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ARSENIC

A Brief Review
of its
Chemistry and Toxicology

June 1977

WALTER W. MELVIN, JR., Colonel, USAF, MC
Director of Environmental Health

EHL, KLM, ASE, JK

ARSENIC: As₄

Physical and Chemical Properties

Physical state: gray, lustrous, crystalline mass, also black amorphous powder (density 3.7) and yellow crystals (density 2.0).

Molecular weight: 299.64 Atomic weight: 74.922

Specific Gravity: 5.73

Melting point: sublimes without melting at 610°C

Vapor pressure: 1 mm Hg (372°C.)

The element arsenic (As) is characterized by its ubiquity in the total environment. Arsenic has frequently been incorrectly identified as a metal. It is not a metal but a metalloid, possessing both metallic and nonmetallic properties. Thus, it can form compounds with the As atom acting as either an anion or a cation. Many compounds are correctly called arsenicals. Different arsenicals have widely differing degrees of toxicity, biological activity and effects on man and his environment.

ARSENIC COMPOUNDS (Except Arsine)

Source, Uses, and Industrial Exposures

The major source of arsenic compounds is the by-product arsenic trioxide recovered from the roasting of arsenic-containing ores.

The compounds of arsenic are used in medicine, in glass manufacture, in pigment production, in rodent poisons, in insecticides, fungicides and herbicides, in textile printing, in tanning and taxidermy preservatives, in antifouling paints, and to control sludge formation in lubricating oils. The most serious exposures to fumes and dusts occur in connection with the smelting of copper, lead, zinc, iron, and other ores, and in the manufacture and

use of insecticides. Non-industrial absorption of arsenic from eating sea food, sprayed fruits and vegetables, and from the use of medicinal arsenicals should always be considered when tracing exposures. In insecticide manufacture exposures to various arsenic compounds, such as calcium arsenate, arsenic trioxide, sodium arsenite, Paris green, Scheele's green, and others, occur. The greatest exposures in this industry are usually in mixing, screening, drying, bagging, and drum-filling operations; concentrations ranging from 0.5 to 45 mg. of arsenic per cubic meter of air are not uncommon. Respirators are frequently, but not universally, worn in such an environment.

In the smelting of arsenical ores many opportunities for exposures within, and even exceeding, the above range exist. Among the highest exposures are those encountered in the cleaning of dust collectors and flues, and in loading and transporting the flue dust. The dust is very fine and disperses readily wherever it is agitated, as in grinding, screening, shoveling, sweeping, transferring from or to wheelbarrows, cars, hoppers, bins, settling rooms, and collectors. The repairing and cleaning of furnaces and other equipment at intervals give rise to high exposures. The effluent from smelter stacks when not properly cleaned poses an atmospheric pollution problem, and vegetation for a considerable distance may have a high arsenic content, up to 350 times normal. Samples of soil in the province of Quebec, Canada, 2 miles distant from smelter stacks have been found to contain as much as 0.06 per cent arsenic. Many orchardists exposed for 2 or 3 months to concentrations of spray mists of up to 4.8 mg. of arsenic per 10 cu. meters of air have not evidenced significant intoxication. The experience under these conditions, however, has not been as adverse as might be expected.

Respirators are sometimes used in industry, but contamination frequently

involves areas where no protection is provided. In occupations where exposures to arsenic compounds exist, workmen prefer respirators in which no rubber touches the face, because of the serious arsenic irritation resulting on the moist surface under and alongside the area covered by rubber. Cotton batting 1/2 to 1 in. thick is popular, and somewhat effective, as a filter when properly adjusted to the face.

Men exposed to arsenic trioxide dust should wear protective clothing over the entire body and take a shower at the end of the day's work.¹

Organic Arsenic Compounds. There are a number of trivalent and pentavalent arsenic compounds produced for medicinal use in the control of protozoan parasites (trypanosomes, amoebae, and plasmodia, as well as spirochetes). In the manufacture of these compounds there exist exposures not only to arsenical raw materials and by-products, but also to the organic, finished products.

These organic arsenicals are nonionized and do not immediately produce arsenic effects when inhaled or ingested. They are only slowly broken down in the body and the ingested portion may be largely excreted unchanged. Inhaled dusts may be more or less readily absorbed in relation to their solubilities, and only slowly produce the toxic effects of inorganic arsenic. The threshold of harm from such exposures is even more obscure than that from inorganic arsenic compounds, but permissible concentrations probably are greater for the organic compounds.

Many organic arsenicals of varied, toxic properties have been investigated for their possible use in chemical warfare.

¹Chemical Data Sheet, SD-60, Arsenic Trioxide. Manufacturing Chemists' Assoc., Washington, D.C., 1956.

ARSENIC ACID, $H_3AsO_4 \cdot 1/2H_2O$

Physical and Chemical Properties

Physical state: white translucent hygroscopic crystals

Molecular weight: 150.94

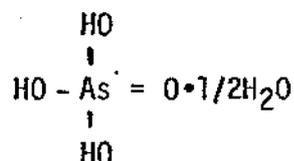
Specific gravity: 2.0 to 2.5

Melting point: $35.5^{\circ}C$.

Boiling point: $160^{\circ}C$.

Solubility: 16.7 g. in 100 ml. of water at $20^{\circ}C$.

Per cent arsenic: 50



ARSENIC TRICHLORIDE, $AsCl_3$

Physical and Chemical Properties

Physical state: yellowish oily liquid (needle-shaped crystals)

Molecular weight: 181.28

Specific gravity: 2.163 ($14^{\circ}C$.)

Melting point: $-18^{\circ}C$.

Boiling point: $130.2^{\circ}C$.

Vapor density: 6.25 (air = 1)

Vapor pressure: 10 mm. Hg, $23.5^{\circ}C$.

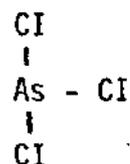
Per cent in "saturated" air: 1.3 ($23.5^{\circ}C$.)

Density of "saturated" air: 1.07 (air = 1)

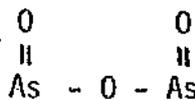
Dissolves in water and decomposes to arsenic trioxide and hydrochloric acid

Per cent arsenic: 76

1 mg./liter \approx 135 p.p.m., 1 p.p.m. \approx 7.4 mg./cu. meter
at $25^{\circ}C$., 760 mm. Hg



ARSENIC TRIOXIDE, As_2O_3 (White Arsenic)



Physical and Chemical Properties

Physical state: transparent crystals or amorphous white powder

Molecular weight: 197.82

Specific gravity: 3.74 to 4.15

Sublimes without melting at $193^{\circ}C$.

Solubility: 2 g. in 100 ml. of water at $25^{\circ}C$. and 11.5 g. in 100 ml. at $100^{\circ}C$.

Not flammable

Per cent arsenic: 76

ARSENIC PENTOXIDE, As_2O_5 (Anhydride of Arsenic Acid)

Physical and Chemical Properties

Physical state: white amorphous powder

Molecular weight: 229.82

Specific gravity: 4.086

Melting point: $315^{\circ}C$. (decomposes)

Solubility: 150 g. in 100 ml. of water at $16^{\circ}C$.; increasingly soluble with temperature rise

Not flammable

Per cent arsenic: 65

CALCIUM ARSENATE, $Ca_3(AsO_4)_2$

Physical and Chemical Properties

Physical state: white amorphous powder

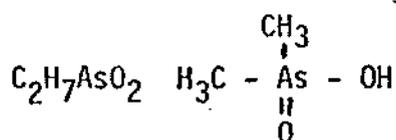
Molecular weight: 398.06

Solubility: slightly soluble in water, soluble in dilute acids

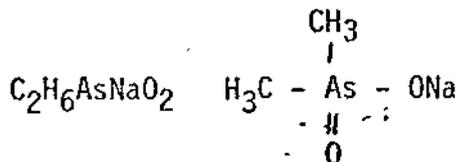
Per cent arsenic: 38; also occurs with 3 moles of water, in which case the molecular weight is 452.11 (per cent arsenic: 33)

CACODYLIC ACID (CA)
(Dimethylarsenic acid)

Molecular weight - 138.0



SODIUM CACODYLATE (Na-CA)



Molecular weight - 160.0

BIOLOGIC EVALUATION

Arsenic absorbed into the human body is excreted in the urine, feces, skin, hair, and nails, and possibly a trace from the lungs. Even at low doses, a proportion of absorbed arsenic is deposited in the skin, hair, and nails where it is firmly bound to keratin.

Arsenic in hair has been used to monitor workers' exposure, but the significance of arsenic in hair is obscured by the difficulty of distinguishing externally deposited arsenic from that systemically deposited in the hair. Once arsenic is deposited on the hair, it resists washing with ether and water. The level of arsenic in fingernail and toenail parings reflects past absorption and is therefore useful forensically, but is less useful if the goal is to monitor current absorption.

Most authors agree that the urine is a major route of arsenic excretion. Arsenic can be detected in the urine of people with no known exposure to arsenic, apparently derived from dietary and general environmental sources. However, the urine of workers occupationally exposed to arsenic may show much higher levels than that of the unexposed, even in the absence of signs of systemic arsenic poisoning.

Urine samples collected from 26 adults and 17 children revealed an average arsenic content of 0.014 mg As/liter with an average specific gravity of 1.017. Corrected to a specific gravity of 1.024, the average was 0.02 mg As/liter.

Seven hundred and fifty-six urine specimens from 29 persons with no known industrial exposure to or abnormal dietary uptake of arsenic had an average urinary excretion of 0.08 mg As/liter, and 79% of the samples were less than 0.1 mg As/liter.

Seafood is considered to be the main source of dietary arsenic. Shellfish in particular elevates the arsenic of test subjects.

Urinary arsenic levels of people with no known arsenic exposure have been reported as 0.014 (0.020 corrected to a specific gravity of 1.024), 0.08, 0.085, 0.129, and 0.13 mg As/liter. Some of the unexposed individuals tested had urinary levels as high as 2.0 mg As/liter, but these high levels may have been due to unusual dietary intake or to unrecognized arsenic exposure.

The urinary arsenic levels of exposed workers vary widely and levels above 4.0 mg As/liter have been reported without apparent adverse effects. On the other hand, signs of mild systemic poisoning have been reported in a worker excreting only 0.76 mg As/liter. This wide variability in urinary arsenic levels, even in an apparently unexposed population, combined with inability to demonstrate a definite association between urinary levels and either observed effects or atmospheric concentrations makes interpretation of urinary data difficult. Nevertheless, a biological threshold limit value of 1.0 mg As/liter of urine has been proposed by Elkins. This is considered to be roughly consistent with a time-weighted average air level of 0.5 mg As/cu m.

Many authors point out the importance of correcting to a mean specific gravity in order to obtain meaningful and consistent results. Testing persons in the United Kingdom resulted in a mean specific gravity of 1.016. However, in the United States the mean value is 1.024. Care must be exercised

when making specific gravity corrections to express the specific gravity of the urine in relation to that of water at the same temperature. If a urinometer calibrated against water at 4 C is used, then a correction for temperature should also be employed.

While no relationship could be shown between urinary arsenic levels and evidence of poisoning, urinary arsenic levels in a group of exposed persons may serve to check the efficacy of control measures and indicate if excessive absorption of arsenic occurs.

Monitoring urinary arsenic cannot replace monitoring atmospheric concentrations as the primary method of characterizing the workers' exposure. It seems reasonable that group averages may be useful as a check on the adequacy of the overall program of engineering controls and work practices designed to protect the workers' health.

Rapid initial excretion of inhaled arsenic (As-74) was reported with 28% of the absorbed As-74 being excreted in the urine within the first day after it was inhaled, and 45% within 10 days. An additional 2.5% had been excreted in the feces after 10 days, but the remaining 52.5% was not accounted for.

The typical symptoms of severe arsenicalism are illustrated in the following case history. The first symptoms were an attack of nausea, vomiting, diarrhea, hot flashes, and progressive anxiety. These symptoms gradually cleared over a period of 10 days. Similar episodes continued intermittently. Within the next 2 years there was a gradual darkening of the skin, and a thickening and scaling of the skin on the soles of the feet. An almost constant pain and feeling of "pins and needles" appeared first in the feet and later in the hands. Muscular weakness became more apparent and the

extremities became numb in a glove and stocking distribution. Three years after the first symptoms, the skin of the trunk had darkened markedly, there had been a gradual loss of vision, and increased pain. Attacks of the initial symptoms continued to occur 3 to 4 times annually for 10 years, until the patient was referred to specialists for management of severe heart failure and muscular dystrophy. The palmar and plantar surfaces were hyperkeratotic and Mees lines were present on the nails. There was an erythematous macular-papular rash below the knees, with indolent, shallow ulcers up to 1 cm in diameter.

At one time, arsenic was considered a beneficial stimulant to the erythropoetic system and was popular as a tonic. Recently, hemotologic abnormalities in association with chronic arsenic intoxication have been reported. Nausea, vomiting, diarrhea, and peripheral neuropathy were present in all cases.

In all cases anemia and leukopenia were present, with thrombocytopenia in 50% of the cases. White counts of less than 1000 were seen, with the major change an absolute neutropenia. All patients had relative eosinophilia, but the absolute eosinophil count was seldom observed. Basophilic stippling was a prominent finding. Disturbed erythropoiesis was observed. Depressed or disturbed myelopoiesis was seen in all cases. Hematologic abnormalities disappeared within 2 to 3 weeks after cessation of arsenic ingestion.

Cold hands or feet or both were common to all and apparently preceded the development of gangrene on the toes or fingers in 6 of the 15 cases. Liver damage was reported in 9 of the 15 cases.

Electrocardiograms were prepared for 80 patients, 45 of whom displayed a broadened Q-R-S interval. The Q-T was almost always prolonged and, frequently, there was an S-T depression and flattening of the T-wave. Six to eight weeks after the first examination, repeat ECGs were obtained in 47 cases. The Q-R-S broadening initially observed was absent or reduced, and the S-T depression and flattened T-wave were observed less frequently.

Prolongation of the Q-T interval and an abnormal T-wave was reported in 2 cases of chronic and 1 case of acute arsenic intoxication. The ECG changes could not be related to disturbances in serum electrolytes and were considered due to a toxic effect on the myocardium.

An extensive study of dermatitis problems in a Swedish copper smelter has been reported. There were symptoms of burning and itching. The dermatitis was broadly classified into two types: eczematous type, with erythema, swelling, and papules or vesicles; and a follicular type, with erythema and follicular swelling or follicular pustules. The dermatitis was primarily localized on the most heavily exposed areas such as the face, back of the neck, throat, forearms, wrists, and hands. However, it also occurred on the scrotum, the inner surfaces of the thighs, the upper chest and back, the lower legs, and around the ankles. Once established, dermatitis continued as long as arsenic exposure continued. To permit the condition to clear up, sick leave was granted. The average length of sick leave required was 13.6 days for initial occurrences and 10.2 days for recurrences.

Patch tests demonstrated that the dermatitis was due to arsenic, not to impurities present in the crude arsenic trioxide. Tests with arsenic trioxide and pentoxide, sodium arsenite, and sodium, calcium, and lead arsenate

demonstrated that all produced dermatitis. Many workers had been sensitized to both trivalent and pentavalent arsenic. It was recommended that workers with mild dermatitis, especially new employees, continue work since this often resulted in hyposensitivity. The incidence of dermatitis was highest in those areas in which arsenic exposure was highest, but occurred in all areas, possibly in sensitized individuals where arsenic exposures were low. Dermatitis also was worse in the summer months, possibly because workers sweat more than in the winter.

RECOMMENDED WORKSHOP CONCENTRATIONS IN AIR

The 1977 TLV recommended by ACGIH is 0.05 mg/m^3 as arsenic for arsenic trioxide production. The same compound is an "A1a Human Carcinogen", i.e., "Substances or substances associated with industrial processes, recognized to have carcinogenic or cocarcinogenic potential, with an assigned TLV." The TLV for arsenic trioxide production is As_2O_3 , 0.05 mg/m^3 as As (as above) with SO_2 , C, 5.0 ppm and Sb_2O_3 , 0.05 mg/m^3 as As and for lead arsenate the TLV is 0.15 mg/m^3 as Pb.