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ASSESSMENT OF ACETYLENE AS A POTENTIAL AIR POLLUTION PROBLEM

VOLUME I

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Volume I

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ABSTRACT

This report is one of a series which assesses the potential air pollution impacts of 14 industrial chemicals outside the work environment. Topics covered in each assessment include physical and chemical properties, health and welfare effects, ambient concentrations and measurement methods, emission sources, and emission controls. The chemicals investigated in this report series are:

Volume I	Acetylene
Volume II	Methyl Alcohol
Volume III	Ethylene Dichloride
Volume IV	Benzene
Volume V	Acetone
Volume VI	Acrylonitrile
Volume VII	Cyclohexanone
Volume VIII	Formaldehyde
Volume IX	Methyl Methacrylate
Volume X	Ortho-Xylene
Volume XI	Maleic Anhydride
Volume XII	Dimethyl Terephthalate
Volume XIII	Adipic Acid
Volume XIV	Phthalic Anhydride.

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SECTION I

SUMMARY AND CONCLUSIONS

Pure acetylene is relatively nontoxic to man. It acts as a simple asphyxiant and produces ill effects only by reducing available oxygen. A concentration of 10 percent produces only slight intoxication, and there is no evidence of adverse effects from chronic exposure. Some damage will occur to sensitive plants at concentrations of the order of 100 ppm. Acetylene does not appear to be a significant component of photochemical smog.

Emissions of acetylene are estimated to have been 9 million pounds in 1974. These occur only from manufacturing and end use. Acetylene production and consumption have declined 47 percent since 1966 to a current production of 617 million pounds per year. Although there are no specific processes mentioned in the literature for the control of acetylene emissions, absorber/scrubber systems are used in manufacturing operations for product purification.

Simple diffusion model calculations place maximum expected 1-hour average ambient concentrations at about 5.5 ppm, and at about 3 ppm for 24-hour values near a plant boundary. Urban concentrations of about 80 ppb and rural values of 1 ppb have been measured.

Based on the low toxicity and expected low ambient concentrations, it appears that acetylene does not pose a health or environmental hazard as an air pollutant. Phosphine, a poisonous gas, is often present as an impurity with acetylene, but at such low concentrations (less than 0.06 percent of the mixture) that it generally poses no hazard.

SECTION II

AIR POLLUTION ASSESSMENT REPORT

PHYSICAL AND CHEMICAL PROPERTIES

Pure acetylene is a colorless, odorless gas made up of two hydrogen and two triple-bonded carbon atoms. Commercially it can be made by the hydrolysis of calcium carbide, by thermal cracking or partial combustion of natural gas.[1] The acetylene obtained from the calcium carbide process, the most usual method of manufacture, has a garlic-like odor due to contamination by phosphine, hydrogen sulfide, and ammonia produced from calcium carbide impurities. The oxygen-acetylene torch is used for welding and cutting of metal. The reactive triple bond makes acetylene an ideal starting material for the synthesis of flexible vinyl plastics, rigid plastics, paints, and chlorinated hydrocarbon solvents. Selected physical and chemical properties are presented in Table 1.

HEALTH AND WELFARE EFFECTS

Effects on Man

Acute Poisoning - Pure acetylene is relatively nontoxic. Only at high concentrations does inhalation of the gas begin to affect man, as shown below:[2]

Concentration	Response
100,000 ppm (10%)	Slight intoxication
200,000 ppm (20%)	Marked intoxication
300,000 ppm (30%)	Incoordination
350,000 ppm (35%)	Unconsciousness in 5 minutes

Table 1. SIGNIFICANT PROPERTIES OF ACETYLENE

Synonyms	Ethine, ethyne, narcylene
Chemical formula	$C_2 H_2$
Molecular weight	26.04
Boiling point (sublimes)	-83.6°C
Melting point	-81.8°C
Vapor density	0.9073 (dry air = 1)
Solubility	1.1 volumes of gas per volume of water at 15.5°C
	The gas is soluble in many organic materials.
Explosive limits	2.5% to 85% in air
	2.8% to 93% in oxygen
Auto ignition temperature	Varies with impurities
Pure grade	644°C (100% gas)
Commercial grade	300°C minimum for mixtures of 30-70% in air. Concentrations other than these require higher ignition temperatures.
At 25°C and 760 mm	1 ppm = 1.065 mg/m^3 1 mg/m^3 = 0.939 ppm

The gas acts as a simple asphyxiant, producing ill effects in man only due to a diminished oxygen concentration in the ambient air. Recovery is complete upon removal from the gas. There is no hazard from skin or eye contact, and ingestion is impossible.

Illnesses attributed to acetylene exposure during welding have not been substantiated due to the presence of other hazardous materials, such as metal fumes.[3] With a lower explosive limit of 2.5 percent in air, it is clear that in the presence of a flame, an explosion would occur long before the acetylene could have any effect on man. Two reported deaths[4,5] attributable to acetylene generators were due to phosphine impurities in one case, and a combination of phosphine and acetylene asphyxiation in the second case. In the second case, it was estimated that the operator was exposed to 80 percent acetylene, resulting in unconsciousness and asphyxiation.

Acetylene has been used as an anesthetic, and has been administered both intravenously saturated in a saline solution, and inhaled under controlled conditions at 25 percent concentration in air. In addition, it has been inhaled at 25 percent concentration to measure pulmonary elimination rate in patients with heart or lung disease as an indication of cardiac or pulmonary output.[6] Acetylene is soluble in live lung tissue with no ill effects.[7]

NIOSH has not established a recommended maximum workplace atmospheric concentration value for acetylene. However, the atmospheric concentration should be maintained below 5000 ppm to reduce the hazard of an explosion, or maintained at a lower value depending on the presence of impurities. In the United States raw materials are selected such that carbide-produced acetylene will not contain more than 0.05 percent phosphine, with actual concentrations usually in the vicinity of 0.00025 percent. Since the NIOSH recommended time weighted average value for exposure to phosphine is 0.3 ppm,[8] acetylene containing 0.05 percent phosphine could have maximum ambient concentration of approximately 500 ppm acetylene.[5]

Chronic Poisoning - There is no evidence that chronic exposure to acetylene at tolerable levels has any ill effects on man.[5]

Effects on Animals - Acute and Chronic Poisoning

Animal exposure to acetylene has not been documented. However, as in man, acetylene will act as an asphyxiant only at high concentrations, depriving the animal of oxygen.

Effects on Vegetation

Acetylene will produce abscission (separation of flowers, fruit, or leaves), epinasty (curling of leaves), and inhibition of growth in sensitive plants. Its toxicity to plants is related to that of ethylene which is widely regarded as the hydrocarbon most toxic to vegetation.[9] Ethylene is a naturally produced plant hormone, active in the regulation of growth, development, and related processes such as the ripening of fruit. Exposure to higher than the biologically permitted level may result in growth retardation, epinasty, or abscission and discoloration of plant parts. Unsaturated hydrocarbons such as acetylene act as ethylene analogues, but must be present in much higher concentrations to produce the identical toxic effects. Atmospheric gases are taken up by plants through their leaves. Thus a primary result of acetylene and ethylene action is the discoloration, abnormal growth, and/or death or plant leaves. No characteristic markings are produced as is the case with sulfur dioxide, ozone, photochemical smog, or fluorides.

Acetylene doses and plant response are presented in Table 2. The concentration of ethylene needed to produce the same response is included as reference.

Table 2. EFFECT OF ACETYLENE AND ETHYLENE ON PLANTS[10,11,12]

Plant	Concentration, ppm		Duration	Response
	Acetylene	Ethylene		
Red kidney bean	125	0.1	4 hours	Abscission
Tomato	50	0.1	2 days	Epinasty
Pea stem	280	0.1	Rate comparison	Growth inhibition
Pea seedlings	250	0.2	3 days	Decimation

Abscission was determined after 4 hours, and refers to the half maximal abscission produced compared to a control.[10] A concentration of 10,000 ppm produced the maximal abscission, 65 percent, after 4 hours. A study of the kinetics of the growth inhibition of the pea stem revealed that 2,800 times more acetylene was needed to produce the same rate of inhibition produced by ethylene.[11]

Other Effects

Effects on Materials - Acetylene will react with copper, silver, and mercury to form spontaneously explosive heavy metal acetylides. Its reaction with the halogens, especially chlorine and fluorine, is rapid and explosive.[5]

Effects on Photochemical Smog - It has been well documented that reactions taking place between hydrocarbons and nitrogen oxides in photochemical smog produce ozone and perotyacyl nitrate (PAN), two chemical species injurious to man, animals, plants, and various materials. Acetylene is not photochemically reactive enough or present in sufficient concentrations in the ambient air to contribute significantly to the atmospheric production of ozone and PAN.[13,14]

AMBIENT CONCENTRATIONS AND MEASUREMENTS

Measurements of acetylene in air have been made in Riverside, California, with morning values of 78 ppb and afternoon values of 27 ppb reported.[15] In contrast, concentrations of about 1 ppb were measured in "pure mountain air" near Riverside. Estimates of likely maximum concentrations near a production facility are presented below.

Ambient Concentration Estimates

The largest production facility for acetylene has a capacity of 180 million pounds per year. Assuming a 1.5 percent loss, this converts to an emission rate of:

$$\frac{(0.015\ \text{emission factor})(180 \times 10^{6}\ \text{lb/yr})(453.6\ \text{g/lb})}{3.1536 \times 10^{7}\ \text{sec/yr}}$$

$$= 38.8\ \text{g/sec of acetylene.}$$

Some assumptions must be made regarding the characteristics of this acetylene release to the atmosphere.

In the first place, it is assumed that the concentrations of acetylene are likely to be highest around production facilities. Secondly, the acetylene emissions do not all come from one source within the plant, but rather from the numerous points of leakage at the facility. Thus the emissions can be characterized as coming from an area source which will be taken to be 100 meters on a side. Finally, the emissions do not occur at ground level, but at different heights, and an average emission height of 10 meters is chosen as a characteristic value.

Ground level concentrations can then be estimated at locations downwind of the facility.[16] To do this a virtual point source of emissions is assumed upwind of the facility at a distance where the initial horizontal dispersion coefficient equals the length of a side of the area divided by 4.3. In this case:

$$\sigma_{yo} = 100\text{m}/4.3 = 23.3\text{m}$$

Assuming neutral stability conditions (Pasquill-Gifford Stability Class D) with overcast skies and light winds, the upwind distance of the virtual point source is approximately 310 meters. With consideration of the plant boundary, it is reasonable to assume that the nearest receptor location is thus about 500 meters from the virtual point source. Finally, taking 2 m/sec as an average wind speed, the ground level concentration may be calculated from:

$$\chi = \frac{Q}{u\pi\sigma_y\sigma_z} e^{-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2}$$

or

$$\chi = \frac{38.8}{(2)\pi(36)(18.5)} e^{-\frac{1}{2}\left(\frac{10}{18.5}\right)^2}$$

$$= 8.01 \times 10^{-3} \text{ g/m}^3$$

for a 10-minute average concentration. Over a period of an hour this becomes:

$$8.01 \times 10^{-3} \text{ g/m}^3 (0.72) = 5.77 \times 10^{-3} \text{ g/m}$$

or 5.5 ppm 1-hour average concentration at the plant boundary (190 m). Over a 24-hour period, the average concentration might roughly be expected to be about 3 ppm.

Measurement Technology

Acetylene at ambient air concentrations may be determined by wet chemical[17] or gas chromatographic[18] techniques. The former method will detect concentrations of between 10 ppb and 10 ppm, while the latter method will detect concentrations as low as 0.01 ppm and can be modified to detect acetylene concentrations to 0.1 ppb by volume.

In the first technique, acetylene is collected by adsorption on silica gel contained in a narrow glass tube cooled by dry ice. A pink to red color is developed in the silica gel by addition of ammoniacal cupric chloride and hydroxylamine hydrochloride. Concentrations of acetylene are determined by comparing the resulting color with colors of tubes containing known concentrations. This method provides reliable results at low concentrations, but the need for handling dry ice in the field makes the method somewhat cumbersome. Also, the method is not specific for acetylene but will determine any alkyne with the triple bond occurring at the end of the chain.

The gas chromatographic method is simpler to perform. Either integrated or grab samples may be collected for subsequent analysis in the lab. A portion of the air sample is injected into a chromatograph column from which it enters a flame ionization detector. The presence of acetylene is determined by its characteristic retention time, and concentrations are determined by comparing the peak height of the recorder response to heights produced by known concentrations.

SOURCES OF ACETYLENE EMISSIONS

Acetylene Production and Consumption

The consumption of acetylene has steadily dropped, for the last 8 years, from 1,161 million pounds in 1966 to 617 million pounds in 1974.[19,20] Competition from other less expensive raw materials has caused the decrease in acetylene consumption. Little, if any, growth is predicted for the future. Approximately 10 percent is used for welding, scarfing and cutting operations and the remainder as a chemical intermediate. Table 3 presents estimated consumption of acetylene for various end products.

Presently five companies with seven locations are manufacturing acetylene from other hydrocarbon sources (see Table 4). The number of locations producing calcium carbide acetylene is estimated to exceed 100 sites.

Table 3. ACETYLENE CONSUMPTION FOR END PRODUCTS

	Million pounds/year
Vinyl chloride	165
Neoprene	122
Vinyl acetate	90
Acrylonitrile	90
Welding	61
Trichloroethylene	45
Acrylic acid and ester	26
Perchloroethylene	8
Other	10
Total	617

Table 4. ACETYLENE PRODUCERS[a]

Company	Location	Capacity, million pounds/year
Dow	Freeport, Texas	15
Monochem	Geismas, La.	180
Rohm and Haas	Deer Park, Texas	35
Tenneco	Houston, Texas	100
Union Carbide	Seadrift, Texas	20
Union Carbide	Taft, La.	12
Union Carbide	Texas City, Texas	25
Total		387

[a]July 1974. Not including producers using the carbide process.

Acetylene Sources and Emissions

Very little data exist in the literature concerning acetylene emissions. Based on other chemical processes, it is estimated that 1.5 percent of total production is lost,[21] resulting in 9 million pounds of emissions. Primary sources of acetylene emissions are acetylene production and end product manufacturing. Acetylene is produced from natural gas or petroleum derivatives by partial oxidation or by electric arc processes, and also by the reaction of calcium carbide with water. This last method accounts for 38 percent of total production. The 61 million pounds (10 percent) of acetylene used for welding and cutting is believed to be produced solely by the calcium carbide method.

Since acetylene is an extremely flammable gas (explosive between concentrations of 2.5 percent and 85 percent), special precautions are taken during its handling and distribution. It is stored in steel cylinders at 250 psi pressure dissolved in acetone. Because there is no venting of the storage tanks, emissions from storage and handling are negligible. Production and end product manufacturing are believed to be the only significant sources of acetylene emissions.

ACETYLENE EMISSION CONTROL METHODS

Presently there are no specific processes mentioned in the literature for the control of acetylene emissions. Industry, however, does use absorber/scrubber systems in manufacturing operations for product pruification. In this process diacetylene and acetylene are separated by using dimethyl formamide. Yields of acetylene ranging from 98.5 to 99.3 percent purity are accomplished by this method.[22] Estimated installed capital costs and operating costs for a general absorber/scrubber system are presented in Table 5.[23]

Table 5. ESTIMATED INSTALLED AND OPERATING COSTS FOR AN ABSORBER/SCRUBBER SYSTEM[23]

System capacity SCFM	1,000	4,000	8,000	20,000
Installed capital cost $	10,900	24,800	37,400	65,500
Annual operating cost $	5,900	12,100	19,500	40,200

SECTION III

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