

Machines that vend carbonated beverages have occasionally been the source of copper poisoning. Poisoning can be prevented if contact between copper lines and carbonated water is precluded.

Copper Poisoning From Vending Machines

SAMUEL H. HOPPER, Ph.D., and HAROLD S. ADAMS, B.S.

SEVERAL health departments have reported cases of illness that appear to be copper poisoning associated with carbonated drinks obtained from vending machines. These machines, the post-mix type, release 1 ounce of a flavored syrup into a cup and then add 5 or more ounces of carbonated water.

In the reported instances of alleged poisoning, the individuals who became ill developed symptoms generally described as acute gastric upset about 12 hours after the vending machine had been in use. The cases of poisoning seemed to occur only after a faulty check valve allowed carbon dioxide to flow into a copper waterline connecting the machine to the building's water supply. Where there is a faulty check valve, the carbon dioxide usually flows back into the water supply because the gas pressure in the tank is greater than the pressure in the building's waterline.

Our investigation at the University of Indiana was conducted to determine whether copper poisoning could result from a carbonated beverage dispensed from a post-mix machine that uses a copper waterline.

Review of Copper Poisoning Cases

Case 1. Twelve persons became ill in a manufacturing plant at Kokomo, Ind., on February 13, 1952. Detailed accounts of sickness were obtained from five persons. There was extensive corrosion of the copper cylinder in a water filter. The carbon in the filter con-

tained 0.43 mg. copper per gram, which is equivalent to 430 ppm.

Case 2. Information from the Office of the Surgeon General, Department of the Army, indicates that defective check valve on a machine at Fort Hamilton, N. Y., in January 1957, resulted in carbonation in the copper waterline. Three persons became ill and laboratory analysis showed 35 ppm copper in the water. Reports of carbonation in a waterline, with no reference to any illness, were also made for First Army Headquarters and a naval receiving station in New York.

Case 3. F. A. Korff of the Baltimore City Health Department reported in a personal communication that a 4-year-old boy was admitted to Union Hospital in Baltimore, Md., on April 3, 1957, with a complaint of vomiting, which started immediately after drinking a carbonated beverage from a vending machine. The child was sufficiently improved to be discharged from the hospital the next day. The laboratory report of his gastric washings showed copper salts, and the attending physician attributed the illness to poisoning from copper salts.

Case 4. J. H. Fritz of the Kansas City (Mo.) Health Department investigated illness of a 2-year-old girl which occurred on February 18,

Dr. Hopper is chairman, department of public health, and Mr. Adams is director, sanitary science course, Indiana University School of Medicine, Indianapolis.

1957, near the city. The child became ill and vomited 15 minutes after drinking part of a carbonated beverage. The remainder of the beverage was taken by the child's grandfather to the city health department. Since the alleged poisoning occurred beyond the jurisdiction of the city health department, the laboratory of the Federal Food and Drug Administration was asked to analyze the sample. The laboratory found approximately 35 ppm copper. Investigation showed that a rubber check valve leaked and allowed carbonated water to lie in a copper waterline overnight. The first few drinks vended the following morning caused illness in eight persons, but only one sample of the beverage was available for analysis. Maintenance men from the company owning the machine replaced a faulty check valve before the Kansas City (Mo.) Health Department personnel arrived on the scene.

Case 5. The Los Angeles Health Department reported that two persons experienced nausea and vomiting within 15 minutes after drinking a carbonated beverage from a vending machine. Investigators found that a defective carbonator valve permitted carbon dioxide to back up into a copper waterline. Chemical analysis of the water from the carbonator indicated 260 ppm of copper (1).

Correspondence with the Los Angeles Health Department revealed that the check valve in question had a single ball held in place by a spring. A small particle which appeared to be a piece of a gasket had lodged under the ball preventing it from closing. A drink drawn from the machine contained 110 ppm copper, while water taken directly from the carbonator contained 260 ppm copper.

Toxicity of Copper

There is no single source of information on copper's toxicity. Information must be gathered from the official publications of a large group of professional agencies. Excerpts from some of these leave the impression that an exact figure for toxicity of copper in man cannot be given.

The Dispensary of the United States of America (2) states that "copper is a constitu-

ent of all tissues of the animal organism; it is absorbed in the intestinal tract from food, which supplies about 2 mgm. daily." It is stored in the liver, and blood contains about 0.14 mg. per 100 ml., or 1.4 ppm. The possible deleterious effect of continued ingestion of considerable quantities of copper has been debated. Copper is not toxic in the same sense that lead, mercury, and nickel are toxic. Many of the soluble salts of copper when taken in a large quantity may give rise to gastroenteritis. The phrase "large quantity" is not defined. Vomiting is usually so prompt that systemic poisoning does not occur.

Davenport (3) in an excellent review states that "there seems to have been, and still is for that matter, no unanimity of opinion regarding the toxicity of copper." She quotes from an editorial (4) on copper which said: "The danger from copper waterlines is slight. Copper is readily attacked by the various acids present in foods such as acetic, citric, malic, tartaric, and oleic. Consequently, any food or drink containing acid will dissolve a certain amount of copper if it comes in contact with that metal. There is no doubt that the human organism can take care of minute amounts of copper, but where the dividing line is between the harmless and the harmful amount cannot yet be said. Individual susceptibility probably enters in to complicate the problem. The danger from copper and brass pipes is negligible. Although copper cooking utensils might possibly be dangerous especially when used for fruits, the real risk comes from industrial hazards and from moonshine liquor."

Gleason and his co-workers state that in general the soluble ionized salts of copper are much more toxic than the insoluble or slightly dissociated compounds (5). The subacetate and the chloride forms are the most poisonous, with cuprous chloride being twice as toxic as the more common cupric salt. They go on to point out that no major toxicological distinctions are recognized between these two valences of copper. Only cupric copper was measured in our series of experiments.

Methods and Results

A post-mix type of machine was obtained on consignment to simulate field conditions for the

study (4). The other materials consisted of 3/8-inch copper tubing cut in 6-foot lengths, some valves, and a cylinder of carbon dioxide.

A 6-foot piece of copper tubing was filled with 100 ml. of carbonated water from the machine, which was connected to the building's water supply. One end of the tube was closed with a valve and the other end was connected to a cylinder of CO₂ under 75 pounds pressure. Tests were repeated 16 times for copper in tap water under pressure. Each ranged from 1 to 4 days in duration. The results varied from 0 to 10 ppm. All tests for copper were made by R. B. Forney, department of toxicology, Indiana University Medical Center, according to the diethyldithiocarbamate method (6).

Since the copper tubing was new, the inside of one tube was etched to see if it would, in this condition, release more copper. The tube was treated with 10 percent nitric acid for 20 minutes and then rinsed thoroughly. Carbonated water was used; the results were not different from those described above.

When an orange drink was used in two separate 24-hour tests, 4.4 and 7.6 ppm copper was obtained from each. At this point all results were regarded as essentially negative.

Table 1. Effect of 75 pounds of carbon dioxide static pressure on water or flavored drink in a copper tube

| Number of trials | Contents of tube ¹ | Length of test (days) | Copper (ppm) |
|------------------|--|-----------------------|--------------|
| 16 | Tap water----- | 1-4 | 0-10 |
| 1 | Tap water ² ----- | 1 | 0-10 |
| 1 | Orange drink ³ (noncarbonated)----- | 1 | 4. 4 |
| 1 | Orange drink (noncarbonated)----- | 1 | 7. 5 |
| 1 | Orange drink (noncarbonated)----- | 1 | 5. 0 |
| 1 | Cola drink (carbonated)----- | 1 | 13. 0 |
| 1 | Cola drink (carbonated)----- | 4 | 25. 0 |
| 3 | Orange drink (carbonated)----- | 1-4 | 20-50 |
| 1 | Orange drink (carbonated)----- | 4 | 200. 0 |

¹ In all cases, the valve at one end of the copper tube was closed. The other end was connected to a cylinder of carbon dioxide.

² The tube was treated with 10 percent nitric acid for 20 minutes before using.

³ The term "noncarbonated" means that the water for the drink did not pass through the carbonator in the machine.

The syrup lines are not connected to the waterline in post-mix machines. Hence a vended drink cannot back up into the waterline in the event of a check valve's failure. Despite this, an orange drink and a cola drink, made with 1 ounce of syrup and 5 ounces of carbonated water, were each kept in a copper tube for 24 hours under 75 pounds CO₂ pressure. The laboratory of the Indiana State Board of Health analyzed these samples in order to check on the previous work and reported that the orange drink contained 5.0 ppm copper and the cola drink 13 ppm copper, which approximated the amount we had obtained. Water under similar conditions showed 6.0 ppm copper.

For the next experiment a cola drink was put into the tube and held under 75 pounds CO₂ pressure for 4 days. The pH was 4.0 when the drink was removed, and it contained 25 ppm copper. An orange drink treated similarly had a pH of 3.5 and 200 ppm copper. Drinks not treated with CO₂ had a pH of 2.0 and less than 1 ppm copper. Carbonated water held for 4 days under 75 pounds pressure at pH 5.2 had 2 ppm copper. Repeated attempts ranging from 1-4 days with the orange drink gave copper in amounts of 20 to 50 ppm. As the summary in table 1 indicates copper was found in the acid drink that was allowed to stand in the tube. But the cause, we reason, could be due to either the acidity or to the type of drink. As a result, buffers were made to check on the effect of acidity.

Buffers were prepared according to Clark's method (7). Their pH varied from 2.6 to 5.0. Potassium acid phthalate and hydrochloric acid up to pH 3.6 were used in the preparation; the phthalate with sodium hydroxide added was used for pH 4.0 to 5.0. The tube was filled with buffer at pH 3.35 and kept at room temperature for 24 hours. No CO₂ was used. When the buffer was removed, its pH was 3.90 and it contained 200 ppm copper. A repeat experiment showed 166 ppm copper. In the next trial CO₂ was bubbled through carbonated water at pH 5.6 for 18 hours. The result was 3.5 ppm copper. However, when the pH was reduced to 5.0 and CO₂ was bubbled through the water for only 2 hours, the result was 25 ppm copper.

We thought that the amount of copper dissolved might be dependent upon whether the tube was new or old. A new tube was filled with buffer at pH 3.60 and was allowed to stand at room temperature for 21 hours. When the buffer was removed, its pH was 3.90 and it contained 600 ppm copper. For an old copper tube, we used the tube which had been etched with nitric acid some months previously and which had been used repeatedly. Buffer at pH 4.75 was put into this tube and kept at room temperature for 20 hours. When the buffer was removed, its pH was 4.80 and it contained 500 ppm copper. Thus, the age of the tube seemed to have no effect.

Table 2. Effect of pH on copper tube

| Buffer (pH) | Time (hours) | Copper (ppm) |
|----------------|--------------|------------------|
| 3.35----- | 24 | ¹ 200 |
| 3.50-3.90----- | 24 | ¹ 166 |
| 5.6----- | 18 | ² 3.5 |
| 3.60----- | 21 | ² 600 |
| 5.0----- | 2 | ² 25 |
| 4.75----- | 20 | ² 500 |
| 4.0----- | 2 | ² 400 |

¹ No CO₂ was used.

² CO₂ allowed to bubble through the tube.

It appeared at this point that copper would dissolve if CO₂ were bubbled through the water at a high enough rate to reduce the pH below 5.0. This reduction was easily accomplished. Carbon dioxide was bubbled through the water until the pH was 4.0 and the amount of copper was 400 ppm (see table 2).

At a pH below 5.0 using a phthalate buffer, large amounts of copper were dissolved. Tap water in a copper tube with CO₂ bubbling through it gave similar results. Thus, it was obvious that copper dissolves as the acidity increases. This lowering of pH occurs when CO₂ bubbles continuously through a copper tube containing water, and is similar to what happens when a faulty check valve is under CO₂ pressure higher than the water pressure.

The explanation for the phenomena reported remains obscure. In all probability the copper which is dissolved is not directly related to the pH, since a very strong acid is needed to

dissolve copper. It would seem that the solubility of copper is dependent upon the presence of dissolved oxygen as well as carbon dioxide. There is ample dissolved oxygen in tap water to form an oxide of copper, which, in the presence of carbonic acid, gives enough copper ions to combine with naturally occurring sulfates and carbonates to appear in the vended drink. A faulty check valve permits carbon dioxide to bubble through the tube and allows enough circulation of water to supply the oxygen needed for the first step in the process.

Public Health Aspects

At the outset, it should be understood that copper poisoning does not represent a public health problem of any great magnitude, since the relatively few cases on record compared with the millions of soft drinks consumed would give an infinitesimally small case rate. To minimize copper poisoning, however, we suggest:

1. Vending machines should adhere to the sanitation code concerning the use of two check valves or a double check valve; or an air gap; or a device to vent the CO₂ to the atmosphere; or a device approved by the health authority (8).

2. A carbonator should not be made of copper. It should be made of an acid resistant nontoxic metal.

3. Water filters and water conditioning devices should not use a copper container.

Summary

If the check valves in a post-mix type vending machine do not function correctly, carbon dioxide may enter the water supply line. In the event that this line is made of copper, then (a) the CO₂ or carbonated water will react with the copper; (b) under certain conditions, the quantities of copper going into solution could be quite large; and (c) copper poisoning could occur from a beverage dispensed from a post-mix type, carbonated beverage machine.

Support is thus given to recommendations that these machines be designed and constructed so as to preclude contact between copper and CO₂ or carbonated water, and such machines be

equipped with a device or devices that provide positive protection against the backflow of CO₂ or carbonated water into the building water supply system.

REFERENCES

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Clinical toxicology of commercial products. Baltimore, Md., Williams and Wilkins, 1957, p. 130.

- (6) American Public Health Association: Standard methods for the examination of water, sewage, and industrial wastes. Ed. 10. New York, N. Y., 1955, pp. 95-99.
- (7) Clark, W. M.: The determination of hydrogen ions. Ed. 3. Baltimore, Md., Williams and Wilkins, 1928, p. 200.
- (8) U. S. Public Health Service: The vending of foods and beverages; a sanitation ordinance and code; 1957 recommendations of the Public Health Service. PHS Pub. No. 546. Washington, D. C., U. S. Government Printing Office, 1957, pp. E3, 13.

EQUIPMENT REFERENCE

- (A) Post-mix type vending machine from Apco, Inc., New York, N. Y.

National Conference on Air Pollution

Municipal, county, and State health personnel, control officials, and scientists and technicians concerned with atmospheric pollution will meet with community leaders representing a wide variety of civic, industrial, and service organizations and agencies at the National Conference on Air Pollution in Washington, D. C., November 18-20, 1958.

Surgeon General Leroy E. Burney has called this conference, open to anyone interested in the subject, for two principal purposes: to create a wider understanding of air pollution problems among civic leaders, and to outline a practicable plan for future action in both research and control.

The program is designed to encourage maximum participation by all conferees. Following a day of orientation, during which participants will hear a status report from the Surgeon General and brief presentations on current knowledge and accomplishments, the assembly will divide into six discussion groups to formulate recommendations for desirable future activities.

On the morning of the third day, the six groups will present their recommendations to a plenary session. The final afternoon's pro-

gram will resemble a "town meeting," with questions and discussion from the floor.

A steering committee comprising representatives of the American Public Health Association, American Municipal Association, Air Pollution Control Association, and other principal governmental, industrial, and scientific organizations have aided the Surgeon General and his staff in planning the conference.

Chairmen and vice chairmen of the discussion groups, in that order, are as follows:

Extent of air pollution: Dr. Arie J. Haagen-Smit and Dr. H. C. McKee.

Sources of air pollution: S. L. Hanauer and Dr. Leslie Chambers.

Health effects of air pollution: Dr. Malcolm H. Merrill and Dr. James P. Dixon.

Economic and social effects of air pollution: Dr. John T. Middleton and Arthur Crago.

Control methods and procedures for air pollution: Dr. Leslie Silverman and W. C. L. Hemeon.

Administrative aspects of air pollution: Dr. Louis C. McCabe and Harold W. Kennedy.



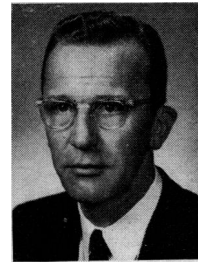
Miss Sleeper



Dr. Dearing



Mr. Mason



Dr. Arnold

New Members of the PHR Board of Editors

The Board of Editors of *Public Health Reports* has gained four new members. Appointed to the board for 3 years, they replace outgoing members Dr. Leo W. Simmons, Dr. H. Trendley Dean, Margaret Arnstein, and Vernon G. MacKenzie.

Francis A. Arnold, Jr., D.D.S., became director of the National Institute of Dental Research, Public Health Service, in 1953. He had served as associate director since establishment of the institute in 1948.

Dr. Arnold's entire professional career has been in the Public Health Service, which he entered in 1934 on graduation from the dental school of Western Reserve University. In 1937, he joined the Dental Research Section, National Institutes of Health, of which he became assistant chief in 1943.

A prolific researcher of international eminence in the dental sciences, Dr. Arnold is a fellow of both the American College of Dentists and the American Public Health Association. He is also a member of the American Dental Association and a former president of the International Association for Dental Research and is now vice president of the *Fédération Dentaire Internationale*.

W. Palmer Dearing, M.D., assistant director for health in the Office of Defense Mobilization, previously served for 9 years as Deputy Surgeon General of the Public Health Service.

After graduation cum laude from Harvard Medical School, Dr. Dearing taught epidemiology in the Harvard School of Public Health. He became a Public Health Service career officer in 1934, serving as an epidemiologist in studies of poliomyelitis and tuberculosis until 1941. That year he was assigned to the Office of Civilian Defense as assistant, and then, chief medical officer. In 1944 he was named personnel chief of the Health Division, United Nations Relief and Rehabilitation Administration, returning to the Public Health Service in 1945 as deputy chief of the Division of Public Health Methods. A year later he became chief of the Division of Commissioned Officers.

Karl M. Mason, M.P.H., was named director of the bureau of environmental health, Pennsylvania Department of Health, in 1954, after having served as the

department's director of professional training since 1951. During 1949 to 1951, he was associated with the Public Health Service following 6 years as director of the division of public health engineering with the Peoria, Ill., Department of Health. Previously, he spent 2 years as public health engineer with two county departments of health in Michigan.

Mr. Mason is a diplomate of the American Academy of Sanitary Engineers and a member of the Advisory Committee to the Surgeon General of the Public Health Service on Water Pollution Control. In addition, he is the Pennsylvania representative on the governing council of the American Public Health Association and a lecturer at both the University of Pittsburgh Graduate School of Public Health and the Robert A. Taft Sanitary Engineering Center in Cincinnati, Ohio.

Ruth Sleeper, R.N., has been director of the School of Nursing and Nursing Service of the Massachusetts General Hospital in Boston since 1946. She began her nursing career in 1922 when she graduated from the Massachusetts General Hospital Training School for Nurses. Miss Sleeper took a master of arts degree from Teachers College, Columbia University, in 1935 and holds the honorary degrees of doctor of humanities from Boston University (1953) and doctor of science from Hood College (1954).

President of the National League of Nursing Education during 1944-48 and of the National League of Nursing in 1952-55, she was also chairman of the Joint Commission for the Improvement of the Care of the Patient.

Her current posts include chairmanship of the Education Committee of the International Council of Nurses and membership on the Expert Committee on Nursing of the World Health Organization and on the Board of Directors of the National League of Nursing.