

# Emission and Determination of Malodorous Compounds from Municipal Solid Waste Sites and Wastewater Treatment Plants

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**Abstract.** Odor in the vicinity of municipal solid waste and waste water treatment plants has often been a real nuisance for the people living in the neighborhood. The attempts were made to identify volatile fatty acids (VFAs) regarded as, at least partially, responsible for the malodorous atmosphere. The procedures, based on solid phase microextraction (SPME) to isolate VFAs from the air and leachate and gas chromatography-mass spectrometry (GC-MS) to separate and identify the VFAs extracted were described. SPME parameters such as extraction temperature and time, and also salt addition and pH of the sample were optimized. PDMS/CAR fiber was selected for extraction. VFAs were determined in the leachate and identified in the air of a municipal solid waste site.

**Keywords:** HS-SPME, malodorous volatile fatty acids, gas chromatography-mass spectrometry, PDMS/CAR fiber.

## 1. Introduction

Biological and chemical processes proceeding in municipal solid waste (MSW) sites and in wastewater lead to the formation of malodorous volatile compounds which are often a nuisance for people living close to the sites. The volatiles are mainly nitrogen and sulfur organic and inorganic compounds and also low molecular mass monocarboxylic acids or volatile fatty acids (VFAs). Hydrogen sulfide has an odor of decaying eggs and volatile mercaptans, organic compounds of bivalent sulfur, are even more malodorous at very low concentrations, e.g. a weapon of skunk, an extremely odorous medium, is a mixture of volatile organosulfur compounds whose main components are crotyl and isopentyl mercaptans, while methyl mercaptan is responsible for a bad smell of flatus. Also some VFAs are characterized by strongly unpleasant smell, e.g. butyric acids of a smell of butter that has gone sour [1].

A “young” landfill contains a large amount of easily biodegradable organic matter. Rapid anaerobic fermentation in such a landfill produces simple fatty acids [2], [3]. The initial phase of processes called the acid phase (acidogenic) leads to the release of large amounts of VFAs (up to 95% organic matter content) [4]. As a result the pH decreases, which results in the release of heavy metals [5]. An intensive growth of acetic bacteria as well as severe consumption of organic substrates and biogenic compounds are observed at this phase which is accompanied by a rapid increase in the content of organics in leachate is also observed.

As the landfill matures, carboxylic acids are consumed just as fast as they are produced [6]. So the odor originating from VFAs depends strongly on the age of landfill and it can be correlated with the presence of the particular VFAs.

Monitoring of selected VFAs can be a measure of quality of the air and their content can be one of parameters indicating if people complains are justified.

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The aim of the paper was to test the possibility of using the combination of SPME (sampling) and GC-MS (separation and quantitation) to determine VFAs and evaluate the air quality in the vicinity of MSW landfills and wastewater treatment plants.

## 2. Experimental

### 2.1. Chemicals

The Volatile Acids Standard Mix containing C1 - C7 (with iC4, iC5 and iC6) monocarboxylic acids was obtained from Sigma–Aldrich (Steinheim, Germany). High purity water was produced using a Milli-Q water purification system. Sodium chloride and 96% sulfuric acid, both “pure for analysis” grade, were from Polskie Odczynniki Chemiczne (Poland). NaCl was heated for 1 hour at temperature of 400 °C before use to remove volatile organic compounds possibly adsorbed on the surface of solid sodium chloride.

### 2.2. VFA Extraction by Means of SPME

SPME experiments were performed with a manual fiber holder. Commercially available fibers with two different coatings: CAR/PDMS and PEG were tested. The fiber holder and fibers were supplied by Supelco (USA). Before use, fibers were conditioned according to the manufacturer’s instructions to remove contaminants. A liquid sample or standard solution (8 mL) was introduced into a 15 mL screw-cap glass vial, with the PTFE/silicone septa (Supelco), NaCl added, the vial closed and placed in a electro-thermostated bath. Magnetic stirring (500 rpm) was applied during the extraction using a PTFE-coated stir bar and the fiber was exposed to the headspace above the aqueous solution. The selected extraction conditions were: 3 g NaCl added to the sample, extraction time 30 min, extraction temperature 30 °C, respectively. After completion of sampling, the fiber was withdrawn into the needle of the manual fiber holder, and then analytes were thermally desorbed from the fiber in the injection port of GC for analysis. In the case of air analysis the same fiber was exposed directly in the air sample.

### 2.3. Experimental Design

A full factorial design was performed to evaluate the influence of different parameters on the extraction of odorous compounds from an aqueous solution. This allowed to determine the influence of all the experimental variables studied. For each analyte, the variable factors that can affect the extraction yield were considered: ionic strength expressed as NaCl concentration (c), temperature (T), extraction time (t) and position of the fiber in the vial (p). Table 1 shows the experimental range for each factor. All experiments were carried out in triplicate in random order.

### 2.4. GC – MS Conditions

GC-MS analysis was performed with a Trace GC coupled to a Finningan Trace DSQ mass spectrometer detector. Analytes were separated in a Stabilwax-DA® capillary column (Restek) (30 m × 0.32 mm i.d.; 0.5 µm film thickness). The split/splitless injection port was equipped with a 0.75 mm ID liner and operated at 250 °C. The carrier gas was helium at a constant inlet flow rate of 1.5 mL min<sup>-1</sup>. The oven temperature program was: initial temperature 40 °C, held for 3 min; then increased by 40 °C/min up to 180 °C, and held for 1 min and by 10 °C/min up to 230 °C, and held for 1 min. MS analyses were conducted in the full-scan and SIM modes; monitored masses were between 40 and 300 amu. Ionization was carried out by the electron impact (EI) mode at 70 eV. The temperatures of the transfer line and the ion source were 240 and 250 °C, respectively. The acquisition of chromatographic data was performed using Xcalibur 1.4 software (Thermo

Table 1: Factor levels considered in the experimental optimization.

Variable	Levels			
c (g)	0	1	3	5
T (°C)	25	30	40	45
t (min)	10	20	30	40
p	in the center of vial		near the wall of vial	

Table 2: Odor threshold concentration (OTC), retention time and m/z ratios of the target compounds.

Compound	OTC [7]	Retention time (min)	m/z	LOD [7]	Corresponding concentration <sup>a</sup>	odour
Acetic Acid	16-50 ppb	7.14	43, 45, 60	20 ppb	< 2 OU/m <sup>3</sup>	
Propionic Acid		7.58	45, 73, 74			
iso-Butyric Acid		7.71	43, 73			
Butyric Acid	1 ppb	8.06	60, 73	20 ppb	20 OU/m <sup>3</sup>	
iso-Valeric Acid		8.31	41, 60, 87			
Valeric Acid	160 ppb	8.75	60, 73	20 ppb	< 1 OU/m <sup>3</sup>	
iso-Hexanoic Acid		9.19	60, 73			
Hexanoic Acid		9.50	60, 73, 87			
Heptanoic Acid		10.32				

<sup>a</sup> calculated by dividing the detection limit concentration of the odorous substance by its threshold odour concentrations (which is equivalent to 1OU/m<sup>3</sup>)

Scientific). Table 2 shows the list of the target compounds, their respective odor threshold concentrations [7] and details of the ions selected for MS monitoring.

### 3. Results and Discussion

In this study, the malodorous organic compounds of interest were VFAs (Table 2), already reported to occur in wastewaters [1], [8] and in the air [9], [10]. They were previously determined using on-fibre silylation [11]. An attempt was made to determine them in the free form in aqueous samples and in the air collected simultaneously at the same place and time to correlate the passage of malodorous VFAs from sewage and leachate to the air.

#### 3.1. Selecting Fibers Coatings

The application of two fiber coatings was studied: PDMS/CAR and PEG. The former has already been used to characterize odorous waste gas emissions [12] and to determine VFAs in wastewaters [13] while the latter to isolate VFAs from water samples [14]. Free VFAs are polar and, a polar fiber coating (as PEG) should be the first choice. PDMS/CAR coating is a composite sorbent, i.e. solid sorbent dispersed in liquid and as such it is efficient extractant for volatile compounds [13], [15]. For the low molecular mass VFAs the extraction yields to PDMS/CAR fibers were higher than to PEG fiber and the former was selected.

#### 3.2. Study of Extraction Conditions

The influence of temperature and time, salt content and the position of fiber in vial on the extraction of odorous compounds from aqueous solutions (Table 1) was studied using a typical procedure based on the evaluation of each variable individually.

Two opposite effects influence the change of the extraction yield with temperature: raising the temperature increases the fraction of analyte transferred from the sample to its headspace but decreases the fraction transferred from the headspace to the fiber. Basing on the data obtained (Fig. 1) a temperature of 30 °C was chosen for extraction. The temperature higher than 30 °C were not used to avoid high water vapor content in the headspace, which can shorten the fiber lifetime.

Extraction times with SPME usually vary from a few minutes to an hour or more, depending on the matrix, analytes, fiber coating and the desired sensitivity. Due to the range in volatility of VFAs, extraction times, between 10 and 40 min were tested to find the best conditions for the majority of the target analytes. Extraction times longer than 40 min were not considered to avoid extending the total analysis time and observed analyte losses (Fig. 2). An extraction time of 30 min seemed the best for most analytes.

Increase in ionic strength decreases organic substance solubility in water resulting in higher fraction of organics in headspace. The effect depends on the polarity of an analyte, the salt concentration and the sample matrix. This was observed for the system studied. Considering such parameters as repeatability, yield of extraction, technical problems, an addition of 3 g NaCl to the sample of 8 mL in a 15 mL vial was assumed

to be the best. With respect to the repeatability and extraction yield the best fiber position was close to the vial wall.

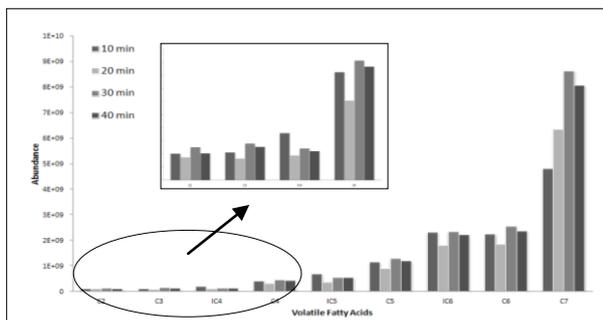


Fig. 1: Effect of extraction temperature on the peak area counts of nine VFAs.

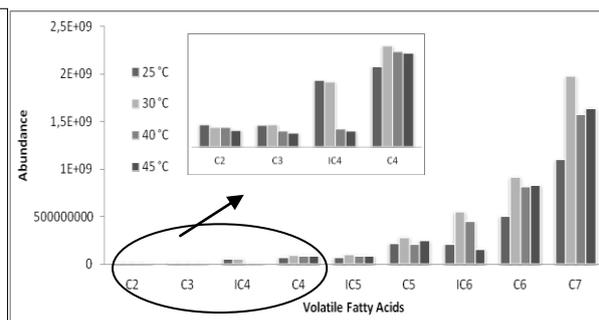


Fig. 2: Effect of extraction time on the peak area counts of nine VFAs.

### 3.3. Analysis of Real Samples

Many analytical tasks of VFAs determination require analyte selective enrichment before injection into a GC. A convenient approach to prepare the sample for GC determination of VFAs should be an SPME technique. If the liquid samples have a very complex and troublesome matrix, analytes of interest can be extracted to SPME fiber from sample headspace, i.e. from the gaseous phase above the sample. If SPME is applicable to extraction of given analytes from HS then it could be effective for the extraction of the same analytes from gas samples.

The developed method based on SPME technique, characterized by LODs ranging from 12.8 ppb for acetic acid to 74.8 ppb for hexanoic acid, was applied to determine VFAs in MSW landfill leachate (a) and landfill air (b). Fig. 3 illustrates the corresponding chromatograms. Quite a few VFAs were detected and identified in the samples.

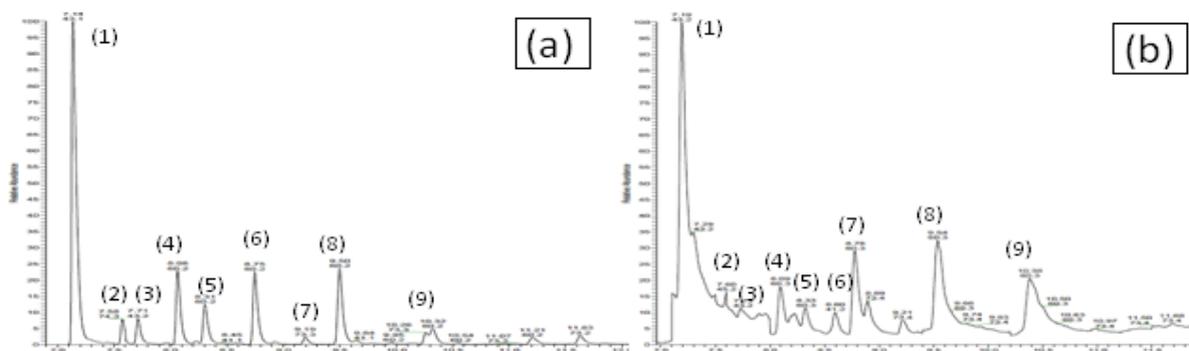


Fig. 3: SPME-GC-MS chromatogram of: (a) wastewater sample headspace; (b) air sample. Peak identification: (1) acetic acid; (2) propionic acid; (3) iso-butyric acid; (4) *n*-butyric acid; (5) isovaleric acid; (6) *n*-valeric acid and (7) iso-hexanoic acid; (8) *n*-hexanoic acid; (9) heptanoic acid

## 4. Conclusion

Processes proceeding in MSW landfills and in wastewater treatment lead to the emission of malodorous substances, including volatile fatty acids. The odours are a nuisance for the people living in the vicinity. To monitor the real threats, VFAs should be determined in the aqueous media and in the air. An analytical procedure based on extraction of VFAs to SPME fibre from a liquid sample headspace as well as directly from the landfill air at a stage of sample preparation and GC-MS for the analysis proper appeared applicable and convenient way to monitor the emission of VFAs. Of the commercial SPME fibres, PDMS/CAR appeared the best with many respects. In the real samples of leachate VFAs could be determined at the concentrations down to ca 13 to 75 ppb depending on an acid. Generally, the same VFAs can be identified in the landfill air collected at the same time and place as leachate samples. Acetic acid is most often present at the highest concentrations.

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