Sulphide (as H₂S)

The presence of sulphide (as hydrogen sulphide) in drinking water results in disagreeable taste and odour; an aesthetic objective of *≤0.05 mg/L (≤50 µg/L)* (expressed as hydrogen sulphide) has therefore been established.

General

Sulphur is a non-metal. Its most common valences are −2, +4 and +6; the −2 reduction state is known as sulphide. Sulphide occurs naturally in mineral ores, oil and coal deposits. In the majority of cases, copper, lead, zinc, nickel and other base metals mined in Canada occur as simple or complex sulphides. Iron sulphides are often associated with these ores.[1]

Hydrogen sulphide, which exists as a colourless gas under normal conditions, also occurs naturally in coal, natural gas, oil, volcanic gases and sulphur springs and lakes. It is a product of the anaerobic decomposition of sulphur-containing organic matter, and other sulphur compounds are nearly always present with the hydrogen sulphide in these natural occurrences. The gas has a characteristic odour of rotten eggs.[2]

Other sulphides are also generated by sulphate-reducing bacteria through anaerobic decomposition of sewage, algae, naturally deposited organic matter[3–5] and the sulphur found in fungicides, pesticides and fertilizers.[6,7] Sulphides are also present in industrial wastes from petroleum and petrochemical plants, gas works, paper mills, heavy water plants and tanneries.[3,4,8,9]

The average concentration of sulphur in the earth's crust is estimated to be in the range of 260 to 520 mg/kg. In seawater, the average concentration of sulphur is 884 mg/L.[10] In living organisms, the mean sulphide concentration is 1.4 mg/kg[11]; sulphur in the −2 reduction state is found directly bonded to carbon in amino acids, vitamins, enzymes and other proteins.[12] Sulphides form an indispensable link in the "sulphur cycle" (the reversible interconversion of sulphide and sulphate) in nature.[13]

Dimethyl sulphide is used as a constituent of artificial flavouring agents.[14] Hydrogen sulphide and other soluble sulphides are utilized in pigment and dye manufacturing, tanning and pulp and chemical processing. They are also employed in the production of cosmetics.[15] Natural waters containing elevated concentrations of hydrogen sulphide are used for therapeutic baths and have been consumed for medical purposes.

Canadian production of hydrogen sulphide by manufacturers of pigments and dye colours amounted to 10.7 tonnes in 1974. Manufacturers of industrial chemicals produced 2461 tonnes of hydrogen sulphide during the same period.[16] Canadian consumption of hydrogen sulphide by manufacturers of industrial chemicals was 3153 tonnes in 1980.[17] The importation of several sulphide compounds into Canada amounted to 1594 tonnes in 1982.[18]

Occurrence

Hydrogen sulphide and sulphides of the alkali and alkaline earth metals are soluble in water.[19] Soluble sulphide salts dissociate into sulphide ions that react with the hydrogen ions in water to form the hydrosulphide ion (HS⁻) or hydrogen sulphide (H₂S). The relative concentrations of these species are a function of the pH of the water; hydrogen sulphide concentrations increase with decreasing pH.[3,4] In polluted waters, therefore, where the pH can be neutral or acidic, the potential for hydrogen sulphide formation is increased.

Temperature, salinity and dissolved oxygen also affect the amount of hydrogen sulphide found in the undissociated form. Temperature affects the dissociation constants of hydrogen sulphide. The proportion of undissociated hydrogen sulphide has been shown to decrease with increasing salinity for a given temperature and pH. However, this effect is negligible in fresh waters and becomes significant only in estuarine and coastal waters.[20] Levels of undissociated hydrogen sulphide were undetectable in Florida Bay,[21] and a maximum concentration of 14 µg/L has been recorded for the Arabian Sea.[22].

Oxidation of hydrogen sulphide is also a function of temperature, pH and ionic strength. The rate of hydrogen sulphide oxidation was found to increase with increasing temperature and pH up to pH 8. Above pH 8, the rate was found to be independent of pH. In addition, the rates of oxidation were higher in seawater than in air-saturated water.[23] In well-aerated water, hydrogen sulphide is oxidized to sulphates or to elemental sulphur

by natural biological systems.[24] Sulphides can also react chemically with dissolved oxygen, but this is thought to be a slow and complex process producing a variety of products, including thiosulphate, sulphite and sulphate.[25]

The oxidation of aqueous sulphide by oxygen is slow in the absence of a catalyst. Catalysis was, in decreasing order, most effective in the presence of Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+} and Cu^{2+}. In the presence of nickel, for instance, the oxidation rate of sulphide was increased from several days to a few minutes.[26]

The reduction of sulphate to sulphide occurs in nature under anaerobic conditions in the presence of sulphate-reducing bacteria and a source of organic carbon. These conditions have been encountered in deep water wells in Elgin, Illinois, where concentrations of 6.4 mg/L of hydrogen sulphide and only 2.0 mg/L of sulphate were measured.[26] Natural waters where dissolved oxygen has been completely exhausted include the Black Sea, the Baltic Sea and certain fjords along the coasts of Norway and western Canada.[20] A concentration of 7 mg/L of undissociated hydrogen sulphide has been reported from an anoxic region of the Black Sea at depths of around 200 m.[21]

At St. Paul, Minnesota, the sulphide concentration in the Mississippi River was found to be 0.092 mg/L; concentrations in pond and well water were somewhat higher — 0.16 and 0.19 mg/L, respectively.[27] In the Rainy River, along the border between Ontario and Minnesota, the mean hydrogen sulphide concentration was 0.07 mg/L within 20 mm of the bottom of sludge beds and ranged from non-detectable to 0.06 mg/L at the surface.[9]

Levels of hydrogen sulphide are not routinely measured in water in the United Kingdom or in other European Community member states. However, two studies of freshwater systems in the United States have reported concentrations of undissociated hydrogen sulphide of 500 μg/L.[28,29] Concentrations of sulphide in Canadian surface water ranged from 1.0 to 11.0 mg/L during the 1980 to 1982 period in western Canada.[30]

Levels of sulphides in drinking water will usually be low because the sulphides are readily oxidized in well-aerated water. Under the aerobic conditions most often encountered in public water supplies, the ultimate product of sulphide oxidation is sulphate. The intermediates, sulphite and thiosulphate, may persist for long periods of time.[26] The presence of sulphate-reducing bacteria in water distribution systems can be a major cause of taste and odour problems in drinking water because of the formation of sulphides from sulphate.

Estimates of air concentrations of hydrogen sulphide due to natural sources range from 0.15 to 0.46 μg/m³.[8] In urban areas, the general population is not usually exposed to concentrations above 1.0 μg/m³.[31] In industrialized areas, hydrogen sulphide

concentrations are significantly higher. At the "Reversing Falls" bridge in Saint John, New Brunswick, which is 400 m downwind from a kraft-process pulp and paper mill, the concentration of hydrogen sulphide in air ranged from 4.56 to 198.0 μg/m³.[32] The National Research Council of Canada has calculated the yearly biogenic discharge of sulphide into the Canadian atmosphere to be 4.02 $\times$ 10^6 tonnes from land and 1.0 $\times$ 10^6 tonnes from oceans.[33]

Soil is an important sink for hydrogen sulphide. Dry and moist soils are equally effective in the sorption of hydrogen sulphide from the air.[32,34] Microorganisms generate sulphides from sulphur compounds in the soil. In the United States, the concentration of sulphides in tidal flat soils in Oregon ranged from 116 to 188 mg/kg.[35]

Sulphides, in various forms, are also present in a number of cooked and raw foods. Generally, concentrations are in the range of 0.0002 to 0.003 mg/g, although the concentration of S-methylmethionine may reach 0.015 mg/g.[36] Dimethyl sulphide is an important flavour compound in British ales (0.0002 to 0.0037 mg/L) and European lager beers (0.003 to 0.114 mg/L).[9] In heated dairy products, hydrogen sulphide is present at concentrations ranging from 0.80 mg/L in skimmed milk with a fat content of 0.1 percent to 1.84 mg/L in cream, which contains 30.5 percent fat.[37]

Canadian Exposure

The daily dietary intake of sulphides by Canadians has not been estimated. Data on the sulphide content of foodstuffs are incomplete. Exposure may result from the consumption of beer and ale, seafood, cooked meat, warm milk, asparagus and other vegetables. Estimation of exposure from foods is further complicated by the evolution of sulphide compounds from cooked foods. In England, the "maximum likely daily intake" of dimethyl sulphide from artificially flavoured candies, soft drinks, creams and jellies was estimated to be 1.7 mg.[38]

The intake of sulphide from drinking water cannot be estimated, as data on sulphide concentrations in drinking water have not been found.

The inhalation of 20 m³ of air containing hydrogen sulphide at natural concentrations would result in a daily intake of 0.003 to 0.02 mg.

Analysis

Methods for the analysis of sulphides in water include the traditional acid displacement procedure, where the hydrogen sulphide liberated by acidification of sulphides is displaced in a stream of carbon dioxide and titrated after absorption in zinc acetate solution. The detection limit of the standard method is approximately 0.25 mg/L.[39] A concentration of 0.06 mg/L has been determined by another method that uses the same principle.[40]

A more recent method involves a gas chromato-graphic technique that uses a modified Hall electrolytic conductivity detector. With this method, simultaneous determination of seven or more different volatile sulphur species in water is possible. Detection limits (as sulphur) of 0.03 ng/L for hydrogen sulphide can be achieved for a 100-mL sample. The precision is better than 10 percent for the range of 1 to 4000 ng/L (as sulphur).[41]

The methylene blue colorimetric method is also generally recognized as a standard analytical procedure for hydrogen sulphide determinations that has quite satisfactory specificity, accuracy and sensitivity.[31] A range of 0 to 20 mg/L may be determined using the methylene blue method of colour development and spectrophotometric determination.[42]

A recent procedure for the determination of total sulphide in zinc acetate-preserved environmental waters has been developed. This method avoids both the turbidity interferences of the methylene blue colori-metric procedure and the need for zinc ion preservation of field samples. The detection limit for this method is 1.9 ng/L, and good agreement was found between gas dialysis/ion chromatography and methylene blue methods.[43]

Treatment Technology

Sulphide control could be undertaken at the raw water source, in the treatment process train or by pre-ventative measures for generation within the distribution system.

Hydrogen sulphide is typically removed from water by aeration or by chemical oxidation. Different configurations of aeration devices utilized at water treatment plants range from simple and mechanical aeration to the more complex packed tower aerators.[44] It was found that optimum hydrogen sulphide removal by aeration occurred below pH 6.[45] Generally, hydro-gen sulphide levels of 0.05 mg/L could be attained using these methods.

Oxidants used for sulphide oxidation include chlorine, potassium permanganate, ozone and ferrate, as well as hydrogen peroxide.

Health Considerations

Absorption, Distribution and Excretion

Hydrogen sulphide is rapidly absorbed into the body, almost exclusively through inhalation. At average physiological pH (around 7), one-half of hydrogen sulphide is undissociated, whereas the remainder exists as the hydrosulphide ion. Undissociated hydrogen sulphide is a lipophilic molecule, capable of diffusing across membranes,[33,46] including skin.[47,48] Soluble sulphides are promptly and completely hydrolysed in body fluids to produce hydrogen sulphide, so that, in terms of their systemic effects, no toxicological distinctions are recognized between them and hydrogen sulphide.[2]

Hydrogen sulphide disposition studies in humans have not been reported. A qualitative disposition study to identify hydrogen sulphide after inhalation exposure in rats and guinea pigs indicated that hydrogen sulphide was distributed to the brain, liver, kidneys, pancreas and small intestine.[49] Other studies reported that absorbed hydrogen sulphide is found in blood plasma, principally bound to albumin,[47] and is distributed in the bones, spleen, lungs, liver, kidneys, pancreas and small intestine.[33,50]

The metabolism of hydrogen sulphide follows three distinct pathways: (1) oxidation to sulphate, which is the major metabolic pathway, (2) methylation[51] and (3) reaction with metallo- or disulphide-containing proteins. The first two pathways could be regarded as detoxif-ication routes, whereas the reaction of hydrogen sulphide with essential proteins is largely responsible for the toxic action of hydrogen sulphide.[50]

Oxidation of sulphide to sulphate and subsequent excretion by the kidney is the major metabolic excretory pathway.[52] It has been shown that the majority of an oral, intraperitoneal or intravenous dose of radiolabelled sodium sulphide in rats was excreted in the urine as sulphate in the first six to 12 hours after dosing.[47] Another study also found that ingested hydrogen sulphide is excreted principally in the urine as sulphate.[10]

Toxic Effects

The oral ingestion of alkali sulphides has been reported to cause nausea, vomiting and epigastric pain, as well as irritate the mucous membranes; it has been estimated that an oral dose of 10 to 15 g sodium sulphide would be fatal to humans.[53,54] As this is a relatively large dose and there is an intestinal enzymatic detoxification system to handle endogenously produced sulphide, the low amounts of sulphide likely to be found in drinking water are not expected to produce toxic effects.

The acute toxicity of inhaled hydrogen sulphide is well documented and includes effects on the respiratory, cardiac and nervous systems.[50,55,56] The chief toxic effects are associated with the deactivation of enzymes, either through the cleavage of their disulphide bridges or by the binding of sulphide to metal co-factors such as Fe^{2+}, Mg^{2+} or Cu^{2+}. In this manner, key enzymes such as cytochrome oxidase, alkaline phosphatase and carbonic anhydrase can be irreversibly denatured.[33]

A study of the human health consequences associated with prolonged low-level exposure to hydrogen sulphide, such as might be encountered under conditions of general urban air pollution, has not yet been carried out.[50]

No reports of toxic effects due to hydrogen sulphide present in drinking water have been found. However, it is worth noting that although sulphites can persist in water for long periods of time, they are not stable.[26]

Few data appear in the open literature on exposure by the oral route or on any ill effects attributable to chronic exposure. The Registry of Toxic Effects of Chemical Substances[57] reported oral LD_{50} values of 205 and 208 mg/kg for sodium sulphide in the mouse and rat, respectively. Sodium sulphide was given intraperitoneally to CD-1 female mice and was found to have an LD_{50} between 40 and 50 mg/kg. When sodium sulphide was administered intravenously to male and female rabbits, 6 mg/kg killed five of six test animals in less than two minutes.[58] A dose of 4 mg hydrogen sulphide per kilogram body weight was lethal in dogs when injected into the jugular vein.[59]

In a subchronic study, dimethyl sulphide administered orally at a dose of 250 mg/kg per day for a period of 14 weeks was found to produce no ill effects in rats.[14]

No studies on chronic exposure to hydrogen sulphide were found in the open literature.

Charles River CD rats (26/sex/group) were administered 9 or 18 mg/kg of sodium sulphide in water by gavage either in the presence or in the absence of a 1 percent thyroid extract. The animals were treated twice a week during the first 56 weeks of the study and given two to three doses per week thereafter. Treatment was terminated at week 78, after which animals were observed for another 26 weeks. Treated males without the 1 percent thyroid extract had a significant association of mortality with dose. However, this association was not found in treated males with the 1 percent thyroid extract. Treated females with thyroid extract did exhibit a higher mortality, but the significance was not specified. Controls were also found to show poor survival. The results were termed "ambiguous" by the authors. No evidence for the carcinogenicity of sodium sulphide was found.[60]

Few *in vitro* studies have been performed with hydrogen sulphide to determine its mutagenic potential. It was tested with strains TA97, TA98 and TA100, both with and without Aroclor-induced hamster and rat liver S-9, and was not found to be mutagenic.[61] In another study, addition of hydrogen sulphide (as sodium sulphide) to the incubation medium in the presence of hydrogen peroxide dramatically increased the toxicity and error-prone mutation rate induction of hydrogen peroxide.[62] This may be significant where hydrogen peroxide is employed as an oxidizing agent in water treatment processes. One *in vivo* study exposed rats (strain unspecified, route probably inhalation) to hydrogen sulphide or carbon disulphide for three to four months, inducing chromosomal aberrations (aneuploidy,

deletions, acentric fragmentation) in the bone marrow of the adult rats and decreasing the mitotic index in the kidney and liver cells of developing embryos.[63]

In a reproduction study, hydrogen sulphide was reported to be embryotoxic and to have an adverse effect upon reproductive function in rats. However, the lack of study details and questionable research methods cast doubt on the results. Thermal mineral waters containing high levels of hydrogen sulphide were used as the test substance where rats (strain and number not specified) were immersed and orally administered (length of time and exact dose not specified) water containing various levels of hydrogen sulphide. Water containing 4 to 12 mg/L of hydrogen sulphide was found to be embryo-toxic (through both oral and dermal exposure), and levels of 2 to 3 mg/L had no effect. The presence of other contaminants in the water was not taken into consideration.[64]

In another study, hydrogen sulphide of mineral origin at levels of <0.2 mg/L in drinking water from an artesian well had little effect on haematological, bacteriological, histological and biological functions of three-month-old chicks (duration of exposure not specified).[65]

Exposure by inhalation of female rats to hydrogen sulphide with carbon disulphide at 10 mg/m^3 for 70 to 90 days before and during gestation was found to be lethal to embryos at the pre- and post-implantation stages. Embryotoxic effects were also observed when hydrogen sulphide was inhaled by males before mating with untreated females. Abnormalities were observed in the urogenital and bone systems of the embryos. Disturbances in ossification and blood formation and dystrophic changes in the liver and kidneys were also observed. However, the contribution of hydrogen sulphide to these effects was unknown because of the presence of carbon disulphide.[66]

Other Considerations

The taste and odour thresholds for hydrogen sulphide in aqueous solutions are estimated to be in the range of 0.05 to 0.104 mg/L[3,6]; for sulphides, the taste and odour threshold is about 0.2 mg/L. It is unlikely, therefore, that any person would consume a harmful dose of hydrogen sulphide in drinking water because of the unpleasant taste and odour.[3]

Hydrogen sulphide solutions have the properties of a weak acid and can therefore promote corrosion.[67] In a few cases, deterioration of asbestos-cement pipe may be curtailed by removing hydrogen sulphide, which may attack the pipe under low-pH conditions.[68] Hydrogen sulphide, in association with soluble iron, produces black stains on laundered items and can cause black deposits in water distribution pipes and on fixtures and silverware.[10,15,69]

Rationale

1. Excessive concentrations of sulphides in drinking water result in disagreeable tastes and odours. Although oral ingestion of large quantities of sulphide can produce toxic effects in humans, it is unlikely that an individual would consume a harmful dose from drinking water because of the unpleasant taste and odour. Therefore, a maximum acceptable concentration has not been set.

2. The taste and odour thresholds for hydrogen sulphide in aqueous solutions are estimated to be in the range of 0.05 to 0.104 mg/L. For other sulphides, the thresholds are higher. The oxidation of sulphide to sulphate in well-aerated waters should ensure that sulphide concentrations in public water supplies are very low.

3. Thus, the aesthetic objective for sulphide (as hydrogen sulphide) in drinking water is ≤0.05 mg/L. The quantity of sulphide ingested from drinking water containing sulphide at this concentration is well below the amount that the body can detoxify.

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