

Occurrence and gas chromatographic determination of volatile fatty acids in landfill leachate. The case of two landfills in Gdansk Pomerania, Poland.

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Abstract. In landfills containing biological matter volatile fatty acids (VFAs) are generated at high rate at the early stage of waste disposal and their content in leachate is high as compared to the leachate from old parts of landfill since they are converted to methane gas. Monitoring of the leachate for the content of VFAs can help determine the processes occurring in waste and possible effect of the leachate on the environment in the case of some leakage. The content of VFAs was determined, using the method developed, in inflow and outflow of ground water and in the brook water passing through one landfill upstream and downstream of the landfill. The data show that some, though rather small, amounts of the acids generated in the landfill are transferred to the above waters. VFAs were determined in the two landfills of similar age and waste composition; their contents in the leachate were not drastically different.

Key words: Volatile fatty acids, Landfill, Leachate, Gas chromatography-mass spectrometry, Gdansk Pomerania

1. Introduction

Volatile fatty acids (VFAs) are aliphatic monocarboxylic acids with 2 to 6 or even 7 carbon atoms. They can be found in many environmental matrices due to numerous sources of natural (biological; geological; transformation of other pollutants) and anthropogenic (agriculture, pig farming, food processing, waste disposal) origin. Municipal solid waste (MSW) generation continues to grow and the sanitary landfill method for the ultimate disposal of solid waste material is increasingly accepted and used. It is so because it is cheaper, minimizes environmental insults and some other inconveniences and allows waste to decompose under controlled conditions into relatively inert, stabilized material [1]. However, the leachate formed, when precipitation water percolates through waste, is generally quite strongly polluted wastewater. In young landfills large amounts of free VFAs are released, due to large quantities of biodegradable organic matter which undergoes rapid anaerobic fermentation, and acids content in the leachate is very high [2]. Degradation is strongly influenced by the composition of MSW. Very high percentage of easily putrescible waste produces acid accumulation and an extremely low pH. This inhibits biological process that follows the particulate matter hydrolysis [3] and limits the

generation of methane [4]. If leachate treated *ex situ* is used the inhibition problem caused by hydrolysed volatile acids can be resolved [5]. The hydrolysis rate was found out to be the highest when an anaerobically pre-treated leachate was used [6]. Later, VFAs are converted to biogas and organic fraction in the leachate is dominated by non-biodegradable compounds. Organic compounds present in the leachate can be composed of VFAs in up to 80%, 5-30% and only of humic and fulvic acids in recent, intermediate and old landfills, respectively [7]. The relation between the age of the landfill and organic matter composition in the leachate may help select an appropriate treatment process [1]. Moreover, VFAs, when released into the environment, may cause some damages. Therefore, the information on VFAs in the leachate and possibly in ground water and surface water in the landfill neighbourhood is of great importance and the content of individual VFAs should be monitored.

Generally gas chromatography (GC) with polar stationary phases and flame ionisation detection is used for the separation and determination of VFAs in aqueous samples [8, 9]. Before the analysis proper leachate and aqueous leachate-related samples must be prepared to make them compatible with GC. For the purpose Manni and Caron used [10] used extraction

with diethyl ether. In many cases, if the sample is not much contaminated with suspended matter, high molecular organics and some other components, aqueous samples can be injected into GC, after removal of solids, provided that specialty separation columns are applied [11]. When the total content of VFAs is to be known titrimetric [12] and spectrophotometric [13] methods were used.

The aim of this work was to test the procedure of determination of VFAs in aqueous samples based on solvent extraction at the step of sample preparation and gas chromatography coupled with mass spectrometry (GC-MS) as a technique of final analysis and then to apply this procedure for the determination of VFAs in aqueous media in two large landfills situated in Gdansk Pomerania, Poland.

2. Experimental

2.1. Characteristics of the landfills studied

Landfill A situated in the former gravel pit has been operated since 1973. A brook flows through the area of the landfill. About 700 ton municipal and some industrial wastes are delivered every day from the area with ca 600,000 inhabitants. Landfill gas is collected and applied to produce energy on site.

Landfill B situated in the former gravel pit was opened in 1979 and has been modernized quite a few times since then. About 250 ton municipal and some industrial wastes are delivered every day from the area with ca 400,000 inhabitants. Presently a landfill gas is collected and applied to produce energy on site.

2.2. Sample collection

Problems with water sampling from landfills result mainly from non-homogeneity of the aqueous media and certain procedures must be followed to select sampling sites and frequency of sampling in order to collect a representative sample.

Leachate. Samples were collected with a scoop from leachate container. In sampling planning vertical stratification was taken into consideration. Care was taken to collect water without particulate matter depositing all the time at the bottom.

Surface water. Samples were collected with a scoop upstream and downstream of the brook. The sample bottle was rinsed with sampled water twice before filling it with the sample proper.

Ground water. Samples were taken using deep-water pump. Care was taken to pump out stagnant water in well before collection of the sample proper. This can

be monitored by measuring pH, conductivity and temperature.

2.3. Sample transport to laboratory

Immediately after collection, samples were transported to the laboratory and subjected to extraction with methyl-*tert*-butyl ether (MTBE). After collection and during transport they were kept at a temperature below 4°C.

2.4. Sample preparation and GC-MS analysis

After filtering solids and suspended matter sulfuric acid to lower pH and sodium chloride to decrease the solubility of the acids in water were added to the samples. VFAs were extracted from water samples twice with 2 cm³ methyl-*tert*-butyl ether each time. Then the two extracts obtained were combined and dried with anhydrous sodium sulfate. A Thermo Finningan Trace GC 2000 gas chromatograph coupled with a Trace DSQ mass spectrometer in SCAN and SIM modes were used to determine the content of acids in the extracts. Separation was performed in GC capillary column (30m x 0.32mm x 500nm) coated with Stabilwax-DA stationary phase (polyethylene glycol modified with terephthalic acid). The chromatographic conditions were as follows: flow rate of helium carrier gas – 1.5 mL/min; oven temperature – 60 °C (2 min), 10 °C/min to 220 °C (1 min); temperature of split/splitless injector operated in splitless mode – 250 °C; transfer line – 250°C. Electron impact ionization was used. The successive steps of the procedure are presented in Fig. 1.

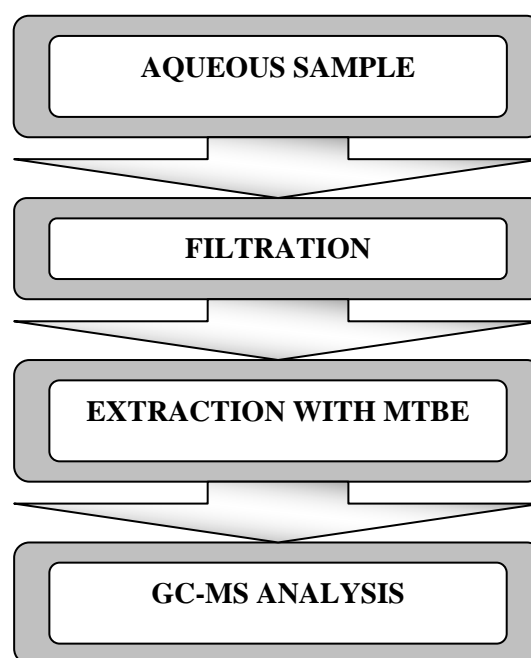


Fig. 1. Successive steps of the procedure of determination of VFAs in aqueous samples.

3. Results

In landfill A VFAs were determined in ground water at the three levels of the upper water-bearing layer in the zone of ground water inflow to the area of the landfill as well as in outflow groundwater; in the brook upstream and downstream of the landfill; and in the leachate. Water in the first level of the upper water layer outflowing the landfill contained acetic acid at a concentration in the range of 0.20-0.50 mg/dm³. The concentrations of the remaining acids were below detection limit of 0.10 mg/dm³. Water in the second level of the upper water layer contained acetic acid at a bit higher concentration, i.e. in the range of 0.57-0.80 mg/dm³ and the remaining acids below the detection limits. In the ground water inflowing the landfill VFAs were not detected. The data indicate that the landfill leachate pollutes the ground water with VFAs to some extent. The acetic acid content in water of the brook downstream was about twice the concentration of acetic upstream, but the concentrations in both cases were close to detection limits of the procedure applied. In the case of Landfill B only the leachate was analyzed.

The comparison of the contents of VFAs in the leachate from Landfill A and Landfill B are presented in Table 1.

Table 1. Comparison of the content of VFAs in the leachate in Landfill A and Landfill B.

Acid	Concentration [mg/dm ³]	
	Landfill A	Landfill B
Acetic	18.0	19.6
Propionic	3.37	6.84
Isobutyric	0.50	1.02
Butyric	1.36	0.67
Isovaleric	0.34	0.44
Valeric	0.28	0.39
Caproic	n.d.	n.d.
Enanthic	n.d.	n.d.
Caprylic	n.d.	n.d.

n.d. – below detection limits

The leachates contain not only acetic acid but also higher VFAs with up to 5 carbon atoms at measurable concentrations which are much higher than in surface and ground water. The differences in concentrations of particular acids in the leachates from these two landfills are not very large. Probably this results from the fact that both landfills are of similar age and the

composition of wastes should not differ drastically. In both cases municipal wastes are predominant.

4. Conclusion

Volatile fatty acids are generated in landfills containing municipal solid waste with the rate dependent on age and composition of the waste. Their content is very high in young landfills. Gas chromatography is a convenient and indispensable technique of individual VFAs determination in landfill leachate and leachate-related aqueous samples. When polar stationary phases are used VFAs in a free form can be separated. If aqueous samples are not much contaminated they can be injected into a GC column after filtration. In other cases organic solvent should be used to extract VFAs. MTBE proved to be an effective and convenient solvent. The analytical procedure based on acids extraction with MTBE and GC-MS determination of VFAs in the extracts is characterized by good selectivity and detection limits on the level of 0.1 mg/dm³. The procedure can be applied to determine VFAs with 2-8 carbon atoms. From the studies of the two landfills in Gdansk Pomerania, Poland results that there can be a slight infiltration of VFAs into ground water and to surface water. The contents of VFAs in the leachates from both landfills are similar. This can be related to the fact that both landfills are of similar age and contain mainly municipal solid waste.

References:

- [1]. Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., Moulin, P., Landfill leachate treatment: Review and opportunity, *Journal of Hazardous Materials*, 150, 2008, 468–493.
- [2]. Welander, U., Henryson, T., Welander, T., Nitrification of landfill leachate using suspended-carrier biofilm technology, *Water Research*, 31, 1997, 2351–2355.
- [3]. Borzacconi, L., Lopez, I., Anido, C., Hydrolysis constant and VFA inhibition in acidogenic phase of MSW anaerobic degradation, *Water Science and Technology*, 36, 6, 1997, 479-484.
- [4]. Vavilin, V.A., Jonsson, S., Ejlertsson, J., Svensson, B.H., Modelling MSW decomposition under landfill conditions considering hydrolytic and methanogenic inhibition, *Biodegradation*, 17, 2006, 389–402.
- [5]. Kim, J., A Bioreactor Landfill Incorporating Innovations in Leachate and Gas Management with a Dedicated Treatment Zone. PhD thesis. University of Pittsburgh, Pennsylvania, USA, 2001, According to *Chemosphere* 59, 2005, 837–844.

- [6]. He, P.J., Shao, L.M., Qu, X. Li, G.J., Lee, D.J., Effects of feed solutions on refuse hydrolysis and landfill leachate characteristics, *Chemosphere*, 59, 2005, 837–844.
- [7]. Chian, E.S.K., DeWalle, F.B., Sanitary landfill leachates and their treatment, *Journal of the Environment Engineering Division*, 103, 1976, 411–431
8. Peldszus, S., Organic Acids (Chapter 13) in *Chromatographic Analysis of the Environment* (Nollet, L.M.L. - editor), Third Edition, Taylor&Francis, 2006.
- [9]. Giecwicz J., Zygmunt B., Oznaczanie lotnych kwasów tłuszczowych w ściekach metodą chromatografii gazowej (Determination of volatile fatty acids in waste water by means of gas chromatography), *Chemia i inżynieria ekologiczna (Ecological Chemistry and Engineering S)*, 10(10), 2003, 1125-1138
- [10]. Manni G., Caron F., Calibration and determination of volatile fatty acids in waste leachates by gas chromatography, *Journal of Chromatography A*, 690, 1995, 237-242
- [11]. Dearman B., Marschner P., Bentham R.H., Methane production and microbial community structure in single-stage batch and sequential batch systems anaerobically co-digesting food waste and biosolids, *Applied Microbiology and Biotechnology*, 69, 2006, 589-596
- [12]. Anderson G.K., Yang G., Determination of bicarbonate and total volatile acid concentration in anaerobic digesters using a simple titration, *Water Environmental Research*, 64, 1992, 53-59
- [13]. Montgomery H.A.C., Dymock J.F., Thom M.S., The rapid colorimetric determination of AIDS and their salts in sewage-sludge liquor, *The Analyst*, 87, 1962, 949-955