REPORT

prepared as part of the implementation of the tasks covered by the project

STEP - Sludge Technological Ecological Progress

Verification of the efficiency of a plasma reactor designed to reduce the emission of volatile chemicals released from compost heaps

Technical recommendations or waste air handling and deodorization techniques

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This report was commissioned by representatives of the Department of Electrical Power Engineering and Electric Drives of the Faculty of Electricity of the West Pomeranian University of Technology in Szczecin. The report was prepared by employees of the Department of Analytical Chemistry of the Faculty of Chemistry of the Gdańsk University of Technology. The report consists of a description of the applied test procedure and obtained results, which may be the basis for the evaluation of the efficiency of the plasma reactor used to remove volatile compounds from gas streams released from compost heaps during their maturation carried out in the sewage treatment plant in Goleniów. The research has been carried out as part of the implementation of the STEP project (Sludge Technological Ecological Progress), the aim of which is to analyse and refine effective methods of sludge utilization, taking into account the energy efficiency of processes, and reducing the nuisance to the environment.

1. Introduction

Municipal and industrial wastewater treatment plants are an example of human activity which carries the risk of creating many harmful chemical compounds, including odorous compounds [1]. One of the main sources of emissions of these compounds is all operations related to the processing and disposal of sewage sludge, which is a by-product of the wastewater treatment process. They are an abundant source of organic matter, rich in a number of compounds with different physicochemical properties [2]. The most frequently identified compounds are: volatile sulfur compounds, volatile odorants, aliphatic hydrocarbons, aldehydes and ketones, esters, alcohols and amines [3,4]. Gaseous mixtures of these compounds entering the atmospheric air can significantly facilitate the deterioration of the living and non-living environment. Compounds particularly arduous in terms of smell may additionally contribute to the occurrence of odour nuisance associated with long-term presence of these substances at concentration levels exceeding the odour detection threshold [5,6]. This problem concerns in particular residents of areas located in the vicinity of municipal facilities such as sewage treatment plants.

One of the forms of sewage sludge management is subjecting them to the composting process. As a result of this process, we get a product that can be used, inter alia, for agricultural purposes [7]. Unfortunately, the compost maturing process, usually taking place in open halls (sediment deposited in the form of compost heaps), generates significant amounts of volatile odorants. To reduce the number of compounds being created, development of new methodological and instrumental solutions is needed, that would allow the reduction of the amount of odorants. One of the solutions that has enjoyed popularity in recent years is the use of plasma techniques that seem to be interesting solutions in the field of environmental research.

The determination of the effectiveness of various solutions enabling the reduction of volatile odorants emission requires the use of appropriate measurement techniques allowing qualitative and quantitative analysis of odorants. The most popular group of techniques used for this purpose are chromatographic techniques, including the technique of gas chromatography coupled with a mass spectrometer (GC-MS) [8]. This solution is in some cases insufficient, as it does not allow for separating the components present in complex matrices (e.g. gas samples) [9]. An alternative to this case is the use of the two-dimensional

gas chromatography (GCxGC) technique, which guarantees a higher degree of separation of analytes present in the tested samples, thanks to the use of a system of two chromatographic columns with different degrees of polarity. The GCxGC technique is increasingly used in various areas of research, mainly food and environmental analysis [10–12].

An alternative to chromatographic techniques, especially in the case of quantitative determinations may be direct measurement techniques in the field of mass spectrometry enabling performing analyses without the need of prior sample preparation [13]. One such technique, developed in the 1980s, is Proton Transfer Reaction Mass Spectrometry (PTR-MS). During the determinations, the tested compounds undergo a reaction of exchanging the proton with hydronium ions generated inside the device. This solution in comparison to chromatographic techniques, in addition to the lack of sample preparation for analysis, is characterized by a shorter time of a single analysis and the possibility of conducting real-time analyses [14,15].

This report presents procedures for the determination of volatile odorants in a gas stream containing compounds released during the process of composting sewage sludge. The determination was carried out for samples taken both before and after the reactor, the task of which was to destroy the main substances responsible for the unpleasant smell accompanying the composting of sediments. The presented results should be helpful in indicating changes occurring in the gas stream purified with the use of a plasma reactor.

2. The test procedure

The gas sampling for testing was carried out in a municipal wastewater treatment plant located in Goleniów (West Pomeranian Voivodeship). In order to carry out the planned tests, 2 compost heaps from the plant were prepared, differing in the ratio of sewage sludge to the added straw. Both piles were located on the indoor compost ripening area; during the gas sampling stage, the given pile was covered in order to limit the exchange of gas stream released from the heap with atmospheric air. The gas sampling took place:

• November 8, 2018 - the first measurement series;

• November 29, 2018 - the second measurement series;

• January 25, 2019 - the third measurement series.

Measurements were carried out at intervals of at least 3 weeks between the series of measurements, so as to examine the effect of aging of compost heaps on the emission level of volatile chemicals released from them. The gas stream released from the heaps was directed to

the plasma reactor in order to remove the compounds responsible for the odour nuisance accompanying the composting process. Gas samples were taken both before the gas entered the reactor and after leaving it. During the tests, 5 reactor operation configurations were checked. In total, 10 gas samples were taken in Tedlar bags and 10 air samples using solid sorbent packed tubes. The diagram of the applied research methodology described in the further part of the report is shown in Fig. 1.
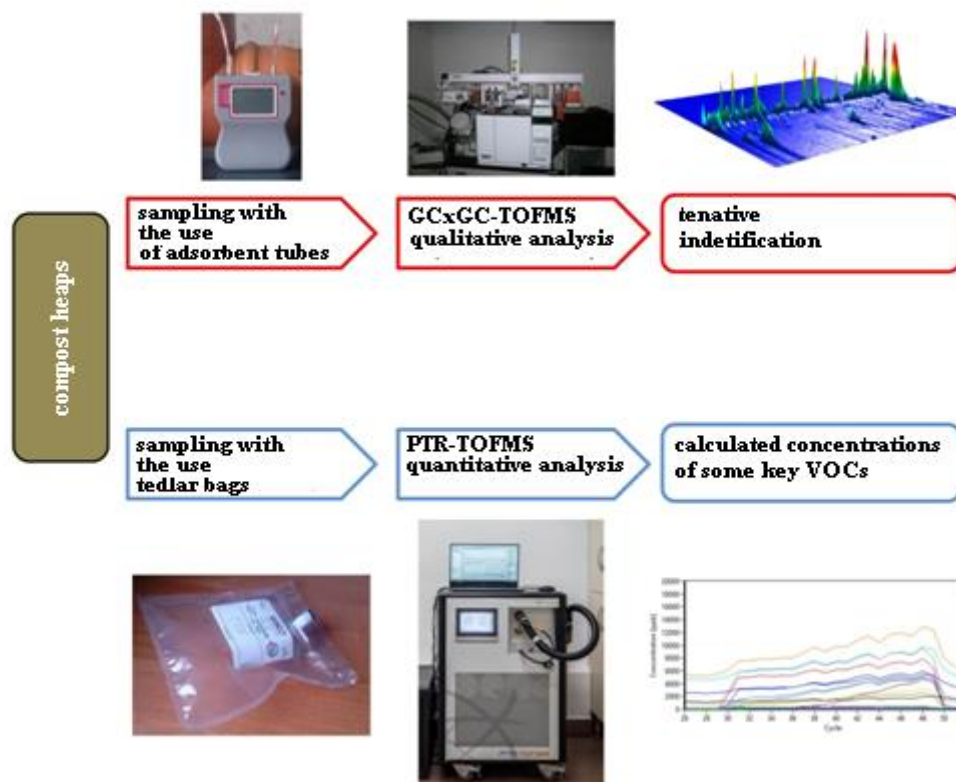

Figure 1. Diagram of the applied research procedure.

Sampling of air containing volatile odorous contaminants was carried out with the use of tubes filled with a solid Tenax TA sorbent (poly (2,6-diphenyl-phenylene oxide)) (Fig. 2). Samples were collected using a Gas Sampling System (Gerstel) with a volume flow rate of 75 ml/min for a period of 10 minutes (Figure 3). This device is a certified tool for use with Gerstel sorption tubes. Each of the tubes on which the adsorbed analytes were located was stored in a refrigerator at +4°C from the day of collection to the day of analysis. After chromatographic analyses, the tubes were desorbed in a thermal desorber (desorption time 180 min, desorption temperature 280 ° C). From the desorption of the tubes to their re-use during sampling, they were also kept tightly closed in a refrigerator at + 4 ° C.

Figure 2. Sorption tubes used during the tests

Figure 3. Sampling of air using the Gas Sampling System

The qualitative analysis of samples containing volatile odorous contaminants was carried out using two-dimensional gas chromatography (Agilent Technologies, Palo Alto, CA, USA), coupled with a mass spectrometer and a time-of-flight mass analyser (LECO Corp., St. Joseph, MI, USA) (Fig. 4). The chromatographic column set consisted of the first column (30m x 0.25mm x 0.25μm, stationary phase Equity 1 (Sigma Aldrich, USA)) and the second column (2.0m x 0.10mm x 0.10μm, stationary phase Sol Gel Wax (SGE Analytical Science, Australia)). The temperature program used during chromatographic analyses is summarized in Table 1.

Table 1. Temperature program used during chromatographic analyses

Parameter	First column	Second column
Initial temperature	40°C	45°C
Time that temperature was sustained	1min	1min
Temperature rise 1	10°C/min up to 90°C	10°C/min up to 95°C
Temperature rise 2	3°C/min up to 240°C	3°C/min up to245°C
Time that temperature was sustained	5 min	5min
Transfer line temperature	250°C	
Ion source temperature	250°C	

The total time of a single chromatographic analysis was 65 minutes. Hydrogen fed to the system with a constant flow rate of $1cm^3$/min was used as the carrier gas. The modulation time was 5 seconds. The detector voltage was 1600V and the mass range recorded during the analyses was $m/z = 40$-500 amu with a spectrum recording rate of 125 spectra/s.

Rysunek 1 GC×GC-TOF-MS apparatus

The data obtained as a result of chromatographic analyses were processed using LECO ChromaTOF ™ 4.44 software (LECO Corporation St. Joseph, MI, USA). Data processing

was carried out automatically using the algorithm of deconvolution of chromatographic peaks. Identification of peaks was performed by comparing the spectra obtained with the spectra found in the NIST (National Institute of Standards and Technology) library and information on the retention times of individual compounds obtained from real sample analyses with respect to data obtained by analysing the standards of the determined substances.

Quantitative analysis of the tested compounds was carried out using a proton transfer reaction mass spectrometry technique (PTR-TOF-MS 1000 Ultra, Ionicon Analytik GmbH, Innsbruck, Austria) (Figure 5). Samples for analyses using this technique were taken into Tedlar bags. Before each series of air sampling, the bags were rinsed 3 times with a N6.0 purity level nitrogen stream to remove any impurities present inside the bags from previous measurement series. Immediately after transporting air samples from the sewage treatment plant to the laboratory located at the Faculty of Chemistry of the Gdańsk University of Technology, they were subjected to immediate analysis in order to avoid possible losses of analytes as a result of long-term storage of samples in the bags.

During the analysis using the PTR-MS technique, the transfer line was heated to 70℃, analytes were introduced into the ionization chamber in a 5 cm3/min stream, and pressure in the drift chamber was 2.6 mbar. The detector voltage during the analysis was 2380 V. The E/N ratio, characteristic for the PTR-MS analysis, was optimized for the value of 130 Td, which allowed the quantitative determination of a wide group of chemical compounds that can be released from the tested compost heaps. The concentrations of the compounds were determined based on the fixed rate of the proton transfer reaction between the ions produced in the ionization chamber and the hydronium ions constituting the source of H^+ ions. Averaged mass spectra were obtained at a rate of 10 seconds. The IonTOF v. 2.4.40 software was used to record the mass spectra. The analysis of the obtained data was carried out using the PTR-MS Viewer v. 3.2.3.0 program (Ionicon GmbH, Innsbruck, Austria).

Rysunek 2 PTR-TOF-MS apparatus

3. Results

The tentative identification of the substance was carried out using the GC×GC-TOFMS equipment. Identification compliance was determined using the 80% criterion of similarity between mass spectra and data found in libraries of mass spectra. However, it should be remembered that the use of the analyte extraction and enrichment step using a sorbent does not reflect the representativeness of the actual composition of the gas samples. This approach, however, serves to detect as many analytes as possible from gas samples. Understanding the actual composition of gas samples is possible by taking them to PTFE (Teflon™) bags and using the PTR-TOFMS apparatus for measurement. After selecting the most intense molecular masses, the results obtained by using the PTR-TOFMS apparatus were linked to the results obtained after GC×GC-TOFMS measurements. This made it possible, in some cases, to assign a specific molecular mass (M), or actually M+1 or M+2, to a specific

structure of a chemical compound. Table 1 shows the identified VOCs in the air samples using the GC×GC-TOFMS apparatus.

Table 1. Summary of the chemical compounds identified in air samples using the GC×GC-TOFMS technique.

chemical class	name of compound	chemical formula	weight	CAS number
Alkanes	Butane, 1-chloro-3-methyl-	$C_5H_{11}Cl$	106	107-84-6
	Butane, 2-iodo-2-methyl-	$C_5H_{11}I$	198	594-38-7
	Cyclohexane, 2-butyl-1,1,3-trimethyl-	$C_{13}H_{26}$	182	54676-39-0
	Cyclohexane, 2,4-diisopropyl-1,1-dimethyl-	$C_{14}H_{28}$	196	0-00-0
	Decane	$C_{10}H_{22}$	142	124-18-5
	Dichloromethane	CH_2Cl_2	84	58165-12-1
	Dodecane	$C_{12}H_{26}$	170	112-40-3
	Dodecane, 2,6,11-trimethyl-	$C_{15}H_{32}$	212	31295-56-4
	Heptane	C_7H_{16}	100	142-82-5
	Heptane, 3-methyl-	C_8H_{18}	114	589-81-1
	Hexadecane	$C_{16}H_{34}$	226	544-76-3
	Hexane	C_6H_{14}	86	110-54-3
	Methane, dichloro-	CH_2Cl_2	84	75-09-2
	n-Hexane	C_6H_{14}	86	110-54-3
	Octane	C_8H_{18}	114	111-65-9
	Pentadecane	$C_{15}H_{32}$	212	629-62-9
	Pentane	C_5H_{12}	72	109-66-0
	Pentane, 2,4-dimethyl-	C_7H_{16}	100	108-08-7
	Tetradecane	$C_{14}H_{30}$	198	629-59-4
Alkenes	1-Decene	$C_{10}H_{20}$	140	872-05-9
	1-Dodecene	$C_{12}H_{24}$	168	112-41-4
	1-Nonene	C_9H_{18}	126	124-11-8
	1-Octene	C_8H_{16}	112	111-66-0
	1-Pentadecene	$C_{15}H_{30}$	210	13360-61-7
	1-Tetradecene	$C_{14}H_{28}$	196	1120-36-1
	2,4-Dimethyl-1-heptene	C_9H_{18}	126	19549-87-2
	3-Heptene, 2,6-dimethyl-	C_9H_{18}	126	2738-18-3
	Cyclodecene, 3-bromo-	$C_{10}H_{17}Br$	216	56325-56-5
	Cyclopentene, 5-hexyl-3,3-dimethyl-	$C_{13}H_{24}$	180	61142-66-3
	Octene	C_8H_{16}	112	0-00-0
Alcohols	1-dodecanol	$C_{12}H_{26}O$	186	112-53-8
	1-Hexadecanol	$C_{16}H_{16}O_2$	240	0-00-0
	1-Hexanol, 2-ethyl-	$C_8H_{18}O$	130	104-76-7
	1-Naphthalenol	$C_{10}H_8O$	144	90-15-3
	1-Tridecanol	$C_{13}H_{28}O$	200	112-70-9

chemical class	name of compound	chemical formula	weight	CAS number
	1,2,3-Propanetriol	$C_3H_8O_3$	92	56-81-5
	2-Decen-1-ol	$C_{10}H_{20}O$	156	22104-80-9
	2-Ethoxyethanol	$C_4H_{10}O_2$	90	110-80-5
	2-Methylpent-4-en-1-ol	$C_6H_{12}O$	100	0-00-0
	2-Propyl-1-pentanol	$C_8H_{18}O$	130	58175-57-8
	2,3-Dimethyl-3-pentanol	$C_7H_{16}O$	116	595-41-5
	3-Hexanol	$C_6H_{14}O$	102	623-37-0
	3-Octanol, 3,7-dimethyl-	$C_{10}H_{22}O$	158	78-69-3
	3,3-Dimethyl-2-butanol	$C_6H_{14}O$	102	464-07-3
	3,4,4,-Trimethyl-1-pentyn-3-ol	$C_8H_{14}O$	126	993-53-3
Aldehydes	Acetaldehyde, chloro-	C_2H_3ClO	78	107-20-0
	3-Furaldehyde	$C_5H_4O_2$	96	498-60-2
	Butanal, 2-methyl-	$C_5H_{10}O$	86	96-17-3
	Decanal	$C_{10}H_{20}O$	156	112-31-2
	Hexanal	$C_6H_{12}O$	100	66-25-1
	Nonanal	$C_9H_{18}O$	142	124-19-6
Ketones	1-phenyl-ethanone	C_8H_8O	120	98-86-2
	1-Propanone, 2,2-dimethyl-1-phenyl-	$C_{11}H_{14}O$	162	938-16-9
	2-Octanone	$C_8H_{16}O$	128	111-13-7
	2-Oxepanone	$C_6H_{10}O_2$	114	502-44-3
	2-Pentadecanone	$C_{15}H_{30}O$	226	2345-28-0
	2-Pentanone	$C_5H_{10}O$	86	107-87-9
	2-Pentanone, 3-methyl-	$C_6H_{12}O$	100	565-61-7
	2-Pentanone, 4-cyclohexylidene-3,3-diethyl-	$C_{15}H_{26}O$	222	313253-65-5
	2-Pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$	116	123-42-2
	2-Propanone, 1-hydroxy-	$C_3H_6O_2$	74	116-09-6
	2-Propanone, 1-methoxy-	$C_4H_8O_2$	88	5878-19-3
	2-Propanone, 1-phenyl-	$C_9H_{10}O$	134	103-79-7
	2-tert-Butylcyclohexanone	$C_{10}H_{18}O$	154	1728-46-7
	2-Tetradecanone	$C_{14}H_{28}O$	212	2345-27-9
	Acetophenone	C_8H_8O	120	98-86-2
	3-Dodecene	$C_{12}H_{24}$	168	7239-23-8
	3-Heptanone	$C_7H_{14}O$	114	106-35-4
	3-Heptanone, 4-methyl-	$C_8H_{16}O$	128	6137-11-07
	Benzophenone	$C_{13}H_{10}O$	182	119-61-9
	Benzyl methyl ketone	$C_9H_{10}O$	134	103-79-7
	Cyclohexanone	$C_6H_{10}O$	98	108-94-1
	Cyclopentanone	C_5H_8O	84	120-92-3
	Methanone, diphenyl-	$C_{13}H_{10}O$	182	119-61-9
Acids	2-Butynoic acid	$C_4H_4O_2$	84	590-93-2

chemical class	name of compound	chemical formula	weight	CAS number
	2-Ketobutyric acid	$C_4H_6O_3$	102	600-18-0
	2-Propenoic acid, 2-propenyl ester	$C_6H_8O_2$	112	999-55-3
	3-Furoic acid	$C_5H_4O_3$	112	488-93-7
	Benzoic acid	$C_7H_6O_2$	122	65-85-0
	Carbamic acid, phenyl ester	$C_7H_7NO_2$	137	622-46-8
	Citraconic acid	$C_5H_6O_4$	130	498-23-7
	Decanoic acid	$C_{10}H_{20}O_2$	172	334-48-5
	Ethanedioic acid	$C_2H_2O_4$	90	144-62-7
	Hexanoic acid	$C_6H_{12}O_2$	116	142-62-1
	Isocyanic acid	CHNO	43	75-13-8
	Nonanoic acid	$C_9H_{18}O_2$	158	112-05-0
	Oxalacetic acid	$C_4H_4O_5$	132	328-42-7
	Pentanoic acid	$C_5H_{10}O_2$	102	109-52-4
	Tetradecanoid acid	$C_{14}H_{28}O_2$	228	544-63-8
Esters	Benzoic acid, phenyl ester	$C_{13}H_{10}O_2$	198	93-99-2
	Formic acid, 2-ethylhexyl ester	$C_9H_{18}O_2$	158	0-00-0
Aromatic compounds	Benzaldehyde	C_7H_6O	106	100-52-7
	Benzene	C_6H_6	78	71-43-2
	Benzene, (1-methyldecyl)-	$C_{17}H_{28}$	232	4536-88-3
	Benzene, (1-methylethyl)-	C_9H_{12}	120	98-82-8
	Benzene, (1-methylpropyl)-	$C_{10}H_{14}$	134	135-98-8
	Benzene, nonyl-	$C_{15}H_{24}$	204	1081-77-2
	Benzene, propyl-	C_9H_{12}	120	103-65-1
	Dibenzofuran	$C_{12}H_8O$	168	132-64-9
	Ethylbenzene	C_8H_{10}	106	100-41-4
	Naphthalene	$C_{10}H_8$	128	91-20-3
	Naphthalene, 1-(phenylmethyl)-	$C_{17}H_{14}$	218	611-45-0
	Naphthalene, 1-methyl-	$C_{11}H_{10}$	142	90-12-0
	Naphthalene, 2-phenyl-	$C_{16}H_{12}$	204	612-94-2
	o-Xylene	C_8H_{10}	106	95-47-6
	p-Isopropenylphenol	$C_9H_{10}O$	134	4286-23-1
	p-Xylene	C_8H_{10}	106	106-42-3
	Phenol	C_6H_6O	94	108-95-2
	Styrene	C_8H_8	104	100-42-5
	Toluene	C_7H_8	92	108-88-3
Nitrogen compounds	Acetonitrile	C_2H_3N	41	75-05-8
	Benzonitrile	C_7H_5N	103	100-47-0
	Formamide, N,N-dimethyl-	C_3H_7NO	73	68-12-2
	Hexanamide	$C_6H_{13}NO$	115	628-02-4
	Methenamine	$C_6H_{12}N_4$	140	100-97-0
	Pentanamide	$C_5H_{11}NO$	101	626-97-1

chemical class	name of compound	chemical formula	weight	CAS number
	Propane, 1-isocyanato-2-methyl-	C_5H_9NO	99	1873-29-6
Sulfur compounds	Trisulfide, dimethyl	$C_2H_6S_3$	126	3658-80-8
	Benzothiazole	C_7H_5NS	135	95-16-9
	Cyclohexane, isothiocyanato-	$C_7H_{11}NS$	141	1122-82-3
	Dimethyl Sulfoxide	C_2H_6OS	78	67-68-5
	Dimethyl trisulfide	$C_2H_6S_3$	126	3658-80-8
	Disulfide, 1,1-dimethylethyl methyl	$C_5H_{12}S_2$	136	35166-82-6
	Disulfide, dibutyl	$C_8H_{18}S_2$	178	629-45-8
	Disulfide, dimethyl	$C_2H_6S_2$	94	624-92-0
	Methanetiole	CH_4S	48	74-93-1

As a result of analyses carried out using the two-dimensional gas chromatography technique coupled with mass spectrometry, it was possible to identify 126 chemical compounds released from compost heaps during the course of three measurement series. Among the identified compounds the predominant groups were: aliphatic hydrocarbons (alkanes and alkenes), aromatic hydrocarbons, aldehydes, ketones and alcohols. In addition, the use of the GC × GC-TOFMS technique made it possible to identify some compounds that belong to the group of volatile organosulfur and organonitrogen compounds. Due to low odour thresholds (OT), these compounds have a relatively high impact on the strength of odour that is produced during the maturation process of compost heaps. Particularly noteworthy are volatile organosulfur compounds, whose OT values fall within the ppbV range. Aromatic hydrocarbons (arenes) are another group of chemical compounds that can significantly contribute to increasing the negative smell effect associated with the composting of sediments. It should also be remembered that some of them exhibit carcinogenic properties (e.g. benzene, toluene), which makes their presence in atmospheric air in the sewage treatment plant and areas located in the immediate vicinity a serious health hazards for both the sewage treatment plant workers and inhabitants of nearby areas.

The presence of the identified chemical compounds in the tested air samples may result from technological factors related to the operation of sewage treatment plants, including the conditions of sludge fermentation process. Some substances, for example toluene, can be formed in significant quantities during the methane fermentation process of sewage sludge. An important role may be played by wastewater delivered to the treatment plant, depending on the characteristics of the area from which the sewage is supplied to the treatment plant. In the case of heavily industrialized areas, the quality of sewage is significantly different from

that originating in with mainly small households. The emission level of volatile odorants released from sewage sludge subjected to the composting process may also be associated with optional additions of coferments during the sludge fermentation process. Coferments of gastronomic origin can contain a significant load of amino acids, which undergo decomposition in anaerobic conditions, and can be a source of volatile organonitrogen compounds.

In the case of tests carried out using GC×GC-TOFMS, the technique of taking analytes present in the gas phase with the use of solid sorbent tubes was used. This approach enables qualitative determination of analytes occurring at relatively low concentration levels, as the analyte enrichment effect occurs. The gas stream containing chemical compounds flows continuously through the sorbent, which has a high adsorption affinity for the test substances. In the case of sampling gas into Tedlar bags, it is not possible to use the enrichment effect of analytes, thus it is much more difficult to carry out a full qualitative analysis. In this case, the concentration of the determined substances is very often slightly higher than the limit of detection of the applied analytical procedure. The use of the Tenax Ta sorbent is justified by numerous studies in which this type of sorbent is indicated as optimal for the determination of a broad spectrum of compounds belonging to the group of volatile organic compounds, including odorants.

The identification of chemical compounds released from compost heaps is an extremely important element of research related to the development of new solutions in the reduction of odour nuisance associated with the functioning of municipal and industrial sewage treatment plants. Knowledge about the physicochemical properties of the main air pollutants emitted from a sewage treatment plant significantly increases the possibilities of optimizing the process of removing volatile odorants in terms of thermal or mechanical processes. Considering the complexity of wastewater treatment processes, as well as solid waste treatment including sewage sludge, simultaneously taking into account legal regulations concerning the implementation of the principles of green chemistry and technology, it can be concluded that developing new methodical and equipment solutions for reducing emissions of volatile atmospheric air pollutants is an extremely important task, and it is necessary to conduct further research on this topic.

Table 2 shows the results of determinations of 10 selected VOCs present in the air samples. Quantitative analyses were carried out using the PTR-TOFMS apparatus.

Table 2. Results of the quantitative analysis of air samples obtained using the PTR-TOFMS apparatus.

Lp.	Chemical name	A	a	b	c	d	e	f	g	h	i	j
			C [ppbV]									
1	Hexane	I	8328	6739	7704	5093	6820	2732	8380	6563	7952	6907
		II	5326	1838	5369	3227	4550	5978	16190	2699	20490	5567
		III	5056	1902	935.4	2869	4175	781.2	2366	2733	5118	1578
2	Dimethyl sulfide	I	7845	8740	6936	3776	6240	2629	6018	4487	5549	3918
		II	4707	675.3	1468	599.3	3448	6353	9015	597.9	4632	2927
		III	2601	910.8	1071	1614	3855	524.5	2333	1278	3208	1376
3	1-methoxypropan-2-ol	I	2901	1431	2178	1418	1708	426.1	3329	2014	2189	1172
		II	691.9	254.5	389.7	352.5	725.0	707.5	2653	314.0	952.2	423.7
		III	701.3	133.6	140.5	241.4	428.4	172.7	335.3	349.1	736.5	205.5
4	Toluene	I	1034	608.4	489.2	378.2	835.5	514.0	702.9	477.1	581.3	455.6
		II	220.7	383.6	112.0	133.0	134.9	266.9	256.5	96.69	297.4	125.2
		III	610.5	284.4	324.0	189.8	316.8	259.9	456.2	329.6	346.1	307.6
5	Pentane	I	962.2	1024	599.6	772.4	697.7	805.2	830.9	885.4	676.7	933.6
		II	294.7	790.1	400.2	2178	233.9	902.9	432.8	1673	1114	221.5
		III	306.9	140.8	129.0	146.9	195.6	171.1	188.1	478.2	204.2	230.2
6	Methanethiol	I	839.8	159.6	470.5	258.6	573.1	524.4	826.2	339.0	769.9	364.8
		II	396.9	268.6	2036	421.4	257.8	317.8	464.9	309.3	1218	129.9
		III	192.5	172.0	108.6	131.4	130.6	129.7	129.9	482.2	217.0	301.1
7	2-methylbutanal	I	786.6	588.7	514.7	629.9	481.9	394.6	847.3	754.6	617.4	573.1
		II	220.1	1560	156.6	961.9	321.5	637.1	863.9	248.3	506.2	237.4
		III	269.5	137.8	131.7	220.5	249.1	132.6	106.7	484.8	255.9	245.7
8	Benzaldehyde	I	198.5	88.04	116.3	114.8	117.4	29.41	269.3	139.8	163.3	67.13
		II	47.34	32.04	93.16	80.76	25.63	49.51	87.84	68.72	73.45	24.03
		III	97.04	70.96	65.13	78.02	84.75	109.7	43.19	85.09	56.58	88.43
9	Benzene	I	3147	4198	4642	10310	4791	7202	3678	4814	10750	5877
		II	723.3	23900	82.87	81.01	644.4	3651	1253	107.8	129.8	1401
		III	2432	1824	1901	1735	1563	1881	1810	2163	2079	2073
10	Dichloromethane	I	332.1	250.2	400.9	407.2	419.6	294.7	477.7	436.7	492.3	427.5
		II	140.9	506.7	132.6	162.3	147.7	314.2	221.9	88.21	345.7	134.3
		III	317.3	302.7	235.1	167.5	253.3	170.3	151.1	258.6	258.0	222.5

a - conditions no. 1 were applied, measured at the reactor inlet
b - conditions no. 1 were applied, measured at the reactor outlet
c - conditions no. 2 were applied, measured at the reactor inlet
d - conditions no. 2 were applied, measured at the reactor outlet
e - conditions no. 3 were applied, measured at the reactor inlet
f - conditions no. 3 were applied, measured at the reactor outlet
g - conditions no. 4 were applied, measured at the reactor inlet
h - conditions no. 4 were applied, measured at the reactor outlet
i - conditions no. 5 were applied, measured at the reactor inlet
j - condition no. 5 were applied, measured at the reactor outlet
A - measurement series number

Performing tests with the use of Tedlar bags and PTR-TOFMS apparatus enables obtaining information on the actual composition of gas samples. The lack of a preliminary sample preparation stage for the analysis, together with direct analysis of the samples using the mass spectrometry technique make it possible to determine the relations between the amounts of volatile components present in a gas mixture. The stage of transporting air samples from Goleniów, where the samples were taken, to Gdańsk, where the final analyses were carried out, had a significant impact on the results of the performed quantitative analyses. The transport of gaseous samples is of key importance to the quality of the obtained results, due to the possibility of losing analytes during the transport of samples. The results obtained using the PTR-TOFMS technique were correlated with the results obtained using the GC×GC-TOF-MS technique. Because of this, it was possible to identify, from among several dozen detected substances using the PTR-TOFMS technique, ten chemical compounds for which the concentration was subsequently determined. Calculation of analyte concentrations (C_{ppbV}) was performed on the basis of calculations taking into account the proton affinity effect for the substance being determined (equation 1).

$$C_{ppbV} = \frac{10^9}{k} \cdot \frac{22400\,\mu_0 U_{drift}}{N_A l^2} \cdot \frac{T_{drift}^2[K]}{T_0^2[K]} \cdot \frac{p_0^2[mbar]}{p_{drift}^2[mbar]} \cdot \frac{C^+}{H_3O^+} \cdot \frac{TR_{H_3O^+}}{TR_{C^+}} \tag{1}$$

$\mu_0 = 2.8\,\dfrac{cm^2}{Vs}$ reduced mobility

$p_0 = 1013.25\,mbar$ Airpressure at standard condition

P_{drift} Drift-tube pressure

$T_0 = 273.15\,K$ Temperature at standard conditic

$T_{drift}[K] = T_0[K] + t_{drift}[C]$ Drift-tube temperature in Kelvin

$t_{drift}[C]$ Drift-tube temperature in Celcius

$N_A = 6.022e23$ Avogadro Number

$l = 9.3cm$ length of the reaction chamber

On the basis of the results presented in Table 2, it can be concluded that it is possible to use appropriate configurations for the reactor operating parameters, which would reduce the amount of VOCs emitted by the compost heaps. However, no optimal setting of the reactor operation was found, for which the amount of all detected substances, including the determined substances, would be reduced.

4. Summary

The conducted research is preliminary. On its basis, it is possible to select appropriate initial plasma reactor configurations, which can be optimized at a further stage. Further model research and development of a statistical method for the presented type of research, for example a method based on the use of artificial neural networks, would enable choosing the optimal method for purifying air samples. Modelling based on monitoring the concentrations of selected analytes before and after the purification process is a good development trend of the presented idea. Among the many substances identified by GC×GC-TOFMS, organosulfur and organonitrogen compounds are found in a really small minority. However, they have the major influence on the type of odour nuisance. On the other hand, the total contribution of all substances belonging to other chemical classes may also have a significant impact on the character of the odour nuisance caused by storing compost heaps. The use of the GC×GC-TOFMS apparatus made it possible to identify 126 substances, and this is only a minority of all detected (but unidentified) chemical compounds in the air samples. Among the dozen or so substances detected using the PTR-TOFMS system, 10 were identified and later subjected to quantitative analysis. Based on the obtained results, it can be concluded that it is possible to control very harmful substances belonging to the BTEX group. A sensible change in the applied measurement procedure would be transport of the PTR-TOFMS device to the place of measurement and monitoring of changes in analyte concentrations in real time. This would make it possible to avoid the problem of losing analytes during their transport in Tedlar bags.

5. References

[1]   Y. Sheng, F. Chen, X. Wang, G. Sheng, J. Fu, Odorous volatile organic sulfides in wastewater treatment plants in Guangzhou, China., Water Environ. Res. 80 (2008) 324–330.

[2]   R.M. Fisher, N. Le-Minh, E.C. Sivret, J.P. Alvarez-Gaitan, S.J. Moore, R.M. Stuetz, Distribution and sensorial relevance of volatile organic compounds emitted throughout wastewater biosolids processing, Sci. Total Environ. 599–600 (2017) 663–670.

[3]   R.M. Fisher, N. Le-Minh, J.P. Alvarez-Gaitan, S.J. Moore, R.M. Stuetz, Emissions of volatile sulfur compounds (VSCs) throughout wastewater biosolids processing, Sci. Total Environ. 616–617 (2018) 622–631.

[4]   H. Byliński, T. Dymerski, J. Gębicki, J. Namieśnik, Complementary use of GCxGC–TOF–MS and statistics for differentiation of variety in biosolid samples, Monatshefte Für Chemie. 149 (2018) 1587.

[5]   J. Gębicki, H. Byliński, J. Namieśnik, Measurement techniques for assessing the olfactory impact of municipal sewage treatment plants, Environ. Monit. Assess. 188 (2016) 32.

[6]   P. Gostelow, S.A. Parsons, R.M. Stuetz, Odour measurements for sewage treatment works, Water Res. 35 (2001) 579–597.

[7]   M.F. Mustafa, Y. Liu, Z. Duan, H. Guo, S. Xu, H. Wang, et al., Volatile compounds emission and health risk assessment during composting of organic fraction of municipal solid waste, J. Hazard. Mater. 327 (2017) 35–43.

[8]   K. Sahil, B. Prashant, M. Akanksha, S. Premjeet, R. Devashish, Gas Chromatography-Mass Spectrometry: Applications, Int. J. Pharm. Biol. Arch. 2 (2011) 1544–1560.

[9]   A.M. Sulej-Suchomska, Ż. Polkowska, T. Chmiel, T.M. Dymerski, Z.J. Kokot, J. Namieśnik, Solid phase microextraction–comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry: a new tool for determining PAHs in airport runoff water samples, Anal. Methods. 8 (2016) 4509–4520.

[10]   M. Adahchour, J. Beens, U.A.T. Brinkman, Recent developments in the application of

comprehensive two-dimensional gas chromatography, J. Chromatogr. A. 1186 (2008) 67–108.

[11]   P.J. Marriott, S.T. Chin, B. Maikhunthod, H.G. Schmarr, S. Bieri, Multidimensional gas chromatography, TrAC - Trends Anal. Chem. 34 (2012) 1–20.

[12]   M. Adahchour, J. Beens, R.J.J. Vreuls, U.A.T. Brinkman, Recent developments in comprehensive two-dimensional gas chromatography (GCxGC). IV. Further applications, conclusions and perspectives, Trends Anal. Chem. 25 (2006) 821–840.

[13]   H. Byliński, J. Gębicki, T. Dymerski, J. Namieśnik, Direct Analysis of Samples of Various Origin and Composition Using Specific Types of Mass Spectrometry, Crit. Rev. Anal. Chem. 47 (2017) 340–358.

[14]   L. Cappellin, F. Loreto, E. Aprea, A. Romano, J. del Pulgar, F. Gasperi, et al., PTR-MS in Italy: A Multipurpose Sensor with Applications in Environmental, Agri-Food and Health Science, Sensors. 13 (2013) 11923–11955.

[15]   F. Biasioli, F. Gasperi, G. Odorizzi, E. Aprea, D. Mott, F. Marini, et al., PTR-MS monitoring of odour emissions from composting plants, Int. J. Mass Spectrom. 239 (2004) 103–109.