Environmental Health Criteria 19

Hydrogen Sulfide

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World Health
Organization

IPCS INTERNATIONAL PROGRAMME ON CHEMICAL SAFETY

ENVIRONMENTAL HEALTH CRITERIA 19

Hydrogen Sulfide

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Published under the joint sponsorship of the United Nations Environment Programme, the International Labour Organisation, and the World Health Organization

World Health Organization

Geneva, 1981

ISBN 92 4 154079 6

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NOTE TO READERS OF THE CRITERIA DOCUMENTS

While every effort has been made to present information in the criteria documents as accurately as possible without unduly delaying their publication, mistakes might have occurred and are likely to occur in the future. In the interest of all users of the environmental health criteria documents, readers are kindly requested to communicate any errors found to the Division of Environmental Health, World Health Organization, Geneva, Switzerland, in order that they may be included in corrigenda which will appear in subsequent volumes.

In addition, experts in any particular field dealing with in the criteria documents are kindly requested to make available to the WHO Secretariat any important published information that may have inadvertently been omitted and which may change the evaluation of health risks from exposure to the environmental agent under examination, so that the information may be considered in the event of updating and re-evaluation of the conclusions contained in the criteria documents.

ENVIRONMENTAL HEALTH CRITERIA FOR HYDROGEN SULFIDE

A WHO Task Group on Environmental Health Criteria for Hydrogen Sulfide met in Geneva from 24 to 28 March 1980. Mr G. Ozolins, Associate Manager, Environmental Health Criteria and Standards, opened the meeting on behalf of the Director-General. The Task Group reviewed and revised the second draft of the criteria document and made an evaluation of the health risks from exposure to hydrogen sulfide.

The first and second drafts were prepared jointly by Dr T. H. Milby of the Environmental Health Associates, Inc., Berkeley, CA, USA, and Dr R. C. Spear of the Department of Biomedical and Environmental Health Sciences, University of California, Berkeley, CA, USA. The comments on which the second draft was based were received from the national focal points for the WHO Environmental Health Criteria Programme in Australia, Belgium, Czechoslovakia, Finland, Federal Republic of Germany, Mexico, New Zealand, Poland, USA and USSR, and from the International Labour Organisation, Geneva, the International Centre for Industry and Environment, France, and the International Petroleum Industry Environmental Conservation Association, London. Comments were also received from Professor M. Katz (Canada) and Professor R. Lilis (USA). Some comments were received after the second draft had been prepared and were reviewed by the Task Group during its meeting. These comments were from the national focal points for the WHO Environmental Health Criteria Programme in Japan and the United Kingdom and from the Commission of the European Communities, Luxembourg, and the International Union of Pure and Applied Chemistry, London.

The collaboration of these national institutions, international organizations and individual experts is gratefully acknowledged. Without their assistance this document could not have been completed.

This document is based primarily on original publications listed in the reference section. However, several recent publications broadly reviewing health aspects of hydrogen sulfide have also been used, including those of the National Research Council, USA (1979) and NIOSH (1977).

Details of the WHO Environmental Health Criteria Programme, including some of the terms frequently used in the documents, can be found in the introduction to the publication "Environmental Health Criteria 1 - Mercury", published by the World Health Organization, Geneva, 1976, now also available as a reprint.

The following conversion factors have been used in this document: hydrogen sulfide: 1 ppm = 1.5 mg/m^3, 1 mg/m^3 = 0.7 ppm.

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Financial support for the publication of this criteria document was kindly provided by the Department of Health and Human Services through a contract from the National Institute of Environmental Health Sciences, Research Triangle Park, North Carolina, USA - a WHO Collaborating Centre for Environmental Health Sciences.

1. SUMMARY AND RECOMMENDATIONS FOR FURTHER STUDIES

1.1 Summary

1.1.1 Properties and analytical methods

Hydrogen sulfide is a colourless gas with a characteristic odour that is soluble in various liquids including water, alcohol, ether, and solutions of amines, alkali carbonates, and bicarbonates. It can undergo a number of oxidation reactions to yield principal products consisting of sulfur dioxide, sulfuric acid, or elemental sulfur. Reaction rates and oxidation products depend on the nature of the oxidizing agent.

The methylene blue colorimetric method has acceptable specificity, accuracy, and sensitivity for hydrogen sulfide determinations, and is generally recognized as a standard analytical procedure. It has been used successfully, in automatic continuous monitoring, but sophisticated maintenance facilities and highly trained technicians are required for this method. Gas chromatography coupled with flame photometric detection is an alternative method for hydrogen sulfide determination, either as a laboratory method or for continuous monitoring in stationary field settings.

Most of the direct-reading methods of hydrogen sulfide determination in the occupational environment are susceptible to various forms of interference. However, methods employing chemical detector tubes appear to be useful in occupational settings, where hazardous levels of hydrogen sulfide can occur. Under these conditions, reliability and accuracy compensate for a certain lack of specificity.

1.1.2 Sources of hydrogen sulfide

Hydrogen sulfide is one of the principal compounds involved in the natural cycle of sulfur in the environment. It occurs in volcanic gases and is produced by bacterial action during the decay of both plant and animal protein. It can also be produced by bacteria through the direct reduction of sulfate. Significant concentrations of hydrogen sulfide occur in some natural gas fields and in geothermally active areas.

Hydrogen sulfide can be formed whenever elemental sulfur or certain sulfur-containing compounds come into contact with organic materials at high temperatures. In industry, it is usually produced as an undesirable by-product, though it is an important reagent or intermediate in some processes. Hydrogen sulfide occurs as a by-product in: the production of coke from sulfur-containing coal, the refining of sulfur-containing crude oils, the production of carbon disulfide, the manufacture of viscose rayon, and in the Kraft process for producing wood pulp.

1.1.3 Environmental levels and exposures

Though concentrations of hydrogen sulfide in urban areas may occasionally be as high as 0.050 mg/m^3 (0.033 ppm) with averaging times of 30 min-1 h, they are generally (below 0.0015 mg/m^3 (0.001 ppm). Peak concentrations as high as 0.20 mg/m^3 (0.13 ppm) have been reported in the neighbourhood of point sources. In a geothermal area, 1-h mean concentrations of up to 2 mg/m^3 (1.4 ppm) have been observed. When hydrogen sulfide was accidentally released in an incident in Poza Rica, Mexico, in 1950, the number of deaths that followed indicated that exposure levels probably exceeded 1500-3000 mg/m^3 (1000-2000 ppm).

It is believed that workers are not usually exposed to hydrogen sulfide concentrations above the occupational exposure limits of 10-15 mg/m^3 (7-10 ppm) (8-h time-weighted average) adopted by many governments. There are, however, numerous reports of accidental exposures to concentrations that have ranged from 150 mg/m^3 (100 ppm) to as high as 18 000 mg/m^3 (12 000 ppm). Such massive exposures to hydrogen sulfide have resulted either from leaks in industrial gas streams containing high levels of hydrogen sulfide or from the slow, insidious accumulation of hydrogen sulfide in low-lying areas. The second case may arise when hydrogen sulfide of biogenic origin is generated from such sources as sewage disposal plants and cesspools.

1.1.4 Effects on experimental animals

In experimental animals, the effects of high doses of hydrogen sulfide and high doses of cyanide are very similar. Cyanide inhibits the enzyme cytochrome *c* oxidase [EC 1.9.3.1] [a], thereby interfering with tissue use of oxygen to the point where metabolic demands cannot be met. Hydrogen sulfide also exhibited an inhibitory action on a purified preparation of cytochrome *c* oxidase.

Results of studies on a number of animal species including canary, rat, guineapig, cat, dog, and goat showed that inhalation of hydrogen sulfide at a concentration of 150-225 mg/m^3 (100-150 ppm) resulted in signs of local irritation of eyes and throat after many hours of exposure; at 300-450 mg/m^3 (200-300 ppm), eye and mucous membrane irritation appeared after 1 h inhalation and slight general effects after prolonged inhalation; at 750-1050 mg/m^3 (500-700 ppm), local irritation and slight systemic signs appeared within 1 h and death after several hours; at 1350 mg/m^3 (900 ppm), serious systemic effects appeared in less than 30 min and death within 1 h; at

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[a] The numbers within brackets following the names of enzymes are those assigned by the Enzyme Commission of the Joint IUPAC-IUB Commission on Biochemical Nomenclature.

2250 mg/m^3 (1500 ppm), collapse and death occurred within 15-30 min; and, at 2700 mg/m^8 (1800 ppm), there was immediate collapse with respiratory paralysis, and death. There is little information on the effects on experimental animals of long-term, low-level exposure to hydrogen sulfide gas.

1.1.5 Effects on man

1.1.5.1 General toxicological considerations

Hydrogen sulfide is both an irritant and an asphyxiant gas. Its direct irritant action on the moist tissues of the eye produces keratoconjunctivitis, known as "gas eye". When inhaled, hydrogen sulfide exerts an irritant action throughout the entire respiratory tract, although the deeper structures suffer the greatest damage. A consequence may be pulmonary oedema. At concentrations of 1500-3000 mg/m^3 (1000-2000 ppm), hydrogen sulfide gas is rapidly absorbed through the lung into the blood, which initially induces hyperpnoea (rapid breathing). This is followed by respiratory inactivity (apnoea). At higher concentrations, hydrogen sulfide exerts an immediate paralysing effect on the respiratory centres. Death due to asphyxia is the certain outcome, unless spontaneous respiration is re-established or artificial respiration is promptly provided. This sequence of events represents the most important toxic effect of hydrogen sulfide.

Acute hydrogen sulfide intoxication can be defined as the effects from a single exposure to massive concentrations of hydrogen sulfide that rapidly produce signs of respiratory distress. Concentrations exceeding about 1500 mg/m^3 (1000 ppm) produce such acute effects. Subacute hydrogen sulfide intoxication is the term applied to the effects of continuous exposure for up to several hours to concentrations ranging from 150 to 1500 mg/m^3 (100-1000 ppm). In this range of exposure, eye irritation is the most commonly observed effect. However, some reports have indicated that the threshold for eye irritation occurs after several hours of exposure to hydrogen sulfide at levels of 16-32 mg/m^3 (10.5-21.0 ppm). Pulmonary oedema may be a more important and potentially fatal complication of subacute hydrogen sulfide intoxication. Chronic intoxication is a largely subjective state characterized by fatigue and believed by some to be a consequence of intermittent exposure to hydrogen sulfide concentrations of 75-150 mg/m^3 (50-100 ppm). Not all research workers accept the existence of such a condition.

The characteristic "rotten egg" odour of hydrogen sulfide is well known. The threshold of perception of this odour varies considerably