

**Special Report**

**No 9**

**Styrene Criteria Document**

**June 1995**

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# ECETOC

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## PREFACE

This report contains an original review and assessment of the toxicological data for styrene and a quantitative risk assessment (chapters 7 to 9) to provide a scientific basis for setting an exposure limit for styrene (chapter 11). Information on occurrence, production and use, exposure and uptake, and measurement techniques (chapters 3 to 6) has been drawn largely from existing reviews.

The report has been prepared for the European Commission Directorate General V responsible for health and safety at the workplace to assist the Group of Scientific Experts (SEG) in its work to provide advice on the basis of available scientific data. This work is being done under Council Directive 80/1107/EEC, as amended with Council Directive 88/642/EEC, on the protection of workers from the risks related to exposure to chemical, physical and biological agents at work. In drafting this report existing guidance was followed closely (EC Commission publ. EUR 13776- 1992).





# STYRENE CRITERIA DOCUMENT

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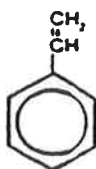
### Table of Abbreviations

AAP	Alanine Amino Peptidase
ABS	Acrylonitrile Butadiene Styrene Copolymer
ACGIH	American Conference of Governmental Industrial Hygienists
ALAT	Alanine Amino Transferase
Alb	Albumin
AM	Alveolar Macrophages
AP	Alkaline Phosphatase
ASAT	Aspartate Amino Transferase
AUC	Area Under blood concentration Curve
BAT	Biological Tolerance Value
BEI	Biological Exposure Index
BM	Bone Marrow
CBI	Covalent Binding Index
CEC	Council of European Community
CNS	Central Nervous System
EDI	Estimated Daily Intake
EDTA	Ethylene Diamine Tetraacetic Acid
EEG	Electroencephalography
EHA	Environmental Health Associates
EPS	Expandable Polystyrene
FDA	Food and Drug Administration (USA)
FID	Flame Ionisation Detector
GAL	$\beta$ -Galactosidase
GLU	$\beta$ -Glucuronidase
GPPS	General Purpose Polystyrene
GPRMC	European Org. of Reinforced Plastics/Composite Materials
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
GSH	Glutathione
GT	Glutamyl Transpeptidase
Hgb	Haemoglobin
HIPS	High Impact Polystyrene
HPLC	High Performance Liquid Chromatography
LDH	Lactate Dehydrogenase

LHC	Lymphatic and Haematopoeietic Cancer
LPG	Liquefied Petroleum Gas
MA	Mandelic Acid
MFO	Mixed Function Oxidase
MN	Micro Nucleus
MS	Mass Spectrometry
NAG	N-Acetyl- $\beta$ -D-Glucosamidase
NCI	National Cancer Institute
NIOSH	National Institute for Occupational Safety and Health (USA)
NPSH	Non-Protein Sulfhydryl groups
OSHA	Occupational Safety and Health Administration (USA)
PB-PK	Physiologically-Based Pharmacokinetic
PBL	Peripheral Blood Lymphocytes
PGA	Phenyglyoxylic Acid
PMCC	Polystyrene Manufacturing Colouring and Compounding Plant
RBP	Retinol Binding Protein
RCC	Renal Cell Carcinoma
RD <sub>50</sub>	50% Decrease of Respiratory Rate
RL	Regenerating Liver
SAN	Styrene Acrylonitrile
SB	Styrene Butadiene Copolymer
SBR	Styrene Butadiene Rubber
SCE	Sister Chromatid Exchange
SDH	Sorbitol Dehydrogenase
SIRC	Styrene Information and Research Center (USA)
SMR	Standard Mortality Ratio
SO	Styrene-7,8-epoxide (Phenyloxirane)
SPI	Society of Plastics Industry
SSB	Single Strand Breaks
STEL	Short Term Exposure Limit
TEAM	Total Exposure Assessment and Management
TWA	Time-Weighted Average
UPR	Unsaturated Polyester Resins
USEPA	Environmental Protection Agency (USA)

## 1. SUBSTANCE IDENTIFICATION

### 1.1 IDENTITY

Common name:	Styrene
CAS registry No:	100-42-5
EEC labelling:	R: 10-20-36/38 S: 23
IUPAC name:	Ethenylbenzene
EINECS No:	2 028 515
Synonyms and Styrene trade names:	Vinylbenzene Ethenylbenzene Phenylethylene Phenylethene Cinnamène
Chemical group:	Unsaturated hydrocarbon
Formula:	$C_8H_8$
Structure:	
Molecular mass:	104.15
Purity of technical product	up to 99.9 %

## 1.2 STYRENE IMPURITIES

Styrene is one of the purest raw materials in the petrochemical technical industry, typically containing a total of less than 2,500 ppm of impurities.

Potential impurities include:

Benzene	<1 ppm
Cumene	10-350 ppm
vinylbenzene	<10 ppm
Ethyltoluene	10-1,000 ppm
Ethylvinylbenzene	<10 ppm
Methylstyrene	50-1,000 ppm
Phenylacetylene	10-100 ppm
Propylbenzene	10-150 ppm
Toluene	<1 ppm
Vinyltoluene	<50 ppm
Xylene	20-1,000 ppm

## 1.3 NECESSARY ADDITIVE

4- <i>tert</i> -Butylcatechol	10-100 ppm
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## 2. CHEMICAL AND PHYSICAL PROPERTIES

### 2.1 PROPERTIES

Styrene is a colourless, highly volatile liquid with a characteristic pungent smell. It polymerises easily at room temperature in the presence of oxygen and oxidises on exposure to light or air.

**Table 1: Chemical and Physical Properties**

Parameter	Value	Reference
Boiling temperature	145.2°C	WHO (1983)
Freezing point	-30.63°C	WHO (1983)
Flash point	31°C	WHO (1983)
Vapour pressure at 20°C	5 mmHg	U.S. Dept Health and Human Services
Colour	Colourless to yellow	U.S. Dept Health and Human Services
Threshold odour concentration	0.02 ppm	Hellman and Small (1974)
Solubility in water	30mg/100ml at 20°C	WHO (1983)
Solubility in organic solvents	ethanol, diethylether, acetone, benzene and petroleum ether	WHO (1983)
Partition coefficient at 20°C	2.95	U.S. Dept Health and Human Services
Flash point	31°C	WHO (1983)
Explosion limit	1.1-6.1%	U.S. Dept Health and Human Services
Auto-flammability, ignition temperature	490°C	WHO (1983)

The technical product is shipped as a liquid. A stabiliser, 4-*tert*-Butylcatechol is added to the styrene which works in conjunction with oxygen to prevent polymerisation.

### 2.2 CONVERSION FACTOR

Conversion factors for styrene concentrations in air, calculated at 20°C and 1,013 hPa are:

$$1 \text{ mg/m}^3 = 0.235 \text{ ppm}$$

$$1 \text{ ppm} = 4.26 \text{ mg/m}^3$$



### 3. OCCURRENCE

#### 3.1 ENVIRONMENTAL

Styrene has been identified in both automobile exhaust (Warner-Selph and De Vita, 1989) and cigarette smoke (Byrd *et al*, 1990). Studies on automobile exhaust suggest that motor vehicles are a primary source of man-made emissions of hydrocarbon gases (National Academy of Sciences, 1976), with Guicherit and Schulting (1985) suggesting that approximately 57% of the styrene present in ambient air is attributable to "mobile" sources. Cigarette smoke probably play a minor role in contributing to styrene levels in outdoor air; it may play a more significant role in contributing to indoor exposures. (For more information see 5.3.1 and 5.3.2).

#### 3.2 WORKPLACE

Emissions of styrene into the environment occurs during monomer production and polymerisation processes. During styrene production fugitive emissions have been estimated to be approximately 20 metric tons for every 260,000 metric tons produced i.e. a loss of approximately 0.0076%. With newer plants the levels of emission have been reduced dramatically with only about 3.5 metric tons of styrene emission occurring per 450,000 tons of styrene produced i.e. an emission 0.0007%. About 33g of styrene emissions can occur for each metric ton of polystyrene produced i.e. a loss about 0.0033%. With increasing upgrading of plant and equipment it can be expected that fugitive styrene emissions will continue to decline.

#### 3.3 FOOD

Styrene has been found in a variety of foods and beverages (van den Berg *et al*, 1993). Because styrene is volatile, reactive and rapidly destroyed by ozone and hydroxyl radicals, it is unlikely to be transported to any significant extent, or to be a source of styrene in water or soil (for review see Alexander, 1990). As there is very little possibility of styrene occurring in drinking water or entering the food chain the presence of styrene in food is unlikely to be caused by environmental contamination.

Sources of styrene in food include natural occurrence and/or migration from polystyrene food packaging. An extensive literature search conducted by the Netherlands Central Institute for Nutrition and Food Research (1983) described the presence of styrene in various foods including: apples, various wild berries (bilberry, blueberry, cloudberry, cowberry, cranberry and loganberry), currants, grapes, peaches, strawberries, onions (roasted), capsicum species, peas, tomatoes, vinegar, parsley, cheese, milk, milk products, eggs, fish, beef, beer, rum, whiskey, cider, white wine, cocoa, coffee, tea, filberts, peanuts, honey, olives, trassi, walnuts, Brazil nuts, oats and soursop. In many instances no quantitative data were supplied and there is always the possibility that the food samples may have come into contact with polystyrene before analysis. Some reports however do provide an estimate of the levels of styrene occurring naturally in foods; for example a study of the volatile constituents found in dried legumes indicated that the concentration of styrene in split peas and lentils was 4 and

5 µg/kg respectively (Lovegren *et al*, 1979) with the level in German beer (Pilsener) being approximately 70 µg/kg. Styrene is also reported to occur extensively in white wine, possibly due to the decarboxylation of cinnamic acid (Tang and Eisenbrand, 1993). The majority of German wines have been found to contain 1 to 3 µg styrene/kg wine (Tang and Eisenbrand, 1993) while Simpson and Miller (1984) reported concentrations of about 1 to 2 µg of styrene per kg of white wine.

Miller *et al* (1993) and van den Berg *et al* (1993) have provided a quantitative estimation of the levels of styrene occurring naturally in a wide variety of foods including meat, fruit and vegetables. In both studies great care was taken to prevent contact with styrene or any type of styrene based polymer. Van den Berg reported that the concentration of styrene in apples, cauliflowers, onions and tomatoes was below 1 µg/kg while levels in black currants and wheat may be as high as 6 µg/kg and 2 µg/kg respectively. Similar levels were reported by Miller *et al* (1993) i.e. levels in beef, coffee beans, peanuts, wheat, oats, strawberries and peaches varying between 0.3 to 8 µg/kg with no styrene being detected in tomatoes, pecans, milk and chicken - detection limit 0.1 µg/kg. The authors did however report exceptionally high levels, range 157 to 39,200 µg/kg, in cinnamon. The results of such studies suggest that styrene may be a natural constituent of many foods being formed in a number of ways including by bacteria and moulds, from carotenoids, from hydrocarbons, from aldehydes, by Maillard reactions, during autoxidation of methyl arachidonate and from 2-phenylethanol (van den Berg *et al*, 1993).

Besides natural occurrence, styrene in food may be due to migration of the monomer from styrene based polymers used for food packaging. (For example see Vamer and Breder, 1981; MAFF, 1983; Gilbert and Starin, 1983 and Society of Plastics Industry, 1993). Migration is dependent on a number of factors including the residual styrene content in the polymer, the nature of the packaged food (migration into fatty foods being higher than aqueous based materials), the contact area, duration of contact, temperature of both storage and package filling, and a variety of other factors. Fatty foods e.g. butter, oil, margarine, dairy products, which have the highest migration levels show styrene concentrations ranging from <5 to 25 µg/kg (Tang and Eisenbrand, 1993).

## 4. PRODUCTION AND USE DATA

### 4.1 PRODUCTION OF STYRENE

The raw materials used to make styrene are obtained from crude oil or liquefied petroleum gas (LPG). A range of processes are required to transform the crude oil or gas into styrene. These processes are described briefly.

The initial step involves a distillation process in which crude oil is refined to produce naphtha heating oil and gasoline. The naphtha fraction from the refinery is subsequently processed by steam cracking into ethylene, propylene and a mixture of monocyclic compounds including benzene. The benzene, after passing through a drying column into a reactor, is mixed with ethylene in the presence of a suitable catalyst. This alkylation reaction is exothermic (the heat being used to generate process steam that can be used in the distillation processes) and can be carried out in liquid phase at low temperatures and pressures with an aluminium chloride catalyst, or in the vapour phase at higher temperatures and pressures with a zeolite catalyst. The crude ethylbenzene is purified by distillation to recover unreacted benzene for recycling. Distillation ends and by-products are used for energy recovery.

The next step in the process is the dehydrogenation of ethylbenzene to produce styrene. More than 90% of styrene produced in the world is made by the iron oxide-catalysed dehydrogenation of ethylbenzene. Continuous chemical reactors are used for this reaction that is carried out at high temperature (typically over 600°C using steam as the energy source) and low pressure. Heat is recovered and the reaction mixture is sent to the fractional distillation units for purification.

The crude styrene from the dehydrogenation reaction is purified in several stages using fractional distillation. The resulting product is commercial polymerisation quality styrene. By-products are recycled or used for their fuel value.