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In memory of prof. dr. Simion Gocan

IDENTIFICATION OF COMPLEX VOLATILE ORGANIC COMPOUNDS IN MUNICIPAL LANDFILL LEACHATE BY HEAD-SPACE SOLID PHASE MICROEXTRACTION AND GCXGC-qMS ANALYSIS

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ABSTRACT. A method for the identification of different classes of volatile organic compounds in the municipal landfill leachate using solid phase microextraction and comprehensive two dimensional gas chromatography coupled with mass spectrometry (SPME-GCxGC-qMS) is elaborated. The results showed that the proposed protocol is able to separate and identify in a single run different classes of volatile organic compounds responsible for the odor of leachate such as carbonyl compounds, aromatic compounds, terpenes, phenolic compounds and nitrogen and sulfur containing compounds. The use of solid phase microextraction not only eliminate the solvent from the samples processing step but also considerably reduces the time and the volume of the sample necessary for this step, being a viable green alternative for this type of analysis. The use of mass spectrometry gives the possibility to indentify many other compounds responsible for municipal landfill leachate odor, creating the premises for a better assessment of chemical composition of leachate. The developed protocol shows good performances in term of repeatability, linearity, limit of detection and limit of quantification being applicable for the real municipal landfill leachate analysis.

***Keywords**: Volatile organic compounds, municipal landfill leachate, solid phase microextraction, GCxGC-qMS*

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1. INTRODUCTION

Leachate is the liquid generated by the percolation of rainwater through the layers of wastes in municipal landfill site. This product can contain both organic and inorganic substances, released from the material deposited or as the result of biotic and abiotic reactions [1-2].

The basal composition of leachates is characterized by dissolved organic matter, xenobiotic organic compounds, inorganic salts, ammonia, heavy metals and other toxicants which are potentially harmful to human and animal health [1, 3].

More than 200 organic compounds have been identified as being dissolved in municipal landfill leachate with upwards of 35 compounds having the potential to cause harm to the environment and human health [4].

The most organic hazardous classes of compounds identified in the municipal landfill leachate are aromatic compounds, chlorinated aliphatic compounds, aliphatic and aromatic acids, polycyclic aromatic hydrocarbons, aldehydes, ketones, terpenes, phenols, phthalates, pesticides, nitrogen containing compounds, organo-phosphoric flame retardants, mercaptans etc. [5-7].

Near the dissolved chemical compounds, municipal landfills are also a potential source of offensive odors which make the areas in the proximity of landfills vulnerable not only to the emissions of potential toxic compounds but also to the nuisance such as odor pollution [8]. The odorous compounds generated by municipal landfill contain generally six classes of substances such as: saturated and unsaturated hydrocarbons, acidic hydrocarbons and organic alcohols, aromatic hydrocarbons, halogenated compounds, sulfur compounds (carbon disulfide and mercaptans), and inorganic compounds [7, 9]. Some of these compounds represent odors causing annoyance for the population, other compounds can be toxic for human and animal health (psychological stress, irritation of mucous membranes, long-term toxic reactions) [10] or can be precursors of photochemical smog formation [9]. From these reasons in the last decades many scientists have been paid attention to the characterization of volatile organic compounds emitted from the municipal landfill.

Over 500 compounds have been reported in landfill gas, these compounds including alkanes and alkenes, cycloalkanes and cycloalkenes, aromatic and polycyclic aromatic hydrocarbons and their derivatives, aldehydes, alcohols, ketones, esters, organohalogens and organosulphur compounds, trichlorethylene, tetrachlorethylene, *b*-pinenes, limonene, *p*-cymene etc. [11-13].

Usually the concentrations of the odorous compounds are very low, but their olfactory thresholds are in some cases lower. Hence, sensitive analytical methods are required for the identification and quantification of odorous substances taking into account that their concentrations are often below the detection limit of measuring equipment [14].

The aim of this study was to develop a sensitive and, in the same time, a comprehensive method for the identification of some classes of compounds responsible for the odor in municipal landfill leachate which may pose health concerns to nearby neighborhoods.

2. RESULTS AND DISCUSSION

2.1. Analytical performances of the SPME-GCxGC-qMS method

The performances of developed method were evaluated in term of repeatability (intra-day precision), linearity, limit of detection (LOD) and limit of quantification (LOQ) calculated based on the ratio of standard deviation (SD) and the slope of calibration curves (Table 1).

Table 1. The performances of developed SPME-GCxGC-MS method

Compound name	Linear curve equations	R^2	SD	Slope	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	RSD (%)
Methyl isobutyl ketone	y=805869x+5E+07	0.9463	10026208	8058691	0.74	2.48	0.9
2-Heptanone	y=5E+06x + 3E+08	0.9785	2623366	5.00E+06	0.32	1.05	0.2
Dimethylbenzene	y=1E+07x + 4E+08	0.9835	310653	1E+07	0.02	0.06	4.0
Isopropylbenzene	y=6E+06x + 3E+08	0.9544	29827885	6.00E+06	3.00	9.94	5.5
Trimethylbenzene	y=2E+07x + 7E+08	0.984	681651	2.00E+07	0.02	0.07	2.9
Phenol	y=7591881x-2E+07	0.9892	15207533	7591881	1.20	4.00	6.6
tert-Butylbenzene	y=6E+06x + 2E+08	0.9855	42115421	6.00E+06	4.20	14.04	9.5
alpha-Terpinene	y=1E+07x + 1E+08	0.9647	47849916	1.00E+07	2.80	9.56	9.8
Limonene	y=2E+07x + 3E+08	0.9599	136306146	2.00E+07	4.00	13.64	10.5
Ocimene	y=9E+06x + 8E+07	0.9827	19865104	9.00E+06	1.32	4.42	6.3
Acetophenone	y=1E+07x - 1E+07	0.9944	42166192	1,00E+07	2.60	8.44	2.2
Cresol	y=3E+06x - 5E+07	0.9554	8847603	3,00E+06	1.76	5.90	2.2
1,3,5-Triisopropyl benzene	y=1E+07x + 2E+08	0.9883	12613977	1.00E+07	3.78	12.6	2.64
5-Nonanone	y=2E+07x + 5E+08	0.9938	62313078	2.00E+07	1.86	6.24	2.6
Terpinolene	y=1E+07x + 2E+08	0.9783	10613977	1.00E+07	0.64	2.12	2.1
Isophorone	y=5E+06x - 5E+06	0.9981	10035259	5.00E+06	1.20	4.02	0.9
Camphor	y=1E+07x + 4E+08	0.9894	76927561	1.00E+07	4.60	15.38	2.4
Benzothiazole	y=1E+07x - 9E+07	0.9888	89652655	1.00E+07	5.40	17.94	5.2

Repeatability was expressed by means of six replicates (n=6) of the standard mixture in concentration of 25 ng mL^{-1}. The results showed a good repeatability, the relative standard deviation RSD being situated under 15-16%, the maximum accepted at the concentration level less than 100 ppb [15]. The method provide also a good linearity with a coefficient of determination

(R^2) ranging between 0.95 and 0.99, a low LOD (0.02-54 ng mL^{-1}) and LOQ (0.05-17.94 ng mL^{-1}) respectively.

The combination of columns chosen for the separation provides a good resolution between the standard compound mixture (Figure 1).

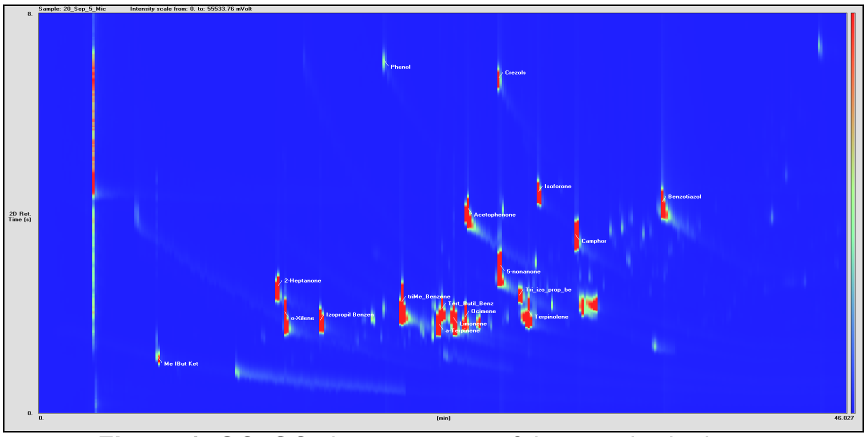


Figure 1. GCxGC chromatogram of the standard mixture

2.2. Analysis of municipal landfill leachate samples

The extraction and the analysis of volatile organic compounds in municipal landfill leachate samples were done under the conditions described in the Experimental part. The results of the performed experiment showed that the landfill leachate contains a huge number of volatile organic compounds with different polarities which are well distributed on the GCxGC chromatogram (Figure 2).

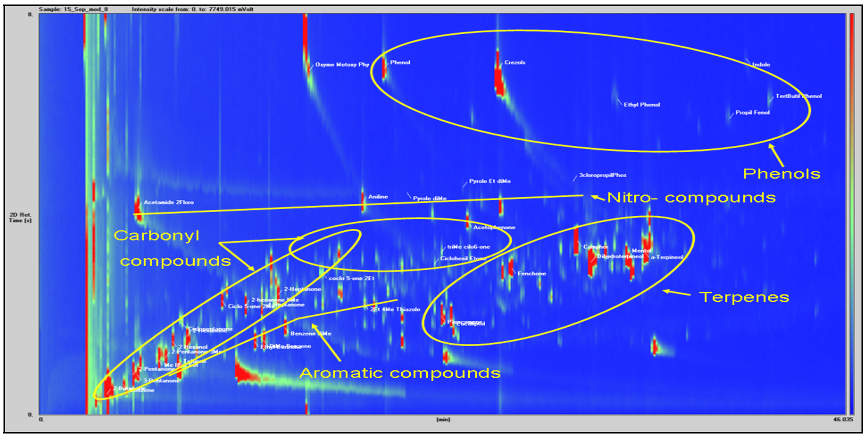
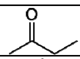
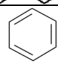
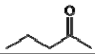
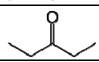
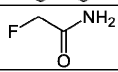
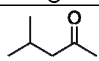
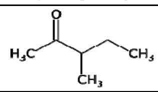
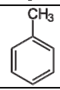
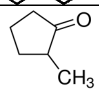
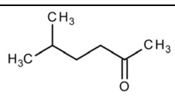
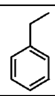


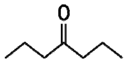
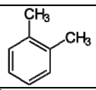
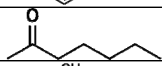
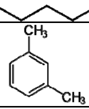
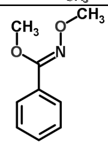
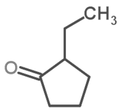
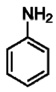
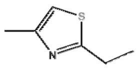
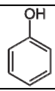
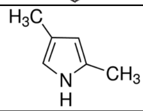
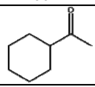
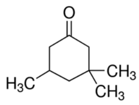
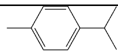
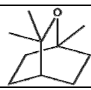
Figure 2. GCxGC chromatogram of the municipal landfill leachate sample and the classes of the identified compounds

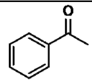
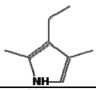
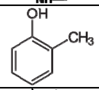
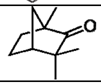
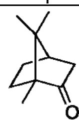
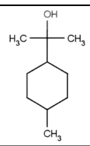
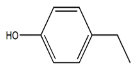
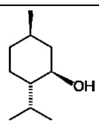
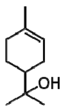
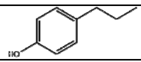
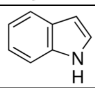
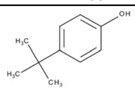
It can be observed that the compounds are grouped on the families according to their physical and chemical proprieties.

Using the standard mixtures, the retention parameters (retention time in the first dimension (RT 1^{st} D) and retention time in the second dimension (RT 2^{nd} D)) and the mass spectra, in the leachate sample 40 compounds were identified. Their name, molecular formula and retention parameters are presented in Table 2. It should be mention that only the compounds with similarity of mass spectra compared with NIST mass spectra library exceeding 70% were taken into consideration.

Table 2. Compounds identified according to standard mixture, their mass spectra and retention parameters

Component name/abbreviation	Molecular formula	RT 1st D (min)	RT 2nd D (sec)
2-Butanone		3.733	0.50
Benzene		4.872	0.64
2-Pentanone		5.333	0.82
3-Pentanone		5.412	0.93
Fluoroacetamide **/** (Acetamide 2Floro)		5.467	4.09
Methyl isobutyl ketone / (Me IBut Ket)		6.800	1.09
3-Methyl-2-pentanone / (2-Pentanone 3Me)		7.200	1.07
Hexanal		7.600	1.55
Toluene		8.000	1.00
2-Hexanone		8.400	1.55
2-Methylcyclopentanone / (Ciclo 5-one 2Me)		10.667	2.52
5-Methyl-2-hexanone / (2-hexanone 5Me)		11.600	2.02
Ethylbenzene / (Ethyl Benzene)		12.267	1.43

Component name/abbreviation	Molecular formula	RT 1st D (min)	RT 2nd D (sec)
4-Heptanone		12.667	2.14
1, 2-dimethylbenzene / (DiMe Benzene)		12.800	1.45
2-Heptanone		13.600	2.55
1, 3-dimethylbenzene / (Benzene diMe)		14.000	1.84
Methyl N-hydroxybenzenecarboximidoate/ (Oxyme Metoxy Phy)		15.067	7.25
2-Ethylcyclopentanone / (coclo 5-one 2Et)		16.000	2.86
Aniline		18.400	4.41
2-Ethyl-4-methylthiazole / (2Et 4Me Thiazole)		18.533	2.25
Phenol		19.600	6.93
2,4-Dimethylpyrrole **/** (Pyrole diMe)		21.200	4.82
Cyclohexyl Ethanone / (Ciclohexil Etone)		22.987	3.02
3,3,5-Trimethylcyclohexanone/ (triMe cilo6-one)		22.933	3.27
p-cymene / (Paracimene)		23.600	1.77
Eucalyptol / (Eucaliptol)		24.267	1.82

Component name/abbreviation	Molecular formula	RT 1st D (min)	RT 2nd D (sec)
Acetophenone		24.400	3.91
3-Ethyl-2,4-dimethylpyrrole / (Pyrole Et diMe)		24.400	4.57
Cresol / (Crezols)		26.133	6.61
Fenchone		26.833	2.84
Camphor		30.667	3.43
Dihydroterpineol		31.467	3.16
Ethyl Phenol		32.800	6.25
Menthol / (Mentol)		33.600	3.07
α-Terpineol		34.400	3.50
Propyl Phenol / (Propil Fenol)		39.067	5.95
Indole		40.000	7.11
4-tert Butylphenol / (TertButil Phenol)		41.923	6.12

It can be also observed that in the analyzed sample the most prevalent compounds are carbonyl group compounds, phenolic compounds, terpenes and aromatic and alkyl aromatic hydrocarbons. Also, nitrogen containing compounds such as fluoroacetamide, aniline, 2,4-dimethylpyrrole, 3-ethyl-2,4-dimethylpyrrole, 2-ethyl-4-methylthiazole, methyl N-hydroxybenzenecarboximidoate have been identified.

Many other compounds could not be identified due to the technical limitation of the instrument. However, the developed method has a big potential and provides information that are difficult to obtain using classical chromatographic methods.

Moreover, the obtained results are in agreement with other studies referring to the odorants of municipal landfill leachate [8-12], but this study provides a better identification of the compounds due to their GCxGC arrangement.

3. CONCLUSIONS

The developed procedure provides a very sensitive method for the analysis of volatile organic compounds in municipal landfill leachate.

Identification of the compounds is improved due to the grouping of the compounds on the families according their physical and chemical proprieties.

The most prevalent families of the identified compounds are carbonyl group compounds, phenolic compounds, terpenes, aromatic and alkyl aromatic hydrocarbons and nitrogen-containing compounds.

SPME-GCxGC-qMS could be a good and green alternative for the screening of volatile organic compounds in municipal landfill leachate, being able to provide better information about the compounds responsible for odors.

4. EXPERIMENTAL SECTION

4.1. Reagents and solutions

For the qualitative and quantitative analysis a standard mixture containing different classes of organic compounds in concentration of 100 µg mL^{-1} dissolved in a solvent mixture of *n*-hexane:acetone (1:1 *v/v*) was used. The composition of the standard mixture is given in Table 1. The standard mixture was prepared from pure substances, of analytical grade purity, purchased from Sigma Aldrich, Supelco and Fluka. The calibration standard solutions in concentration of 10, 25, 50, 100 and 150 ng mL^{-1} were prepared by dilution of different volumes of standard mixture in 5 mL of Milli-Q water. Acetone and *n*-hexane (99.99% purity) were provided from Merck (Germany) and helium in purity of 99.9999% from Air Liquide, France. The Milli-Q water was prepared using a Milli-Q Plus water system from Millipore (USA).

4.2. Instrumentation, chromatographic and SPME conditions

For the analysis of volatile organic compounds in municipal landfill leachate, a Thermo Trace GC×GC gas chromatograph equipped with a dual CO_2 cryogenic modulator and coupled to a quadrupole mass spectrometer (qMS) model ThermoISQ (Courtaboeuf, France) was used. Helium of high purity at a constant pressure of 156 kPa was used as carrier gas. The mass spectrometer frequency of acquisition was 50 Hz, and the SCAN mode was used for data collection, setting a mass range from 45 to 250 m/z. The ionization was performed by Electron Impact Ionization using a voltage of 70 eV. The ion source temperature was 210°C and 280°C for the transfer line. The inlet temperature was set at 280ºC and the injection was made in split mode using a split ration of 10.

For the separation, a Factor Four VF-1 ms column (100% dimethylpolysiloxane), 30 m × 0.25 mm ID, 0.25 µm film thickness (Varian) was used in the first dimension and a DB-1701 column ((14%-cyanopropyl-phenyl)-methylpolysiloxane), 1.5 m × 0.10 mm ID, 0.10 µm film thickness (Agilent) was used for the second dimension. The separation of compounds was performed with a gradient temperature program, by a heating of 2.0ºC/min from 40 to120ºC, with 5 minutes final hold time. The modulation period was 8 seconds and the initial off-set was 0.5 second.

The data acquisition was performed using the X-Calibur software and the GC×GC representation was realized by the Chrom-Card software. The identification of the compounds was done comparing the obtained mass spectra with those from NIST (classical) mass spectral library.

The solid phase microextraction (SPME) of the target compounds was performed using a SDVB/carbowax/pdms fiber, 20 mm length using a TriPlus Autosampler. For the extraction, the following conditions were used: incubation temperature 60ºC in constant mode, extraction time 10 minutes and desorption time 15 minutes.

For the analysis of volatile organic compounds in real samples, 5 mL of municipal landfill leachate collected from a municipal solid waste landfill from Romania was used. The extraction was done according to the protocol described above.

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