

Osmium Tetroxide

Safety Data Sheet

Division of Occupational Health and Safety
National Institutes of Health



WARNING!

This compound is toxic and mutagenic. It is readily absorbed through the respiratory and intestinal tracts. It may cause severe irritation of the skin, eyes, mucous membranes, and lungs. Avoid formation and breathing of aerosols or vapors.

Laboratory operations should be conducted in a fume, glove, box, or ventilated cabinet.

Avoid skin contact; If exposed, wash with soap and cold water. Avoid washing with solvents. Avoid rubbing of skin or increasing its temperature.

For eye exposure, irrigate immediately with large amounts of water. For ingestion, induce vomiting. Drink milk or water. Refer for gastric lavage. For inhalation, remove victim promptly to clean air. Administer rescue breathing if necessary. Refer to physician.

In case of laboratory spill, wear protective clothing during cleanup. Avoid skin contact or breathing of aerosols or vapors. Use water to dissolve compound. Use absorbent paper to mop up spill. Wash down area with soap and water. Dispose of waste solutions and materials appropriately.

A. Background

Osmium tetroxide is a pale yellow volatile crystalline solid with a characteristic acrid odor. It is readily absorbed by inhalation of its vapors. It is highly irritating to the eyes, nose, and mucous membranes of the respiratory tract and discolors the skin on contact. There are few reliable estimates of animal toxicity but it is believed that severely toxic exposures of man under industrial or laboratory conditions are unlikely because of the repugnant odor of this compound. The strong oxidizing power of osmium tetroxide is used industrially in the oxidation of olefins to glycols, and of sterols and sugars. In the laboratory the main uses are in tissue fixation and staining for visible and electron microscopy, and as a catalyst in other oxidations (cf. Rylander, 1973). It has also been recommended for the treatment of some arthritic conditions.

The permissible exposure limit for osmium tetroxide (8 hour time-weighted average) is 0.002 mg/m³ (ACGIH, 1987).

B. Chemical and Physical Data

1. Chemical Abstract No.: 20816-12-0.
2. Synonyms: Osmic acid (usually applied to 1-2% aqueous solutions used in histological work); osmic acid anhydride; osmine tetroxide.

3. Chemical structure and molecular weight: OsO_4 ; 254.20.
4. Density: 4.906
5. Absorption spectroscopy: The ultraviolet spectrum shows four peaks in the range of 282-312 nm (Goldstein et al., 1961a). Data for Raman and infrared spectra have been tabulated (Woodward and Roberts, 1956).
6. Volatility: The vapor pressure at 27° C is 11 mm Hg. Weast (1982), p_A D-201, lists vapor pressures over the range of -5.6° C to 130° C.
7. Solubility: Osmium tetroxide is soluble in water to the extent of 7.24 g/100 ml at 25° C. It is highly soluble in inert organic solvents (350 g/100 ml in carbon tetrachloride; also soluble in ethanol, ether) and in ammonia with which it forms adducts.
8. Description: Pale yellow monoclinic crystals. Acrid odor, variously described as chlorine- or ozone-like.
9. Boiling point, melting point: Osmium tetroxide begins to sublime to 30° C. Its melting point is 40.6° C; its boiling point has been variously listed as 121.2° C (Griffin, 1974), 130° C (Weast, 1982), and 131.2° C (Griffith, 1967). (The first figure might be a misprint.)
10. Stability: There are no data but it appears to be quite stable in the absence of impurities, since it can be distilled at 100° C without decomposition. However, osmium tetroxide is very readily reduced in the presence of slight amounts of organic impurities, such as dust or grease, to black osmium dioxide, thus accounting for the frequently found black deposits at the mounts of storage containers. In aqueous solution it forms the hydrate H_4OsO_6 or $\text{OsO}_2(\text{OH})_4$ which gives a neutral reaction to litmus paper ($\text{pK}_1 = 7.2$) (Bavay et al., 1967).
11. Chemical reactivity: As mentioned above, osmium tetroxide is a powerful oxidizing agent which is used as a reactant in the oxidation of olefins, steroids, and sugars, and as a catalyst in chlorate, peroxide, periodate, and other oxidations. Its ready reduction to osmium dioxide (or osmium metal) is the basis for its use in tissue fixation and staining in visual and electron microscopy.
12. Flashpoint: None.
13. Autoignition temperature: No data.
14. Explosive limits in the air: No data.

C. Fire, Explosion, and Reactivity Hazard Data

1. Major hazards of osmium tetroxide to fire-fighting personnel are due to its volatility (effects on eyes, nose, and throat). Complete protective clothing and air-supplied respirators should be worn.
2. OsO_4 is not combustible.
3. Conditions contributing to instability are likely to include presence of any organic materials. If significant amounts of osmium tetroxide are present in a fire-fighting situation, reaction with these materials could possibly be explosive (although there are no literature data to this effect).
4. No hazardous decomposition products have been identified. The products of reduction of osmium tetroxide (osmium dioxide and osmium metal) are stated to be nontoxic (Smith *et al.*, 1974).

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D. Operational Procedures

The NIH Guidelines for the Laboratory Use of Chemical Carcinogens describe operational practices to be followed when potentially carcinogenic chemicals are used in NIH laboratories. The NIH Guidelines should be consulted to identify the proper use conditions required and specific controls to be implemented during normal and complex operations or manipulations involving osmium tetroxide.

It should be emphasized that this data sheet and the NIH Guidelines are intended as starting points for the implementation of good laboratory practices when using this compound. The practices and procedures described in the following sections pertain to the National Institutes of Health and may not be universally applicable to other institutions. Administrators and/or researchers at other institutions should modify the following items as needed to reflect their individual management system and current occupational and environmental regulations.

1. Chemical inactivation: Methods have been reported (Smith *et al.*, 1974).
2. Decontamination: Turn off equipment that could be affected by osmium tetroxide or the materials used for cleanup. If there is any uncertainty regarding the procedures to be followed for decontamination, call the NIH Fire Department (dial 911) for assistance. Use absorbent paper to mop up spill. Wipe off surfaces with alkali in 50% aqueous ethanol, then wash with copious quantities of water. Glassware should be rinsed in a hood with alkali in 50% aqueous ethanol, followed by soap and water. Animal cages should be washed with water.
3. Disposal: No waste streams containing osmium tetroxide shall be disposed of in skins or general refuse. Surplus osmium tetroxide or chemical waste streams contaminated with osmium tetroxide shall be handled as hazardous chemical waste and disposed of in accordance with the NIH chemical waste disposal system. Nonchemical waste (*e.g.*, animal carcasses and bedding) containing osmium tetroxide shall be handled and packaged incinerations in accordance with the NIH medical-pathological waste disposal system. Potentially infectious waste (*e.g.*, tissue cultures) containing osmium tetroxide shall be packaged for incineration, as above. Burnable waste (*e.g.*, absorbent bench top liners) minimally contaminated with osmium tetroxide shall be handled as potentially infectious waste and packaged for incineration, as above. Absorbent materials (*e.g.*, associated with spill cleanup) grossly contaminated shall be handled in accordance with the chemical waste disposal system. Radioactive waste containing osmium tetroxide shall be handled in accordance with the NIH radioactive waste disposal system.
4. Storage: store solutions of osmium tetroxide in dark-colored, tightly closed containers, preferably under refrigeration. Store solid osmium tetroxide in sealed ampoules or in bottles with caps with polyethylene cone liners inside a sealed secondary container. Avoid exposure to dust or other organic materials. Store working quantities of osmium tetroxide and its solutions in an explosion-safe refrigerator in the work area.

E. Monitoring and Measurement Procedures Including Direct Field Measurements and Sampling for Subsequent Laboratory Analysis

1. Sampling: No methods have been published for sampling of osmium tetroxide in environmental air, evidently because the need has not been established. A Russian publication mentions sampling by absorption in 0.01 M sodium hydroxide (Lukovskaya and Terletskaya, 1974).
2. Analysis: Most methods have been developed for the purpose of determining osmium metal in ore samples; however, since these methods involve as intermediary steps oxidation to the tetroxide (*e.g.*, with potassium permanganate) they should be applicable to osmium tetroxide directly. Customarily it is extracted into chloroform for separation from interfering substances. A colorimetric method, involving distillation, reduction with stannous chloride, and addition of thiourea to form a pink color,

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has been a standard procedure for many years. The useful range is 0-1,000 $\mu\text{g Os}$ (McLaughlin et al., 1946). Direct ultraviolet spectroscopy or colorimetry of the complex of osmium tetroxide with 1,5-diphenylcarbohydrazide has been adapted to cover a variety of sensitivity ranges (Goldstein *et al.*, 1961a, 1961b, 1961c). Osmium tetroxide as a catalyst in the reaction $\text{As(III)} \text{ (colorless)} + 2\text{Ce(IV)} \text{ (yellow)} - \text{As(V)} \text{ (colorless)} + 2\text{Ce(III)} \text{ (colorless)}$ has been used to determine nanogram amounts of osmium (Sauerbrunn and Sandell, 1953; Sandell and Onishi, 1978), and lower amounts have been determined by the catalyzed reaction of hydrogen peroxide with cyanocuprate. This reaction may be monitored by amperometry or potentiometry, or by chemiluminescence after addition of luminal. The lowest determinable concentration is 0.03 ng Os per ml (Ling and Svehla, 1984).

F. Biological Effects (Animal and Human)

1. Absorption: Osmium tetroxide is absorbed mainly by inhalation. Exposure of the eyes, skin, and nose produces severe irritant effects, but it is not known if systemic intoxication follows exposure by these routes.
2. Distribution: No data. A great deal of inhaled osmium tetroxide is reduced and “plated out” along the respiratory tract immediately upon contact with mucous membranes.
3. Metabolism and excretion: No data.
4. Toxic effects: The acute and chronic toxicity of osmium tetroxide is difficult to assess. The Registry of Toxic Effects of Chemical Substances cites LD50 values of 14 mg/kg (rat, oral and mouse, intraperitoneal) and 162 mg/kg (mouse, oral) from an unpublished Shell Chemical Company report. Inhalation studies were carried out on rabbits (Brunot, 1933). The author of the latter study has pointed out that the vapor concentration to which the animals were exposed could not be evaluated because of the rapid reduction of osmium tetroxide by the skin, hair, mucous membranes, and excreta of the experimental animals as well as by the chamber walls. All rabbits exposed to initial amounts of 250 and 1,000 mg in a 190 liter chamber died in an average of 4 days and 30 hours, respectively, with purulent bronchopneumonia and kidney involvement.

Seven cases of exposure of industrial workers to osmium tetroxide vapors during osmiridium refining operations have been reported (McLaughlin et al., 1946). Exposure concentrations were estimated at 130-640 $\mu\text{g Os per m}^3$. Exposed individuals evidenced a “gritty” feeling in the eyes (shown to be due to particles, possibly of osmium metal, on the cornea) with pain and lacrimation, and a typical halo effect around all lights which prevented clear vision for several hours. There was strong irritation of the mucous membranes of nose, throat, and bronchi. All effects lasted for 12-24 hours and there appeared to be no chronic or cumulative effects. Only one death due to accidental inhalation of osmium tetroxide, attributed to bronchial pneumonia, has been reported (Raymond, 1874). In a review (Sittig, 1979) it has been noted that prolonged exposure may lead to corneal damage and blindness and that skin contact results in a green or black discoloration which on prolonged contact may produce dermatitis and ulceration. It is unlikely that any of these systems develop under usual laboratory conditions because of the early warning effects (eye irritation, odor) of exposure.

5. Carcinogenic effects: None have been reported.
6. Mutagenic and teratogenic effects: A mutagenic effect of osmium tetroxide on *B. subtilis* has been reported (Kanematsu et al., 1980).

G. Emergency Treatment

1. Skin and eye exposure: For skin exposure, remove contaminated clothing and wash skin with soap and water. Skin should not be rinsed with organic solvents. Avoid rubbing of skin or increasing its

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temperature. For eye exposure, irrigate immediately with copious quantities of running water for at least 15 minutes. Obtain ophthalmological evaluation.

2. Ingestion: Drink plenty of water or milk. Induce vomiting. Refer for gastric lavage.
3. Inhalation: Remove victim promptly to clean air. Administer rescue breathing if necessary.
4. Refer to physician at once. Consider treatment for pulmonary irritation.

H. References

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