Silver

It is not considered necessary to specify a maximum acceptable concentration for silver in drinking water. Ingestion of excessive quantities of silver may result in argyria, a condition characterized by a blue-grey discoloration of the skin, eyes, and mucous membranes. The exact quantity of silver required to produce argyria is unknown, but it is believed to be in the order of 1000 mg. Drinking water contributes negligibly to a person's intake of silver; also, the data available on levels of silver in food and water indicate that the combined intake of silver from these sources is below levels at which adverse health effects would occur.

General

Silver, a white, lustrous, malleable metal, has the highest known electrical and thermal conductivities of all metals. Silver occurs in nature in elemental form and in ores such as argentite (Ag_2S), horn silver ($AgCl$), proustite (Ag_3AsS_3), and pyrargyrite (Ag_3SbS_3). In the Earth's crust, it is generally found at concentrations of the order of 0.1 mg/kg.[1,2]

Silver is commonly associated with lead and zinc sulphide ores. In Canada, most silver (about 70 percent) is produced as a by-product of base-metal production, and about 30 percent is obtained from silver ores; a small amount may also be refined from gold ores. In 1983, total production in Canada was about 1106 tonnes. Canadian consumption was about 180 tonnes, and the remainder was exported (the United States was by far the largest customer) either as the refined metal or as silver-ore concentrate.[3]

Silver is used in brazing alloys and solders, in electrical and electronic applications, such as storage batteries and electroplating, and in the manufacture of fungicides, photographic films, silverware, and jewellery. Silver is used most extensively in the photographic industry. In Canada, photography and coin production are the major uses of silver.[3]

Occurrence

Silver occurs in soils as a result of geochemical processes at concentrations ranging from less than 0.01 to 5 mg/kg, with an average concentration of 0.1 mg/kg.[2] In New Brunswick, however, "normal" soils contain 1.6 mg/kg in the surface horizons.[4]

Little information is available on the levels of silver in food. A paper published in 1940 suggested that the occurrence of silver in prepared foods is usually the result of contact with silver utensils.[5]* Unusually high concentrations, several hundred milligrams per kilogram, have been recorded in mushrooms; wheat flour and bran are reported to contain 0.4 and 1.0 mg/kg dry weight, respectively; molluscs 0.1 to 10 mg/kg dry weight; and meat (beef, pork, mutton, and lamb) 0.004 to 0.024 mg/kg wet weight.[6]

Many silver salts, such as the chloride, sulphide, phosphate, carbonate, and arsenate, are sparingly soluble (pK_{sp} 10 to 50); as a result, dissolved silver concentrations in natural waters are very low. A recent study has suggested that the dissolved silver found in river water comprises silver species complexed by chloride and unidentified constituents (perhaps dissolved humic matter) that strongly bind silver.[7] Measurements of silver in Canadian surface waters (measured at NAQUADAT stations) indicated that the silver concentrations in 90 percent of the water samples were below detection limits (which ranged from 0.004 to 0.01 mg/L), and none was greater than 0.01 mg/L.[8] Measurements at seven points along the length of the Ottawa River, Ontario, found concentrations of silver that ranged between 0.00001 and 0.00006 mg/L.[9] Similar results have been reported for U.S. surface waters. In one survey of 1577 surface waters, only 6.6 percent of the samples had detectable quantities of silver (>0.0001 mg/L); the mean concentration of silver in these samples was 0.0026 mg/L.[10]

In a survey of Canadian tap water, silver was found in only 0.1 percent of 239 sampled waters; the detection limit for silver in this study, which used neutron activation analysis, was 0.000001 to 0.000005 mg/L.[11] In one U.S. study, 23 percent of 969 drinking water supplies had detectable levels of silver (>0.0001 mg/L);

* It is hard to believe that, even in 1940, much food was prepared using silver or silver-plated utensils.

of these samples, the average concentration was 0.0008 mg/L, and the highest concentration recorded was 0.026 mg/L.[12] Silver concentrations in excess of 0.05 mg/L may occur when silver is used as an antimicrobial agent in water treatment devices.[13] Silver is used to treat potable water for Swiss ski resorts, German breweries, soft drink bottlers, British ships, Shell Oil Company tankers, drilling rigs, and over half the world's airlines.[6] Concentrations of 0.1 to 0.2 mg/L of silver are sufficient to ensure antimicrobial action.[6]

There are few data concerning levels of silver in the atmosphere. Smith and Carson have noted that the "ambient concentrations of silver found at locations near anthropogenic sources range from 0.00000017 to 0.000007 mg/m^3".[1] The World Health Organization (WHO), however, estimates that "a typical level in urban air would not be expected to exceed 0.00005 mg/m^3".[18]

Canadian Exposure

There is considerable variation in estimates of the amount of silver ingested daily by man. A recent study measured the silver intake (and that of a number of other trace elements) of 84 Canadian women consuming self-selected diets.[14] The silver intake was measured by neutron activation analysis of aliquots from 1-day food composites (which included the drinking water component) collected by the subjects. The distribution of silver concentrations in the composites was non-Gaussian, and the median daily intake was found to be 0.0071 mg. Much higher daily intakes have been reported: for example, Tipton *et al*. found the average daily intake of silver in the diets of two individuals in the United States (one male, one female) to be 0.035 and 0.04 mg, respectively;[15] Hamilton *et al*. determined that the average daily dietary intake of silver in the United Kingdom was 0.027 ± 0.017 mg;[16] and, in an early (1940) study, Kehoe *et al*. measured an average daily dietary intake of 0.088 ± 0.077 mg.[5] Much lower daily dietary intakes of silver have also been estimated: Clemente *et al*. reported an average silver intake in the typical diets of the population in three Italian cities (measured by neutron activation analysis of composite food samples) of only 0.0004 mg/day.[17] The WHO has commented that "there is inadequate information to provide a precise average dietary intake, but estimated values within the range 0.02 to 0.08 mg/day might be reasonable".[18]

The data concerning levels of silver in drinking water and in ambient air presented in the previous section, coupled with the estimates of dietary intake discussed above, suggest that drinking water would normally contribute a negligible amount to an individual's total daily intake of the element. The exception would be individuals who receive all their drinking water from water treatment devices that employ silver as the antimicrobial agent.

Treatment Technology[19]

Silver is readily removed from water by conventional coagulation and lime-softening techniques. Tests have shown that alum and ferric sulphate coagulation achieve removal in the order of 80 percent in the pH range 6 to 8. Above pH 8, alum removals decrease with increasing pH because of poor alum floc formation under alkaline conditions. Lime softening removes from 75 to 90 percent silver in the pH range 9 to 11.5.

Health Considerations

Essentiality

Silver is a non-essential element and normally occurs in animal and human tissues only in trace amounts (see Table II-14 of reference 1, for examples). Silver, however, slowly accumulates in the body with age.[20]

Uptake and Excretion

Information dealing with the uptake, distribution, and subsequent fate of silver ingested by mammalian species is sparse. The data that do exist, however, indicate that most ingested silver is rapidly excreted and that little is absorbed.

Dequidt *et al*. found that, in rats ingesting colloidal silver over a 12-day period, almost 5 percent of the total dose was absorbed.[21] Furchner *et al*. presumed that, in an experiment involving the oral dosing of radiolabelled silver nitrate in beagle dogs, 10 percent of the dose was absorbed, as only 90 percent was lost very rapidly.[22] In some earlier experiments involving intragastric administration of carrier-free radiolabelled silver to rats, Scott and Hamilton concluded that only 0.1 percent of the single dose was absorbed, because by 4 days after dosing 99.0 and 0.18 percent of the original dose had been eliminated in the faeces and urine, respectively.[23] Furchner *et al*., however, stated that the findings of Scott and Hamilton indicate about a 4 percent absorption from the gastrointestinal tract.[22]

In a 28-day experiment involving a "normal adult American", the silver content in duplicate samples of all the food eaten daily by the individual and in 24-hour samples of the individual's faeces and urine was analysed.[5] Daily intake of silver was found to be 0.088 mg (standard deviation, ± 0.077 mg; probable error, ± 0.01 mg), and daily excretion of the element in faeces was 0.058 mg (standard deviation, ± 0.035 mg; probable error, ± 0.005 mg). No silver was detected in the individual's urine. Although these data indicate that some silver in the diet is absorbed by humans (at least by a “normal adult American”), the large standard deviations shown by the data do not permit reliable quantification of the amount absorbed. In another similar study, analyses were made of the diets and excreta (faeces and urine) of one male and one female (husband and wife) for 30 days.[15] Average daily intake of silver was 0.035 mg for the man and 0.040 mg for the woman; the man excreted, on average, 50 percent more silver than he ingested (no explanation of this anomaly was given), whereas the woman retained an average of 16 percent of the silver ingested.

In the face of these conflicting data, the WHO has assumed that approximately 10 percent of silver ingested is absorbed.[18] The absorption of silver from the diet probably varies widely from individual to individual and, indeed, with the type of diet. The primary sites of deposition in the body are the liver, skin, adrenals, lungs, muscle, pancreas, kidney, heart, and spleen.[6]

Health Effects

Very large iatrogenic doses of silver and silver compounds have been associated with a number of severe acute effects in humans, including death.[20] However, there have been no reports of adverse health effects arising from ingestion of silver at levels encountered in the diet.

All the data concerning chronic toxicity of silver compounds in humans have arisen from their use as therapeutic agents. Prolonged or careless administration of silver-containing compounds can in some cases cause accumulation of silver in the tissues, primarily in the skin and mucous membranes. Deposition of large amounts in the subepithelial portions of the skin imparts a characteristic bluish pigmentation, a condition known as argyria.[20] The pigment is partly silver sulphide and partly metallic silver that has been produced by photolytic reduction of the sulphide.[24] In a review of more than 200 cases of argyria, it was stated that there is often a long-delayed appearance of discoloration; no cases resulted from an idiosyncrasy to silver.[20] Considerable variability in predisposition to argyria has been noted, the causes of which are unknown. The quantity of silver causing argyria in man is not precisely known, but Hill and Pillsbury noted that the injection of 1000 mg of silver as silver arsphenamine produced this condition.[20]

There has been a comparatively large number of animal experiments in which the effects of silver compounds in drinking water were investigated. These experiments have recently been described and reviewed by the U.S. Environmental Protection Agency (EPA).[6] The EPA concluded that, for laboratory animals, concentrations of silver ions up to 0.2 mg/L in drinking water caused no deleterious effects when given continuously for up to 11 months. Ill effects appeared at 0.4 mg/L; by 0.5 mg/L, conditioned-reflex activity and immunological activity were reduced.

There are no reports linking ingested silver or silver compounds with carcinogenic effects. Nor have there been any reports of either mutagenic or teratogenic effects.

Conclusion

1. Ingestion of excessive quantities of silver may result in argyria, a condition characterized by a blue-grey discoloration of the skin, eyes, and mucous membranes. There is considerable variability in individual predisposition to argyria, and the exact quantity of silver required to cause this effect is unknown. Argyria has been produced by injection of 1000 mg of silver (as silver arsphenamine) in a single dose, an amount 10 times smaller than the dose of silver (as the nitrate) that produces death.

2. Food is the main source of silver for persons not occupationally exposed to this element. Raw and finished drinking waters in both Canada and the United States have not been found to contain concentrations of silver higher than 0.005 mg/L; the highest levels reported in most drinking waters are 50 times less than this value. Therefore, drinking water contributes a negligible amount to an individual’s intake except when silver is used as an antimicrobial agent in water treatment devices. Moreover, daily intake of silver from food and water is considerably below the level at which adverse effects would occur.

3. A maximum acceptable concentration is therefore not specified for silver.

References

1. Smith, I.C. and Carson, B.L. Trace metals in the environment. Vol. 2. Silver. Ann Arbor Science Publ., Ann Arbor, MI (1977).

2. Boyle, R.W. Geochemistry of silver and its deposits with notes on geochemical prospecting for the element. Geol. Surv. Can. Bull. 160 (1968), cited in reference 1.

3. Law-West, D. Silver. In: Canadian minerals yearbook 1983–1984: review and outlook. Catalogue No. M38-5/33E, Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa (1985).

4. Present, E.W. and Tupper,W.M. Trace elements in some N.B. soils. Can. J. Soil Sci., 45: 305 (1965).

5. Kehoe, R.A., Cholak, J. and Story, R.V. Manganese, lead, tin, aluminum, copper, and silver in normal biological material. J. Nutr., 20: 85 (1940).

6. U.S. Environmental Protection Agency. Ambient water quality criteria: silver. NTIS Document No. PB81-117822, Environmental Criteria and Assessment Office, October (1980).

7. Whitlow, S.I. and Rice, D.L. Silver complexation in river waters of central New York. Water Res., 19: 619 (1985).

8. National Water Quality Data Bank (NAQUADAT). Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa (1985).

9. Merritt, W.F. Variation in trace element concentrations along the length of the Ottawa River. Can. J. Earth Sci., 12: 850 (1975).

10. Kopp, J.F. The occurrence of trace elements in water. In: Proc. 3rd Annu. Conf. on Trace Elements in Environmental Health. p. 59 (1969).

11. Neri, L.C. *et al*. Health aspects of hard and soft waters. J. Am. Water Works Assoc., 67: 403 (1975), cited in reference 6.

12. Craun, G.F. and McCabe, L.L. Problems associated with metals in drinking water. J. Am. Water Works Assoc., 67: 593 (1975).

13. Smith, D.K., Thomas, G.H., Christison, J. and Chatfield, E. Survey and test protocols for point-of-use water purifiers. Publ. 77-EHD-8, Department of National Health and Welfare, Ottawa (1977).

14. Gibson, R.S. and Scythes, C.A. Chromium, selenium, and other trace element intake of a selected sample of Canadian premenopausal women. Biol. Trace Elem. Res., 6: 105 (1984).

15. Tipton, I.H. *et al*. Trace elements in diets and excreta. Health Phys., 12: 1683 (1966), cited in references 1, 6.

16. Hamilton, E.I. *et al.* The concentrations and distribution of some stable elements in healthy tissues from the United Kingdom: an environmental study. Sci. Total Environ., 1: 341 (1972/73), cited in reference 6.

17. Clemente, G.F. *et al*. Trace element intake and excretion in the Italian population. J. Radioanal. Chem., 37: 549 (1977), cited in reference 6.

18. World Health Organization. Guidelines for drinking-water quality. Vol. 2. Health criteria and other supporting information. Ch. 15. Geneva (1984).

19. U.S. Environmental Protection Agency. Manual of treatment techniques for meeting the interim primary drinking water regulations. Report No. EPA-600/8-77-005, Cincinnati, OH, May. pp. 32–33 (1977).

20. Hill, W.B. and Pillsbury, D.M. Argyria: the pharmacology of silver. Williams and Wilkins, Baltimore, MD (1939), cited in references 1, 6, 18.

21. Dequidt, M. *et al*. Étude toxicologique expérimentale de quelques dérivés argentiques. l. Localisation et élimination. Bull. Soc. Pharm. Lille, 1: 23 (1974), cited in reference 6.

22. Furchner, J.E. *et al*. Effective retention of silver-110 by dogs after oral administration. In: Annual reports of the Biological and Medical Research Group (H-4) of the Health Division. Report No. LA-3610-MS, Los Alamos Science Laboratories, Berkeley, CA. p. 191 (1966), cited in reference 6.

23. Scott, K.G. and Hamilton, J.G. The metabolism of silver in the rat with radiosilver used as indicator. Univ. Calif. Publ. Pharmacol., 2: 241 (1950). (Chem. Abstr., 45: 30751 [1950].)

24. Goodman, L.S. and Gilman, A. The pharmacological basis of therapeutics. 5th edition. MacMillan Publ. Co., New York, NY (1975).