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CASE REPORT

A serial analysis of hydrogen sulfide poisoning: three group accidents

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Abstract

Hydrogen sulfide (H2S) is a powerful toxic gas in workplace incidents, and it poses a threat to colleagues or family members involved in rescues, leading to a "domino effect" of multiple deaths. In this report, we describe three incidents in which 10 people died, and we present the results of the analyses performed in different incidents, including paper pulp pit, sewer, and sewage well. We provide the macroscopic and morphological findings of ten victims, which include conjunctival hemorrhage, corneal erosion, pulmonary edema, and pulmonary hemorrhage. Additionally, we observed large amounts of waste paper pulp or black sludge in the upper and lower respiratory tracts or upper and lower gastrointestinal tracts of six victims. Furthermore, we conducted a toxicological examination of the victims' blood sulfide using an alkylation extraction approach combined with gas chromatography/mass spectrometry. The sulfide concentrations in the 10 victims ranged from 0.06 to 6.72 mg/L.

Keywords Hydrogen sulfide poisoning · Forensic toxicology · Onsite environmental assessments · Autopsy

Introduction

Hydrogen sulfide (H_2S) is a colorless gas that is soluble in water and denser than air. H_2S is commonly known for its rotten egg odor, which can be detected at a concentration of 0.025 parts per million (ppm), becomes noticeable at 0.30 ppm, can cause local irritation of the conjunctiva, sclera, and upper respiratory tract at 3–5 ppm, and is intense but not unbearable at 20–30 ppm [1, 2]. At higher concentrations (> 100 ppm), the sense of smell is swiftly paralyzed, and no odor can be recognized, but toxicity persists, clearly increasing the risk of H_2S poisoning. When H_2S concentrations in the air approach 0.25–0.30 ppm and remain, they can have an impact on the health of individuals in adjacent communities [3]. H_2S poisoning occurs predominantly in chemical factories, fertilizer plants, paper mills, sewage treatment systems, fisheries, and other places where sulfur-containing organic matter decays [4]. Although H_2S poisoning has traditionally been thought to occur in confined settings, a number of fatal cases in open spaces have been reported in recent years [5]. Fatal poisoning from H_2S exposure is not uncommon in forensic science judgments, and despite its well-known risks, it remains an occupational safety issue that requires immediate attention. The combined findings of histopathology, toxicology, and environmental testing at the scene are critical in determining the cause of death from H_2S poisoning [6]. Air testing at the accident site would be useful in evaluating the results of toxicological analysis, but this has typically been lacking in previous reports.

In this paper, we present a report on 10 fatal occupation-related accidents involving H_2S poisoning that occurred in paper pulp pits, sewers, and sewage wells. We evaluated the results of environmental chemical analyses at the accident sites. Although the victims of each accident died almost simultaneously, their macroscopic and morphological findings, and toxicological results of sulfide levels in the blood were different.

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Materials and methods

To study the characteristics of cases of deaths caused by H_2S poisoning, a review of autopsy documents from 2016 to 2022 was conducted at the Hubei Chongxin Judicial Expertise Center. A total of three accidents resulting in 10 deaths were identified, in which eight victims were analyzed according to the following methods:

Postmortem examination

The bodies were initially examined at the scene and then frozen for preservation until an autopsy could be performed. The time interval from death to autopsy varied for each victim. At autopsy, heart blood was extracted using a blood collection tube and promptly transferred to the laboratory for analysis. The remaining organs were preserved in formalin solution and subjected to histopathological examination using standard forensic pathological examination procedures.

Toxicological examination

An alkylation extraction procedure and gas chromatography/mass spectrometry (GC/MS) analysis, as previously published by Kage [7, 8], were used to determine the sulfide content of the blood. Routine toxicological tests were also carried out by technicians on each victim's blood to rule out the presence of alcohol and typical forensic poisons/drugs.

Onsite environmental assessments

Following the accident, technicians will perform air sampling of the work site. The environmental concentration of H_2S will be detected according to the Chinese method "Air quality determination of hydrogen sulfide, methyl mercaptan, methyl sulfide and dimethyl disulfide by gas chromatography" (GB/T 14678–1993) with a detection limit of 0.2×10^{-3} mg/m^3 [9].

Case presentation

Case 1

The accident took place at a small factory that produced paper plates for eggs. The factory had been shut down for over a month due to a failed environmental inspection. During this time, an abandoned pulp pond was left unattended, and a large amount of sulfur-containing organic material decayed, producing H_2S. Three factory employees (victims 1, 2, and 3) entered the pulp pond for equipment maintenance while stirring the remaining waste pulp, and all three employees quickly collapsed. Victim 4, who was the father of Victim 2, discovered the situation and attempted to rescue the employees without any protection but also immediately collapsed in the pool.

Case 2

The incident occurred in a sewage pipe inspection well that was filled with black sludge. Victim 5 suddenly collapsed during the inspection operation. Victim 6, who attempted to rescue, also fell into the black sludge and collapsed.

Case 3

Another tragic incident occurred in a sewage well, which was approximately 6.5-m deep with an internal diameter of about 0.65 m. A climbing ladder was installed on the well wall. The day before the incident, workers wearing basic safety masks entered Sewer Well A to open the blocked pipe 1 (refer to Fig. 1). After about 40 min of work, the diameter of pipe 1 expanded to 0.3 m, causing an increase in water flow and sewage rate, releasing H_2S into the sewage, and creating a slight rotten egg smell. The workers returned to the surface, closed well cover A, and left. The next morning, four other workers again carried out the work and responded without caution or extensive protective equipment due to no danger identified by previous workers. However, after a full night of sewage flow, a large amount of H_2S had accumulated at the bottom of the sewer well. Although manhole covers A and B were opened for ventilation for approximately 14 min, it was clearly not adequate. Victim 9 was the first to enter the well and immediately collapsed. Victims 7, 8, and 10 were rescued in turn by going down the well, but they all quickly collapsed after shouting or coughing.

A schematic diagram of the accident scene is shown in Fig. 1.

Results

Autopsy findings

The 10 victims, whose ages ranged from 34 to 67 years (victims 9 and 10 were unknown), were all male, normally developed, and well nourished. Autopsies revealed pulmonary hemorrhage, pulmonary edema, bronchial mucosa detachment and necrosis, and marked conjunctival congestion and pinpoint hemorrhages. Only two of the bodies (victims 7 and

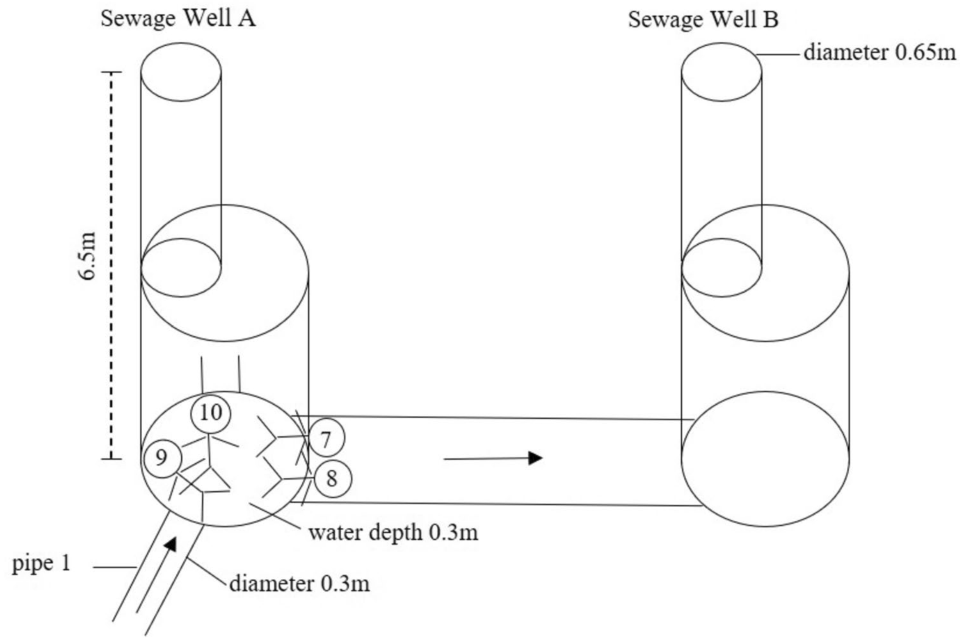

Fig. 1 Direction of water flow; Victims 7 and 8 fell side by side in the sewage channel

8) showed apparent grey–green lividity (Fig. 2a, b). Victims 9 and 10 were not autopsied. The autopsy results of the 8 victims are shown in Table 1 (Figs. 3a–f and 4a, b).

Toxicology test results

The sulfide concentrations in the blood samples obtained during the autopsies were as follows, case 1 = 0.06 mg/L, 0.08 mg/L, 0.07 mg/L, and 0.09 mg/L; case 2 = 4.80 mg/L and 6.72 mg/L; and case 3 = 3.40 mg/L and 2.00 mg/L (Table 2). Routine toxicological tests were carried out by technicians on each victim's blood to rule out the presence of alcohol and typical forensic poisons/drugs, and the results were negative.

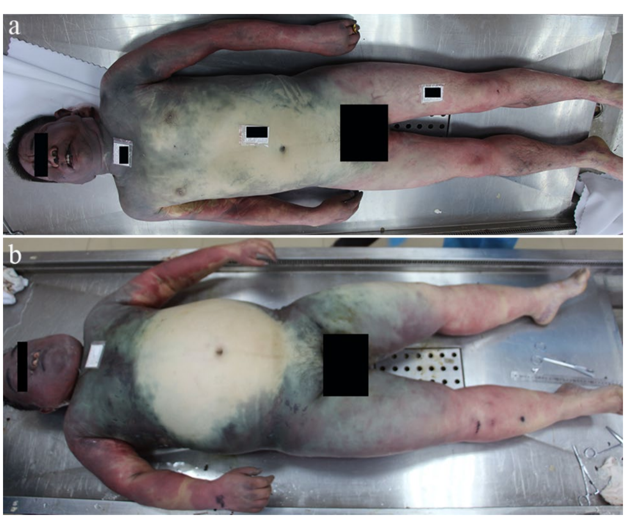

Fig. 2 Macroscopic findings of grey-green lividity. **a** Victim 7 and **b** Victim 8

Onsite environmental test results

As shown in Table 2, the technicians detected different concentrations of H_2S at the three accident sites, which were 63 ppm, 1 ppm, and 490 ppm. Other components found in Case 3 included oxygen (20.3%) and carbon monoxide (0%).

Discussions

H_2S is a highly toxic gas that, much like cyanide, obstructs aerobic cellular respiration by inhibiting cytochrome oxidase and preventing mitochondrial oxygen consumption [10]. H_2S poisoning is an important cause of industrial fatalities. The knockdown effect, characterized by sudden loss of consciousness and respiratory depression, is a prominent and unavoidable aspect of H_2S poisoning [5, 11]. Meanwhile, coworkers or family members who enter the accident site without any protective measures become victims as well, leading to a "domino effect" of death [12, 13]. In addition to accidental poisoning, cases of suicide involving H_2S in confined spaces (homes or cars) have been reported in recent years in countries such as Japan and the United States, where they produce large amounts of H_2S by mixing bathroom sulfur or litho-sulfur compound (a tree spray) with common household cleaners sold in stores [14–18]. However, reports of H_2S suicide in China are still relatively rare.

H_2S is denser than air and can dissolve in water [19]. Accidental H_2S poisoning is commonly associated with

Table 1 The main pathological manifestations of all victims

Cases	Victims	Conjunctiva	Pulmonary findings			Gastrointestinal contents	Other findings
			Edema	Hemorrhage	Other		
1 (paper pulp pit)	1 (male, 43 years old)	Hyperemia	+	+	Deep aspiration of paper pulp, vegetable cells in the bronchi	Paper pulp	Cerebral edema
	2 (male, 44 years old)	Hyperemia	+	-	Deep aspiration of paper pulp, vegetable cells in the bronchi	Paper pulp	Cerebral edema
	3 (male, 63 years old)	Hyperemia	+	-	Deep aspiration of paper pulp	Paper pulp	Several abrasions on the body, cerebral edema, subarachnoid hemorrhage
	4 (male, 67 years old)	Hyperemia	+	+	Deep aspiration of paper pulp, vegetable cells in the bronchi	Paper pulp	Cerebral edema
2 (sewer)	5 (male, 65 years old)	Hyperemia	+	+	Massive aspiration of black sludge, surface bleeding point, diatoms in their lung	Black sludge	Several abrasions on the body, cerebral edema
	6 (male, 58 years old)	Hyperemia	+	+	Massive aspiration of black sludge, diatoms in their lung	Black sludge	Several abrasions on the body, subarachnoid hemorrhage, pleural hemorrhages
3 (sewerage well)	7 (male, 51 years old)	Hyperemia, erosion	+ (high-grade)	+	Surface dark green, Bronchial mucosal necrosis	NO	Gray–green lividity, few abrasions on the body, cerebral edema, tracheal mucosal hemorrhage
	8 (male, 34 years old)	Hyperemia, erosion	+ (high-grade)	+	Bronchial mucosal necrosis	NO	Gray–green lividity, several abrasions on the body, cerebral edema, tracheal mucosal hemorrhage
	9,10 (male, -)	NT	NT	NT	NT	NT	NT

NT not tested

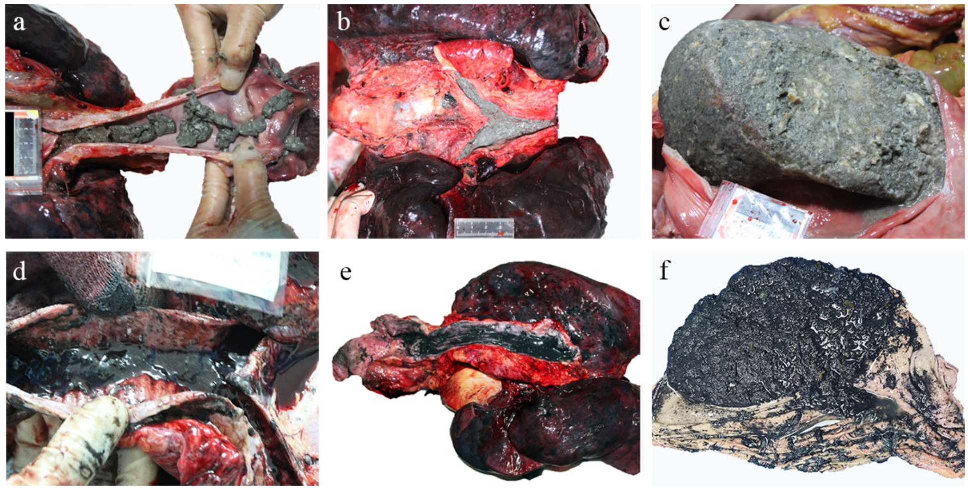

Fig. 3 Macroscopic findings. **a** Aspiration of paper pulp in victim 3. **b** Aspiration of paper pulp in victim. **c** Paper pulp in the stomach of victim 3. **d** Aspiration of black sludge in victim 6. **e** Black sludge residue on the entire esophageal wall of victim 5. **f** Black sludge in the stomach of victim 6

first-time entry into a sewer well. However, in case 3 of this study, the construction workers were safe on the first day before fatal poisoning occurred on the second day. This indicates that the gas in the sewer system is gradually released with increasing water flow, causing the concentration of H_2S to gradually increase and collect at the bottom of the sewer well, eventually leading to tragedy.

In H_2S poisoning, there are no specific pathological findings. However, all victims had similar pulmonary pathology and signs of local irritation, such as pulmonary edema, pulmonary hemorrhage, conjunctival hemorrhage, and corneal erosion [20, 21]. The gray–green lividity, as described in traditional forensic textbooks, is not commonly found in the literature and is only clearly described in the reports of Mihoko Ago and Nunziata Barbera [12, 22]. It is formed by the combination of sulfide and hemoglobin [23, 24]. In the present report, only two victims from case 3 showed grey–green lividity. Several abrasions and contusion injuries were detected on the bodies in victims 3, 5, 6, 7, and 8, who likely lost consciousness and collapsed rapidly after exposure to large amounts of H_2S [20]. Interestingly, paper pulp or black sludge from the accident site was found in the upper and lower respiratory tracts as well as in the upper and lower digestive tracts of the six victims in this study. Similar studies by Kimura and Oesterhelweg also described the discovery of diatoms or feces in the upper and lower respiratory tracts of H_2S poisoning victims, suggesting that they died by accidental inhalation and asphyxiation [25, 26].

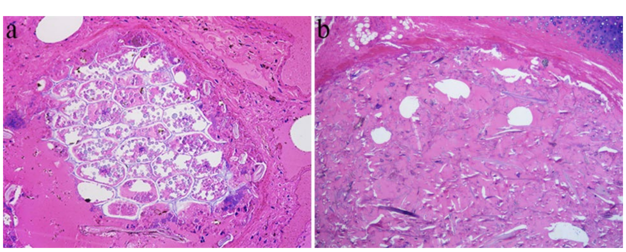

Fig. 4 Morphological findings in case 1. **a** Vegetable cells in the lungs of victim 2 (HE, 40×). **b** Fibers in the lungs of victim 4 (HE, 100×)

Blood sulfide testing is a useful indicator of reaction to H_2S poisoning. Our study reported sulfide concentrations of 0.06–6.72 mg/L in the victims' blood, which were essentially similar to the 29 cases of death due to accidental inhalation of H_2S gas (0.08–9.36 mg/L) reported by Kyoko Maebashi [27]. In a study of clinical blood samples from 100 randomly selected normal patients, sulfide concentrations were always below 0.05 mg/L [28]. Although postmortem decay can produce sulfide, McAnalley reported that it can be suppressed if the specimens are refrigerated or frozen, with no significant effect on toxicological analysis results, and that the amount of H_2S ingested in vivo has a much stronger effect on blood sulfide concentrations than postmortem factors [27]. However, the four victims in case 1 had relatively low concentrations of sulfide in their bodies, presumably because they lost consciousness after inhaling lower concentrations of H_2S at the scene and then fell into the pulp pool, where they died of asphyxiation from inhaling large amounts of pulp. This may also be due to the long postmortem interval between their deaths, resulting in sulfide volatilization or oxidative decomposition [29].

The main limitation of this study is that blood concentrations of thiosulfate (TS), the main metabolite of H_2S entering the body, were not analyzed [30, 31]. By comparing the concentration of blood sulfide and TS, it is possible to infer the duration of survival and the order of events in cases of H_2S poisoning, helping law enforcement to reconstruct the actual situation of the accident [23, 25]. However, it has been demonstrated that in situations of fatal H_2S poisoning, the TS test may be negative since death occurs quickly and there is no time for H_2S to be transported to the liver and

Table 2 All victims' blood sulfide concentrations and ambient H_2S gas detection

Case	Victim	PMI (days)	Blood sulfide concentrations (mg/L)	Death to environmental testing (days)	H_2S concentrations onsite (ppm)
1	1	16	0.06	2	63
	2	16	0.08	2	63
	3	16	0.07	2	63
	4	16	0.09	2	63
2	5	2	4.80	3	1
	6	2	6.72	3	1
3	7	11	3.40	0.4	490
	8	11	2.00	0.4	490
	9,10	NT	NT	0.4	490

NT not tested

metabolized to thiosulfate [1, 27]. In some similar cases of fatal poisoning, such as those involving trucks and tankers, thiosulfate was found to be absent from the blood, and the results of the site environmental analysis were not reported [5, 6].

Lack of elevated blood sulfide or TS concentrations does not immediately rule out H_2S poisoning. In cases where sudden unconsciousness and asphyxiation lead to death, environmental chemical testing at the scene of death can provide sufficient evidence to confirm H_2S poisoning [6, 24, 32]. According to the Chinese occupational exposure limits for hazardous factors in the workplace, the maximum limit value for H_2S is 6.59 ppm (10 mg/m^3) [33]. In previous cases of H_2S poisoning resulting in multiple deaths, there were only a few reports of detecting onsite H_2S concentrations (Table 3). As with previous reports, the diagnosis of H_2S poisoning in both case 1 and case 3 will be confirmed by the detection of H_2S concentrations above the standard in the environment. Unfortunately, in case 2, the site had been vented after the accident, and the technician testing on the third day found that the H_2S concentration was within the maximum limit, contradicting the victims' toxicological analysis result. Therefore, there are issues with measuring H_2S in the incident environment, as technicians arrive at the site to perform tests after victims have been transferred or even after ventilation, which often leads to mixing of H_2S with outside air at the site [25].

In conclusion, unilateral findings in cases involving suspected H_2S poisoning can vary significantly, and a combination of autopsy findings, toxicological results, and early environmental examination is essential in determining the cause of death. It is important to emphasize that mass H_2S poisoning still occurs in some workplaces where hazards are known to exist. We need to increase awareness of these risks and establish safe work procedures. In the e vent of poisoning, victims should be moved promptly to an open environment, but rescue attempts should not be made without a self-contained breathing apparatus.

Table 3 Field environmental testing and toxicological analysis of blood in other fatal cases

Accident summary	H_2S concentrations in the environment (ppm)	Blood sulfide concentrations (mg/L)	Blood TS concentrations (mg/L)	Number of deaths
Removal of heavy oil from cargo ship [33]	30 ppm	NT	9.97	2
Repaired in the sewer [20]	34 ppm	NT	0.09	2
Transferred organic fertilizer to tank [5]	102 ppm	NT	1.21, 4.5	2
Woman suicided in the room [34]	110 ppm	0.66	1.71	1
Drainage pump house of fish farm [7]	123 ppm	0.96,30.4	13.4	2
Underground tank for waste water in a hospital [35]	150 ppm	0.22	2.8	1
Indoors next to the biogas plant [25]	> 2000 ppm	NT	NT	4
Family of three fell into volcanic crater [31]	2200 ppm	3.84–12.48	0.22–4.44	3

NT not tested

Key points

1. The authors describe three fatal H2S poisoning accidents resulting in 10 deaths.
2. The death of the workers in case 3 occurred during the second entry into the sewage well.
3. Sludge or paper pulp was found in the respiratory and digestive tracts of six of the victims.
4. Relatives involved in the rescue also died as a direct result.
5. Blood sulfide concentrations in all cases ranged from 0.06 to 6.72 mg/L.

Data availability The data underlying this article can be found in the article.

Declarations

Informed consent Written informed consent for publishing this scientific report was obtained from the direct relative of the decedent in these cases.

Conflict of interest The authors declare no competing interest.

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