CASE REPORT

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Chloropicrin Found in Industrial Grade Nitrogen

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ABSTRACT: Industrial grade nitrogen cylinders were analyzed for the presence of adulterants after several individuals became ill following a nonfatal exposure. A preliminary report from another laboratory indicated the presence of chloropicrin and phosgene, a known decomposition product of chloropicrin. Our results confirmed the presence of chloropicrin and demonstrated phosgene to be an artifact of GC/MS analysis. A possible contamination scenario is discussed.

KEYWORDS: forensic science, chloropicrin, trichloronitromethane, poisoning, forensic toxicology, industrial nitrogen cylinders

Chloropicrin (trichloronitromethane, CCl_3NO_2) is a colorless, slightly oily liquid with a boiling point of 112.4°C. It is used as an insecticide, fungicide, and weed and grass seed killer in soil. It is commonly used in combination with or as an alternative to other fumigants (1). It also has applications as a warning agent for compounds such as methyl bromide (2). The Occupational Safety and Hazard Administration's (OSHA) permissible exposure limit for chloropicrin is 0.1 PPM over an eight-hour time weighted average (PEL-TWA) (3). The LD_{50} in rats is 250 mg/kg and concentrations of 340 and 110 PPM are lethal in 1 and 20 min, respectively (4). Undiluted chloropicrin is highly toxic by ingestion or direct contact with the skin or eyes. According to the American Conference of Governmental Industrial Hygienists (5), airborne exposure to 0.3–0.37 PPM (2–2.5 mg/m cubed) for 3–30 seconds results in eye irritation. This response is reported to be highly variable among individuals and tearing (lacrimation) may occur at airborne exposures of 0.15–0.3 PPM (1–2 mg/m cubed). Inhalation exposure to 4 PPM (26 mg/m cubed) for a few seconds may cause some degree of incapacitation and an exposure of a few seconds to 15 PPM (100 mg/m cubed) can cause injury to the respiratory track. Exposure to concentrations above 15 ppm can result in lacrimation, vomiting, and if allowed to continue for a minute or longer, can cause pulmonary edema and possibly death (5).

Case History

Four individuals in a dental office became ill during and after a surgical procedure utilizing pneumatic tools powered by industrial grade nitrogen. After the delivery and use of a new tank of nitrogen during and following an afternoon dental surgery, individuals assisting in and present during the procedure experienced symptoms of dizziness, burning throat, burning eyes, blurred vision, tightness of the chest, confusion, headache, nausea, and coughing. These effects were experienced within minutes of the initial operation of the surgical tool. While investigating the medical office for the source of the problem, a representative from the pneumatic tool company entered the office and activated the tool. The representative inhaled the exhaust gas from the tool to demonstrate that nitrogen gas is inert and innocuous. He began coughing, rubbing his eyes, and gasping for air. He went immediately to a local emergency room were he was treated and released. In addition, the other individuals exposed during the procedure continued experiencing symptoms that day and eventually went to the emergency room. The residual effects from the exposure and subsequent treatments for the victims continued from two weeks to three months.

Our laboratory was contacted pursuant to a possible product tampering case following preliminary testing from an environmental laboratory of this nitrogen gas cylinder. The preliminary report revealed the presence of chloropicrin and phosgene in the nitrogen gas cylinder.

Experimental

Materials

Chloropicrin standard was purchased from Absolute Standards, Inc., Hamden, Connecticut. All reagents (analytical grade) were purchased from Baxter. Powder-free latex gloves were purchased from Safeskin, Boca Raton, Florida. Vacu-Sampler® (MDA Scientific, INC., Lincolnshire, IL) cans were a gift from David Copeland, Occupational Safety and Health Administration (OSHA).

Instrumentation

The gas samples were analyzed on a model 5890 series II plus gas chromatogram with a 5972 mass selective detector (GC/MS, Hewlett-Packard, Palo Alto, CA). The column used was a Restek (Bellefonte, PA) 30 m RTX-5 with a 0.25-mm internal diameter and a 0.25-μm film thickness. Initial oven temperature was 40°C for 4 min, the temperature was ramped to 280°C at 40°/min, and this temperature was held for 6 min for a total run time of 17 min. Helium flow rate was 0.906 mL/min. Injection port and detector temperature were 120°C, and 280°C respectively.

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Collection and Analysis

Gas for GC/MS analysis was collected via two methods. The first method of collection employed a powder-free latex glove and cellophane tape. This glove was placed directly to the cylinder and filled with sample gas. A knot was tied in the glove to prevent escape of the gas and cellophane tape was placed on the filled glove. A gas-tight syringe (Hamilton, Reno, NV) was used to puncture this taped site and collect 0.1 to 0.5 mL of gas. The second method employed an evacuated collection vessel (Vacu-Sampler). Gases were collected with this by attaching a Tygon® tube from the gas source (i.e., gas cylinder) to the nipple of the Vacu-Sampler. The gas source was opened and the button on the vessel was depressed allowing the vessel to draw the sample gas into the vessel. During analysis the button was removed revealing a septum from which the collected gas was sampled with a gas tight syringe.

Samples were analyzed by GC/MS according to the parameters described above by injection of 0.1 to 0.5 mL of gas sample. Swabs were analyzed by rinsing in methyl-t-butyl ether (MTBE) and injecting the solution into a GC/MS.

Results and Discussion

The local law enforcement agency was notified about the exposure due to the possibility of "product tampering." The agency submitted the nitrogen gas cylinder to the Toxicology Department of the South Carolina Law Enforcement Division (SLED). The gas cylinder from the medical office was analyzed as described above in the Experimental Section. The cylinder contained chloropicrin, and the GC/MS chromatogram recorded for its contents is shown in Fig. 1. Both phosgene and chloropicrin were identified, however, phosgene is known to be a thermal decomposition product of chloropicrin (6). The analysis was, therefore, performed under a lower injection port temperature. The results of this GC analysis confirmed that only chloropicrin was present in the nitrogen gas, and the phosgene detected was merely an artifact due to thermal degradation of chloropicrin.

Another nitrogen gas cylinder was present at the dental office, and it was also submitted for analysis. The second nitrogen gas cylinder was also found to contain chloropicrin. It was believed that this was most probably an isolated incident that involved the intentional contamination of the cylinders found at the dental office. However, to ensure the safety and well being of others who may be using industrial grade nitrogen gas, other nitrogen gas cylinders were sampled from the distribution center where the contaminated cylinders were purchased. The results of the analysis of nitrogen gas cylinders with various lot numbers from this distribution center are listed in Table 1.

The presence of chloropicrin in the nitrogen gas cylinders at the dental office was not an isolated case. Almost all of the nitrogen gas cylinders analyzed from the distribution center were contaminated with chloropicrin (Table 1). The lot numbers on the cylinders indicate the dates in which they were filled, and all of the cylinders contaminated with chloropicrin were filled at the same filling station. The investigation of the contamination of the nitrogen gas cylinders subsequently focused on this filling station.

A preliminary analysis indicated that chloropicrin was present in

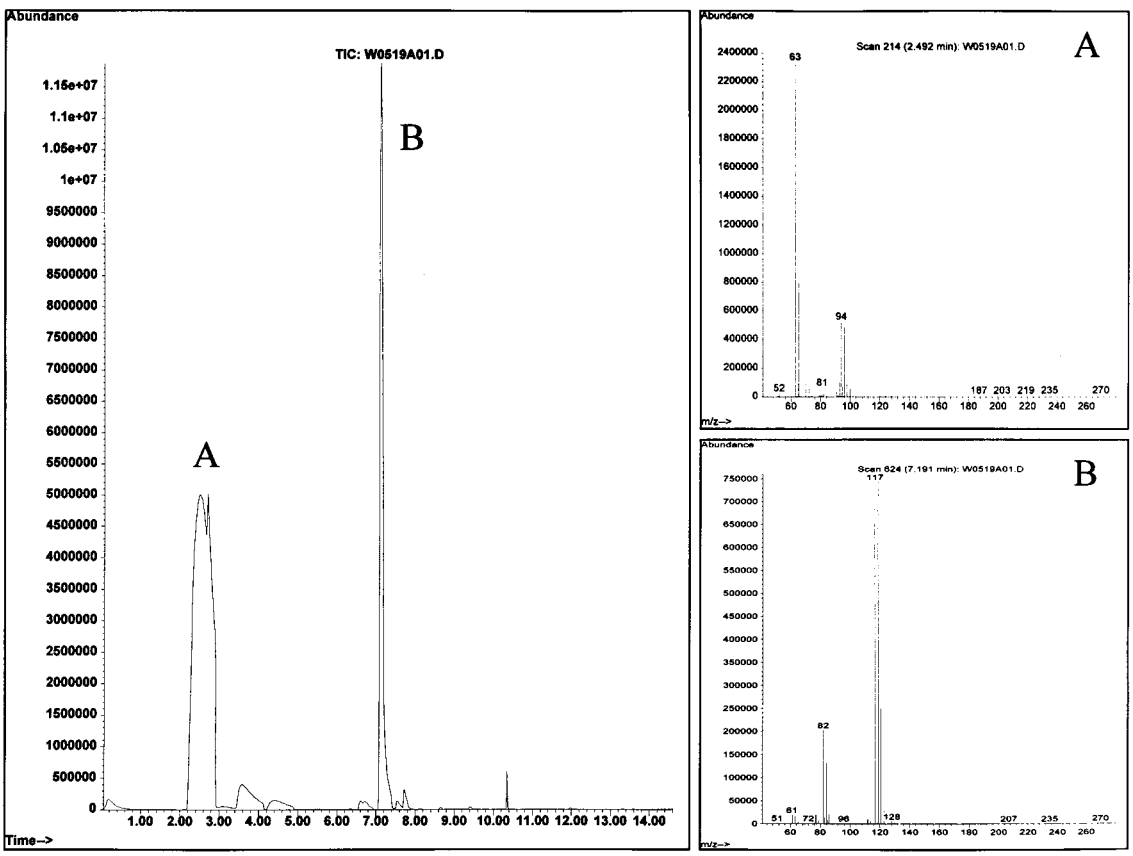

FIG. 1—*Total ion chromatogram of 0.1 mL of a chloropicrin standard analyzed as described under "Instrumentation" except injection port temperature was 225°C. Insert A corresponds to the mass spectrum of phosgene at 2.492 min and insert B corresponds to the mass spectrum of chloropicrin at 7.191 min.*

TABLE 1—*Results from analysis of all samples.*

Sample	Chloropicrin
Lot A*	present
Lot B*	present
Lot C‡	present
Lot D†	present
Lot E†	present
Lot F†	present
Lot G†	no analysis
Lot H†	Present
Refilling Manifold A‡	inconclusive
Refilling Manifold B‡	not present
Swabs (5) from filling manifold§	not present
Internal nitrogen port§	not present
Gas sample A§	not present
Gas sample B§	not present
Gas sample C§	not present
Gas sample D§	not present

*Sample collected 5-15-97 (approx. fill date, 4-14-97) from initial incident at the medical office on 5-8-97.

†Sample collected 5-16-97 (approx. fill dates, 4-14-97 to 5-15-97) from distribution station.

‡Sample collected 5-16-97 (approx. fill date from tank, 5-6-97) from filling station.

§Sample collected 5-21-97 from filling station.

the nitrogen gas at the filling station (number ‡, Table 1). The refilling manifold is a metal line that numerous gas cylinders can be connected to and filled with nitrogen gas simultaneously. If the nitrogen gas was intentionally contaminated with chloropicrin, it was believed that this manifold would contain high levels of this compound. Swabs of the manifold were taken with cotton tip applicators and were all negative for chloropicrin. Nitrogen gas from several of the refilling manifolds was also analyzed to ensure that the gas was free from contamination, and all of these samples were negative for chloropicrin. The results from the swabs suggest that the contamination of the nitrogen gas cylinders may not have been intentional.

As a result of SLED, OSHA, and The Department of Health and Environmental Control (DHEC) investigations, it was learned that chloropicrin is used prior to the planting season as a soil fumigant in tobacco fields. The time frame of this contamination coincided with the tobacco field planting season. Because industrial grade nitrogen is used as a propellant for the application of chloropicrin, there exists some probability for a tank or several tanks to be contaminated by a back flow event during the application process. The nitrogen gas cylinders are filled by attaching them to the refill manifold, evacuating the cylinders, and refilling them with nitrogen gas. It is possible that one or several contaminated cylinders caused the contamination of the refill manifold, which in turn caused the contamination of gas cylinders attached to the contaminated manifold. This secondary contamination event was sufficient to cause the contamination of several lots of nitrogen but was insufficient for detection by the time the investigation took place. It was believed that the contamination of the nitrogen gas cylinders was accidental due to the use of chloropicrin as a fumigant.

Conclusion

The cause of the nonfatal exposure in this case was a result of the use of industrial grade nitrogen (for the purpose of powering a pneumatic medical tool) contaminated with chloropicrin. The contamination was most likely due to the use of chloropicrin as a fumigant of tobacco fields. The refilling manifold was most likely contaminated by one or several nitrogen gas cylinders that were contaminated by a "back flow" as farmers used the nitrogen as a propellant for the chloropicrin. The contaminated manifold led to the contamination of a number of lots of nitrogen, of which several were delivered to a distribution station that supplied the medical office. In conclusion, medical grade gases should be used in any clinical procedures.

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References

1. Wilhelm S, Storkan RC. Large scale soil fumigation growth response. Phytopathology 1990;49:530–1.
2. Thomson WT. Agricultural Chemicals Book III. Miscellaneous Agricultural Chemicals. Fresno, CA, Thomson Publications, 1991–2.
3. Hayes WJ Jr., Laws ER Jr. Handbook of Pesticide Toxicology. Vol. 2. New York: Academic Press.
4. Sax NI, Lewis RJ Sr. Hazardous Chemicals Desk Reference. New York: Van Nostrand Reinhold Company Inc., 1987.
5. American Conference of Governmental Industrial Hygienists. Documentation of Threshold Limit Values and Biological Exposure Indices, Sixth Ed. Cincinnati, 1992:299–300.
6. Budavari S, editor. The Merck Index, Eleventh edition. New Jersey: Merck and Co. Inc.

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