

Acute collective gas poisoning at work in a manure storage tank

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Abstract

Cases of deaths in manure or septic tanks are rare in legal-medical practice, more frequently as unfortunate occupational accidents. Poisoning with toxic gases, especially with hydrogen sulfide, is reported as the cause of death, while the exhaustion of oxygen in the air is omitted with the simultaneous excess of carbon dioxide. In such cases, determination of the direct cause of death constitutes a big problem because post-mortem examination does not reveal the specific changes. A case of acute collective poisoning by gases in a manure storage tank is presented of 5 agricultural workers, 2 of whom died. While explaining the cause of poisoning and deaths, toxicological blood tests were performed in the victims of the accident, as well as gases inside the manure storage tank. The post-mortem examinations and toxicological blood tests performed did not allow determination of the direct cause of death. Toxicological tests of gases from inside the manure tank showed a very low concentration of oxygen, with a simultaneous very high concentration of carbon dioxide, and a considerable level of hydrogen sulfide. The cause of fainting of three and deaths of two workers was not the poisoning with hydrogen sulfide, but oxygen deficiency in the air of the tank.

Key words

acute poisoning, collective poisoning, manure gas poisoning, gases, work in a manure storage tank

INTRODUCTION

In the countries of the European Union the problems of environment protection and labour protection in association with agricultural production, especially breeding and raising of livestock, are considered as important. At present, the conditions for breeding and raising animals must satisfy a number of requirements, including the storage and disposal of faeces, which are a valuable natural fertilizer. Inadequacies associated with the storage of animal faeces may cause the contamination of ground and surface waters, as well as human poisonings with the produced gases. The faeces are stored in manure tanks, which are above ground or underground, without the necessity to enter them for service purposes. In such tanks – apart from a considerable amount of water – there are animal faeces and a large amount of fermenting organic substances. As a result of anaerobic decomposition of organic substances, various hazardous gases are produced, such as: methane, hydrogen sulfide, ammonia, carbon dioxide, and in addition, chemical compounds which are defined as odours (fetors) [1-7].

Hydrogen sulfide (H₂S) is a colourless, flammable, extremely toxic gas. At low concentrations it has a characteristic rotten-egg smell, but can be present at dangerously high concentrations, with no perceivable odour. In low concentrations, hydrogen sulfide has an irritating effect on the respiratory tract mucosa, causes inflammatory changes and

conjunctivitis. High levels of this compound cause a rapid loss of consciousness, neurological disorders, respiratory failure, and even death due to suffocation, which occurs within few minutes. The suspicion of a fatal poisoning with H₂S should be based on a precise analysis of the circumstances of the event. The diagnosis should be confirmed by a qualitative, and if possible, quantitative H₂S analysis.

Ammonia (NH₃) is a colourless gas with a characteristic pungent odour (which acts as a warning), produced by reduction of nitrogen compounds and in the decaying processes of plant and animal material. Ammonia is absorbed mainly in the airways, in higher concentrations, in contact with the humid surface of the mucous membranes it produces ammonium hydrate which has strong irritating properties, causing bronchitis, and, in acute poisonings – pulmonary oedema, bronchial pneumonia, oedema of the glottis, respiratory centre depression, which leads to death.

Methane (CH₄) – also known as swamp or mine gas – is the main component of natural gas. This gas is odourless and colourless, absorbed mainly in the lungs, and through this route may induce the symptoms of a general poisoning by exerting a depressant effect on the central nervous system.

Carbon dioxide (CO₂) is a colourless, odourless and non-flammable gas, well soluble in water; it accumulates near the ground surface (is 1.5 times heavier than air), especially in silos, manure tanks, and wells, displacing oxygen. It is the product of combustion, fermentation and respiration. In low concentrations, carbon dioxide is non-toxic, however, in high concentrations it is harmful for health or even lethal, causing the development of hypercapnia and respiratory acidosis. In liquid manure are also produced other, volatile substances (so-called odours), such as: amines, carbonyl compounds,

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merkaptans, various alcohols, ketones, aldehydes, and additionally, especially putrescent smelling indoles and skatoles.

In confined spaces, such as manure storage tanks, the concentration of toxic gases may be high, even life-threatening, especially with the lack of adequate aeration. Individuals who enter inside the manure storage tank are exposed, among other things, to poisoning with the above-mentioned gases by the respiratory route. Due to this, one should never enter the tank or pit which had not been previously aired and cleaned from sewage. It is not possible to determine the direct effect of death of a victim in a manure storage tank, septic tank or silo based only on postmortem examination. In such cases, the results of examinations at the site of the event and circumstances preceding death are very useful in establishing the cause of death. In the cases of death in manure storage or septic tanks described, various causes of death have been reported, most frequently an acute poisoning with hydrogen sulfide, and only sporadically an oxygen deficiency [4, 8-14].

The employees operating manure storage tank should be familiar with the principles of providing first aid in the case of accident or poisoning. In the majority of reports it is absolutely recommended that these workers should apply protective masks with proper absorbers, this is incorrect, because the main cause of death is oxygen deficiency caused by an insufficient amount of oxygen in the inhaled air. Therefore, in these conditions it is necessary to wear oxygen apparatus [3, 15, 16].

Quick and reliable detection of dangerous concentrations of toxic gases or low oxygen concentration is crucial for employees working in hazardous conditions. A wide variety of portable and stationery gas detectors are available on the market. Detectors are designed for simultaneous measurement of explosive, toxic and flammable gases, as well as oxygen loss. For measurement of explosives and combustibles, catalytic sensor are used. Detection of toxic gases and oxygen utilizes high-quality electrochemical and infrared sensors [17].

OBJECTIVE

- 1) Determination of the concentration of gases most often occurring in a manure storage tank.
- 2) Presentation of a case of acute, collective poisoning in a manure storage tank – with 2 fatal and 3 fainting victims.

CASE DESCRIPTION

In September 2008, on a farming enterprise, several employees carried out maintenance activities in a manure storage tank with a depth of approximately 3 m, situated in an excavation below ground level. One of them entered into the tank in order to install a seal on the pump at the bottom. After a while, this employee fainted and fell off the third step of the ladder by which he had descended to the bottom of the. The other workers went into the tank to help him, but they also started to faint or feel bad after getting out of the tank into the fresh air. As a result of the rescue action, two people died, and three were taken to hospital due to fainting with the symptoms of acute poisoning.

METHODS AND MATERIALS

Gas samples for toxicological tests were collected into two containers from the site of accident, from inside the manure storage tank – the respiratory zone of the victims of the poisoning. The samples were taken over the surface of the liquid in the tank into two plastic containers marker No.1 and No. 2. Analyses were performed by the headspace gas chromatographic (HSGC) method developed for using chromatograph Chrom 5 (Prague, Czech Republic), equipped with a thermal conductivity detector (TCD) working at 50°C. A glass column (L. 3.5 m, I.D. 2 mm) packed with: HayeSep Q 80/100 (Alltech, USA) was used for the analysis of volatile inorganic compounds of the character of acyl anhydrides (carbon dioxide – CO₂, sulfur dioxide – SO₂, nitrogen dioxide – NO₂), acids (hydrogen sulfide – H₂S, hydrogen cyanide – HCN) – also water. The glass column (L. 3.5 m, I.D. 2 mm) packed with Molecular Sieve 5A 80/100 (Alltech USA) was applied for the analysis of neutral compounds (carbon monoxide – CO, oxygen – O₂, nitrogen – N₂, methane – CH₄). Hydrogen was used as the carrier gas. Gas flow was 20 ml/min. Analysis was performed under isothermal conditions i.e. 35°C for both columns. Injection port temperature was 40°C for HayeSepQ column and 35°C for Molecular Sieve 5A. 0.5 ml of gas sample was introduced by gastight syringe to the injection port.

The two fatal victims were subjected to autopsy, which did not show neither pathological changes nor injuries explaining the cause of death. Post-mortem examinations showed only a passive hyperemia of the internal organs, presence of fluid blood in the cardiac chambers and blood vessels, and pleural petechiae. Also, histopathologic tests of specimens of the internal organs did not show any pathological changes or injuries.

The remaining three victims were provided with medical assistance in the hospital where they had been hospitalized for 2-3 days for observation. In the hospital, no organic changes were diagnosed which would be the result of poisoning.

Blood and the vitreous body of the eye were collected from the fatal victims, and blood from victims who were provided hospital care.

RESULTS

Toxicologic analysis of the gas collected over the liquid into plastic containers numbered 1 and 2, column packed with HAYE SEP Q, when calculated into percentages (%), showed the presence of the following (Table 1):

Table 1 Toxicologic analysis of the gas collected over the liquid into plastic containers numbered 1 and 2, column packed with HAYE SEP Q.

	air collected in chemical-toxicological laboratory	gas from over liquid container No.1	gas from over liquid container No.2
air – N ₂ , O ₂	98.4%	75%	73.7%
methane – CH ₄	–	5.1%	4.4%
carbon dioxide – CO ₂	0.1%	14.5%	14.1%
water vapour – H ₂ O	1.5%	3.4%	5.9%
hydrogen sulfide – H ₂ S	–	2%	1.9%

Analysis of the gas from over the liquid collected into plastic containers No.1 and No. 2, column packed with molecular sieve 5A, when calculated into percentages (%), showed the presence of the following (Table 2):

Table 2 Analysis of the gas from over the liquid collected into plastic containers No.1 and No. 2, column packed with molecular sieve 5A.

	air collected in the chemical-toxicological laboratory	gas from over the liquid container No.1	gas from over the liquid container No.2
oxygen – O ₂	20.99%	1.57%	1.44%
nitrogen – N ₂	79.01%	90.86%	91.65%
methane – CH ₄	–	7.57%	6.91%

The tests for the presence of volatile organic compounds performed by the headspace gas chromatography method in the blood and vitreous body of the eye collected from the corpses confirmed the lack of ethyl alcohol, whereas in the survivors of the accident, no ethyl alcohol was found in the blood: however, trace amounts of acetone were present. Examinations of blood samples taken from all the victims, carried out by the headspace gas chromatography method, did not confirm the presence of any other volatile organic compounds.

DISCUSSION

In Polish literature, apart from press releases, there are few reports concerning the causes of deaths in confined spaces, such as in the above-analyzed case, while performing maintenance work activities or cleaning. Two cases of deaths in silos have been described, which also occurred in September; therefore, this month seems to be especially dangerous in agriculture with respect to the poisonings described. In one case, the silo was half-filled with cut sweet corn, and in the other there were the remains of sour cabbage and water. The toxicological studies conducted in the air of the silo with corn did not show the presence of H₂S and CO, while CO₂ was found within 26% volume range and O₂ within 12% volume range. In the second case, the toxicological examinations of a jar with sour cabbage collected from the silo showed the presence of CO₂ within volume range 17%, O₂ 25%, and CO, and CH₄ within the volume range 26.4%. In both cases, based on the results of autopsy and auxiliary tests, it was determined that the cause of death of the victims was acute poisoning with carbon dioxide [15].

Cases of deaths in manure storage pits and septic tanks have been more frequently described in the international literature. The descriptions of cases of death after entering such tanks show that there were many other fatal victims among them who, in an unskilled way attempted to render assistance to the victims of poisonings, and themselves sustained fatal acute poisonings. On private farms these were often family members. In such cases, the cause of death poisoning with hydrogen sulfide or other toxic gases (carbon dioxide) were most frequently reported, and suffocation due to oxygen deficiency was sporadically mentioned [6, 7, 18-20]. In the presented case of acute collective poisoning, the determinations were based on toxicological tests of the air in the manure storage pits. It was found that in the manure

tank, toxic gases were produced, the mean concentration of which was within the following volume range: methane – 50-80%, CO₂ – 20-50%, H₂S – 2-8%, and additionally, small amounts of other gases, such as O₂, N₂, NH₃, CO – within the volume range 1-5% [5, 18-20]. Even small concentrations of toxic gases present inside the manure tank may cause bronchospasm resulting in dyspnea. The lack of rotten egg odour, characteristic of hydrogen sulfide may be misleading, because this odour disappears with an increase in the concentration of this gas. The poisonous effect of this mixture is mainly due to the concentration of H₂S and CO₂ [3, 5, 16, 21].

Studies conducted in the years 1980-1989 in the USA, showed that, on average, there were 89 deaths annually during work in any types of confined spaces. In this group, there were approximately 20 victims (22%) who attempted to rescue others, and unfortunately sustained fatal poisoning themselves, because they could not act in a safe way [16]. Similar studies during the period 1982 - 1992 indicated that in 68 such events there were 104 fatal victims, 36 (35%) of whom were employees who died while unskillful rescuing others [3, 21]. Harmful gases are produced in manure storage tanks during each season of the year; nevertheless, in summer, there occur optimum conditions for the activity of microbes, which may result in an increased gas production. In the years 1980-1989, 22 deaths were noted during the period from April-September [16]. The release of gas from manure storage tanks also depends on the period of its storage, adding water, re-pumping to collectors, and homogenization [3, 5, 16, 22].

In confined spaces such as manure storage tanks, with limited entry and exit apertures, and also unfavourable natural ventilation, due to the decomposition and fermentation of manure and wastes, toxic gases are produced, such as methane, hydrogen sulfide, ammonia and carbon dioxide, and also oxygen deficiency. Low oxygen concentrations are mainly the result of the activity of bacteria and fungi, which use up oxygen for their needs, producing excessive amounts of carbon dioxide. In pure ambient air, the oxygen content is 21% and carbon dioxide 0.033%. Based on literature, with oxygen concentration in inhaled air within the range of 10-15%, there occur disorders in the assessment of the situation and motor coordination, with the concentration of 8-10% - loss of consciousness, and death occurs at concentrations of 8% or lower. Loss of consciousness occurs rapidly, within less than a minute (about 40 seconds), and death – within several minutes, with oxygen concentration in the environment of 4-6% [18-20, 23-25].

The cause of fainting, and even death of people present in such confined spaces may result from low oxygen concentration in inhaled air and/or the direct effect of toxic gases. Although suffocation was reported as the primary cause of death of victims of such accidents, the precise pathomechanism of death was often difficult to establish. The results of autopsy of such victims are non-specific, and most frequently the specific gases which might have caused death were not determined. In the cases of deaths in small, confined spaces, suffocation due to oxygen deficiency or its low concentration in the air of these spaces was reported, caused by its replacement by carbon dioxide [6, 21, 23].

In the presented case, in the manure storage tank where the workers were performing maintenance work activities in order to install a seal, intensive fermentation processes

were taking place, with the lack of aeration of the tank or its insufficient aeration before starting work, which resulted in the production of toxic gases with a considerable accumulation of carbon dioxide in the air of the tank. In the case analyzed, physico-chemical examinations confirmed that the concentrations of gases remained within the following ranges: CH_4 – 5.1-7.57%, CO_2 – 14.1-14.5%, O_2 – 1.44-1.57%, H_2S – 1.9-2.0%. Thus, own studies showed a very low oxygen concentration, very high concentration of carbon dioxide, and a considerable concentration of hydrogen sulfide in the atmosphere of the manure storage tank. This allows the presumption that the cause of death of two of the workers and fainting by the remaining three workers was oxygen deficiency, caused by a considerable oxygen deficit in the air of the manure storage tank.

CONCLUSIONS

1. Cases of deaths in manure storage and septic tanks are rare, and happen mainly in rural areas.
2. In confirmed spaces of manure storage tanks, the concentration of toxic gases may be high, even life threatening, especially without proper aeration, accompanied by a considerable oxygen deficiency.
3. The cause of death in manure storage and septic tanks is oxygen deficiency due to the exhaustion of its resources during the decaying process. Work in such spaces is dangerous and may be threatening to health and life.
4. Agricultural workers should be educated never to enter manure storage tanks without oxygen apparatus, even to rescue victims. The workers may enter the manure storage tanks only provided that the tanks have been previously properly aerated and cleaned from sludge. They should be equipped with oxygen apparatus and insured by others.

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