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1,4-dioxane:
an emergent pollutant which can be useful

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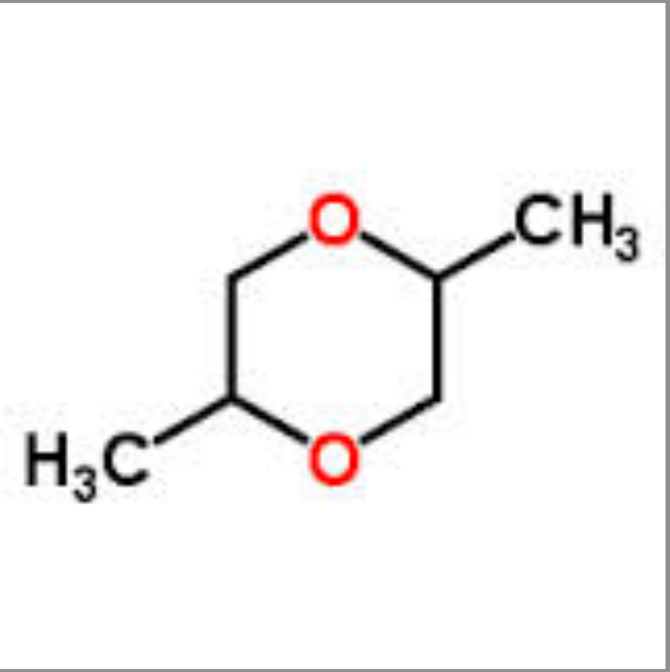
20 ans meme pas peur !

Introduction



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Introduction

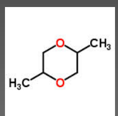
1,4-dioxane has many uses beyond its key role as a stabilizer for methyl chloroform (1,1,1-TCA). It is used directly in several industrial and commercial processes and is found in a wide range of consumer products.

1,4-dioxane also occurs as a by-product in the production of certain surfactants, synthetic textiles, plastics and resins. As a result of its widespread use, 1,4-Dioxane is found in ambient air, surface water and groundwater, but also more commonly in wastewater, landfill leachate and landfill gas.

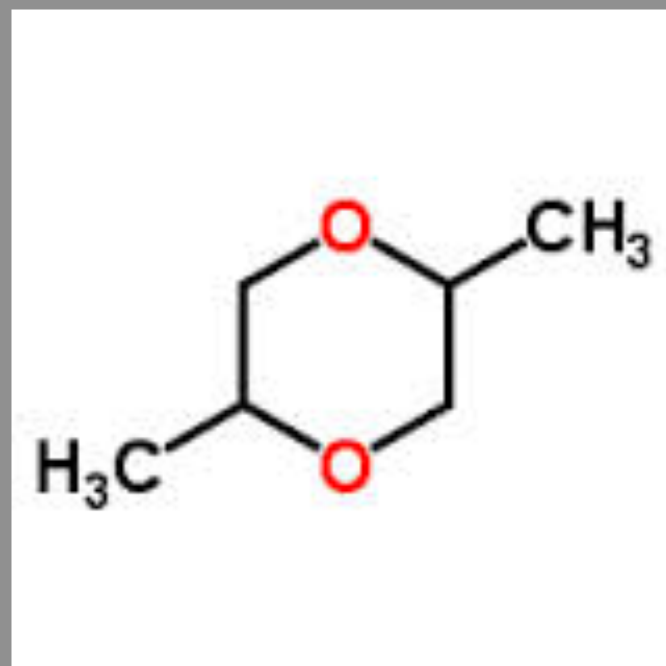
Introduction

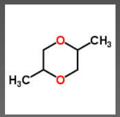
Documenting the uses, occurrence and history of the 1,4-dioxane production provides practical information for consultants investigating 1,4-dioxane releases in soil and groundwater.

Knowledge of the many uses of 1,4-dioxane may also be helpful in reconstructing release histories by forensic investigative techniques.



1 – Chemistry of 1,4-Dioxane

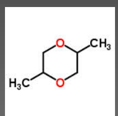




1 - Chemistry of 1,4-dioxane

A. V. Lourenço first described 1,4-dioxane in 1863 as the product of reacting ethylene glycol and 1,2-dibromoethane. In the same year, A. Wurtz described the derivation of 1,4-Dioxane from ethylene oxide.

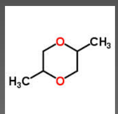
1,4-Dioxane is also known as *p*-dioxane, diethylene oxide, 1,4- diethylene dioxide and glycol ethylene ether. 1,4-dioxane is a cyclic ether that has four carbon atoms, resulting in two ether functional groups in the same molecule. Cyclic ethers have a ring structure in which the oxygen has become part of the ring.



1 - Chemistry of 1,4-dioxane

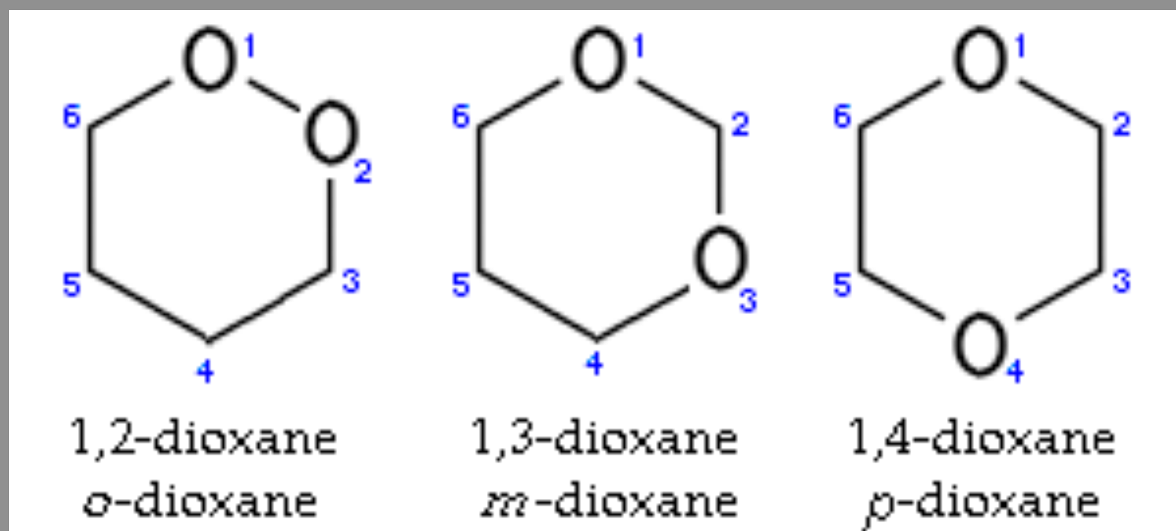
In 1,4-dioxane, the oxygen atoms occur directly opposite each other to form symmetrical either linkage. This structure makes 1,4-dioxane highly stable and relatively immune to reactions with acids, oxides and oxidizing agents. The symmetry of the 1,4-dioxane ring should impart only a very small dipole moment to the molecule; nevertheless, it has good solvency.

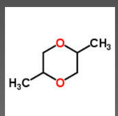
1,4-dioxane has a slight odor similar to butanol. It is fully miscible with water and most organic solvents and water is fully soluble in dioxane. 1,4-dioxane is favored as a solvent for cellulose derivatives, polymers, chlorinated rubber, resins and it has many other uses, as described further.



1 - Chemistry of 1,4-dioxane

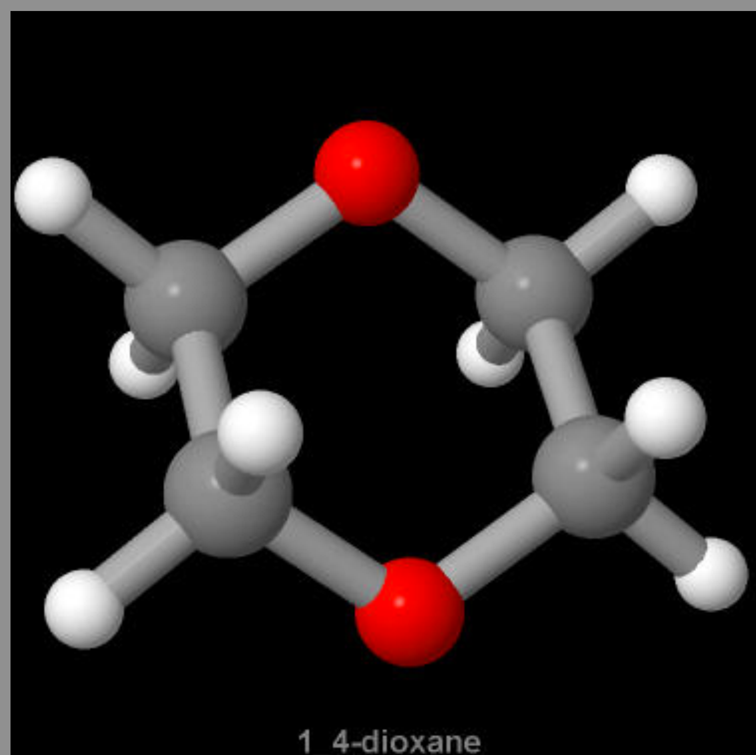
There are two other dioxane isomers, 1,2-dioxane and 1,3-dioxane:

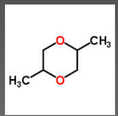




1 - Chemistry of 1,4-dioxane

The molecular structure of 1,4-dioxane is shown below. Its two oxygen atoms (in red) make it hydrophilic and infinitely soluble in water.





Chemistry of 1,4-dioxane

Properties	
Colorless	
Molecular formula	$C_4H_8O_2$
Molecular weight (g)	88.2
Melting point	11.8 °C
Freezing point	-57 °C
Boiling point (°C at 760 mm Hg)	101°C
Vapor pressure (mm Hg)	30 mm at 20°C
Vapor density (relative to air = 1)	3.03
Density (g/ml at 20°C)	1,033 g/cm^3
Saturation concentration in air	148 g/m^3 at 20°C - 232 g/m^3 at 30°C
Viscosity at 20°C	0.012 poise
Solubility	Completely miscible
$LogK_{oc}$	1.07 – 1.23
$LogK_{ow}$	-0.27 -0.43

2 – History of the 1,4-Dioxane production

2 - History of the 1,4-dioxane production

1,4-dioxane is produced from ethylene glycol. The most commonly used process involves heating ethylene glycol to 160°C and reacting it with concentrated sulfuric acid under a vacuum.

1,4-dioxane was first produced for commercial sale and use in 1929. The US began larger-scale production of 1,4-dioxane in 1951. A company in Japan began production in 1958. The largest demand for 1,4-dioxane arose in the late 1950s and the early 1960s with its use in stabilizing methyl chloroform (1,1,1-TCA).

2 - History of the 1,4-dioxane production

In 1985, the worldwide production of 1,4-dioxane was estimated at 14.000 tons.

In the mid 1980s, about 90% of the 1,4-dioxane produced annually was used to stabilize methyl chloroform.

By 1995, the year in which ozone depleting substance regulations severely curtailed the use of methyl chloroform, the production of 1,4-dioxane decreased to 10.000 tons.

Uses of 1,4-dioxane

3 – Uses of 1,4-Dioxane

3 – Uses of 1,4-dioxane

3.1 - Direct uses of 1,4-dioxane

- ✓ Some lacquers, paints, varnishes and paint and varnish remover
- ✓ Wetting and dispersing agent in textile processing
- ✓ Dyes baths and stain and printing composition
- ✓ Solvent for fats, oils, waxes and natural and synthetic resins
- ✓ Solvent for brominated fire retardants

3 – Uses of 1,4-dioxane

3.1 - Direct uses of 1,4-dioxane

- ✓ Reaction media in various organic synthesis reactions
- ✓ Stabilizer for chlorinated solvents
- ✓ Some cleaning and detergent preparations, adhesives, cosmetics, deodorants, fumigants, emulsions and polishing agents

3 – Uses of 1,4-dioxane

3.1 - Direct uses of 1,4-dioxane

- ✓ 1,4-dioxane can be used in food
  - Chicken flavor
  - Fried chicken volatile flavor compounds
  - Tomato fruit juice volatiles

  …
- ✓ But also in pharmaceutical industry

3 – Uses of 1,4-dioxane

3.2 – 1,4-dioxane as a by-product of manufacturing

1,4-dioxane occurs as a reaction by-product in several chemical processes used to produce polyester, soaps and plastics. This is for example:

- ✓ Personal care products: detergents, shampoos and cosmetics
- ✓ Contraceptive sponges and spermicidal lubricants

3 – Uses of 1,4-dioxane

3.2 – 1,4-dioxane as a by-product of manufacturing

✓ Polyethylene glycol

- Pharmaceuticals
- Cosmetics such as deodorant sticks, lipsticks, shaving creams, toothpastes and lotions
- Detergents in laundry soaps and dish-washing soaps
- Textile and leather processing
- Plastics and resins
- Paper
- Printing inks
- Lubricants
- Mold-release agents in the rubber industry
- Metal corrosion inhibitors in the petroleum industry

3 – Uses of 1,4-dioxane

3.2 – 1,4-dioxane as a by-product of manufacturing

- ✓ Polyethylene glycol
  - Anticracking and preservation in woodworking
  - Brake fluid lubricants
  - Petroleum refining and gasoline antiknock agent
- ✓ Inert ingredient in Glyphosphate herbicides (Roundup,…)
- ✓ Pesticides
- ✓ …

Now the question is:
why 1,4-dioxane can be useful?

4 – Forensic opportunities

Forensic investigations in environmental contamination are usually oriented toward attributing responsibility to parties who used and released a contaminant and must therefore share the burden of investigation and remediation.

Perhaps, the most important and least available feature of solvent contamination sites is the timing of release. The potential utility of solvent stabilizers to assist in establishing the timing (or rate and duration of the release) depends on whether the mass fraction of the stabilizer is sufficient to be detected in the environment and whether the stabilizer compounds persist in the subsurface.

4 – Forensic opportunities

When 1,4-dioxane and methyl chloroform (1,1,1-TCA) are present in an environmental sample, a number of forensic interpretative opportunities are available, including the following:

1) TCA with 1,4-dioxane was likely manufactured no earlier than the early 1950s. While 1,4-dioxane is also associated with other industrial and commercial uses, its association is primarily as a stabilizer with chlorinated solvents

4 – Forensic opportunities

Forensic opportunities

2) If 1,2-butylene oxide is present with 1,4-dioxane and 1,1,1-TCA it suggests that the 1,1,1-TCA was used in a vapor degreasing capacity and that aluminum parts may have been degreased
3) If 1,1,1-TCA is detected without 1,4-dioxane, it may indicate that the 1,1,1-TCA was used for cold cleaning and not vapor degreasing
4) If the initial concentration of 1,4-dioxane in the 1,1,1-TCA is known and the presence of 1,4-dioxane in an environmental sample is significantly greater (≈ > 50%), it may indicate that the 1,4-dioxane was released as a spent solvent, rather than from virgin product released during delivery

4 – Forensic opportunities

5) A forensic opportunity with 1,4-dioxane is its propensity to accumulate in vapor degreaser sludge, along with other additives, owing to is higher boiling point
6) Another forensic opportunity exists in cases where 1,4-dioxane and 1,1,1-TCA are detected at an automotive repair facility, as indication of the release of a brake cleaning fluid. While methyl chloroform was historically the primary ingredient in most aerosol brake cleaner, it was replaced in the late 1990s with PCE due to the impacts of methyl chloroform on stratospheric ozone depletion.

4 – Forensic opportunities

7) 1,4-dioxane may provide a mean to distinguish between a release of solvents from distillation of sludge and new solvent using 1,4-dioxane, due to the difference in the boiling point between 1,4-dioxane and 1,1,1-TCA (101°C versus 78°C)

   Partitioning experiments indicate that 27% of the 1,4-dioxane will remain in the liquid; with continued additions to the solvent, the 1,4-dioxane is enriched in the spent solvent. If sufficient information is available, it may be possible to distinguish between a release of new TCA and spent TCA, prior to distillation, based on the 1,4-dioxane to TCA ratio.

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