarbons

Major air contaminants emitted in fertilizer and other petroleum industries are as follow:

TABLE 4 - (continued)

Process of Operation	Air Contaminants Emitted
Phosphate fertilizers: crushing grinding and calcining	Particulates (dust)
Hydrolysis of P_2O_3	PH_3 $P_2O_5PO_4$ mist
Acidulation and curing	HF, SiF_4
Granulation	Particulates (dust) (product recovery)
Ammoniation	NH_3. NH_4Cl. SIF_4 HF
Nitric acid acidulation	NO_2 gaseous fluoride compounds
Super phosphate storage and shipping	Particulates (dust)
Ammonium nitrate reactor	NH_3, NO_2
Prilling tower	NH_4, NO_3
NGL units	Hydrocarbon
Oil production units	H_2S odor
Gas compression station	" "
Gas injection plant	" "
Sulphur unit	" "
Oil wells	" "
Cooling tower	Emission of hydrocarbons (HC+VOCs)
Waste water system	Emission of hydrocarbons (HC+VOCs)

*** VOCs: Volatile Oil Components**

6.4 Standard Level

6.4.1 Ambient air quality standards

Standard for desirable community levels in term of concentrations and sample arranging time periods, associate with measurements of these pollutants in community air as described in “Human Environmental Laws, Regulation Criteria and Standards”, Pages 187 & 188, Tables 3-7 & 3-8, By Department of Environment of Iran(1st ed. Nov. 2012).

Certain materials have been designated as hazardous air pollutants, to which no ambient air quality standard is applicable, and for which national emission standards will be used.

Various pollutants in different sources that should be considered with Emission standard is given in Table 6.

TABLE 6

SOURCE	POLLUTANT CONSIDERED
PETROLEUM REFINERIES	PM, NO_x, TRS, Odor, CO, H_2S, HC
ASPHALT BATCH PLANTS	PM, NO_x, Odor, HC
PHOSPHATE FERTILIZER PLANTS	PM, F
PHOSPHORUS REDUCTION PLANTS	PM, F
INDUSTRIAL SIZE FUEL-BURNING PLANTS	PM, SO_2, NO_x
STORAGE VESSELS FOR PETROLEUM LIQUIDS	HC
SEWAGE TREATMENT PLANTS	
OIL & GAS. NGL, GAS INJ./COMP. UNITS & WELLHEAD SEPRATOR	PM, HC, CO, CO_2, H_2S, NOX, SMOKE
GAS SWEETING PLANT	PM, HC, H_2S, RSH, CO, CO_2, NOX, SMOKE
DESALTING PLANTS	PM, HC, SMOKE, CO, CO_2, H_2S

a) From Wagman, Ref. 113.

b) PM means Particulate Matter.

c) TRS means Total Reduced Sulfur.

6.4.2 Emission standard

Emission Standards may be written in several ways:

1) Process weight rate or mass of emitted pollutant per mass of raw material (eg, 0.15 kg particulate per metric ton of feed to a kiln).

2) Mass of emitted pollutant per mass of product (eg, 1.5 kg of nitrogen oxide per metric ton of nitric acid pro- duced).

3) Mass of emitted pollutant per volume of emitted gas (eg. 90 mg of particulate per dry standard cubic meter).

4) Mass of emitted pollutant per heat input (eg, 0.34 grams of sulfur dioxide per 10 6 joules of heat input).

5) Plume opacity (eg, plume not to exhibit more than 20 % opacity). Other emission standards include the limitation of sulfur content of fuel and the restriction on pollutant mass emitted by new vehicles during a specified dynamometer test cycle.

For emission standard the following figures can be considered.

Pollutant		
SH_2	**10 mg/m^3**	**6.62 ppm**
Carbon monoxide	**187.5% mg/m^3**	**150 ppm**
Sulfur oxide	**----**	**800 ppm**
Particles	**50 (mg/m^3)**	**----**
Hydrocarbons	**20% opacity**	----
Photochemical	**20 mg/m^3**	**----**
Nonphotochemical	**300 mg/m^3**	**----**
Nitrogen Oxides	**432mg/m^3**	**210 ppm**

The latest Standard by Department of Environment of Iran should be considered (Refer to Section 2.References).

Note:

Based on the high sulphur content of present fuel oils burned in furnaces the emission standard specified can not be generally achieved. However the subject matter shall be considered in future projects case by case.

6.5 Measurement of Air Pollution

Pollution measurements may be divided into two categories: ambient and source measurements. For more details see Appendix F.

6.6 Cleaning Equipment for Air and Other Gases

6.6.1 Classification of dust separators

For classification of dust separators refer to ISO 6584.

6.6.2 Condensation

For Engineering Design of TEMA Type Shell and Tube Heat Exchangers refer to IPS-E-PR-770.

6.6.3 Flare, flare stack and furnaces

For design of Flare and Blow down systems, Flare and Flare Stacks, and Furnaces refer to the following standards respectively.

IPS-E-PR-460

IPS-G-ME-210

IPS-E-PR-810

6.7 Process Control

6.7.1 Refineries

Refinery atmospheric emissions and control procedures are customarily considered by types of equipment employed rather than by refinery process operation.

6.7.1.1 Storage tanks

Hydrocarbon vapors may be released through a number of mechanisms in storage tanks, including tank breathing due to temperature changes, direct evaporation, and displacement during filling. The principal source of potential loss is from crude oil and light distillate products. The hydrocarbon content of crude oil is substantially saturated and, as explained above, is not believed to be involved in the photochemical smog complex. Light distillates have considerable value and are normally controlled to a practical economic level. Vapor conservation storage may involve tanks with floating roof covers, pressurized tanks, and connections to vapor recovery systems.

For materials exhibiting a true vapor pressure (TVP) at storage conditions of below 78 mm of Hg, no controls are required; for materials with a TVP between (78 and 570 mm of Hg), the storage vessel shall be equipped with a floating roof or equivalent; for materials with a TVP exceeding 570 mm of Hg, the vessel shall be equipped with a vapor recovery system or equivalent.

6.7.1.2 Catalyst regeneration units

Coke formed on the surface of catalysts during catalytic cracking, reforming, and hydrogenation is burned off in regenerating vessels by controlled combustion. Flue gases from regenerators may contain catalyst dust, carbon monoxide, hydrocarbon (principally methane), and sulfur and nitrogen oxides. The catalyst dust may be controlled by mechanical or electrical collecting equipment. The carbon monoxide and unburned hydrocarbons are generally dispersed in the atmosphere, but may be eliminated by burning in a waste heat boiler which also generates additional steam. Amount of catalyst emitted from fluid catalytic cracking regenerator should not exceed one kg of catalyst per 1000 kg of coke make, and carbon monoxide to 500 ppm by volume.

In-situ type operation is finding wider use in fluid catalytic cracking unit.

6.7.1.3 Waste water separators

Waste water gravity separators are commonly used to trap and recover oil discharged to the sewer system from equipment leaks and spills, shutdowns, sampling, process condensate, pump seals, etc. Depending on the quantity and type of oil in the sewers, some hydrocarbon vapors may evaporate from the drainage and separator system. If this vaporization is sizable and control is indicated, the front end of the separators may be covered. Catch basin liquid seals, manhole covers, and good house-keeping practices will likewise control drainage system vapor losses.

6.7.1.4 Loading facilities

While most petroleum products leave the refinery though pipelines with no emission to the atmosphere, loading into tank trucks, tank cars, and drums can result in hydrocarbon vapor loss by displacement or evaporation. Careful operation to minimize spillage, and vapor collection and recovery equipment will control vapor loss from this operation.

6.7.1.5 Pipeline valves

The typical refinery contains a maze of piping, mostly above grade. The effects of heat, pressure, vibration, and corrosion may cause leaks in valved connections. Depending on the product carried and the temperature, the leaks may be liquid, vapor, or both. Regular inspection and prompt maintenance will correct vapor loss from this source.

6.7.1.6 Pumps and compressors

Hydrocarbons can leak at the contact between the moving shaft and stationary casing in pumps and compressors. Asbestos or other fibers are packed around the shaft to retard leakage from shaft motions. Mechanical seals, consisting of two plates, perpendicular to the shaft, forced tightly together, and also used. Wear can cause both packed and mechanical seals to leak product. Inspection and maintenance, sealing glands under pressure, and use of mechanical seals in light hydrocarbon service are useful control measures.

6.7.1.7 Blow down system, flares, and shutdowns

Refinery process units and equipment are periodically shut down for maintenance and repair. Since these turnarounds generally occur about once a year, losses from this source are sporadic. Hydrocarbons purged during shutdowns and start-ups may be manifolded to blowdown system for recovery, safe venting, or flaring. Vapors can be recovered in a gas holder or compressor and discharged to the refinery fuel gas system. Flares should be of the smokeless type, utilizing either steam or air injection. Design data for smokeless flares are readily available from combustion equipment manufacturers and in industry technical manuals. For aesthetic purposes, ground flares are becoming more popular.

6.7.1.8 Boilers and process heaters

Refineries depend on boilers and heaters to supply high pressure steam at elevated temperatures. Fuels may include refinery or natural gas, heavy fuel oil, and coke, often in various changing combinations. Sulfur oxides in the flue gas are, of course, a result of the sulfur in the fuel feed. Nitrogen oxides and small quantities of hydrocarbons, organic acids, and particulate matter are also present. Sulfide stripping of fuel gas prior to burning and selective blending of fuels may be employed to control sulfur emissions. Normally, good combustion practices will control smoke and particulate matter.

Stacks on boilers and heaters are elevated to improve atmospheric dispersion and further diminish resulting ground-level concentrations of gases such as sulfur dioxide and nitrogen oxides.

6.7.1.9 Sulfur recovery units

The potential for H_2S loss to the atmosphere occurs at two points in the Claus process:

a) The interface between the H_2S recovery process and the feed to the unit.

b) The tail gas from the plant. If the Claus plant breaks down and cannot take the feed, H_2S has to be flared. Some refineries utilize spare Claus capacity so that flaring is minimized.

The presence of H_2S in the tail-gas indicates that the conversion of H_2S to S is not complete. This tail-gas is either incinerated at 538°C to 649°C temperature thus releasing all sulfur compounds as sulfur oxides, or further treated in a tail-gas recovery system. The tail-gas treating systems generally convert all sulfur compounds to H_2S, after which the stream is scrubbed to remove the H_2S.

6.7.1.10 Incinerators

There are a number of incineration processes available for the incineration of refinery sludges, solids, and spent caustics. Fluid bed incinerators can be installed in refineries. These fluid bed incinerators operate at temperatures of 704°C. As the sludge is burned, the solids from the sludge remain in the bed while gaseous products of combustion, water vapor and fine particulate matter pass overhead through a cyclone separator and a water scrubber before venting to the atmosphere.

6.7.1.11 Miscellaneous

Various other miscellaneous emission sources, usually of lesser significance, will be found in refinery operations. Pressure relief valves may be manifolded into vapor recovery or flare systems to control leakage and relief discharged. Steam-driven vacuum jets, employed to induce negative pressure in process equipment, may discharge light hydrocarbons with the exhaust steam. These gases may be vented and burned in an adjacent boiler or heater firebox.

Fumes from air blowing operations may be consumed by incineration or absorbed by scrubbing. Gases from spent caustic and mercaptan disposal may be burned in fireboxes.

Hydrogen sulfide and mercaptans are the principal potential pollutants that may cause odors. These gases can be released from process steam condensates, drain liquids, barometric condenser sumps, sour volatile product tankage, and spent caustic solutions from treating operations.

Odorous compounds in steam condensates can be removed by stripping with air, flue gas, or steam and offensive gases can be burned in furnaces or boilers. Drain liquids can be collected in closed storage systems and recycled to the process.

Barometric condensers are being replaced by more modern surface condensers, and the noncondensables may be burned in process heaters or in a separate incinerator.

Spent caustic can be degasified, neutralized with flue gas, and/or stripped before disposal. Sulfides can also be removed from sour process water and spent caustic solutions by air oxidation to thiosulfates and sulfates.

Refinery waste gases that contain hydrogen sulfide are generally scrubbed with appropriate solutions for extraction of the sulfide by nonregenerative or heat-regenerative procedures. In the former method, the waste gases are scrubbed with a caustic solution, producing a solution of sodium sulfide and acid sulfide. As described above, the spent caustic may be oxidized by air blowing or sold. Vent gas from the blowing operation should be burned.

Heat-regenerative methods involve scrubbing sour gases with various types of amine, phenolate, or phosphate solutions which absorb hydrogen sulfide at moderately low temperatures and release it at higher temperatures. These methods are cyclic and consist of an absorption step, in which the hydrogen sulfide is scrubbed from the absorbing solution at approximately 38°C followed by a regeneration step in which the solution is reactivated for use by heating it to its boiling point to drive off the hydrogen sulfide. The released hydrogen sulfide is then burned or oxidized to form sulfur.

Refinery process changes may have the net effect of reducing overall emissions to the atmosphere. Examples of such process changes include substitution of hydrogen treating for chemical treatment of distillates use of harder catalysts to reduce attrition losses, and regeneration of spent chemicals for reuse.

Odor control methods for refinery are described in Appendix E.

6.7.2 Petrochemical processes

Petrochemical process that use air-oxidation-type reaction, normally have large continuous amounts of gas emissions to the atmosphere. The six processes considered in this section employ reactions using air oxidation.

Acrylonitrile-Carbon black-Ethylene-dichloride-Ethylene oxide-Formaldehyde-Phthalic anhydride.

6.7.2.1 Acrylonitrile

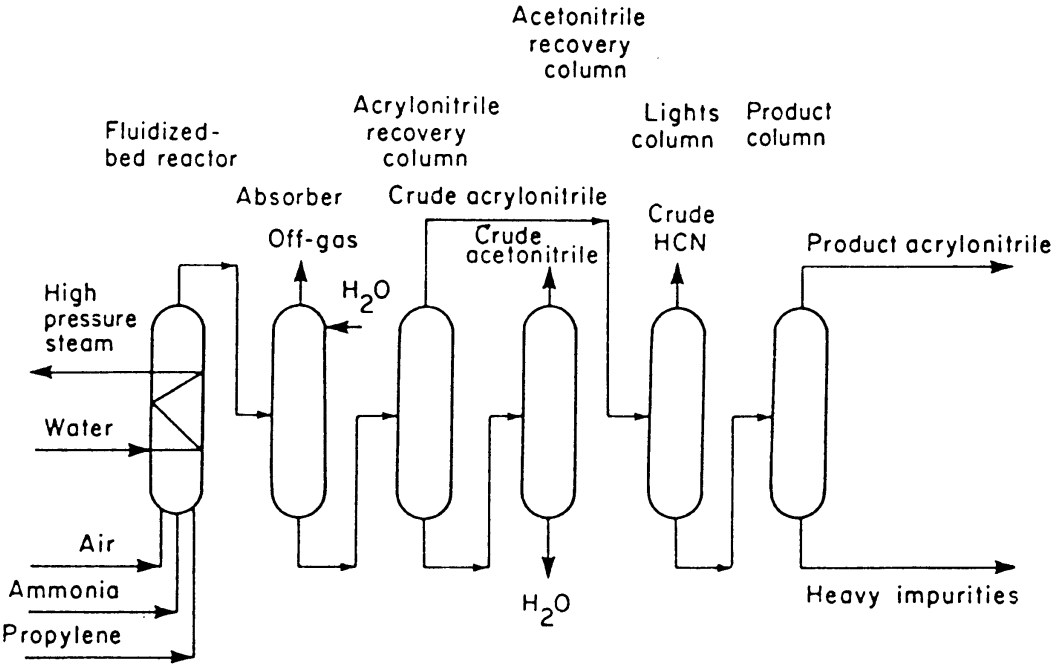
Air pollution emissions and their control. The major source of emissions from an acrylonitrile plant is the exit gas stream from the product absorber. For a typical plant producing 90 million kg a year of acrylonitrile, the gas flow rate would be 1284 scmm. The pollutants in kilograms per metric ton of acrylonitrile produced are shown in Table 7.

TABLE 7

POLLUTANT	KILOGRAM PER TON OF ACRYLONITRILE PRODUCED [a]
CARBON MONOXIDE	122
PROPYLENE	38
PROPANE	61
HYDROGEN CYANIDE	0.5
ACRYLONITRILE	0.25
ACETONITRILE	6.5

a) With no control.

In Fig. 1 flow manufacture of acrylonitrile has been shown.



FLOW DIAGRAM OF THE SOHIO PROCESS FOR THE MANUFACTURE OF ACRYLONITRILE, NOTING POTENTIAL AIR POLLUTION SOURCES

Fig. 1

The composition of the stream will depend primarily on the selectivity of the catalyst in the reactor and the efficiency of the absorber.

A second, less important, source of emissions from this process is the by-product incinerator. About 1 to 3% of the nitrogen content of the excess hydrogen cyanide and acetonitrile is converted into nitrogen oxides in a commercial incinerator operating at 871°C. There is presently no demonstrated control device for the oxides of nitrogen. The amount of the emission depends upon the amount of by-product gas burned, the temperature of combustion, and the percent of excess air.

A thermal incinerator will oxidize essentially all of the contaminants from the main process vent stream. However, the gas has such a low heat content that supplemental fuel must be added to achieve stable flame control and complete combustion. Various combinations of heat exchange could be used. Because acrylonitrile plants generate more steam than they can utilize, any steam generated by the incinerator has to be exported. The most feasible air pollution control system for new plants would be a thermal incinerator with process vent gas preheat, combustion air preheat, and a waste heat boiler.

6.7.2.2 Carbon black

Of all carbon black produced about 84% is manufactured by the furnace process. The thermal process which produces 14% of the carbon black is a minor source of air pollution. The plants using the channel process presently account for less than 2% of production.

6.7.2.3 Furnace process

In the furnace process, natural gas and a high carbon aromatic oil are preheated and introduced into a furnace with a limit amount of air (Fig. 2). A combination of cracking and combustion occurs.

$$CH_4 + 1\tfrac{1}{2}\,O_2 \rightarrow CO + 2\,H_2O + \text{heat}$$
$$(\_\_CH_2\_\_) \xrightarrow{\text{heat}} C + H_2$$
$$H_2 + \tfrac{1}{2}\,O_2 \rightarrow H2O + \text{heat}$$

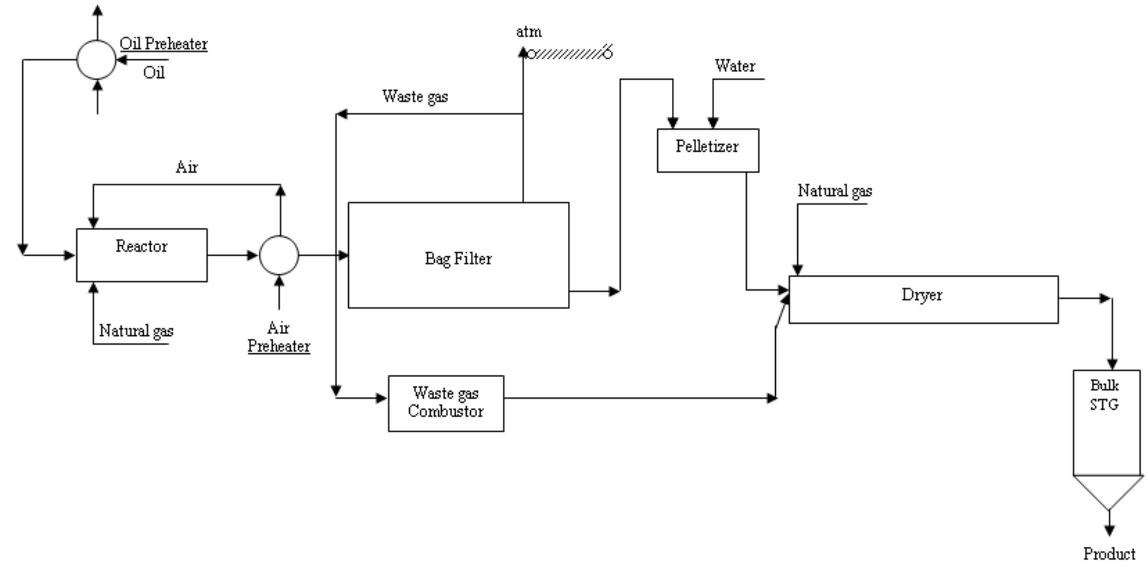


Fig. 2

6.7.2.4 Air pollutant emissions and their control

The major source of emissions from a furnace black plant is the exit gas stream from the bag collector. For a typical plant producing 41 million kg of black per year the gas flow rate would be 1440 scmm. The pollutants in pounds per ton of black produced are shown in Table 8. The exact composition of the stream will depend upon the grade of black produced and the composition of the aromatic oil. Grades which require a larger proportion of gas feed will have increased emissions of carbon monoxide. The amount of hydrogen sulfide formed is proportional to the sulfur content of the aromatic oil.

TABLE 8 - POLLUTANT PRODUCTION IN THE FURNACE BLACK PROCESS

POLLUTANT[a]	KILOGRAM PER TON OF CARBON BLACK PRODUCED
HYDROGEN	116.5
CARBON MONOXIDE	1270
HYDROGEN SULFIDE	27.5
SULFUR DIOXIDE	trace
METHANE AND ACETYLENE	54.5
PARTICULATE MATTER (BLACK)	2

a) No control after baghouse.

Any type of incineration device will oxidize most of the carbon monoxide and hydrogen sulfide in the vent stream. However, a carbon monoxide boiler or thermal incinerator would be more efficient than a flare. Because off-gas is low in heat content [about 40 BTU per scf (356,000 cal per scm)], most combustion devices require supplemental fuel (natural gas) to maintain combustion. Various combinations of heat exchange, supplemental fuel addition, and heat recovery can be used. The choice is an economic one determined by the costs of fuel and equipment and the ability to use any steam generated. The most efficient air pollution control system for new plants under most circumstances would be a process vent gas thermal incinerator with combustion air heat exchange plus a waste heat boiler and steamdriven process equipment. This should oxidize all the carbon monoxide, hydrogen sulfide, and hydrocarbons.

6.7.2.5 Ethylene dichloride

Ethylene dichloride produced by the direct chlorination or oxyclorination of ethylene. The atmospheric pollutants from direct chlorination processes are much less than those from the oxychloration process. Almost all ethylene dichlrodie used for the manufacture of vinyl chloride monomer.

6.7.2.6 Oxychlorination process

Vaporized ethylene, anhydrous hydrogen chloride, and air are fed to a catalytic reactor which operates at (2.3 to 6.1 atm) and 200°C to 315°C. The reaction is

$$2\ CH_2{=}CH_2 + O_2 + 4\ HCl \rightarrow 2\ CH_2Cl - CH_2Cl + 2\ H_2O$$

6.7.2.7 Air pollutant emissions and their control

The major source of emissions from an ethylene dichloride plant is the exit-gas stream from the solvent scrubber.(see Fig. 3)

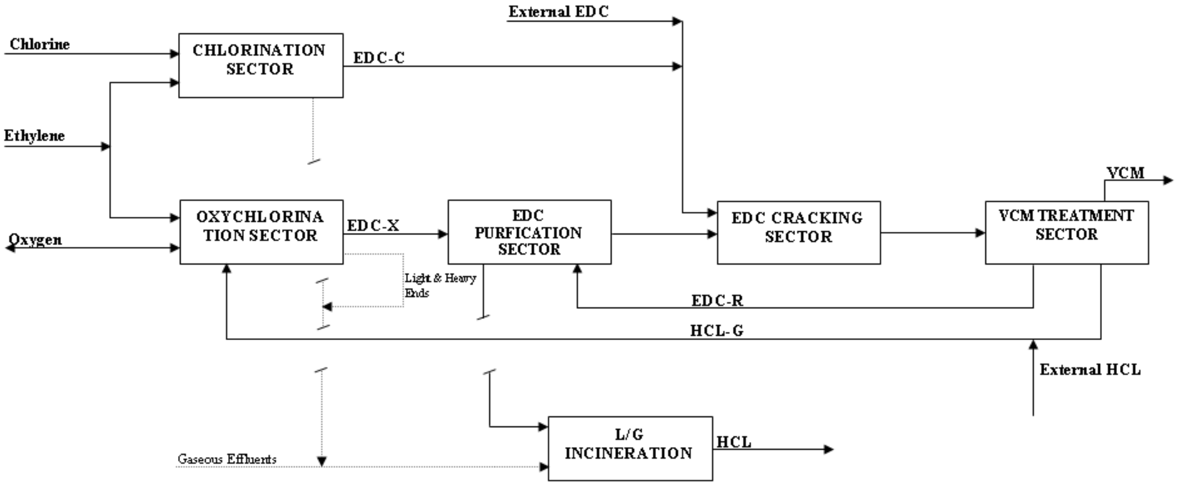


Fig. 3

For a typical plant of the type described producing 317 million kg per year, the gas flow rate would be 489 scmm.

The pollutants in (kilograms per metric ton) of ethylene dichloride produced are shown in Table 9. The values given are average values for several different oxychlorination processes. The composition of the stream will depend on catalyst activity, reactor operating conditions, and the solvent scrubber efficiency. All existing ethylene dichloride plants vent this stream directly to the atmosphere with no treatment. Any one of several combustion devices could be used to destroy the contaminants present. A water or caustic scrubber could be used after the combuster to remove the hydrogen chloride generated. Several different types of incineration would be feasible. The most efficient method for new plants would be a thermal incinerator followed by a waste heat boiler and a final caustic scrubber. The steam generated could be used in the plant. Because this system has not been demonstrated, it is possible that there might be significant operating problems. Careful control of temperature would be necessary to prevent condensation of hydrogen chloride and resultant corrosion of metal. Also, because of the low heating value of the gas stream 267,000 to 445,000 cal per scm, supplemental fuel would have to be added to achieve complete combustion and satisfactory flame control.

TABLE 9 - POLLUTANT PRODUCTION IN ETHYLENE DICHLORIDE MANUFACTURE BY OXYCHLORINATION

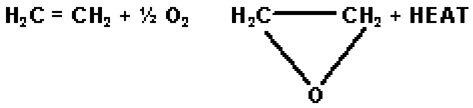
POLLUTANT	KILOGRAM PER TON OF ETHYLENE DICHLORIDE PRODUCED [a,b]
CARBON MONOXIDE	0.65
METHANE	2.0
ETHYLENE	4.8
ETHANE	6.3
ETHYLENE DICHLORIDE	6.9
ETHYL CHLORIDE	5.9
AROMATIC SOLVENT	1.1

The most feasible air pollution control system for an existing plant would be a thermal incinerator and scrubber on the main process vent.

6.7.2.8 Ethylene oxide

The oxidation of ethylene is the most widely used process for the production of ethylene oxide. The production of ethylene glycol, used primarily as automotive antifreeze, consumes more than half the ethylene oxide produced. The second largest use of ethylene oxide is in the manufacture of nonionic surfactants.

Ethylene oxide is produced by passing ethylene and air (or oxygen) over a silver catalyst and recovering ethylene oxide from the gas stream by water absorption. Ethylene oxide is stripped from the water solution and refined. The reaction is



$$H_2C = CH_2 + \tfrac{1}{2}\, O_2 \qquad H_2C \text{---} CH_2 + \text{HEAT} \;\; (\text{bridged by } O)$$

Flow diagrams for the air and oxygen processes are given in Figures 4 and 5. In the air process, air and ethylene are added to a recycle gas stream and fed to the main reactor where the reaction takes place in tubes containing silver catalyst.

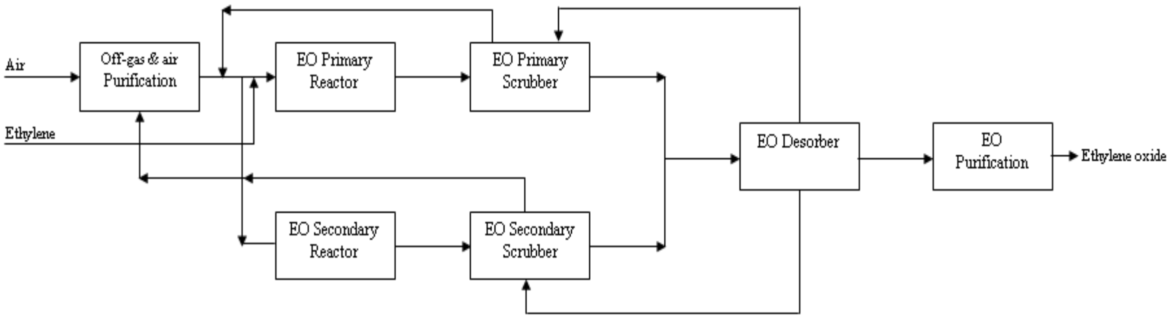
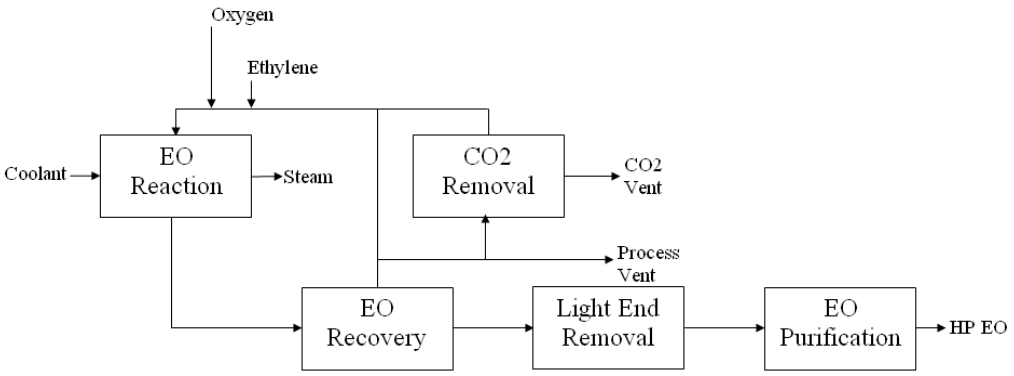


Fig. 4



FLOW DIAGRAM OF THE DIRECT OXIDATION PROCESS FOR THE MANUFACTURE OF ETHYLENE OXIDE USING AIR, NOTING POTENTIAL SOURCES OF AIR POLLUTION

Fig. 5

After heat exchange with recycle gas, the reactor effluent gases pass to the main absorber where the ethylene oxide is absorbed in a water solution. Approximately two-thirds of the absorber overhead gas (which contains nitrogen, carbon dioxide, unreacted ethylene, and air) is returned as recycle to the main reactor. The remaining onethird of the main absorber overhead gas is purged from the system. Most of the ethylene in the purge stream is recovered as ethylene oxide which is formed in the purge reactor and removed in the purge absorber. The vent from the purge absorber, mostly nitrogen and carbon dioxide, contains some unreacted ethylene, a small amount of ethylene oxide, and all the ethane in the ethylene raw material. The ethylene oxide in the main absorber and purge absorber bottoms is removed by desorption, refined, and sent to storage.

Although the oxygen process is similar to the air oxidation process, there is usually no purge reactor or absorber. Also, because the conversion of ethylene per pass is lower, the recycle is larger. Product is recovered by absorption as in the air oxidation process. A carbon dioxide absorber, used on a portion of the recycle stream, controls the build-up of carbon dioxide. Other inert gases are removed by a small absorber vent gas purge. In a variation of the process, methane is added to the recycle gas to act as an inert in the reactor and yield a high calorie vent gas which burns easily in a boiler.

TABLE 10 - POLLUTANT PRODUCTION IN ETHYLENE OXIDE MANUFACTURE BY AIR OXIDATION

	KILOGRAM PER TON OF ETHYLENE OXIDE PRODUCED-PURGE ABSORBER VENT [a]	
POLLUTANT	**WITH NO CONTROL**	**WITH COMBUSTION**
ETHANE	6	Nil
ETHYLENE	92	Nil
ETHYLENE OXIDE	1	Nil

a) Values are kilograms per metric ton.

6.7.2.9 Air pollutant emissions and their control

The only important source of emissions from ethylene oxide manufacture are the purge vents. Typical pollutants for the purge absorber vent of an ethylene oxide plant using air oxidation are shown in Table 11. For a typical 90 million kg per year plant the vent gas rate would be 9775 scmm. Typical main process vent pollutants for a plant using oxygen oxidation are shown in Table 11. For a 90 million kg per year plant the main process vent gas rate would be 3.4 scmm. Because the carbon dioxide vent of 164 scmm contains an insignificant amount of contaminants, it can be vented or sold as carbon dioxide.

The most efficient method to control emissions from an ethylene oxide plant is to feed the main process vent to a catalytic combuster and use the hot gases from this unit in expanders to drive the process compressors. More than 99% removal of combustible gases would be expected.

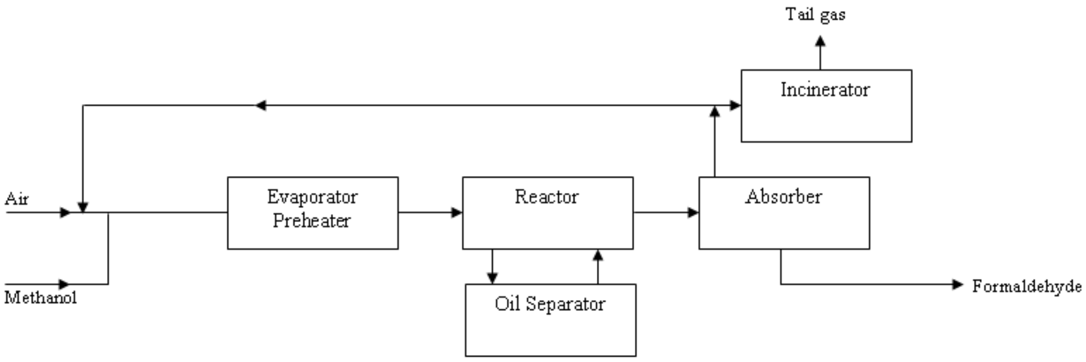
TABLE 11 - POLLUTANT PRODUCTION IN ETHYLENE OXIDE MANUFACTURE BY OXYGEN OXIDATION

	KILOGRAM PER TON OF ETHYLENE OXIDE PRODUCED-MAIN PROCESS VENT [a]	
POLLUTANT	**WITH NO CONTROL**	**WITH COMBUSTION**
ETHANE	3	Nil
ETHYLENE OXIDE	2.5	Nil

a) Values are kilograms per metric ton.

6.7.2.10 Formaldehyde

All formaldehyde was produced by the air oxidation of methanol. About 57% was used in combination with phenol, urea, or melamine to form resins and adhesives. The largest and fastest growing use of phenol-formaldehyde resins is as an adhesive for plywood. Urea formaldehyde resin is primarily used as an adhesive for particle board. Formaldehyde is also used to manufacture hexamethylenetetramine, pentaerythritol, and several miscellaneous resins.



FLOW DIAGRAM OF THE METHANOL PROCESS FOR THE MANUFACTURE OF FORMALDEHYDE, NOTING POTENTIAL SOURCES OF AIR POLLUTION

Fig. 6

6.7.2.11 Air pollutant emissions and their control

The major source of emissions from a formaldehyde plant is the exit-gas stream from the scrubber. The amount and composition of gaseous emissions and the type of control device that can be used depend upon the type of process.

For the mixed metal oxide catalyst process the pollutants in points per ton of 37% formaldehyde solution produced are shown in Table 12. The values given are for a plant operating at maximum recycle; for nonrecycle operation these values would be higher. For a typical plant producing 45 million kg per year of 37% formaldehyde, the exit-gas flow rate at maximum recycle would be 9.6 scmm. Water scrubber could be used to remove formaldehyde.

TABLE 12 - MAXIMUM ABSORBER VENT GAS RECYCLE POLLUTANTS IN FORMALDEHYDE PRODUCTION BY MIXED-OXIDE CATALYST PROCESS [a]

	WITH NO CONTROL	WITH INCINERATION	WITH WATER SCRUBBING
FORMALDEHYDE	0.8	Nil	0.1
METHANOL	2	Nil	0.2
CARBON MONOXIDE	17	Nil	17
DIMETHYLE ETHER	0.8	Nil	0.8

a) Values are for kiolograms per metric ton.

An incinerator is used to oxidize all contaminants from this stream but because of the very low heat content of the gas, considerable auxiliary fuel should be required.

For the silver catalyst process the pollutants in pounds per ton of 37% formaldehyde solution produced are shown in Table 13. For a typical plant producing 100 million 1b (45 million kg) per year of 37% formaldehyde, the gas flow rate would be 62 scmm with a heat content of about 552,000 cal/scm. The composition of the vent gas depends again on design and operating conditions of the absorber, but the absorption is easier because of the lower gas volume. Incineration can be used to oxidize all the contaminants in this stream.

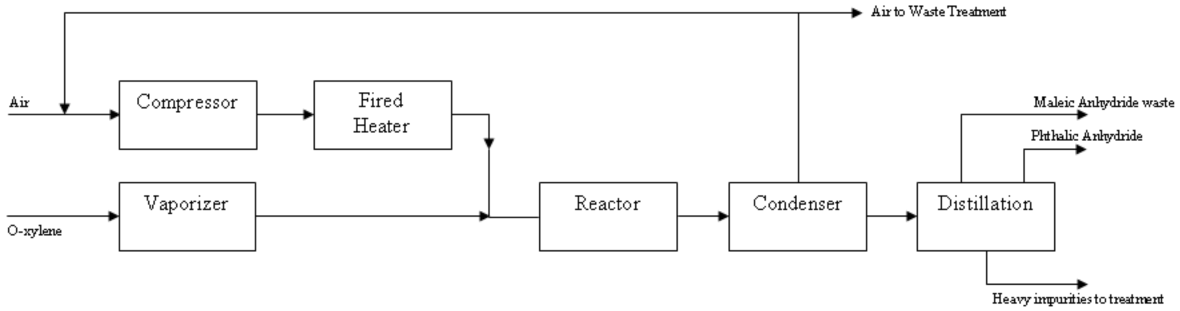
TABLE 13 - POLLUTANT PRODUCTION IN FORMALDEHYDE MANUFACTURE BY SILVER CATALYST PROCESS

	KILOGRAM PER TON 37% FORMALDEHYDE SOLUTION PRODUCED [a]	
POLLUTANT	WITH NO CONTROL	WITH COMBUSTION
FORMALDEHYDE	0.6	Nil
METHANOL	2.5	Nil
CARBON MONO-OXIDE	5.2	Nil
HYDROGEN	10.0	Nil

a) Values are kilograms per metric ton.

6.7.2.12 Phthalic anhydride

All phtalic anhydride is produced by the vapor phase air oxidation of either o-xylene or naphthalene. About 56% goes into the production of plasticizers for vinyl resins, and phthalic-based alkyd resins, used primarily for exterior surface coatings, account for about 22% of the material produced. About 17% is used in the manufacture of polyester resins, most of which are glass reinforced.



FLOW DIAGRAM OF THE OXIDATION O-XYLENE OR NAPHTHALENE FOR THE MANUFACTURE OF PHTALIC ANHYDRIDE, NOTING POTENTIAL SOURCES OF AIR POLLUTION

Fig. 7

The major source of emissions from phthalic anhydride manufacture is the off-gas from the switch condensers. For a typical (58 million kg per year) plant this stream has a flow rate of 3680 scmm). The composition of this stream is shown in Table 15 for plants using oxylene feedstock. The organic acids and anhydrides are malodorous lachrymators.

The most common type of emission control is water scrubbing. A typical combination for this application is a venturi scrubber followed by a cyclone separator and a packed countercurrent scrubber. The absorption efficiencies of the various scrubbers will vary considerably, but typical emission are given in Table 14. The scrubbing liquid must be incinerated in a small natural gas incinerator.

TABLE 14 - POLLUTANT PRODUCTION IN PHTHALIC ANHYDRIDE MANUFACTURE

	KILOGRAM PER TON PHTHALIC ANHYDRIDE PRODUCED[a]		
POLLUTANT	**WITH NO CONTROL**	**WITH INCINERATION**	**WITH WATER SCRUBBING**
ORGANIC ACIDS AND ANHYDRIDES	65	2.5	3
SULFUR DIOXIDE	5	5	5
CARBON MONOXIDE	140	0.1	140
PARTICULATE MATTER	Trace	-	Trace

a) Values are kilograms per metric ton.

6.7.2.13 Emission reduction during air pollution episodes

Atmospheric emissions from the petrochemical processes described in this section can be reduced significantly or stopped completely within a period of 1-3 hours. Petrochemical plants usually have several independent trains of processing equipment, and these trains may be shutdown as required to reduce emissions. Most operators also have the option of reducing production by leaving all trains on line and reducing the throughout per train. In either case the emissions from the process would be approximately proportional to operating level.

6.7.3 Fertilizer industries

Pollutant Consider	Process of Operation	Control System
dust	Phosphate fertilizers: crushing, grinding,and calcining	Exhaust system, scrubber, cyclone, baghouse
PH_3, P_2O_5, PO_4 mist	Hydrolysis of P_2O_5	Scrubbers, flare
HF, SiF_4	Acidulation and curing	Scrubbers
Particulates	Granulation	Exhaust system, scrubber,
NH3, NH_4Cl, HF, SiF_4	Ammoniation precipitator, baghouse, high-energy scrubber	Cyclone, electrostatic
NO_2 gases	Nitric acid acidulation	Scrubber, addition of urea
Particulates	Superphosphate storage and shipping	Exhaust system, cyclone, or baghouse
NH_3 , NO_2	Ammonium nitrate reactor	Scrubber
	Prilling tower	Proper operation control, scrubbers
NH_4, NO_3		

6.7.4 Crude oil terminals:

Several types of crude terminals are encountered throughout the industry based upon the sources and final destinations of the crude oil. The types of terminals to be considered in the following discussion are: inland pipeline terminals, marine shipping terminals, onshore marine receiving terminals, offshore marine receiving terminals, barge shipping terminals and barge receiving terminals.

A large amount of storage capacity is required at crude oil terminals, not only to enable the crude to be brought into the terminal from numerous producing regions (which may include several different quality crudes), but also to provide the tankage for segregation, batching, blending and inventorying necessary for continuous pipeline operations before the crude oil can be moved to refineries. Similar operations are necessary for marine terminals both for shipping and receiving of crude oil.

The sources of pollutants are based on the type of operation (receiving or shipping) and the type of transportation used (pipeline, tanker, or barge).

6.7.4.1 Air pollution control

The most significant of the air pollutants emitted by a terminal operation are hydrocarbon, which occur at all types of crude facilities. Other air pollutants include odors, SO_x, NO_x,, CO, and particulates are also concerned.

6.7.4.2 Hydrocarbons

Emission sources include storage tanks (normally onshore), transportation vessel tanks, tanker refueling, tank cleaning (both storage and vessels), tank degassing (preparation for inspection and maintenance), ballasting and fugitive emissions. In the case of onshore or permanent facilities, the mechanisms for limiting hydrocarbon emissions or collecting the vapors for incineration are similar to those discussed for refineries. The emissions from operations such as tanker refueling and tank degassing may incorporate vapor recovery or vapor collection/disposal (flaring) systems depending on whether an on-shore or off -shore facility is involved . Several operational control techniques have been considered as alternatives to the use of vapor control systems. These approaches include segregated ballasting, tank cleaning, slow loading, short loading, and the routing of vapors into tanks that are being emptied. The hydrocarbon emissions from ballasting on the other hand are normally uncontrolled. Hydrocarbon vapors can also be created by crude oil washing of cargo tanks during unloading.

6.7.4.2 (a) Emissions from tankers ballasted tanks

The emission of hydrocarbon gas from ballasted tanks can be avoided in one of three ways or any combination thereof;

By the use of permanent ballast tanks of sufficient capacity to provide the minimum departure drought (International Marine Organization standards should be used). For more information please refer to environmental management practices in oil refineries and terminals United Nation environment programme 1987.

6.7.4.3 Sulphur oxides (SO_x)

Emissions result from the flaring of H_2S containing gases, space heating with fuel oil, fuel combustion and tankers. The flaring emissions are uncontrolled while the fuel combustion emissions may be "controlled" by using the low-sulphur fuel oil.

6.7.4.4 Nitrogen oxides (NO_x)

Sources include space heating, the flare and tankers. Emission controls are normally not employed due to the small quantities emitted.

6.7.4.5 Particulates

Emissions at the terminal should be limited to fugitive emissions such as dust which can be controlled by methods such as paving or vegetation cover.

6.7.4.6 Odors

Odors from a crude terminal are usually caused by H_2S, mercaptans and hydrocarbon emissions. The most effective means of controlling odorcausing emissions, especially those containing H_2S, is vapor collection and incineration.

6.8 Environment Related Guarantee

Due consideration must also be given to air pollution, noise control, waste water control and other environment related control measures which are regulated by laws, regulations, national standards, etc. (IPS-E-PR-250 Sec. 6.4)

6.9 Threshold Limit Values

Introduction to the Chemical Substances

Threshold Limit Values (TLVs) refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects.

These limits are intended for use in the practice of industrial hygiene as guidelines or recommendations in the control of potential health hazards and for no other use, e.g., in the evaluation or control of community air pollution nuisances; in estimating the toxic potential of continuous, uninterrupted exposures or other extended work periods; as proof or disproof of an existing disease or physical condition.

The third edition of Iranian Health Ministry booklet, related to TLVs limited (1391, pp: 22-75) shall be considered as the expose level allowable in workplace.

Definitions

Three categories of Threshold Limit Values (TLVs) are specified herein, as follows:

a) Threshold Limit Value-Time-Weighted Average (TLV-TWA)-the time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

b) Threshold Limit Value-Short-Term Exposure Limit (TLV-STEL)- the concentration to which workers can be exposed continuously for a short period of time without suffering from:

1) Irritation,

2) Chronic or irreversible tissue damage, or,

3) Narcosis of sufficient degree to increase the likelihood of accidental injury, impair self-rescue or materially reduce work efficiency, and provided that the daily TLV-TWA is not exceeded. It is not a separate independent exposure limit; rather, it supplements the timeweighted average (TWA) limit where there are recognized acute effects from a substance whose toxic effects are primarily of a chronic nature. STELs are recommended only where toxic effects have been reported from high short-term exposures in either humans or animals.

A STEL is defined as a 15-minute TWA exposure which should not be exceeded at any time during a workday even if the 8-hour TWA is within the TLV-TWA. Exposures above the TLV-TWA up to the STEL should not be longer than 15 minutes and should not occur more than four times per day. There should be at least 60 minutes between successive exposures in this range. An averaging period other than 15 minutes may be recommended when this is warranted by observed biological effects.

c) Threshold Limit Value-Ceiling(TLV-C)the concentration that should not be exceeded during any part of the working exposure.

In conventional industrial hyginic practice if instantaneous monitoring is not feasible, then the TLV-C can be assessed by sampling over a 15-minute period except for those substances that may cause immediate irritation when exposures are short.

For some substances, e.g., irritant gases, only one category, the TLV-Ceiling, may be relevant. For other substances, one or two categories may be relevant, depending upon their physiologic action. It is important to observe that if any one of these types of TLVs is exceeded, a potential hazard from that substance is presumed to exist.

The Chemical Substances TLV Committee holds to the opinion that TLVs based on physical irritation should be considered no less binding than those based on physical impairment. There is increasing evidence that physical irritation may initiate, promote, or accelerate physical impairment through interaction with other chemical or biologic agents.

Time-Weighted Average (TWA) vs Ceiling (C) Limits. TWAs permit excursions above the TLV provided they are compensated by equivalent excursions below the TLV-TWA during the workday. In some instances, it may be permissible to calculate the average concentration for a workweek rather than for a workday. The relationship between the TLV and permissible excursion is a rule of thumb and in certain cases may not apply. The amount by which the TLVs may be exceeded for short periods without injury to health depends upon a number of factors such as the nature of the contaminant, whether very high concentrations-even for short periods-produce acute poisoning, whether the effects are cumulative, the frequency with which high concentrations occur, and the duration of such periods. All factors must be taken into consideration in arriving at a decision as to whether a hazardous condition exists.

Excursion Limits

For the vast majority of substances with a TLV- TWA, there is not enough toxicological data available to warrant a STEL. Nevertheless, excursions above the TLV-TWA should be controlled even where the 8-hour TLV-TWA is within recommended limits. Earlier editions of the TLV list included such limits whose values depended on the TLV - TWAs of the substance in question.

While no rigorous rationale was provided for these particular values, the basic concept was intuitive: in a well-controlled process exposure, excursions should be held within some reasonable limits. Unfortunately, neither toxicolohy nor collective industrial hygiene experience provide a solid basis for quantifying what those limits should be. The approach here is that the maximum recommended excursion should be related to variability generally observed in actual industrial processes. In reviewing large numbers of industrial hygiene surveys conducted by the National institute for Occupational Safety and Health, Leidel, Busch, and Crouse(1) found that short-term exposure measurements were generally lognormally distributed with geometric standard deviations mostly in the range of 1.5 to 2.0.

While a complete discussion of the theory and properties of the lognormal distribution is beyond the scope of this section, a brief description of some important terms is preseneted. The measure of central tendency in a lognormal description is the antilog of the mean logarithm of the sample values. The distribution is skewed, and the geometric mean is always smaller than the arithmetic mean by an amount which depends on the geometric standard deviation. In the lognormal distribution. The geometric standard deviation (sd_g) is the antilog of the standard deviation of the sample value logarithms and 68.26% of all values lie between m_g/sd_g and $m_g \times sd_g$.

If the short-term exposure values in a given situation have a geometric standard deviation of 2.0,5% of all values will exceed 3.13 times the geometric mean. If a process displays a variability greater than this, it is not under good control and efforts should be made to restore control. This concept is the basis for the following excursion limit recommendation which apply to those TLV- TWAs that do not have STELS:

Excursions in worker exposure levels may exceed 3 times the TLV - TWA for no more than a total of 30 minutes during a workday, and under no circumstances should they exceed 5 times the TLV-TWA, provided that the TLV-TWA is not exceeded.

The approach is a considerable simplification of the idea of the lognormal concentration distribution but is considered more convenient to use by the practicing industrial hygienist. If exposure excursions are maintained within the recommended limits, the geometric standard deviation of the concentration measurements will be near 2.0 and the goal of the recommendations will be accomplished.

When the toxicological data for a specific substance are available to establish a STEL, this value takes precedence over the excursion limit regardless of whether it is more or less stringent.

“Skin” Notation

The designation “Skin” in the “Notations” column refers to the potential significant contribution to the overall exposure by the cutaneous route, including mucous membranes and the eyes, either by contact with vapors or, of probable greater significance, by direct skin contact with the substance. Vehicles present in solutions or mixtures can also significantly enhance potential skin absorption. It should be noted that while some materiais are capabel of causing irritation, dermatitis, and sensitization in workers, these properties are not considered relevant when assigning a skin notation. It should be noted, however, that the development of a dermatological condition can significantly affect the potential for dermal absorption.

While relatively limited quantitative data carrently exist with regard to skin absorption of gases, vapors, and liquids by workers, the chemical Substances TLV Committee recommends that the integration of data from acute dermal studies and repeated dose dermal studies in animals and /or humans, along with the ability of the chemical to be absorbed, be used in deciding on the appropriateness of the skin notation. In general, available data which suggest that the potential for absorption via the hands/forearms during the workday could be significant, especially for chemicals with lower TLVs, could justify a skin notation. From acute animal toxicity data, materials having a relatively low dermal LD_{50} (1000 mg/kg of body weight or less) would be given a skin notation. Where repeated dermal application studies have shown significant systemic effects following treament, a skin notation would be considered. When chemicals penetrate the skin easily (higher octanol -water partition coefficients) and where extrapolations of systemic effects from other routes of exposure suggest dermal absorption may be important in the expressed toxicity, a skin notation would be considered.

Substances having a skin notation and a low TLV may present special problems for operations involving high airborne concentrations of the material, particularly under conditions where significant areas of the skin are exposed for a long period of time. Under these conditions, special precautions to significantly reduce or preclude skin contact may be required.

Biological monitoring should be considered to determine the relative contribution of exposure via the dermal route to the total dose. The TLV/BEI Book contains a number of adopted Biological Exposure indices, which provide an additional tool when assessing the worker's total exposure to selected materials. For additional information, refer to "Dermal Absorption" in the "Introduction to the Biological Exposure indices," Documentation of Threshold Limit Values and Biological Exposure indices, and to Leung and Paustenbach.(2) Use of the skin designation is intended to alert the reader that air sampling alone is insufficient to accurately quantitate exposure and that measures to prevent significant cutaneous absorption may be required.

"Sensitizer" Notation

The designation "SEN" in the "Notations" column refers to the potential for an agent to produce sensitization, as confirmed by human or animal data. The SEN notation does not imply that sensitization is the critical effect on which the TLV is based, nor does it imply that this effect is the sole basis for that agent's TLV. If sensitization data exis, they are carefully considered when recommending the TLV for the agent. For those TLVs that are bases upon sensitization, they are meant to protect workers from induction of this effect and are not intended to protect those workers who have already become sensitized.

In the workplace, respiratory, dermal, or conjunctival exposures to sensitizing agents may occur. Similary, sensitizers may evoke respiratory, dermal, or conjunctival reactions. At this time, the notation does not distinguish between sensitization involving any or these organ systems. The absence of a SEN notation does not signify that the agent lacks the ability to produce sensitization but may reflect the paucity or inconclusiveness of scientific evidence.

Sensitization often occurs via an immunological mechanism and is not to be confused with other conditions or terminology such as hyperreactivity, susceptibility, or sensitivity. Initially, there may be little or no response to a sensitizing agent. However, after a person is sensitized, subsequent exposure may cause intense responses, even at low exposure concentrations (well below the TLV).These reactions may belife-threatening and may have an immediate or delyed onset. Workers who have become sensitized to a particular agent may also exhilbit cross- reactivity to other agents with similar chemical structures.

A reduction in exposure to the sensitizer and its structural analogs generally reduces the incidence of allergic reactions among sensitized individuals. For some sensitized individuals, however, complete avoidance in occupational and nonoccupational settings provides the only means to prevent the immune responses to recognized sensitizing agents and their structural analogs.

Agents having a SEN notation and a low TLV present special problems in the workplace. Respiratory, dermal, and conjunctival exposures should be significantly reduced or eliminated using personal protective eqipment and process control measures. Education and training (e.g., review of potential health effects, safe handling procedures, emergency information) are also necessary for those who work with known sensitizing agents.

For additional information regarding the sensitization potential of a particular agent, refer to the Documentation for the specific agent.

Although the TWA concentration provides the most satisfactory, practical way of monitoring airborne agents for compliance with the TLVs, there are certain substances for which it is inappropriate. In the latter group are substances which are predominantly fast acting and whose TLV is more appropriately based on this particular response. Substances with this type of response are best controlled by a ceiling limit that should not be exceeded.

It is implicit in these definitions that the manner of sampling to determine noncompliance with the limits for each group must differ; a single, brief sample, that is applicable to a ceiling limit, is not appropriate to the TWA; here, a sufficient number of samples are needed to permit a TWA concentration throughout a complete cycle of operations or throughout the workshift.

Whereas the ceiling limit places a definite boundary that concentrations should not be permitted to exceed, the TWA requires an explicit limit to the excursions that are permissible above the listed TLVs. It should be noted that the same factors are used by the Chemical Substances TLV Committee in determining the magnitude of the value of the STELs, or whether to include or exclude a substance for a ceiling listing.

Mixtures

Special consideration should be given also to the application of the TLVs in assessing the health hazards that may be associated with exposure to mixtures of two or more substances. A brief discussion of basic considerations involved in developing TLVs for mixtures and methods for their development, amplified by specific examples, are given in Appendix C.

Particulate Matter

For solid and liquid particulate matter, TLVs are expressed in terms of total particulate, except where the terms inhalable, thoracic, of respirable particulate are used. Refer to Endnotes. See Appendix D, Particle Size-Selective Sampling Criteria for Airborn Particulate Matter, for the definitions of inhalable, thoracic, and respirable particulate matter. The term total particulate refers to airborne material sampled with the 37 - mm closed face cassette traditionally used in the United States for aerosol sampling.

The intent of the Chemical Substances TLV Committee is to replace all total particulate TLVs with inhalable, thoracic, or respirable particulate matter TLVs. All proposed changes will be included on the Notice of Intended Changes and comments invited. Publication of the results of side-by-side sampling studies using older total and newer inhalable, thoracic, or respirable sampling techniques is encouraged to aid in the appropriate replacement of current total particulate TLVs.

Particulates (Insoluble) Not Otherwise Specified (PNOS)

There are many substances with TLVs and many more without TLVs for which there is no evidence of specific toxic effects. Those that are particulates have frequently been called "nuisance dusts" Although these materials may not cause fibosis or systemic effects, they are not biologically inert. At high concentrations, otherwise nontoxic particulates have been associated with the occasionally fatal condition known as alveolar proteinosis. At lower concentrations, they can inhibit the clearance of toxic particulates from the lung by decreasing the mobility of the alveolar macrophages. Accordingly, the Chemical Substances TLV Committee recommends the use of the term "Particulates (Insoluble) Not Otherwise Specified (PNOS)" to emphasize that all materials are potentially toxic and to avoid the implication that these materials are harmless at all exposure concentrations .Particulates identified under the PNOS heading are those containing no asbestos and <1% crystalline silica. To recognize the adverse effects of expo-sure to otherwise nontoxic particulate matter. A TLV-TWA of 10 mg/m^3 for inhalable particulate and a TLV_TWA of 3 mg/m^3 for respirable particulate have been established and are included in the adopted TLV section. Refer to the PNOS Documentation for a complete discussion of this subject.

Simple Asphyxiants-"Inert" Gases of Vapors

A number of gases and vapors, when present in high concentrations in air, act primarily as simple asphyxiants without other significant physiologic effects. A TLV may not be recommended for each simple asphyxiant because the limiting factor is the available oxygen. The minimal oxygen content should be 18% by volume under normal atmospheric pressure (equivalent to a partial pressure, pO_2 of 135 torr). Atmospheres deficient in O_2 do not provide adequate warning and most simple asphyxiants are odorlless. Several simple asphyxiants present an explosion hazard. Account should be taken of this factor in limiting the concentration of the asphyxiant.

Biological Exposure Indices (BEIs)

The note "BEI" is lidted in the "Notations" column when a BEI is also recommended for the substance listed. Biological monitoring should be instituted for such substances to evaluate the total exposure form all sources, including der-mal, ingestion, or nonocccupational. See the BEI section in this Book and the Documentation of the TLVs and BEIs for the substance.

Physical Factors

It is recognized that such physical tactors as heat, ultraviolet and ionizing radiation, humidity, abnormal pressure (altitude), and the like amy place added stress on the body so that the effects from exposure at a TLV may be altered. Most of these stresses act adversely to increase the toxic response of a substance. Although most TLVs have built-in safety factors to guard against adverse effects to moderate deviations from normal environments, the safety factors of most substances are not of such a magnitude as to take care of gross deviations. For example, continuous, heavy work at temperatures above 25°C WBGT, or overtime extending the workweek more than 25% might be considered gross deviations. In such instances, judgment must be exercised in the proper adjustments of the TLVs.

Unlisted Substances

The list of TLVs is by no means a complete list of all hazardous substances of of all hazardous substances used in industry. For a large number of materials of recognized toxicity, little or no data are available that could be used to establish a TLV. Substances that do not appear on the TLV list should not be considered to be harmless or nontoxic. When unlisted substances are introduced into workplace, the medical and scientific literature should be reviewed to identify potentially dangerous toxic effects. It may also be advisable to conduct preliminary toxicity studies. In any case, it is necessary to remain alert to adverse health effects in workers which may be associated with the use of new materials. The TLV Committee strongly encourages industrial hygienists and other occupational health professionals to bring to the Committee's attention any information which would suggest that a TLV should be established. Such information should include exposure concentrations and correlated health effects data (dose-esponse) that would support a recommended TLV.

Unusual Work Schedules

Application of TLVs to workers on work schedules markedly different from the conventional 8-hour day, 40- hour week requires particular judgment in order to provide, for such workers, protection equal to that provided to workers on conventional work shifts.

As tentative guidance, field hygienists are referred to the "Bried and Scala model" which is described and explained at length in Patty.(3)

The Brief and Scala model reduces the TLV proportionately for both increased exposure time and reduced recovery (nonexposure) time. The model is generally intended to apply to work schedules longer than 8 hours/day or 40 hours / week. The model should not be used justify very high exposures as "allowable" where the exposure periods are short (e.g., exposure to 8 times the TLV - TWA for one hour and zero exposure during the remainder of the shift). In this respect. The general limitations on TLV excursions and STELs should be applied to avoid inappropriate use of the model with very short expo-sure periods or shifts.

Since adjusted TLVs do not have the benefit of historical use and long - time observation, medical supervision during initial use of adjusted TLVs is advised. In addition, the hygienist should avoid unnecessary exposure of workers even if a model shows such exposures to be "allowable" and should not use models to justify higher-than-necessary exposures.

The Brief and Scala model is easier to use than some of the more complex models based on pharmacokinetic actions. However, hygienists thoroughly familiar with such models may find them more appropriate in specific instances. Use of such models usually requires knowledge of the biological half-life of each substance, and some models require additional data.

Short workweeks can allow workers to have tow fulltime jobs, perhaps with similar exposures, and may result in overexposure even if neither job by itself entails overexposure. Hygienists should be alert to such situations.

Conversion of TLVs in ppm to mg/m^3

TLVs for gases and vapors are usually established in terms of parts per million of substances in air by volume (ppm). For convenience to the user, these TLVs are alse listed with molecular weights. where 24.45 = molar volume of air in liters at normal temperature and pressure (NTP) conditions (25°C and 760 torr) , the conversion equation for mg/ m^3 is.

$$TLV\ in\ mg/m^3 = \frac{(TLV)(gram\ molecular\ weight\ of\ substance)}{24.45}$$

Conversely, the equation for converting TLVs in mg/m^3 to ppm is:

$$TLV\ in\ ppm = \frac{\left(TLV\ in \frac{mg}{m^3}\right)(24.45)}{(Gram\ molecular\ weight\ of\ substance)}$$

The above equation may be used to convert TLVs to any degree of precision desired. When converting TLVs to mg/m^3 for other temperatures and pressures, the reference TLVs should be used as a starting point. When converting values expressed as an element (e.g., as Fe, as Ni), the molecular value of the element should be used, not that of the entire compound.

In making conversions for substances with variable molecular weights, appropriate molecular weights should be estimated or assumed (see the TLV Documentation).

References:

1. Leidel, N.A: Busch, K.A.: Cuouse, W.E.: Exposure Measurement Action Level and Occupational Environmental Variability. DHEW (NIOSH) Pub. No. 76 -131; NTIS Pub. No. PB-267-509. National Technical Information Service, Springfield, VA (December 1975).

2. Leung, H.: Paustenbach, D.J.: Techniques for Estimating the Percutaneous Absorption of Chemicals Due to Occupational and Environmental Exposure. Appl. Occup. Environ. Hyg. 9(3): 187-197 (March 1994).

3. Paustenbach, D.J.: Occupational Exposure Limits, Pharmacokinetics, and Unusual Work Schedules. In: Patty's Industrial Hygiene and Toxicology , 3rd ed., Vol . 3A, the Work Environment , Chap. 7, pp. 222 - 348. R.I. Harris, L.J. Cralley and L.V. Cralley, Eds John Wiley and Sons, Inc., New York (1994).

Respirable and Total Dust

For solid substances and liquified mists, TLVs are expressed in terms of total dust, except where the term "respirable dust" is used. See Appendix D, Particle Size-Selective Sampling Criterial for Airborne Particulate Matter, for the definition of respirable dust.

Particulates Not Otherwise Classified (PNOC)

In contrast to fibrogenic dusts which cause scar tissue to be formed in lungs when inhaled in excessive amounts, socalled "nuisance" dusts have a long history of little adverse effect on lungs and do not produce significant organic disease or toxic effect when exposures are kept under reasonable control. Such dusts have also been called (biologically) " inert" dusts, but the latter term is inappropriate to the extent that there is no dust which does not evoke some cellular response in the lung when inhaled in sufficient amount.

However, the lung-tissue reaction caused by inhalation of PNOCs has the following characteristics:

1) The architecture of the air spaces remains intact;

2) Collagen (scar tissue) is not formed to a significant extent; and

3) The tissue reaction is potentially reversible.

Excessive concentrations of PNOCs in the workroom air may seriously reduce visibility; may cause unpleasant deposits in the eyes, ears, and nasal passages (e.g., Portland cement dust); or cause injury to the skin or mucous membranes by chemical or mechanical action or by the rigorous skin cleansing procedures necessary for their removal.

A TLV-TWA of 10 mg/m^3 of total dust containing no asbestos and < 1% crystalline silica is recommended for substances in these categories and for which no specific TLVs have been assigned.

Conversion of TLVs in ppm to mg/m^3

TLVs for gases or vapors are usually established in terms of parts per million of substance in air by volume (ppm). For convenience to the user, these TLVs are also listed here in terms of milligrams of substance per cubic meter of air (mg/m^3). The conversion is based on 760 torrbarometric pressure and 25°C, giving a conversion equation of:

$$\textbf{TLV in mg/m}^3 = \frac{(\text{TLV in ppm})\,(\text{gram molecular weight of the substant})}{24.45}$$

Resulting values are rounded to two significant figures below 100 and to three significant figures above 100. This is not done to give any converted value a greater precision than that of the original TLV, but to avoid increasing or decreasing the TLV significantly merely by the conversion of units.

In the Appendix G you will find the exposure levels that are allowed in your work place you must not exceed these levels.

APPENDICES

APPENDIX A

CARCINOGENICITY

ACGIH has been aware of the increasing public concern over chemicals or industrial processes that cause or contribute to increased ridk of cancer in workers. More sophisticated methods of bioassay, as well as the use of sophisticated mathematical models that extrapolate the levels of risk among workers, have led to differing interpretations as to which chemicals or processes should be categorized as human carcinogens and what the maximum exposure levels should be. The goal of the Chemical Substances TLV Committee has been to synthesize the available information in a manner that will be useful to practicing industrial hygienists, without overburdening them with needliss details. The categories for carcinogenicity are:

A1-Confirmed Human Carcinogen: The agent is carcinogenic to humans based on the weight of evidence from epidemiologic studies.

A2-Suspected Human Carcinogen: Human data are accepted as adequate in quality but are conflicting or insufficient to classify the agent as a confirmed human carcinogen; OR, the agent is carcinogenic in experimental animals at dose (s), by route (s) of exposure, at site (s), of histologic types (s), or by mechanism (s) considered relevant to worker exposure. The A2 is used primarily when there is limited evidence of carcinogenicity in humanse and sufficient evidence of carcinogenicity in experimental animals with relevance to humans.

A3-Confirmed Animal Carcinogen with Unknown Relevance to Humans: The agent is carcinogenic in experimental animals at a relatively high dose, by route (s) of administration, at site (s), of histologic types (s), or by mechanism (s) that may not be relevant to worker exposure. Available epidemiologic studies do not confirm an increased risk of cancer in exposed humans. Available evidence does not suggest that the agent is likely to cause cancer in humans except under uncommon or unlikely routes or levels of exposure.

A4-Not Classifiable as a Human Carcinogen: Agents which cause concern that they could be carcinogenic for humans but which cannot be assessed conclusively because of a lack of data. In vitro or animal studies do not provide indications of carcinogenicity which are sufficient to classify the agent into one of the other categories.

A5-Not Suspected as a Human Carcinogen: The agent is not sus-pected to be a human carcinogen on the bisis of properly conducted epidmiologic studies in humans. These studies have sufficiently long follow-up, reliable exposure histories, sufficiently high dose, and adequate statistical power to con-clude that exposure to the agent dose not convey a significant risk of cancer to humans; OR, the evidence suggesting a lack of carcinogenicity in experimental animals is supported by mechanistic data.

Substances for which no human or experimental animal carcinogenic data have been reported are assigned no carcinogenicity designation.

Exposures to carcinogens must be kept to a minimum. Workers exposed to A1 carcinogens without a TLV should be properly equipped to eliminate to the fullest extent possible all exposure to the carcinogen. For A1 carcinogens with a TLV and for A2 and A3 carcinogens, worker exposure by all routes should be carefully controlled to levels as low as possible below the TLV. Refer to the "Guidelines for the Classification of Occpational Carcinogens" in the Introduction to the Documentation of the Threshold Limit Values and Biological Exposure Indices for a complete description and derivation of these designations.

APPENDIX B

SUBSTANCES OF VARIABLE COMPOSITION

B1. Polytetrafluoroethylene * decomposition products

Thermal decomposition of the fluorocarbon chain in air leade to the formation of oxidized products containing carbon, fluorine, and oxygen. Because these products decompose in part by hydrolysis in alkaline solution, they can be quantitatively determined in air as fluoride to provide and index of exposure. No TLVs are recommended at this time, but air concentration should be controlled as low as possible.

(* Some trade names include: Algoflon, Fluon, Teflon, Tetran)

B2. Welding Fumes – Total Particulat (not otherwise specified): TLV-TWA, 5 mg/ m^3

Welding fumes cannot be classified simply. The composition and quantity of both are dependent on the alloy being welded and the process and electrodes used. Reliable analysis of fumes cannot be made without considering the nature of the welding process and system being examined; reactive metals and alloys such as aluminum and titanium are arc-welded in a protective, inert atmosphere such as argon. These arcs create relatively little fume, but they do create an intense rediation which can produce ozone. Similar processes are used to arc-weld steels, also creating a relatively low level of fumes. Ferrous alloys also are arc-welded in oxidizing environments that generate considerable fume and can produce carbon monoxide instead of ozone. Such fumes generally are composed of discrete particles of amorphous slags containing iron, manganese, silicon, and other metallic constituents depending on the alloy system involved. Chromium and nickel compounde are found in fumes when stainless steels are arc-welded. Some coated and flux-cored electrodes are formulated with fluorides and the fumes associated with them can contain significantly more fluorides than oxides. Because of the above factors, arc-welding fumes frequently must be tested for individual constituents that are likely to be present to determine whether specific TLVs are exceeded. Conclusions based on total concentration are generally adequate if no toxic elements are present in welding rod, metal, or metal coating and conditions are not conducive to the formation of toxic gases.

APPENDIX C

THRESHOLD LIMIT VALUES MIXTURES

When two or more hazardous substances which act upon the same organ system are present, their combined effect, rather than that of either individually, should be given primary consideration. In the absence of information to the contrary, the effects of the different hazards should be considered as additive. That is, if the sum of

$$\frac{C_n}{T_n} + \ldots \frac{C_2}{T_2} + \frac{C_1}{T_1}$$

exceeds unity, then the threshold limit of the mixture should be considered as being exceeded. C_1 indicates the observed atmospheric concentration and T_1 the corresponding threshold limit (see Example A.1 and B.1)

Exceptions to the above rule may be made when there is a good reason to believe that the chief effects of the different harmful substances are not in fact additive, but are independent as when purely local effects on different organs of the body are produced by the various components of the mixture. In such cases, the threshold limit ordinarily is exceeded only when at least one member of the series (C_1 /T_1+ or C_2 /T_2, etc.) itself has a value exceeding unity (see Example B.1).

Synergistic action or potentiation may occur with some combinations of atmospheric contaminants. Such cases at present must be determined individually. Potentiation or synergistic agents are not necessarily harmful by themselves. Potentiating effects of exposure to such agents by routes other than that of inhalation are also possible, e.g., imbibed alcohol and inhaled narcotic (trichloroethylene). Potentiation is characteristically exhibited at high concentrations, less probably at low.

When a given operation or process characteristically emits a number of harmful dusts, fumes, vapors or gases, it will frequently be only feasible to attempt to evaluate the hazard by measurement of a single substance. In such cases, the threshold limit used for this substance should be reduced by a suitable factor, the magnitude of which will depend on the number, toxicity, and relative quantity of the other contaminants ordinarily present.

Examples of processes that are typically associated with two or more harmful atmospheric contaminants are welding, automobile repair, blasting, lacquering, certain foundry operations, diesel exhausts, etc.

Examples of TLVs for Mixtures

A. Additive effects

The following formulae apply only when the components in a mixture have similar toxicologic effects; they should not be used for mixtures with widely differing reactivities, e.g., hydrogen cyanide and sulfur dioxide. In such case, the formula for Independent Effects should be used.

1. General case, where air is analyzed for each component, the TLV of mixture=

$$\text{TLV of mixture} = \frac{C_n}{T_n} + \ldots + \frac{C_2}{T_2} + \frac{C_1}{T_1} \leq 1$$

Note: It is essential that the atmosphere be analyzed both qualitatively and quantitatively for each component present in order to evaluate compliance or noncompliance with this calculated TLV.

Example A.1:

Air contains 400 ppm of acetone (TLV, 500 ppm), 150 ppm of sec - butyl acetate (TLV, 200 ppm) and 100 ppm of methyl ethyl keone (TLV, 200 ppm).

Atmospheric concentration of mixture=400+150+100=650 ppm of mixture.

$$\frac{100}{200} + \frac{150}{200} + \frac{400}{500} = 0.8 + 0.75 + 0.5 = 2.05$$

Threshold Limit is exceeded.

2. Special case when the source of contaminant is a liquid mixture and the atmospheric composition is assumed to be similar to that of the original material, e. g, on time-weighted average exposure basis, all of the liquid (solvent) mixture eventually evaporates. When the percent composition (by weight) of the liquid mixture is known, the TLVs of the constituents must be listed in mg/m^3

$$TLV\ in\ mixture = \frac{1}{\frac{fn}{TLVn} + \cdots + \frac{fc}{TLVc} + \frac{fb}{TLVb} + \frac{fa}{TLVa}}$$

Note: In order to evaluate compliance with this TLV, field sampling instruments should be calibrated,in the Laboratory, for response to this specific quatitative and qualitative air-vapor mixture, also to fractional concentrations of this mixture (e.g., 1/2/ the TLV; 1/10 the TLV; 2 ×the TLV; 10 ×the TLV; etc.)

Example A.2:

Liquid contains (by weight):

50% heptane: TLV=400 ppm or 1640 mg/m^3

1 mg/m^3 =0.24 ppm

30% methyl chloroform: TLV=350 ppm or 1910 mg/m^3

1 mg/m^3 =0.18ppm

20% perchloroethylene: TLV = 25 ppm or 170 mg/m^3

1 mg/m^3 =0.15 ppm

$$TLV\ in\ mixture = \frac{1}{\frac{0.2}{170} + \frac{0.3}{1910} + \frac{0.5}{1640}} = \frac{1}{0.00164} = 610\ mg/m^3$$

Of this mixture

50% or (610)(0.5)= 305 mg/m^3 is heptane

30% or (610)(0.3)=183 mg/m^3 is methyl chloroform

20% or (610)(0.2)=122 mg/m^3 is perchloroethylene

These values can be converted to ppm as follows:

Heptane: 305 mg/m^3 ×0.24= 73 ppm

Methyl chloroform: 183 mg/m^3 × 0.18 = 33 ppm

Perchloroethylene: 122 mg/m^3 × 0.15 = 18 ppm

TLV of mixture = 73+33+18= 124 ppm, or 610 mg/m^3

B. Independent effects

$$TLV\ for\ mixture = \frac{C_3}{t_3} \leq 1 \text{ یا } \frac{C_2}{t_2} \leq 1 \text{ یا } \frac{C_1}{t_1} \leq 1\ ; etc$$

$$X = \frac{Ln\ (dae/T)}{Ln\ (\sum)}$$

Example B.1:

Air contains 0.05 mg/m^3 of lead (TLV, 0.05) and 0.7 mg/m^3 of sulfuric acid (TLV, 1).

$$\frac{0.05}{0.05} = 1\ ;\ \frac{0.7}{1} = 0.7$$

Threshold limit is not exceeded.

C. TLV for mixtures of mineral dusts

For mixtures of biologically active mineral dusts, the general formula for mixtures given in A.2 may be used.

Rpm (dae) = IPM (dae) [1-f(x)]

APPENDIX D

PARTICLE SIZE – SELECTIVE

Sampling Criteria for Airbome Particulate Matter

For chemical substances present in inhaled air as suspensions of solid particles or droplets, the potential hazard depends on particle size as well as mass concentration because of: 1) effects of particle size on the deposition site within the respiratory tract, and 2) the ten-dency for many occupational diseases to be associated with material deposited in particular regions of the respiratory tract.

ACGIH has recommended particlesize-selective TLVs for crys-talline silica for many years in recognition of the well-established asso-ciation between silicosis and respirable mass concentrations. The Chemical Substances TLV Committee is now re-examining other chemical substances encountered in particulate form in occupational environments with the objective of defining: 1) the size-fraction most closely associated for each substance with the health effect of con-cern, and 2) the mass concentration within that size fraction which should represent the TLV.

The Particle Size – Selective TLVs (PSS-TLVs) are expressed in three forms:

1. Inhalable Particulate Mass TLVs (IPM-TLVs) for those materials that are hazardous when deposited anywhere in the respiratory tract.

2. Thoracic Particulate Mass TLVs (TPM-TLVs) for those materials that are hazardous when deposited anywhere within the lung air-ways and the gas-exchange region.

3. Respirable Particulate Mass TLVs (RPM-TLVs) for those materials that are hazardous when deposited in the gas-exchange region.

The three particulate mass fractions described above are defined in quantitative terms in accordance with the following equations: (1-3)

A. IPM consists of those particles that are captured according to the following collection efficiency regardless of sampler orientation with respect to wind direction:

$0.5[1+\exp(-0.06\, d_{ae})])=\mathrm{IPM}(d_{ae}$

for $0 < d_{ae} \leq 100\ \mu$ m

where: IPM (d_{ae})= the collection efficiency

d_{ae} = aerodynamic diameter of particle in μ m

B. TPM consists of those particles that are captured according to the following collection efficiency:

$$\mathrm{TPM}(d_{ae}) = \mathrm{IPM}(d_{ae})\,[1-f(x)]$$

Where: f(x) = cumulative probability function of the standardized normal variable, x

$$\frac{In(d_{ae}/T)}{In(\Sigma)} \quad X=$$

In= natural logarithm

= 11.64 µ m Γ

= 1.5 $\sum$

C. RPM consists of those particles that are captured assording to the following collection efficiency:

Rpm (d $_{ae}$) = IPM (d $_{ae}$) [1.f(x)]

Where F (x)= same as above, but withΓ= 4.25 µ m and Σ= 1.5

The most significant difference from previous difinitions is the in-crease in the median cut point for a respirable particulate matter sam-pler from 3.5 µ m to 4.0 µ m; this is in accord with the International Organization for Standardization / European Standardization Committee (ISO/ CEN) protocol. (4.5) At this time, no change is recommended for the measurement of respirable particulates using a 10-mm nylon cyclone at a flow rate of 1.7 liters per minute. Two analyses of avail-able data indicate that the flow rate of 1.7 liters per minute allows the 10-mm nylon cyclone to approximate the particulate matter concentra-tion which would be measured by an ideal respirable particulate sam-pler as defined herein. (6.7)

Collection efficiencies representative of several sizes of particles in each of the respective mass fractions are shown in Tables 1, 2, and 3. Documentation for the respective algorithms repesentative of the three mass fractions is found in the literature. (2-4)

TABLE 1. Inhalable

Particle Aerodynamic Diameter (µ m)	Inhalable Particulate Mass (IPM) (%)
0	100
1	97
2	94
5	87
10	77
20	65
30	58
40	54.5
50	52.5
100	50

TABLE 2. Thoracic

Particle Aerodynamic Diameter (µ m)	Thoracic Particulate Mass (TPM)(%)
0	100
2	94
4	89
6	80.5
8	67
10	50
12	35
14	23
16	15
18	9.5
20	6
25	2

TABLE 3. Respirable

Particle Aerodynamic Diameter (µ m)	Respirable Particulate Mass (RPM) (%)
0	100
1	97
2	91
3	74
4	50
5	30
6	17
7	9
8	5
10	1

References:

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4. International Organization for Standardization (ISO): Air Quality-Particle Size Fraction Definitions for Health-Related Sampling.

Approved for publication as CD 7708. ISO, Geneva (1991)

5. European Standardization Committee (CEN): Size Fraction Definitions for Measurement of Airborne Particles in the workplace. Approved for publication as pr EN 481. CEN, Brussels (1992)

6. Bartley, D.L.: Letter to J.Doull, TLV Committee, July 9, 1991.

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APPENDIX E

ODOR CONTROL METHODS FOR REFINERY PURPOSES

1. ALKYLATION UNITS AND ASPHALT OXIDIZERS

Odor emissions are effectively prevented by afterburners or the collection and feeding the off-gases to process heaters.

2. BAROMETRIC CONDENSERS AND VACUUM TOWERS

Odor prevention has been achieved by venting all off-gases, including vacuum jet gases, to process heaters or where necesary, flares. If the off-gases contain high concentrations of sulphur compounds, further improvement may be obtained by pretreating the off-gases prior to burning. Condensing the vacuum jet stream and adding the condensate to the foul-water stripper has also been effective. In many refineries, the barometric condensers are being replaced with closed units which effectively eliminate this source.

3. BIO-OXIDATION UNITS

Odor emissions have been controlled by separating and pretreating particularly odorous streams. Proper maintenance of pH levels and mechanical aeration have also decreased odor emissions. In addition, proper handling of the biooxidation unit sludge improves odor prevention.

4. CATALYTIC CRACKING UNITS

Many odor problems have essentially been eliminated by the replacement of older moving bed units with new fluid catalytic cracking units. In addition, desulphurizing the feedstock has been effective.

5. CAUSTIC TREATMENT

Odor problems have been diminished by condensing the off-gases, recovering spent caustic by air blowing and burning the off-gases, or converting the thiols and extracting the resulting disulphides.

6. COKERS

Odor emissions are controlled by extracting the off-gas with gas-oil streams or condensing the off-gases and feeding the non-condensables to a process heater unit. The water quench is also a source of odors which can be eliminated by feeding the quench vapors to a flare or condensing it and adding the condensate to the foul-water stripper. The use of an amine scrubber on the off-gases with the scrubbed stream added to the fuel gas line is also effective.

7. DESALTER

Odors have been prevented by feeding the desalted water to a sour-water stripper, or in some circumstances by disposal in deep wells.

8. INCINERATOR

Odor emissions can be controlled by increasing the combustion temperature.

(to be continued)

APPENDIX E (continued)

9. LUBE OIL

Odors can be significantly reduced through the use of solvent extraction in place of acid treatment. Further improvement has been obtained by adding vapor control systems to the solvent storage tanks, installing blower-scrubber systems to the vents from blending and canning areas, and the use of hydrotreating instead of H_2SO_4 in the production of white oil.

10. PROPANE LOADING

Odor problems are commonly produced during the addition of an odorant. The use of a totally enclosed odorant system and a flush of the piping with the propane after odorant addition eliminates the major source of odor.

11. PUMPS AND COMPRESSORS

Odors are controlled by the replacement of packed seals with mechanical seals. Where mechanical seals cannot be used, the pump seals can be enclosed and vented to flare system with flare gas recovery and led to the refinery fuel system.

12. SAFETY FLARES

Flares should only be used for upset conditions to minimize odor problems.

13. SEWER SYSTEMS

Odor problems may be prevented by adding oil separators to each process unit, pretreating the effluent before discharge to the sewer and flashing the desalted water before it discharged to the sewer. Where possible, all hot spent process water should be cooled before dumping in the sewer.

14. SOUR-WATER STRIPPING

Odors created can be prevented by collecting the off-gases and sending them to a sulphur recovery unit, or by incineration.

15. SPILLS AND LEAKS

Odor problems may be minimized by collecting the spill in vacuum trucks for quick disposal.

16. STEAMING OF TOWERS AND VESSELS

Odor emissions can be reduced by conducting a more complete pumpout and through the use of a water or gasoline wash prior to steaming. Improvement can also be obtained by containing the first steam and venting it to a flare and treating the waste water.

(to be continued)

APPENDIX E (continued)

17. STORAGE TANKS FOR VOLATILE MATERIALS

Storage tank odors prevention has been improved by the use of floating roofs and not pumping below the level where a proper seal is maintained. Odor prevention from asphalt tanks or during cleaning may be improved by venting through a charcoal cannister.

18. SULPHUR RECOVERY UNIT

Odor prevention may be obtained by maintaining adequate temperatures in the process unit and storing the sulphur in molten form in a closed system.

19. VAPOR COLLECTION SYSTEM

Odors are reduced by recovery of all off-gases and vapor emissions in a completely closed system for use as fuel gas, recycle for reprocessing, or to be sent to a combustion device for incineration.

20. HYDROGEN TREATING

Odors compounds are treated with hydrogen to produce desirable products and H_2S.

APPENDIX F

MEASUREMENT OF AIR POLLUTION

Air samples often require detection and measurement in the ppmv to ppbv (parts by volume) range; source concentrations range from tenths of a percent to a few hundred ppmv. In areas of high population density, extensive community sampling networks have been eastablished using continuous monitors installed at strategic locations with the data telemetered to a central data-processing center. Less complex sampling techniques are used in remote areas, in metropolitan areas with limited budgets, or in determining sites for fixed monitors. Special problems may be investigated with portable, vehicle-carried, or airborne sampling equipment. Air sampling may fullfill one or more of the following objectives :

1) Establishing and operating a pollution alert network;

2) Monitoring the effect of an emission source;

3) Predicting the effect of a proposed installation,

4) Establishing seasonal or yearly trends,

5) Locating the source of an undesirable pollutant,

6) Obtaining permanent sampling records for legal action, and,

7) Correlating pollutant dispersion with Environmental Protection Organization of Iran (EPOI).

Source sampling has problems which are distinct and different from ambient sampling. Source gas temperature may be high and contain high concentrations of water vapor or entrained mist, dust, or other interfering substances; and particulates and gases may be deposited on or absorbed in extractive probes before reaching the measuring instrument. Typical objectives in source sampling are:

1) Demonstrating compliance with regulations;

2) Providing emission data;

3) Measuring product loss or optimizing process variables;

4) Obtaining engineering data for design;

5) Acceptance testing of control equipment, and;

6) Determining need for maintenance of process or control equipment. Depending on the objective, source sampling may be infrequent, occasional, intermittent, or continuous.

Source sampling

Source test methods for air pollutants fall into two broad categories, based on the physical state of the target pollutant, solid or fluid.

Details are given in IPS-G-SF-860.

Methods for the measurement of the concentration of particulate matter in ducts carrying gases is also in IPS-G-SF-860.

(to be continued)

APPENDIX F (continued)

Equipment

List of equipment for measurement of particulate content are given in IPS-G-SF-860.

Principle of isokinetic sampling

In order to have a representative measurement of the dust content in the duct, an isokinetic sample has to be taken at each measuring point. Details are given in IPS-G-SF-860.

Gaseous pollutants

Modern source-test methods for sampling gaseous pollutants from stacks involve two basic approaches: Continuous emissions monitoring, or CEM, and wet chemistry. In CEM, the pollutant is monitored in real-time using analyzers to detect the chemical in situ (in the stack) or in a sample of the gas that has been extracted from the stack and conditioned.

CEM analyzers are available for monitoring carbon monoxide, NO_x, SO_2, total hydrocarbons, hydrogen sulfide and hydrochloric acid. Many contractors who perform source tests have mobile vans outfitted with CEM systems for short term monitoring programs.

The second approach, wet chemistry, involves collecting the sample in a container, solid adsorbent or liquid-impinger train that must be manipulated manually in the field and then removed to a laboratory for analysis. All the gases that can be measured with CEM also have their respective "wet chemistry" method.

In addition, there are wet-chemistry methods for the class of gaseous pollutants that includes benzene, vinyl chloride, and formaldehyde. EPA method 106 for vinylchloride. The EPA volatile organic sampling train (VOST) for organics, and California Air Resources Board (CARB) Method 430 for formaldehyde is accepted.

Whole-air sampling

EPA Method 106 is an example of "whole air" sampling, in which a sample of the stack gas is extracted from the stack into a container called a Tedlar bag. The whole air sample is then transported to the laboratory for gas chromatography (GC) analysis.
Although Tedlar bags are used to collect several types of compounds, their use requires care. Different compounds behave differently in the bags, thus influencing the reproducibility of the analytical results.
EPA’s gas-chromatographic technique specifies flame ionization detection (FID) for analyzing vinyl chloride. However, the GC-FID analyzer can sometimes give erroneous results because it may actually be detecting compounds other than vinyl chloride.
To increase the level of confidence of an analysis, the laboratory technician should perform a second-column confirmation (by running the sample on another GC column). Otherwise, by the time the error is discovered, the sample’s "holding time" can have expired and it may no longer be representative of the emissions stream.
The mass spectrophotometer (MS) detector is a better alternative for gas analysis. Although a GC-FID analysis is generally less expensive than one using GC-MS, the mass spectrometer provides the actual proof (or disproof)

- Without second-column confirmation
- That a peak on the gas chromatograph is the target compound.

However, compared with FID and other GC detectors, the mass spectroscopy suffers from low detection limits. This limitation is being overcome with cryogenic concentration techniques, which are now being incorporated into modern GC-MS systems for the analysis of air.

(to be continued)

APPENDIX F (continued)

Volatile-organics sampling

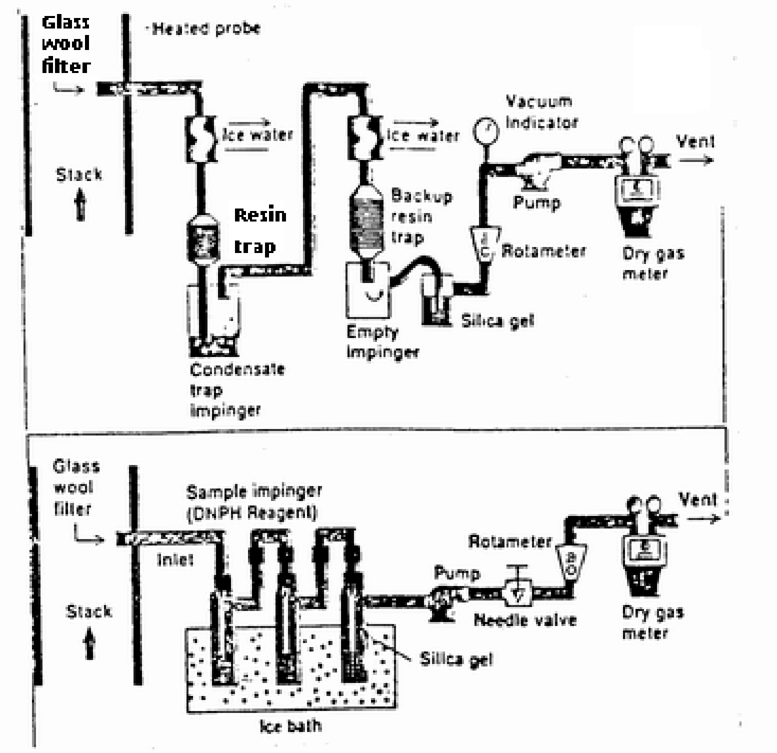
EPA’s Volatile Organics Sampling Train (VOST) can sample vinyl chloride and a much-larger host of volatile organic gases than can be handled by Tedlar bags. In VOST, stack gas is extracted from the source, cooled, and passed through a pair of adsorbent traps (Fig. F-1, TOP). The first trap is of Tenax; the second, Tenax and charcoal. The traps are then taken to the laboratory, where they are thermally desorbed onto the cryogenic trap of the GC-MS system.

This method allows for longer sample-holding times. Further, the traps can be spiked with isotopically labeled target compounds-the ultimate in quality assurance because it provides for a high degree of confidence in the test result if the spike is present. Good spike-recovery means that the target compound survived the rigors of sampling and was thermally desorbed from the sample tube without degradation.

Another sampling train for gases is CARB’s Method 430 for formaldehyde (Fig. F-1, bottom). This is an example of "wet impingement" and is particularly interesting in that part of the analytical chemistry is accomplished in the impinger during sampling.

The emissions gas is extracted from the stack and bubbled through impingers containing an acidic solution of 2,4- dinitrophenylhydrazine (DNPH); formaldehyde (and other aldehydes) reacts with the DNPH to form a stable derivative. The sample is recovered from the sampling train and transported for analysis.

In the laboratory, the derivative is extracted with an organic solvent and analyzed by high-pressure liquid chromatography (HPLC) fitted with an ultraviolet detector. It should be noted that contamination is a real problem with this method. Rigorous steps must be taken to ensure that the impinger solutions are clean and protected from exposure to ambient air during the entire course of use.



SAMPLING TRAINS FOR VOLATILE ORGANICS (PHOTO AND TOP SCHEMATIC) AND A "WET IMPINGEMENT" METHOD FOR FORMALDEHYDE
Fig. F-1

(to be continued)

APPENDIX F (continued)

Determination in work place air

Determination of vinyl chloride-charcoal tube/gas chromatographic method

It is said that even 1 ppm of monomer in vinyl chloride is carcinogenic. The method is for determination of the vinyl chloride monomer concentration in work place air in the range from 250 Mg/m^3 (= 100 Ml/m^3) to 25 Mg/m^3 (= 10 ml/m^3) when sampling of 30 lit of air is taken.

Principle

A known volume of air sample is passed through a glass or metal tube packed with activated charcoal. The vinyl chloride is adsorbed onto the charcoal. The collected vinyl chloride is desorbed using carbon disulfide and analyzed with a gas chromatograph equipped with a flame ionization detector.

Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent quality.

a) Vinyl chloride liquid in a small gas cylinder.

Warning

Vinyl chloride is recognized as a human carcinogen. Avoid any exposure by inhalation or skin contact. Personal protection (e.g.an effective respirator shall be available in all cases where exposure to vinyl chloride is possible.

Vinyl chloride vapor is highly flammable. Usage shall be restricted to a well-ventilated fume cupboard. An effective fire extinguisher shall be permanently available.

b) Carbon disulfide (CS_2), chromatographic quality, previously checked for compounds coincident with the vinyl chloride peak. The CS_2 shall not contain impurities that coelute with vinyl chloride giving a response greater than 0.06 ng of vinyl chloride at an injection volume of 1 µl. This requirment shall be checked for each batch of CS_2.

Warning

Carbon disulfide vapor is toxic. Avoid any exposure by inhalation or skin contact. Carbon disulfide is highly flammable. Usage shall be restricted to a well ventilated fume cupboard. An effective fire extinguisher shall be permanently available.

Small waste quantities of carbon disulfide shall be disposed of only in accordance with local regulations and accepted practices.

c) Activated coconut shell charcoal, particle size 0.35 mm to 0.85 mm. Before packing the tubes, the charcoal shall be heated in an inert atmosphere, e.g. high-purity nitrogen, at approximately 600°C for 1 h. To prevent recontamination of the charcoal, it shall be kept in a clean atmosphere during cooling to room temperature, storage and loading into the tubes.

Note:

Suitable tubes containing pretreated coconut charcoal are commercially available.

(to be continued)

APPENDIX F (continued)

d) Vinyl chloride standard solutions for the preparation of the calibration graph.

1) Vinyl chloride standard solution, containing 260 mg of C_2H_3Cl per liter.

Pipette 10.0 ml of the carbon disulfide (b) into a vial, cap the vial and cool in dry ice. Obtain pure vinyl chloride vapor at atmospheric pressure by partially filling a previously evacuated gas bag with pure gas from the small gas cylinder (a).

Fill a syringe (5.8) with 1.0 ml of the vinyl chloride vapor from the gas bag and close the valve of the syringe. Insert the tip of the needle through the septum cap into the carbon disulfide. Open the valve and withdraw the plunger slightly to allow the carbon disulfide to enter the syringe. The action of the vinyl chloride dissolving in the carbon disulfide creates a vacuum and the syringe becomes filled with the solvent. Return the solution to the vial. Flush the syringe twice with the solution and return the flushings to the vial.

1 ml of this standard solution contains 260 µg of C_2H_3Cl.

Note:
The vinyl chloride concentrations are given for the case in which the vinyl chloride vapor is injected at 20°C and 101.3 kPa.

2) Vinyl chloride standard solution containing 52 mg of C_2H_3Cl per liter.

Add approximately 5 ml of the carbon disulfide to a 10 ml one-mark volumetric flask. Pipette 2 ml of the standard solution into this flask, dilute to the mark with the carbon disulfide and mix well.

1 ml of this Standard solution contains 52 µg of C_2H_3Cl.

3) Vinyl chloride standard solution containing 5.2 mg of C_2H_3Cl per liter.

Add approximately 5 ml of the carbon disulfide to a 10 ml one-mark volumetric flask.

Pipette 1 ml of the standard solution into this flask, dilute to the mark with the carbon disulfide and mix well.

1 ml of this standard solution contains 5.2 µg of C_2H_3Cl.

4) Vinyl chloride standard solution containing 0.52 mg of C_2H_3Cl per liter.

Add approximately 5 ml of the carbon disulfide to a 10 ml one-mark volumetric flask. Pipette 1 ml of the standard solution into this flask, dilute to the mark with the carbon disulfide and mix well.

1 ml of this standard solution contains 0.52 µg of C_2H_3Cl.

5) Vinyl chloride standard solution containing 0.052 mg of C_2H_3Cl per liter.

Add approximately 5 ml of the carbon disulfide to a 10 ml one-mark volumetric flask. Pipette 1 ml of the standard solution item 3 into this flask, dilute to the mark with the carbon disulfide and mix well.

1 ml of this standard solution contains 0.52 µg of C_2H_3CL.

(to be continued)

APPENDIX F (continued)

e) Vinyl chloride control solutions for checking the calibration graph.

1) Vinyl chloride control solution, containing 130 mg of C_2H_3Cl per liter.

Prepare this solution as described in d.1, but inject 0.5 ml instead of 1.0 ml of the vinyl chloride vapor.

1 ml of this control solution contains 130 µg of C_2H_3Cl.

2) Vinyl chloride control solution, containing 52 mg of C_2H_3Cl per liter.

Use the solution prepared as described in e.I.

1 ml of this control solution contains 0.52 µg of C_2H_3Cl.

Apparatus

Standard for:

Ordinary laboratory apparatus are given in IPS-G-SF-860.

Expression of results

Standard for calculation, precision and test report are given in IPS-G-SF-860.