Comparison of storage stability of hydrogen sulfide in Tedlar bags in different sampling temperatures

Porównanie stabilności przechowywania siarkowodoru w workach tedlerowych w różnych temperaturach pobierania próbek

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Keywords: air pollution; chromatography; hydrogen sulphide; odour; Tedlar; sampling; storage.

Abstract

The purpose of this study was to investigate the stability of storage losses of hydrogen sulphide in Tedlar sampling bag materials at different sampling temperatures (between 4°C and 37°C). Conditions of samples storage were as follows: 20°C storage temperature, exterior relative humidity – 40%, without any light exposure. After first 8 hours of H2S storage, two groups of sampling temperature ranges were distinguished – with more than 50% reduction (range of sapling temperatures from 13°C to 20°C) and with less than 50% reduction of hydrogen sulfide concentration (temperatures between 4°C and 13°C and from 23°C to 37°C). This trend continued up to 25 h and 29 h when the reduction of the hydrogen sulfide concentration became greater than 50% (the temperatures, respectively, 13-14°C and 15-17°C). The highest reduction of H2S was observed for the extreme temperatures (4-6°C and 37-38°C), with the biggest differences between sampling and storage temperature values. Present study draw attention to the temperature as an important factor (between i.a. humidity and pressure) which should be considered not only during the storage, but also in the sampling phase of air analysis. Difference between temperature in both phases can cause important changes in compound concentrations.

Słowa kluczowe: chromatografia; odór; pobieranie próbek; przechowywanie próbek; siarkowodór; Tedlar; zanieczyszczenia powietrza

Streszczenie

Celem badania było zbadanie stabilności oraz strat stężenia siarkowodoru podczas przechowywania w workach Tedlarowych, w różnych temperaturach pobierania próbek (pomiędzy 4°C i 37°C). Warunki przechowywania próbek były następujące: temperatura przechowywania: 20°C, wilgotność względna na zewnątrz: 40%, brak ekspozycji na światło. Po pierwszych 8 godzinach przechowywania H2S, wyróżniono dwie grupy zakresów temperatur pobierania próbek – z ponad 50% redukcją (zakres temperatur od 13°C do 20°C) i z mniej niż 50% redukcją stężenia siarkowodoru (temperatury od 4°C i 13°C oraz od 23°C do 37°C). Trend ten utrzymywał się do 25 h i 29 h, kiedy redukcją stężenia siarkowodoru przekroczyła 50% (temperatury odpowiednio 13-14°C i 15-17°C). Największą redukcję siarkowodoru zaobserwowano w skrajnych temperaturach (4-6°C oraz 37-38°C), przy największych różnicach między wartościami temperatury pobierania próbek i przechowywania. Niniejsze badania zwracają uwagę na temperaturę jako ważny czynnik (pomiędzy innymi wilgotnością i ciśnieniem), który powinien być brany pod uwagę nie tylko podczas przechowywania, ale także w fazie pobierania próbek do analizy powietrza. Różnica między temperaturą w obu fazach może powodować istotne zmiany w stężeniach związków.

Introduction

Odour complains which arise from the volatile sulfur compounds (VSCs) emissions sources, such as feedlots, poultry sheds, municipal and landfills, wastewater treatment plants, as well as composting and mechanical-biological waste treatment plants, are the major issue of waste and wastewater management (Gostelow et al. 2001; Trabue et al. 2006; Le et al. 2013). Those sources emit i.a. onerous volatile chemicals: aldehydes and ketones, inorganic nitrogen, alcohols, fatty acids and sulfur compounds, such as reduced sulfur compounds (RSCs) (Borras et al. 2016). RSCs are particulary responsible for unpleasant, odour nuisance to local populations. Among them, the common odourants of wastewarte treatment processes are, especially, mercaptans and sulphides. The existence of so many different odourous compounds associated with above activities and processes creates potential problems while individual compounds are used as the basis for odours assessment. Also, it is noteworthy, that, cited in the literature as well as regulations, odour annovance threshold levels are highly variable for, i.a., hydrogen sulphide and other compounds (Mahin 2001). Domestic wastewater includes 3-10 mg/L organic sulfur, especially from proteinaceous material (e.g. sulfur containing amino acids - cysteine and methionine), sulfonates originating from household detergents as well as 30-60 mg/L inorganic sulphur as sulphates (Gostelow & Parsons 2000). The highest concentrations of H₂S were noticed in sewers and influent of WWTPs. The main problem is, that sulphur compounds have a low odour threshold value – for example, this value for H_2S is below 100 ppb (Haydt 2001). Concentration of 30 ppb could be detected by over 80% of population (Maasikmets et al. 2015). The main process causing odour emission in wastewater treatment plants is an organic matter anaerobic degradation, which results a generation of i.a. hydrogen sulphide and mercaptans. Sulphur compounds emitted into the atmosphere or comes from sulphate aerosols and acids (mainly sulphuric or methanesulphonic acid) occur as a sub-micrometer size

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particles (Maasikmets et al. 2015). VOCs odour, because of its unpleasant nature, can also give rise to concern among health hazard of public. Although, in most cases, this is not a real health threat. Odorous air can be seen as "non-healthy" among people (Zarra et al. 2008). Sulvok et al. (2001) mentioned, that the analysis of those compounds is difficult due to absorption processes in the surfaces. Additionally, mercaptans my undergro partial oxidation. The European standard for dynamic olfactometry defines three types of sample bags: tetrafluoroethylene hexafluoropropylene copolymer (FEP), polyvinylfluoride (PVF, Tedlar TM) and polyethyleneterephthalate (PET, Nalophan NATM). During industrial routine analysis, Tedlar (polyvinylfluoride) and/or Nalophan bags are usually chosen. Tedlar is commonly used as sampling bags material in the USA, while Nalophan is more widely used in Europe and Australia. Their main advantage is inertness as well as low cost (Sulyok et al. 2001; Trabue et al. 2006; Le et al. 2013), the main disadvantages: storage losses caused by leakage and sorption on the material surface. Also, the problems in storage of most of VSCs are metal catalytic and photo oxidation (Sulyok et al. 2001). Guillot and Beghi (2008), during analysis of Tedlar, Teflon and Mylar bags show H₂S concentration losses due to permeation of that compound through sampling bag material. It has been shown that the concentration of reduced sulfur compounds, amines, carboxylic acids, phenols and indoles decreases during the storage due to sorption to the bag material and diffusion out of the bags (Trabue et al. 2006; Guillot & Beghi 2008; Hansen et al. 2011). Odor decay rates depend on bag materials and kind of analyzed compounds. Covne et al. (2011) wrote, that the best for collection of VOCs are: SamplePro FlexFilm, FlexFoil PLUS, and Tedlar, while FlexFoil PLUS is an optimal alternative for the sulfur compounds. SamplePro Flex-Film, FlexFoil PLUS and Tedlar are suitable for CO, CO₂, and methane analysis, and FlexFoil PLUS is the optimal alternative for hydrogen. Zarra et al. (2012) wrote, that ammonia and H₂S easily escapes from Nalophan sample bags, so that material is not recommended for those compounds. According to Bakhtari (2014), Tedlar has a better holding properties than Nalophan, when decay of sulfur compounds concentration is considered. Furthermore, that author wrote, that, due to specific smell of virgin Tedlar, it can contaminate a weaker sample of odour. It was demonstrated that PVC, silicone and stainless steel was less suitable for sample introduction of VOCs analysis than PTFE (Teflon) (Sulyok et al. 2001; Kim et al. 2006). Also, the potential loss could be the result of surface and reaction with gases and particles during the dilution phase. The short storage time is one of the most important limitation of odorous chemical compounds (Borras et al. 2016). For example, samples collected by Tedlar bags must be evaluated before 24 h or high losses are reported. On the other hand Laor et al. (2010) wrote, that storing sample for 30 hours before measurement is acceptable. Unfortunately, there is lack of data that can be used to assess the potential impact of storage of samples from different sources of unpleasant odors. Temperature and relative humidity may also - in addition to chemical compounds - affect the olfactory sensation and change in environment condition could affect the sensory response. Reinikainen et al. (1992) found, that the perception of indoor air quality increased, when humidification increases from 30% to 40%, while. Le et al. (2013) wrote, that there were still no verification studies on the effect of various temperatures on the transformation and loss of VSC in sample bags despite the fact, that the temperature is a very important factor affecting the chemical reactions, the rate of diffusion and permeation through the bag material.

The purpose of this study was to investigate the stability of storage losses of hydrogen sulphide in Tedlar sampling bag materials at different sampling temperatures (between 4°C and 38°C), with 20°C storage temperature, exterior relative humidity of 40% and without any light exposure. H_2S was chosen as one of the compound that as a significant impact on the disadvantages of smell and very low odour threshold value.

Methods

Tedlar bags were flushed with odour free air (pure nitrogen) to reduce odour background levels. Air contaminated by generated hydrogen sulphide, as only air contaminant, was taken to 10 L Tedlar bags by a suction-embossing pump, through silicon hoses, in different temperatures from 4°C to 38°C (n=40). After that, bags were stored in standard conditions: 20°C storage temperature, exterior relative humidity of 40% and without any light exposure. Concentration of hydrogen sulphide was determined using Photovac Voyager chromatograph.

Tedlar gas sampling bags of 50 μ m thickness used for determinations are recommended in many US EPA methods including TCLP and methods TO-3 (VOCs), TO-12 (NMOC), TO-14A (VOCs), TO-15 (VOCs), ASTM D-5504 (reduced sulfur compounds) and a variety of atmospheric gas methods.

Photovac Voyager is a portable, automatic gas analyzer for identifying airborne chemicals and measuring their concentrations. Voyager uses a gas chromatograph (GC) to analyze air samples and collects a sample of air and automatically introduces the sample into the GC. It uses photoionization detector (PID), precolumn and three columns for heavy (C7-C12), middle (C3-C7) and light (C1-C3) compounds): 4 m×53 mm×2.0 µm SPB-35 (precolumn), 8 m×0.25 mm BLANK Fused Silica (column A), 20 m×0.32 mm×1.0 µm Supelcowax10 (PEG)(column B), 15 m×0.32 mm×12 µm Quadrex 0071 (column C). Carrier gas used for determinations was a high purity nitrogen. Column oven in Photovac Voyager is isothermal 55°C to 80°C. The Voyager can be effectively used to monitor many of the volatile organic compounds listed in EPA Method 8240A, including chlorinated and aromatic hydrocarbons. Method detection limits (MDLs) for VOCs range from parts per trillion (ppt) in water to about 500 parts per million (ppm) in ambient air, depending upon the type of compound and detector used. (Szyłak-Szydłowski 2015)

For the analysis, sampling temperatures were grouped into eight compartments: (4-6°C), (7-8°C), (13-14°C), (15-17°C), (17-20°C), (20-22°C), (23-26°C), (37-38°C). The relative recoveries were normalized. In case of significance for a number of variances, the Bartlett test was used. This test concerns of k normal populations $N(\mu,\sigma_i^2)$, which the hypothesis of equality of variance in all populations was verified. Hypotheses are as follows:

$$H_0: \sigma_1^2 = \sigma_1^2 = \cdots = \sigma_k^2$$
$$H_1: \sim H_0$$

It is based on statistics having the asymptotic distribution χ^2 , and the convergence of the distribution of χ^2 is very fast. Because of this, Bartlett test can be used to very small populations (for example nⁱ ≥ 6). If:

$$c = 1 + \frac{1}{3(k-1)} \left(\sum_{i=1}^{k} \frac{1}{n_i - 1} - \frac{1}{n-k} \right)$$

then, test statistics is:

$$\chi^{2} = \frac{1}{c} \left[(n-k) \ln \frac{\sum_{i=1}^{k} n_{i} S_{i}^{2}}{n-k} - \sum_{i=1}^{k} (n_{i}-1) \ln \frac{n_{i} S_{i}^{2}}{n_{1}-1} \right]$$

and the critical area:

$$C = \left[\chi^2_{1-\alpha,k-1},\infty\right)$$



Fig. 1 Changes of content of hydrogen sulphide during 56 hours storage in Tedlar bags Rys. 1 Zmiany zawartości siarkowodoru podczas 56-godzinnego przechowywania w workach Tedlarowych

Because the test is very sensitive to deviations from the normal distribution, also the test Flinger-Killeen was used, which is more resistant to outliers. The use of the Hartley test was considered, but it is robust on a derogation from the normal distribution. So the Levene test was performed. It's a version of the F-test, which uses, instead of the original populations, $|X_t - \bar{X}|$. The idea of the test is reduced to compare the significance of the differences of the average deviation instead of variance.

Results and discussion

Table 1 contains Bartlett's, Fligner-Killens and Levene's test results for different ranges of the temperature values. Table 1 Results of Bartlett's, Flinger-Killen's and Levene's tests for different ranges of the temperature values

Temperature ranges (°C)	Bartlett		Flingen-Killen		Levene	
	χ²	р	χ²	р	F	Pr (>F)
4-6	15,16	0,0017	7,12	0,0680	1,47	0,2292
7-8	11,90	0,0770	14,22	0,0026	2,54	0,0608
13-14	0,19	0,9097	0,22	0,8961	0,05	0,9498
15-17	13,72	0,0012	25,25	0,0041	1,72	0,1742
17-20	11,69	0,0029	27,35	1,15·10 ⁻⁶	12,60	1,9·10 ⁻⁵
20-23	1,39	0,7077	3,35	0,3141	1,80	0,1520
23-26	15,94	0,0012	6,50	0,0897	1,59	0,1977
37-38	16,38	0,0009	1,29	0,7323	1,40	0,2482





Differences in mean levels of R

Fig. 3 Visualization of Tukey's test results of temperature influence of hydrogen sulphide changes (95% family-wise confidence level) Rys. 3. Wizualizacja wyników testu Tukeya wpływu temperatury na zmiany siarkowodoru (poziom ufności 95%)

In most cases, there is no reason to reject the hypothesis that the examined variances differ significantly. At the significance level of 0.01, that case existed for temperatures 13-14°C and 20-23°C. This result was influenced by two test series (one from each temperature range). It was considered that it could be a mistake caused by two leaking bags – those results were removed from the analysis. Figure 1 contains changes of hydrogen sulphide content during 56 hours storage in Tedlar bags.

The average rate of hydrogen sulphide change were expressed by the difference between chain index and the one:

$$\overline{l_g} = \sqrt[n-1]{\frac{Y_n}{Y_1} - 1}$$

In addition, the ANOVA test was performed to check whether the temperature has an effect on the changes in the concentration of hydrogen sulphide, in terms of both individual temperatures and the selected temperature ranges. F values for both cases were, respectively, 4.037 and 51.27, and the critical values were: 1.00 and 1.94. For this reason, the null hypothesis of ANOVA test was rejected, co the temperature significantly affects the changes in the concentration of hydrogen sulphide in the tested samples. Visualization of the analysis of variance for the selected temperature ranges is shown in figure 2.

To answer the question, which among compared populations were responsible for rejecting the null hypothesis, a post-hoc tests (multiple comparisons) were performed. Selected tests were: Tukey HSD and Duncan. Tukey's test results of the study showed



4 Heatmap with dendrograms of the Spearman correlation coefficient between all temperature ranges and time od hvdrogen sulfide storage 4 Мара cieplna wraz z dendrogramami współczynnika korelacji Spearmana pomiędzy wszystzakresami temperatur i czasem przechowywania siarkowodoru w workach

that 22 (out of 28 pairs of population) pairs were responsible for the rejection of the null hypothesis. Consistent with the null hypothesis were pairs: 23-26°C and: 37-38°C, 4-6°C, 7-8°C; 37-38°C and: 4-6°C, 7-8°C; 7-8°C and 4-6°C. To verify these results, a comparison of pairs corrected for multiple were performed. The results of this test are presented in table 2 and the figure 3.

Figure 4 contains heatmap with dendrograms of the Spearman correlation coefficient between all variables.

Table 2 The results of pairwise comparisons corrected for multiple testing Tabela 2 Wyniki porównania parami skorygowane o wielokrotne testowanie

	1	2	3	4	5	6	7
2	0,9564	-	-	-	-	-	-
3	2,1·10 ⁻⁷	0,0001	-	-	-	-	-
4	4,7·10 ⁻⁹	5,3·10 ⁻⁶	1,0000	-	-	-	-
5	2·10 ⁻¹⁶	2·10 ⁻¹⁶	6·10 ⁻¹⁴	6·10 ⁻¹²	-	-	-
6	2·10 ⁻¹⁶	3,6·10 ⁻¹⁴	0,0016	0,0163	0,0001	-	-
7	0,9310	1,0000	0,0002	1,3·10 ⁻⁵	2·10 ⁻¹⁶	1,4·10 ⁻¹³	-
8	1,0000	0,9564	2,5·10 ⁻⁷	5,9·10 ⁻⁹	2·10 ⁻¹⁶	2·10 ⁻¹⁶	0,9310

Ekpa et al. (2020) evaluated carotenoid retention after 180 days of storage in aluminium, laminated paper and double-layered polyethylene bags at 4°C and 37°C was determined to assess the stability. The lowest amount of total carotenoids was found in flour stored in laminated paper bags at 37°C (only 16% retention after 180 days), attributable to the high storage temperature and oxygen permeability of the packaging material. The highest concentration of hexanal was in flour milled by rotor mill or freezer mill, and stored in laminated paper bags at 37°C after 180 days, while the lowest concentrations were for flour in aluminium bags and double-layered polyethylene bags stored at 4°C. Considerable degradation of carotenoids in maize during grain and flour storage has been reported. Other authors reported similar trends. Mugode et al. (2014), Ortiz et al. (2016) and Taleon et al. (2017) and proved, that the double-layered polyethylene bags showed better retention, followed by the aluminium bags. Szyłak-Szydłowski (2015) examined the decreasing of concentration of following compounds within 78 h of holding in the Tedlar bags: i.a. benzene, acetone, 1,1-dichloroethylene, c-1,2-dichloroethylene, t-1,2-dichloroethylene, methyl ethyl ketone and vinyl chloride. Author noticed the increase of the chlorobenzene and m-xylene concentration during the first 30 h and increase of bromomethane concentration in the last 48 h. In other cases, the average rate of loss was from 0.01 to 2.50 % for the first 30 h and from 0.35 to 18.50 % during the last 48 h of examination. In present examinations, the average rate of loss of hydrogen sulphide during the first 30 hours was from 0.07% (temperature range: 17-20°C) to 7.01% (temperature range: 37-38°C), while during 48 hours - from 1.42% to 100% (extreme temperature ranges: 4-6°C, 7-8°C and 23-26°C, 37-38°C). Zarra et al. (2012) proved, that, due to easily escape of hydrogen sulfide from Nalophan bags, the 30 h expiration period for all samples, regardless of the kind of the compound, could not be performed. Present examinations confirmed that conclusion only in the sampling temperature range between 17°C and 20°C reduction after 30 h expiration period was less than 10%. In other cases that value was between 97% (for 37-38°C range) and 42% (for 20-23°C range). Hansen et al. (2011) shown the decreasing of H₂S concentration by approx. 30% during the 24 h of storage in Tedlar and Nalophan bags. Conclusions of those researchers were confirmed in present examinations for 20-23°C range, while hydrogen sulphide reduction value was 35%. Additionally, Blazy et al. (2015) shown that most odourants can be lost during first

24 hours. For example, dimethyl sulphide and hydrogen sulphide was lost in Tedlar and Nalophan bags, after, respectively, 4 and 8 hours of storage. In addition, Lau (1989) examined the stability of a six sulphur compounds gas mixture at the ppb (v/v) (ppbv) concentration level in a 5 L Tedlar bag over 21 days. Half-lives of examined gases were as follows: SO2: 0.02 day, H₂S: 10 days, ethyl mercaptan: 25 days, methyl mercaptan: 29 days, CS2: 58 days, COS: 100 days. The author concluded that Tedlar bags are not suitable for examinations of SO2 and H₂S, unlike the other compounds, which stability is good enough to collect samples and send to the laboratory. Van Harreveld (2003) showed that the stability of odour in Nalophan bags is acceptable only for a period of 4 to 12 hours. After 30 hours, decay level was about 50% as that measured at the fourth hour. Kasper et al. (2018) suggested, that that double Nalophan bags with sample air in outer bags can improve recovery of odorants of phenols and carboxylic acids by a few percent. At the present studies, similar values were achieved for the sampling bags after 30 h, in the sampling temperature range 15-17°C (reduction value 54%) and 20-23°C (reduction value 42%). Therefore, relatively stable between first 12 h after sampling were samples taken in the temperature range between 17°C and 20°C (reduction value 10%). Moderate stable (reduction between 1% and 15%) were, during 4 hours, samples taken in the temperature ranges: 15-17°C, 7-8°C, 17-20°C20-23°C. In the other hand, Coyne concluded, that in 24 hours sulphur compounds in Tedlar bags have losses of less than 5% (Coyne et al. 2003, 2011). Different examinations of Le (2015) were connected with the stability within 72 hour storage of VSC samples in Tedlar, Mylar and Nalophan sampling bags, at three temperatures: 5, 20, and 30°C. The results have shown the 46-50% reduction of H_2S after 24 hours at 30°C as well as the loss of that compound concentration at 5°C or 20°C (of up to 27% at 24 hours) in all three bag materials. In other hand, Man et al. (2020) noticed no significant drop in recovery for dimethyl sulphide, during the first 24 h of storage in all the four types of sampling bags. Even at the end of the investigation period (72 h), storage recovery for dimethyl sulphide reached 92% in Tedlar bags, 88% in FEP bags, 89% in BOPET bags and 86% in Fluode bags. Those researchers pointed out, that poor recovery was generally observed for the storage of both indole and skatole in all the types of sampling bags - after 24 h, the averaged recovery rates for indole in Fluode, Tedlar, FEP and BOPET sampling bags were 8.4%, 9.3%, 39.6% and 12.2%, respectively, while the averaged recovery rates for skatole were 9.7%, 13.6%, 34.9% and 17.8%, respectively. Le concluded, that with the increasing of the storage temperature, a consistent increasing trend in the concentration loss in Mylar and Nalophan sampling bags was observed for H₂S, MeSH, EtSH, BuSH, and t-BuSH. In addition, changing the storage temperature from 20°C to 30°C resulted slightly higher extent of loss than temperature changing from 5°C to 20°C. Relative recoveries factors higher than 100% were noticed for H₂S at 6 hour, with storage relative humidity of 80% and temperature 30°C. Irregularity in that result could be the effect of changes in the VSCs equilibrium between gas and the bag because of high moisture content and temperature. H₂S is the most hydrophilic compound and have the lowest boiling point, so it is more susceptible to this alteration (Le 2015). In present examinations, after first 8 hours of H₂S storage in the temperature 20°C, two groups of sampling temperature ranges can be distinguished - those characterized by more than 50% reduction (range of sapling temperatures from 13°C to 20°C) and those with less than 50% reduction of hydrogen sulfide concentration (temperatures between 4°C and 13°C and from 23°C to 37°C). This trend continued up to 25 h and 29 h when the reduction of the hydrogen sulfide concentration became greater than 50% at the temperatures, respectively, 13-14°C and 15-17°C.

Recent changes in analytical methodology have contributed to improve the characterization of emissions of odours. Determination of the main types of gases in the samples derived from the sources of malodorous substances is still a major challenge because of the high reactivity leading to losses during the uptake and analysis phase (Borras et al. 2016). In present study, significant differences between reduction of hydrogen sulphide concentration had been found depending on the sampling temperatures. The highest reduction was observed for the extreme temperatures (4-6°C and 37-38°C), with the largest differences – 16-18°C – between sampling and storage temperature values. Sampling bags can be still used in those examinations, but not only a better control of temperature and humidity conditions during the storage phase is necessary. Also, monitoring the conditions during the sampling phase is very important. In the case of sulphur compound analysis (especially with reduced compounds), particular attention to the concentration changes and interaction between compounds and sampling device materials should be paid. Also, the atmospheric factors, like i.a. temperature, humidity and pressure, are very important in the analytical methodology. When we consider them, not only a high differential gradient of humidity (between inside and outside the bag), but also a difference between sampling and storage temperatures, can cause important changes in compound concentrations.ies.

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