Exposure to an accidental trichlorosilane spill: three case reports

Chang Won Park¹, Seong Hun Kim², Soo Hyung Lee², Shinwoo Kim², Woo Young Nho²

¹Department of Emergency Medicine, Fatima Hospital, Daegu, Korea
²Department of Emergency Medicine, CHA Gumi Medical Center, CHA University School of Medicine, Gumi, Korea

Chlorosilane is a hazardous chemical compound which is used as a raw material in the production of silicone. Despite strict restrictions, accidental spillage of chlorosilane is often reported. However, human exposure was rarely reported in the past decades and the effect on humans is barely known. We report cases of human exposure to an accidental trichlorosilane spill. Three middle aged male industrial workers visited our emergency department after exposure to trichlorosilane. They presented with shortness of breath and burns on multiple sites. Chest radiograph and laboratory studies were performed. None of the reports showed serious results and were discharged after conservative management.

Keywords Silicones; Trichlorosilane; Occupational medicine; Chemical hazard release; Case reports

What is already known
The human clinical data after chlorosilane exposure has not been reported worldwide.

What is new in the current study
Various symptoms, including skin, respiratory, and gastrointestinal, could be developed after chlorosilane exposure.
INTRODUCTION

Chlorosilane is a chemical compound that consists of chlorine and silicone atoms. After a chemical process, purified silicone can be derived from chlorosilane. This material is widely used in the modern industries like semiconductor manufacture. Physiological effects of chlorosilane exposure have been reported in some animal studies. However, human exposure has rarely been reported and clinical effect on humans are barely known.

We report three cases of human exposure to an accidental trichlorosilane spill.

CASE REPORTS

On 21 July 2020, at 1:47 a.m., trichlorosilane gas spilled out from an underground chemical storage tank of an industrial plant in a city. The government announced that some part of the storage tank valve was broken. A total of 113 kL of trichlorosilane gas was released and seven plant workers were exposed to the gas. They were mechanics who came to the scene to fix the problem without adequate protective equipment. Evacuation of citizens was conducted following the national disaster protocol, and no injuries resulting from exposure to the gas among citizens were reported. Among the seven exposed workers, three visited our emergency medical center at 2:03 a.m. on the same day. They were at the scene during the early stages of the event. Each of them was exposed to trichlorosilane for a few minutes, but the exact amount of contact with the toxic material was not reported. On arrival, they appeared acutely ill, and all of them presented with mild shortness of breath and irritation of the skin. Oxygen supplementation was administered by the first responders at the scene, but the patients reported to the emergency department (ED) without oxygen. Oxygen therapy via non-rebreather mask with reservoir bag was initiated. Chest radiography and laboratory examinations were performed. General characteristics and clinical information are provided in Table 1.

### Table 1. General characteristics and clinical information

| Variable                  | Case 1 | Case 2 | Case 3 |
|---------------------------|--------|--------|--------|
| Age (yr)                  | 51     | 46     | 57     |
| Sex                       | Male   | Male   | Male   |
| Underlying disease        | None   | None   | Hypertension |
| Vital signs on arrival    |        |        |        |
| Blood pressure (mmHg)     | 130/80 | 170/100| 130/80 |
| Pulse rate (/min)         | 100    | 120    | 115    |
| Respiratory rate (/min)   | 20     | 20     | 22     |
| Body temperature (°C)     | 36.3   | 36.2   | 36.8   |
| Oxygen saturation (%)     | 100    | 100    | 100    |
| Arterial blood gas analysis |      |        |        |
| pH                        | 7.397  | 7.382  | 7.381  |
| pCO₂ (mmHg)               | 33.2   | 36.1   | 42.4   |
| pO₂ (mmHg)                | 85.7   | 78.8   | 83.1   |
| HCO₃⁻, actual (mmol/L)    | 20.0   | 21.0   | 24.6   |
| Base excess, vitro (mmol/L) | -3.8   | -3.4   | -0.6   |

Clinical presentations

| Skin               | Location                  | Degree of burn | Respiratory | Gastrointestinal |
|--------------------|---------------------------|----------------|-------------|------------------|
| Both shoulder to hand | Anterior and posterior neck | 1st degree     | Mild        | Nausea           |
| Both knee to foot  | Both shoulder to wrist     | 1st degree     | Mild        | Nausea           |
|                    | Genital area to anus       | 1st degree     | Mild        | Bitter taste     |
|                    | Both scapular area         |                |             |                  |
|                    | Both ankle and foot        |                |             |                  |

Fig. 1. Chest radiographs of the patients. (A) Case 1, (B) case 2, and (C) case 3. L, left side.
showed no significant abnormality in any of the three patients (Fig. 1). There was no significant hypoxemia in any of the patients and the amount of oxygen was gradually reduced. Injury to the skin was limited to localized redness with pain. There was no swelling, bullae formation, or necrotic changes to the skin in any patients. Symptomatic management including control of pain was provided. Respiratory symptoms were relieved 3 hours after exposure, and the patients were discharged with ointment for managing skin irritation. None of them visited the outpatient clinic or ED after the event. One month after exposure, no specific sequelae were noted in any patients. The patients provided informed consent for publication of the research details and clinical images.

DISCUSSION

The city Gumi is one of the main industrial areas in the country. The main products that are manufactured are electronics such as mobile devices, household appliances and computer parts. Several accidental chemical spills have previously been reported in this city. This is the first report of human exposure to the chlorosilane chemical in our country.

Chlorosilane is a chemical compound which is used as a raw material in the production of silicone. It is produced by synthesis of silicon and hydrochloride by the Muller-Rochow process. Tri-chlorosilane (CAS RN 10025-78-2) is the main product of this process and pure silicone can be derived from hydrolysis of trichlorosilane. For this reason, chlorosilane is widely used in semiconductor and photovoltaic industries, which need ultrapure silicone for their manufacture. Chlorosilane is classified as a hazardous substance. In several countries, protocols for handling, storage, transportation and a response plan of exposure control are in force. According to the National Fire Protection Association hazard classification in the United States, trichlorosilane is classified as level 3 (extremely dangerous) as a health hazard, level 4 (extreme) regarding flammability, and level 2 (moderate) regarding instability. Further, this material is classified as level 4 for acute oral toxicity (H302), level 3 for acute inhalation toxicity (H331), and level 1 for skin corrosion (H314), by the hazard classification of Korea. Our government legally stipulated the essential level of personal protection equipment for any person who handles trichlorosilane. Trichlorosilane is mentioned in division 4.3 of the Hazardous Material Classification of the Department of Transportation in the United States, which means ‘dangerous when wet’ hazardous material. Storage and transportation of the trichlorosilane, like the material of the storage container, degree of filling in the storage or maintenance temperature, are strictly controlled by documented protocols.

Despite precautions, around 70 cases of chlorosilane spills were reported during a period of 18 years in the United States. One case of human exposure of chlorosilane was reported in 1984. In that case, 4,560 L of tetrachlorosilane were spilled which is thousands of times less than the spill in our case. A total of 28 people visited medical facilities and no death or hospitalizations were reported in that spill in the United States.

Trichlorosilane is a liquid in its standard state and vaporizes quickly on exposure to air. Once it spills, it reacts with water in the air rapidly. Hydrochloride gas, one of the main products of hydrolysis, is released concurrently with chlorosilane. Clinical effects of chlorosilane exposure should be considered as exposure to hydrochloride acid. Skin and eyes are the major route of direct contact. Nasal or intraoral mucosa may be injured. Both chlorosilane and hydrochloric acid have a corrosive effect. Irritation of the nasal, oral, oropharyngeal, respiratory tract or skin after exposure causes clinical symptoms and signs. In severe cases, esophageal and/or deep gastric burns or mucosal necrosis could develop after oral ingestion. Permanent visual loss after ocular exposure, tissue necrosis after skin exposure and acute lung injury after inhalation has been reported rarely. Systemic toxicity including hypotension, cardiac arrhythmia, metabolic acidosis, renal failure, disseminated intravascular coagulation, and cardiac arrest could develop in fatal cases. The metabolic pathway of the substance and accumulation in the human body after exposure to the material is under investigation. In the previous report of chlorosilane exposure in 1984, they reported that the patients had lacrimation, rhinorrhea, headache, coughing, and burning sensation of the mouth and throat. In our case, patients mostly showed skin irritation and shortness of breath. There is no specific antidote for chlorosilane exposure. Supportive care with symptomatic management is the mainstay of treatment. No delayed complications of chlorosilane exposure have been reported yet; no data on carcinogenicity, developmental or reproductive problems have been reported either.

In conclusion, we report three cases of massive trichlorosilane exposure to humans. Symptoms are relatively minimal and those exposed were discharged after management in the ED without hospitalization. Long-term complications should be evaluated, and industrial safety instructions must be strictly followed to prevent such accidents in the future.

CONFLICT OF INTEREST

No potential conflict of interest relevant to this article was reported.
REFERENCES

1. Jean PA, Gallavan RH, Kolesar GB, Siddiqui WH, Oxley JA, Meeks RG. Chlorosilane acute inhalation toxicity and development of an LC50 prediction model. Inhal Toxicol 2006;18:515-22.
2. Kizer KW, Garb LG, Hine CH. Health effects of silicon tetrachloride: report of an urban accident. J Occup Med 1984;26:33-6.
3. Kim JA, Yoon SY, Cho SY, et al. Acute health effects of accidental chlorine gas exposure. Ann Occup Environ Med 2014;26:29.
4. Choe MSP, Lee MJ, Seo KS, et al. Application of calcium nebulization for mass exposure to an accidental hydrofluoric acid spill. Burns 2020;46:1337-46.
5. Rochow EG. The direct synthesis of organosilicon compounds. J Am Chem Soc 1945;67:963-5.
6. Wireless Information System for Emergency Responders. Trichlorosilane [Internet]. Bethesda, MD: US National Library of Medicine; 2020 [cited 2021 Jan 31]. Available from: https://webwiser.nlm.nih.gov/substance?identifier=Trichlorosilane&identifierType=name&substanceId=360.
7. National Institute of Environmental Research. Trichlorosilane [Internet]. Incheon: National Chemicals Information System; 2015 [cited 2021 Jan 31]. Available from: https://ncis.nier.go.kr/main.do.
8. Ministry of Environment. Chemical Substances Control Act, Article 14 [Internet]. Sejong: Korean Law Information Center; 2019 [cited 2021 Jan 30]. Available from: https://www.law.go.kr/LSW/eng/engLsSc.do?menuId=2&section=lawNm&query=chemical+substance+control&txt=Query=0&ly=0#ilBgcolor0.
9. National Institute of Chemical Safety, Ministry of Environment. Rule of personal protective equipment in hazardous chemical material handling, rule 2017-7, article 4 [Internet]. Cheongju: National Institute of Chemical Safety; 2017 [cited 2021 Feb 2]. Available from: https://me.go.kr/ysg/file/readDownloadFile.do;jsessionid=CybMslFxdaJJKcTQmUVcG0.mehome1?fileId=194394&fileSeq=1.
10. New Jersey Department of Health. Hazardous substance fact sheet [Internet]. Trenton, NJ: New Jersey Department of Health; 2010 [cited 2021 Jan 30]. Available from: https://nj.gov/health/eh/rtkweb/documents/fs/1903.pdf.
11. United States Coast Guard. National Response Center standard data report [Internet]. Washington, DC: United States Coast Guard; 2007 [cited 2020 Sep 25]. Available from: https://nrc.uscg.mil/FOIAFiles/CY07.xlsx.
12. National Research Council. Acute exposure guideline levels for selected airborne chemicals. Vol. 11. Washington, DC: National Academies Press; 2012.