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Hydrogen Sulfide in Drinking-water

Background document for development of
WHO *Guidelines for Drinking-water Quality*

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Preface

One of the primary goals of WHO and its member states is that "all people, whatever their stage of development and their social and economic conditions, have the right to have access to an adequate supply of safe drinking water." A major WHO function to achieve such goals is the responsibility "to propose regulations, and to make recommendations with respect to international health matters ...."

The first WHO document dealing specifically with public drinking-water quality was published in 1958 as International Standards for Drinking-Water. It was subsequently revised in 1963 and in 1971 under the same title. In 1984–1985, the first edition of the WHO Guidelines for drinking-water quality (GDWQ) was published in three volumes: Volume 1, Recommendations; Volume 2, Health criteria and other supporting information; and Volume 3, Surveillance and control of community supplies. Second editions of these volumes were published in 1993, 1996 and 1997, respectively. Addenda to Volumes 1 and 2 of the second edition were published in 1998, addressing selected chemicals. An addendum on microbiological aspects reviewing selected microorganisms was published in 2002.

The GDWQ are subject to a rolling revision process. Through this process, microbial, chemical and radiological aspects of drinking-water are subject to periodic review, and documentation related to aspects of protection and control of public drinking-water quality is accordingly prepared/updated.

Since the first edition of the GDWQ, WHO has published information on health criteria and other supporting information to the GDWQ, describing the approaches used in deriving guideline values and presenting critical reviews and evaluations of the effects on human health of the substances or contaminants examined in drinking-water.

For each chemical contaminant or substance considered, a lead institution prepared a health criteria document evaluating the risks for human health from exposure to the particular chemical in drinking-water. Institutions from Canada, Denmark, Finland, France, Germany, Italy, Japan, Netherlands, Norway, Poland, Sweden, United Kingdom and United States of America prepared the requested health criteria documents.

Under the responsibility of the coordinators for a group of chemicals considered in the guidelines, the draft health criteria documents were submitted to a number of scientific institutions and selected experts for peer review. Comments were taken into consideration by the coordinators and authors before the documents were submitted for final evaluation by the experts meetings. A "final task force" meeting reviewed the health risk assessments and public and peer review comments and, where appropriate, decided upon guideline values. During preparation of the third edition of the GDWQ, it was decided to include a public review via the world wide web in the process of development of the health criteria documents.

During the preparation of health criteria documents and at experts meetings, careful consideration was given to information available in previous risk assessments carried out by the International Programme on Chemical Safety, in its Environmental Health

Criteria monographs and Concise International Chemical Assessment Documents, the International Agency for Research on Cancer, the joint FAO/WHO Meetings on Pesticide Residues, and the joint FAO/WHO Expert Committee on Food Additives (which evaluates contaminants such as lead, cadmium, nitrate and nitrite in addition to food additives).

Further up-to-date information on the GDWQ and the process of their development is available on the WHO internet site and in the current edition of the GDWQ.

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GENERAL DESCRIPTION

Identity

CAS no.: 7783-06-4
Molecular formula: H_2S

Physicochemical properties *(1,2)* [Conversion factor in air: 1 mg/m^3 = 0.670 ppm]

Property	*Value*
Physical appearance	Colourless gas
Melting point	-85.5 °C
Boiling point	-60.7 °C
Density	1.54 g/litre at 0 °C
Water solubility	4370 ml/litre at 0 °C; 1860 ml/litre at 40 °C
Vapour pressure	1875 kPa at 20 °C

Organoleptic properties

Hydrogen sulfide has an offensive "rotten eggs" odour that is detectable at very low concentrations in air, below 8 µg/m^3 (*3*). At concentrations of 50–150 mg/m^3 in air, it has a deceptively sweet smell; above this range, it deadens the sense of smell (*4*). In water, the taste and odour thresholds for hydrogen sulfide are estimated to be between 0.05 and 0.1 mg/litre. The taste and odour threshold for sulfides is about 0.2 mg/litre (*5*).

Major uses

The major uses of hydrogen sulfide include its conversion into sulfur and sulfuric acid and the manufacture of inorganic sulfides, thiophenes, thiols, thioaldehydes, and thioketones. It is used in dye manufacturing, tanning, the production of wood-pulp, chemical processing, and the manufacture of cosmetics. Spring waters that contain elevated concentrations of hydrogen sulfide are used for therapeutic medicinal baths (*1*).

Environmental fate

Hydrogen sulfide is formed when soluble sulfides are hydrolysed in water. In water, hydrogen sulfide dissociates, forming monohydrogensulfide(1-) (HS^-) and sulfide (S^{2-}) ions. The relative concentrations of these species are a function of the pH of the water, hydrogen sulfide concentrations increasing with decreasing pH. At pH 7.4, about one-third exists as undissociated hydrogen sulfide and the remainder largely as the monohydrogensulfide(1-) anion (*6*). The sulfide is present in appreciable concentrations above pH 10 (*1*). In well aerated water, hydrogen sulfide is readily oxidized to sulfates and biologically oxidized to elemental sulfur. In anaerobic water, microbial reduction of sulfate to sulfide can occur (*7*).

ANALYTICAL METHODS

Hydrogen sulfide is traditionally determined using an acid displacement procedure (*8,9*); the hydrogen sulfide is displaced by acidification, followed by analysis by gas chromatography using a flame photometric detector. The procedure has been used for water, sewage, and effluents containing 0–2.0 mg of sulfide per litre with a detection limit of about 0.25 mg of sulfur per litre (*9*). A estimated lower detection limit of 0.06 mg/litre has been reported for a similar method (*10*). The methylene blue colorimetric method is another standard analytical procedure for hydrogen sulfide determination, at concentrations ranging between 0.1 and 20

mg/litre (*11*). A number of methods have been developed for the determination of sulfide (*11,12*).

ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

Air

Hydrogen sulfide is present in air primarily as a result of natural emissions. Concentrations generally vary from 0.1 to 1 μg/m^3 in ambient air, although concentrations above 100 μg/m^3 have been reported near industrial plants (*3*). An estimated daily intake of 2–20 μg can be calculated on the assumption that 20 m^3 of air containing hydrogen sulfide at natural concentrations is inhaled.

Water

Most of the hydrogen sulfide present in raw waters is derived from natural sources and industrial processes. It is particularly noticeable in some groundwaters, depending on source rock mineralogy and microorganisms present (*13*). In the USA, a maximum concentration of 500 μg of undissociated hydrogen sulfide per litre has been reported in fresh water (*14*).

Food

A number of foodstuffs and drinks may contain sulfides. However, estimation of exposure from food is complicated by the formation of sulfides in cooked foods. Levels in heated dairy products range from 0.8 mg/litre in skimmed milk (0.1% fat) to 1.84 mg/litre in cream (30.5% fat). The hydrogen sulfide content of cooked meat ranges from 0.276 mg/kg for beef to 0.394 mg/kg for lamb. Hydrogen sulfide is formed principally from the sulfur-containing amino acids in meat protein, levels being higher in anaerobically packaged meat. Dimethyl sulfide is used in the manufacture of jellies, candy, soft drinks, and cream in the United Kingdom, where the maximum probable intake has been estimated at 1.7 mg/day (*15*).

KINETICS AND METABOLISM IN LABORATORY ANIMALS AND HUMANS

Hydrogen sulfide and soluble alkali sulfides are rapidly absorbed following ingestion (*7*). Inhaled hydrogen sulfide has been shown to be distributed to the brain, liver, kidneys, pancreas, and small intestine (*16*). It is metabolized mainly by the liver, the two routes being oxidation to sulfate and methylation to methanethiol and dimethyl sulfide (*17*). Sulfides and sulfates are rapidly excreted via the kidneys in experimental animals, but a small proportion of the sulfides may also be excreted via the lungs. Some metallic sulfides are excreted in the faeces (*1*).

EFFECTS ON LABORATORY ANIMALS AND *IN VITRO* TEST SYSTEMS

Acute exposure

Oral LD_{50} values of 205 and 208 mg/kg of body weight were reported in the mouse and rat, respectively, for sodium sulfide (Registry of Toxic Effects of Chemical Substances, 1989, unpublished data).

Short-term exposure

Dimethyl sulfide given daily at an oral dose of 250 mg/kg of body weight for 14 weeks was found to produce no ill effects in rats. This dose is equivalent to a daily intake of 15 g by a 60-kg adult. However, hydrogen sulfide has been reported to be more toxic than dimethyl sulfide by a factor of 50 (*18*).

Reproductive toxicity, embryotoxicity, and teratogenicity

The ingestion of "thermal" mineral water containing 4–12 mg of hydrogen sulfide per litre was embryotoxic in rats, whereas water containing 2–3 mg/litre had no effect. However, the significance of these findings is doubtful, as few experimental details were published and the mineral water contained numerous other substances (*19*). No effects on pregnancy were seen other than a dose-dependent increase in delivery time in female rats exposed to 112 mg/m^3 hydrogen sulfide from day 6 of gestation until day 21 postpartum. In addition, no significant effects on the growth and development of pups were seen (*20*).

Mutagenicity and related end-points

Hydrogen sulfide was not mutagenic in *Salmonella typhimurium* strains TA97, TA98, or TA100, with or without metabolic activation (*21*). Chromosomal aberrations have been reported in the bone marrow of adult rats exposed to 10 mg/m^3 for 3–4 months (*22*). Hydrogen sulfide has been shown to increase the mutagenicity of hydrogen peroxide in *S. typhimurium* strain TA102 (*23*). This may be significant where hydrogen peroxide is employed as an oxidizing agent in water-treatment processes.

Carcinogenicity

In a study in which Charles River CD male and female rats were administered 9 or 18 mg of sodium sulfide per kg of body weight in water by gavage in either the presence or absence of a 1% thyroid extract at least twice a week for 78 weeks, no evidence of carcinogenicity was found. Because of the high mortality in all treated and control groups, the validity of the results is questionable (*24*).

EFFECTS ON HUMANS

No data are available on the oral toxicity of hydrogen sulfide. However, alkali sulfides irritate mucous membranes and can cause nausea, vomiting, and epigastric pain following ingestion. The oral dose of sodium sulfide fatal to humans has been estimated at 10–15 g (*1*).

When inhaled, hydrogen sulfide is highly acutely toxic to humans (*25*). Its rapid mode of action involves the formation of a complex with the iron(III) ion of the mitochondrial metalloenzyme cytochrome oxidase, thereby blocking oxidative metabolism (*4,25*). Other enzymes reported to be inhibited by sulfides are succinate dehydrogenase, adenosinetriphosphatase, DOPA oxidase, carbonic anhydrase, dipeptidase, benzamidase, and some enzymes containing iron such as catalase and peroxidases (*1*). Reduction of disulfide bridges in proteins has been suggested as a mechanism whereby enzyme function could be altered (*3*). Irritation of the eyes and respiratory tract can be observed at concentrations of 15–30 mg/m^3, and concentrations of 700–1400 mg/m^3 can cause unconciousness and respiratory paralysis resulting in death (*3*).

Few studies on prolonged exposure to low concentrations of hydrogen sulfide have been undertaken. In one study, the reticulocytes of 17 workers engaged in wood-pulp production who were exposed to low levels of hydrogen sulfide and methylthiols were analysed (*26*). The activities of a number of enzymes involved in the haem biosynthetic pathway were inhibited, although the mechanism is unclear.

CONCLUSIONS

The taste and odour threshold for hydrogen sulfide in water has been estimated to be as low as 0.05 mg/litre. Although oral toxicity data are lacking, it is unlikely that anyone could

consume a harmful dose of hydrogen sulfide in drinking-water. Consequently, no health-based guideline value is proposed. However, hydrogen sulfide should not be detectable in drinking-water by taste or odour

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