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Development of measurement techniques for determination main and hazardous components in biogas utilised for energy purposes

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ABSTRACT

One of the problems that encounter most biogas plants is the fouling that takes place due to the poor quality of biogas utilised for energy purposes. In such a situation it is necessary to measure and control concentrations of main and hazardous components in a biogas. Indeed, the purification systems become a crucial elements of operational plants. In the presented work the analytical procedures and standardisation of analytical methods for determination of main biogas components: trimethylsilanol, volatile methylsiloxanes, volatile organic compounds, oil mist, and halogenated components originating in biogas were developed. For this, gas chromatography has been coupled with various kinds of detection methods i.e. electron capture, thermal conductivity, flame ionization, and mass spectrometry. Furthermore, the sampling procedure based on direct biogas absorption allowed to exclude the extraction process. Consequently, the time of analysis was significantly reduced. The field study showed clearly, that concentration of siloxanes in analysed samples was determined in the range from 20.6 to 361.8 mg/N m^3. Therefore, the impact of biogas silica-contaminants on a running gas-motor was explained and extensively discussed. VMSs and TMSOH concentrations were recalculated and expressed in toluene equivalent, as well as the interpretation of obtained data was provided. Although, we have successfully proven, that the toluene equivalent (T_{eq}) is not an appropriate differentiating factor for siloxanes concentration, although the content of TMSOH might be expressed as T_{eq}. The promising results obtained in this study indicate that this novel sampling procedure, and the standardisation of analytical routines can become a promising approach to accomplish the procedure of biofuel analysis.

1. Introduction

Landfill and digester biogases are widely used as a biofuel to produce electricity, to drive pumps, and fire boilers. Unlike the natural gas, they have an inherent drawback from saturation with moisture, they contain the quantities of sulphur, chlorine and silicon compounds. This however has not deterred the successful application of these at large number of biogas utilisation plants [1,2]. In 2008 Helmut Kaiser Consulting Company has estimated the potential of biogas worldwide market [3]. In the report there was a broad discussion on the rapid profits growth from biogas utilisation, from 2 billion euro in 2006 to 25 billion euro in 2020. Moreover, European countries are indicated to be significant biogas producers in context to the global market of renewable energy. Renewable energy resources are implemented with profits, as indicates it Poland example [4,5]. According to calculation evaluated in Poland in 2010, the theoretical biogas potential arising from an organic fraction on municipal wastes amounted to more than 400 million m^3 [6]. This trend will be progressing and as the International Energy Agency reported, the energy recovery from municipal landfill gas will make a great expansion in the near future, particularly in Asia [7] and East Europe. Many countries have been recently developing an energy sector based on biogas. This has been influenced by both economic factors and care for environment. Moreover, still growing prices and limited resources of fossil fuels altogether with technological progress render the biogas utilisation as an alternative, pointing it as a good way to produce cheap and clean green-energy [6,8]. The most popular technologies concerning biogas utilisation are based on two solutions. The first one is based on the micro [9], small [10], and standard [11] combined heat and power (CHP) systems, the latter, on the biogas enrichment processes and its conversion into the transport fuel. The presence of hydrogen sulphide, ammonia, halogens, volatile organic compounds (VOCs), oil mist (OM > C_{10} – hydrocarbons forming a structure of more than ten carbon atoms), volatile methylsiloxanes (VMSs) and trimethylsilanol (TMSOH) in biogas considerably hamper the biogas utilisation for energy purposes.

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Moreover, these compounds are coming from decomposition of organic substances and they are characterised by different solubility, vapour pressure, volatility and polarity, hence these prosperities cause a serious problem for control and measurement of the biogas stream. Especially VMSs are not decomposed in natural processes, they have a significantly lower solubility in water and are more adsorptive than many other organic compounds [12]. They do not accumulate in water phase during biogas production, but are effectively volatilize to gas phase from fermentation products. The biogas can contain up to eight different linear and cyclic VMSs. This specific group is characterised by totally methylated silicon-oxygen-backbone including methyl groups, all represent a subgroup of silicones. VMSs are non-toxic and have some useful prosperities, a low surface tension and water repelling properties explaining their widespread use [12]. The main cause of its appearance in biogas is polydimethylsiloxane (PDMS), because VMSs are final products of PDMS decomposition, being the component used in multiple industry applications e.g. additives to oil, car polish, cleaners and car waxes, in customer products as nappies, protective creams, cosmetics components, as an elastomer in silicone, and finally in medical implants, in cosmetic surgery and in coating pacemakers [13–15]. Additionally, high vapour pressure index (0.02–31.0 mmHg at 25 °C) of VMSs leads to easy volatilization from deposited waste or waste water treatment sludge into the biogas [1]. Moreover, different VOCs with more than four carbon atoms in their structure are generally present in biogas, they are still unsatisfactorily characterised in context to the biogas matrix complexity. To this group belong aromatic heterocyclic compounds, and organic acids. In order to better understand the problems of most engine operators, many biogas aspects have been studied i.e. biogas composition, processes of biogas combustion and content of contaminants. Furthermore, application of biogas as a fuel in CHP units needs to be analysed in details and harmful compounds that affect the engine during the biogas combustion should be removed. The appearance of more or less problematic components depend on biogas source and on the type of biogas production process afterwards. The presence of VMSs and TMSOH causes serious problems for biogas engines operators. During the combustion inside the engine, silicon atoms combine with oxygen and other elements, thus changing into powdered silica-deposit. The engine silica deposit coming form the inner parts of engine combustion chamber is shown in Fig. 1 and it consists of silica dioxide predominantly, as well as can contain atoms of calcium, copper, sulphur and zinc. The analysed deposit was sampled directly from the combustion chamber and analysed by SEM–EDX without any sample pre-treatment. The SEM–EDX, type 1430 VP (LEO Electron Microscopy Ltd., UK) was equipped with XFlash 4010 Quantax 200 AXS detector (Bruker, Germany) and the 3000× zoom was set for the further analysis of samples. Most of the analysed residues are white to light brown in colour with a powdery-looking surface or varying texture, smooth, rough and grainy surface. Mentioned micro-crystal deposit adheres to the working parts and covers the engine surface with several millimetres thick layer. Chemical composition of silica deposit makes the layer difficult to be removed by chemical or mechanical means. The propensity of silica deposition depends on flame front, area of surface heated, tip speed, post combustion equipment, heat recovery and catalyst. However, it leads to fouling in the combustion chamber, on the valves, valve seats, piston crowns and cylinder walls. This process significantly reduces compression and engine efficiency. In engines, deposits are formed in the hottest areas, mainly on the first few rows of nozzles and blades, so many manufacturers have already set very low limits of VMSs concentration in biogas in warranty restrictions.

The VMSs conversion during the biogas combustion in engines and the harmful influence of silica-deposition on motor can be concisely explained in two general steps. At first, in combustion chamber, under prevailing extreme conditions, the silica components present in the biogas convert into amorphous glass form. After engine cooling the amorphous compounds crystallise and form an even layer of micro-glass deposit that can lead to engine damage. This micro-crystal glass deposit can cause changes in geometry of the combustion chamber, inducting higher emission of air pollutants and violating air emission regulations [16]. Moreover, the significant high concentration of discussed compounds causes overheating of sensitive motor parts and leads to malfunction of pistons and spark plugs [17,18]. The monitoring of biogas contaminants is essential for the safe working of the motor whilst the information on VMSs and TMSOH concentration is important for engine manufacturers and operators. Therefore, engine operators have to make a decision, either to remove the siloxanes, or to operate without the manufacturer's warranty [19]. At the same time acid gases cause corrosion, as well as the amounts of hydrogen sulphide and halogenated components (chlorinated and fluorinated) influenced by humidity evolve into H_2S_{aq}, HCl_{aq} and HF_{aq} acids leading to drastic decrease of engine oil pH.

This paper provides a reliable information concerning the biogas-to-energy application. In addition, this information can feedback the future development in this area, particularly the on-line measurement and monitoring processes [20]. In this paper, we present the methods of analysis and discuss these results taking into account the concentration of biogas components in samples originating from different sources. Moreover, in contrast to existing papers [21,22], this work provides a modern sampling proce-

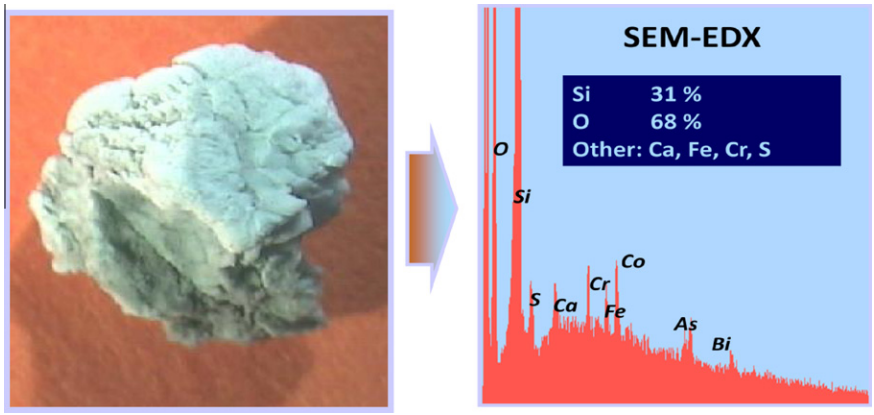

Fig. 1. SEM–EDX analyse and elemental composition of engine deposit.

dure, that eliminates the extraction process and suggests an appropriate analytical routine for methylsiloksanes, trimethylsilanol, volatile organic compounds, as well as oil mist determination. To the best of our knowledge, this work extends the current knowledge by providing reliable information on recognising the biogas matrix composition, on analytical methods of biogas analysis, and the impact of contaminants on operation of CHP units.

2. Experimental set-up and procedures

2.1. Measurements sites

The measurements were carried out at nine sites: four active municipal landfills, four working municipal waste water treatment plants (WWTPs) and one agricultural bioreactor (ABR), which are located at Germany and at Poland. The Landfill A is located in the central part of Poland, in Lodzkie region. The biogas was collected from 43-extraction well systems deployed at area of 4.5 ha. In the case of Landfill B the biogas samples were collected from 41-extraction well systems deployed at area of 4.2 ha and the landfill was located at Lubuskie region in west part of Poland. The Landfills C and D are located at Baden-Wurttemberg and Sachsen–Anhalt region in Germany, respectively. Additionally, the biogas purification system in the form of active carbon filter, introduced for humidity and hydrogen sulphide removal was operated. In above, the raw biogas samples were collected from 42-extraction well systems disposed at area of 6.8 ha and 61-extraction well systems deployed at 7.3 ha area, respectively. Biogas samples originating from three WWTPs in Germany and one sample from Poland were taken. In A–C WWTPs the operated ceramic filter purifies the raw biogas from moisture. The mesophilic nature of processes is prosecuted in all described WWTPs. The biogas is produced in 1500 m^3 digester tanks, where the primary and secondary sludge is decomposed. The ABR is located at Bavaria region, Germany. In one bioreactor (1200 m^3, filled to 75–80%) the silage and field corn is decomposed under specified biological mesophilic processes (temperature of process: 37–39 °C). Table 1 presents an overview of the measurements at locations, containing information on the type of biogas, applied purification systems, and kinds of its utilisation.

2.2. Gas collection and sampling

The biogas samples from the landfills, WWTPs and ABR were collected during the spring season (March–June) from 2010 to 2011. At each above sites, raw landfill gas samples were taken from main pipe located after drilling extraction well system, whilst biogas samples from WWTPs and ABR were collected from the main pipe with raw biogas, before the purification appliance, directly. A total of 72 samples were taken for this study (eight samples from each site). For determination of methane, carbon dioxide, oxygen, nitrogen, VOCs and halogenated compounds, the biogas samples were collected in LINDE PLASTIGAS Bags (PETP/AL/PE max. pressure 0.1 bar, vol.2.5 L). In case of VMSs, TMSOH and OM measurements, the samples were collected by means of impingers with an organic sorbent. Methanol, *n*-hexane and acetone were tested for organic solvents. The best results with respect to sorption were obtained for acetone (data not provided) thus, this solvent was chosen as a trapping liquid for our study. For the experiment two series of connected impingers were employed. The impingres containing approx. 30 g of acetone were arranged as it is indicated at Fig. 2. The sampling was done by passing raw biogas through two series of connected impingers, which were coupled with a calibrated rotameter (Dwyer, Dwyer Instruments Inc. USA) and a special flowmeter provided by Ritter Company – (Ritter, Germany). The trapping solvent – acetone Suprasolv (99.99%) was provided by Merck (Merck, Germany). Thereafter, the biogas flow rate was set to 0.5 L/min for 40 min, and approx. 20 L of biogas went through the sampling system. The 2nd – impinger was adopted as a control sample in order to verify if all target compounds were absorbed in the 1st impinger. To ensure, that the absorption of the VMSs, TMSOH and OM in a trapping solvent is complete, the process was additionally carried out in low temperature (<0 °C), as well as the sampling was three times repeated. The temperature of sampling was measured on-line by TESTO metre. Finally, 72 samples were taken. Obtained samples were gently stored under dark and cold conditions (0–4 °C) during transport to the laboratory. Thereafter, the collected samples were kept one day under room conditions and analysed by chromatography means.

2.3. Analysis

Different detection methods with respect to the quantification of biogas components and contaminants were employed for recognising the biogas matrix complexity. The hyphenated chromatographic method with detection types: GC–ECD (gas chromatography coupled with electron capture detector), GC–FID (gas chromatography coupled with flame ionization detector), GC–TCD (gas chromatography coupled with thermal conductivity detector) and GC–MS (gas chromatography coupled with mass spectrometry detector) were applied in order to obtain an extensive information on analysed biogas samples. Furthermore, the main advantage of applied techniques was a comprehensive infor-

Table 1
Biogas measurement location.

Type/location of measurement	Region	Digester feed/disposed waste	Biogas flow (m^3/h)	Purification gas system (Yes/No)	Gas utilisation
Landfill A – Poland	Woj. Lodzkie	Municipal solid waste	500–600	No	CHP gas engine
Landfill B – Poland	Woj. Podlaskie	Municipal solid waste	400–450	No	CHP gas engine
Landfill C – Germany	Baden-Wurttemberg	Municipal solid waste	350–400	Yes – active carbon filter	CHP gas engine
Landfill D – Germany	Sachsen–Anhalt	Municipal solid waste	450–500	Yes – active carbon filter	CHP gas engine and fuel cell
Bioreactor – Germany	Bavaria	Agricultural biowaste	100	No	Microturbine (only energy production)
WWTP A – Germany	Niedersachsen	Sewage sludge	65	Yes – ceramic filter	Microturbine (only energy production)
WWTP B – Germany	Hessen	Sewage sludge + industry waste	250	Yes – ceramic filter	CHP gas engine
WWTP C – Germany	Hessen	Sewage sludge	55	Yes – ceramic filter	Microturbine (only energy production)
WWTP D – Poland	Woj. Pomorskie	Sewage sludge + agricultural waste (animal fats and proteins)	85	No	Microturbine (only energy production)

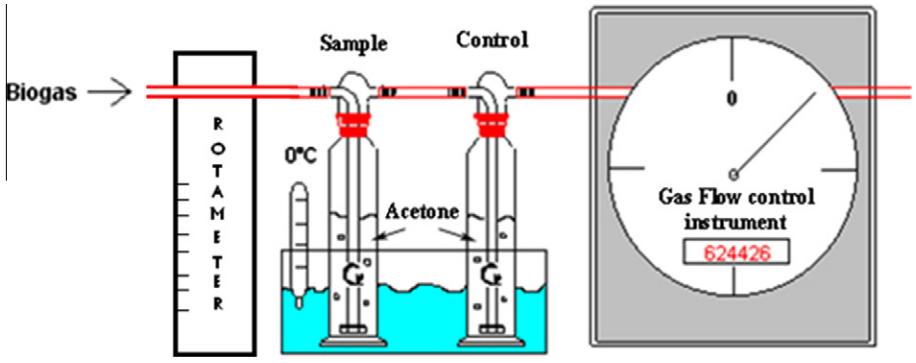

Fig. 2. The employed sampling system.

mation on the biogas components in context to biogas matrix. Therefore, the main and trace components, also contaminants contained in biogas have a significant impact on the efficiency of energy production. Both, the analytical procedures at site and off site were tested. The biogas components were divided into major and minor groups for the analysis. The concentration of major (methane, carbon dioxide, oxygen, nitrogen, VMSs, TMSOH, VOCs, OM, halogenated compounds) and minor (ammonia, hydrogen sulphide, relative humidity) components was determined. The minor components were determined at site, whereas sampling for the major components has been carried out on spot, and collected samples were subsequently analysed in the laboratory. In all cases, the blank sample was verified before the analysis.

The biogas components, such as methane, carbon dioxide, nitrogen and oxygen were analysed in GC coupled with TC detector. The biogas samples were measured by GC–TCD System HP 5890 Series II (Hewlett–Packard, Germany) equipped with Carboxen column having 30 m × 0.25 mm, 0.10 μm film thickness, operated from 50 °C (5 min isothermal) to 190 °C (5 min isothermal) at 10 °C/min. Helium was used as a carrier gas. Inject: 2 μL, state of sample: gas-sample. Moreover, the concentration of halogenated components in the biogas samples was performed by Varian CP 3800 GC system fitted with EC detector. Initial oven temperature was set to 60 °C. This temperature was kept for 5 min, after which the temperature was linearly increased to 240 °C at rate of 10 °C/min. The gas sample was injected into described GC–ECD system, directly. The separation was carried out in the non-polar DB-5 column characterised by 30 m × 0.20 mm, 0.25 μm film thickness, provided by Agilent Technologies (Agilent Technologies, USA). Standards were provided by SAS (SAS, Germany). TubeDetectors (certified detectors tubes ISO 9001, Dräger Röhrchen and MSA AUER ISO 9001, Germany) were employed for hydrogen sulphide, methylmercaptans, triethylamin-5 and ammonia determination. The humidity and temperature of biogas were analysed by portable TESTO metre (TESTO AG, Testo System 635-2, Germany).

The analyses after absorption processes were done with the use of GC system coupled with MS and FID detectors. Each VMSs and the unstable in its pure form TMSOH existing in the analysed samples were qualified and quantified by GC–MS. The analysis of the biogas samples was performed by applying a VARIAN 3800 gas chromatograph with a CTC Analytics Combi PAL autosampler, coupled with a Selective Mass Spectrometry Detector, S2200. The mass selective detector was characterised by the temperature of transfer line at 210 °C. The mass spectrometric detector was operated in electron impact ionization mode with an ionizing energy of max. 60 eV. The selected mode and the mass window were set at the selected ion monitoring (SIM) in the range from 15 m/z to 500 m/z. Additionally, the GC–MS conditions were as follows: initial oven temperature 60 °C and the initial ramping rate 10 °C/min. to 210 °C with subsequent sample conditioning in 50 °C during 5 min. isothermal conditioning. Optional parameters of the system: injector temperature – 240 °C, detector temperature – 230 °C carrier gas: helium (linear gas velocity: 2 mL/min.). The separation was carried out on Cabrox capillary column (Agilent Technology, Germany) with the parameters specified: 30 m × 0.32 mm, 0.25 film thickness. The GC inlet septum Teflon was used. The auto-injection sample volume was 1 μL.

The hexamethyldisiloxane (abbreviated as L2), octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), were obtained from Aldrich (Aldrich, Germany), whilst hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), dodecamethylcyclohexasiloxane (D6) and TMSOH with purities 99.9% were provided by Merck (Merck, Germany) and SAS (SAS, Germany), respectively. For the quantification of VMSs and TMSOH the calibration curves with the linearity ranging from 0.01 to 55.6 μg/g were prepared in acetone. The calibration levels were chosen to mirror typical concentrations of VMSs and TMSOH in different types of investigated biogases. Consequently, the mixture of standards was injected into the GC–MS System directly. Injection was three time repeated for each measurement. The limit of detection (LOD) and limit of quantification (LOQ) in amounts of 0.01 μg/g and 0.04 μg/g, respectively, were obtained for the analysis. The results were identified comparing obtained mass spectra with data from NIST 2010 MS – spectra library. All peaks were identified with a correlation higher than 99.9%.

The concentration of VOCs and OM in biogas samples were identified and quantified by GC–MS and GC–FID, simultaneously. For OM determination VARIAN CP 3800 chromatograph coupled with non-polar column DB-5 with parameters specified: 30 m × 0.20 mm, film 0.5 μm (Agilent Technology, Germany), was applied. As a standard for VOCs and OM determination *n*-decane (99.9%, Merck, Germany) was used. All peaks before and after *n*-decane retention time (RT) were integrated for VOCs and OM determination, respectively. Parameters of applied GC system were as follows: 40 °C – 5 min. isothermal, threshold 20 °C/min, at 250 °C, 15 min isothermal and optional settings: injector temperature: 250 °C, detector temperature: 290 °C, carrier gas: helium (linear velocity: 1.6 mL/min), inject: 1 μL.

3. Results and discussion

For all tested biogases, a significant concentrations of minor and major components were observed. Table 2 provides a summary results on main and trace biogas components in the analysed samples in the form of records from Tube Detectors, TESTO metre, and applied chromatograph. Additionally, in Table 3 the results

Table 2
Concentrations of biogas components.

Compound	CH_4[a] (%)	CO_2[a] (%)	N_2[a] (%)	O_2[a] (%)	Humidity[b] (%)/(°C)	NH_3[a] (mg/N m^3)	H_2S[a] (mg/N m^3)	Halogens[a] (F, Cl, Br, I) (mg/N m^3)	Oil mist[a] (mg/N m^3)
Landfill A	61.5 ± 0.6	35.0 ± 1.0	3.5 ± 0.2	n.d	97.9/26.2	43.0 ± 3.0	607.0 ± 3.7	79.5 ± 0.1	3500.0 ± 13.9
Landfill B	59.2 ± 1.0	39.8 ± 1.1	1.0 ± 0.3	3.0 ± 0.1	90.0/26.7	3.5 ± 1.0	437.0 ± 2.4	12.2 ± 0.1	1610.0 ± 11.0
Landfill C	60.2 ± 1.3	31.8 ± 1.1	7.0 ± 0.3	3.0 ± 1.0	92.8/24.2	15.8 ± 2.0	452.8 ± 1.9	36.6 ± 0.1	n.a
Landfill D	58.3 ± 1.7	38.2 ± 1.8	2.3 ± 0.2	3.0 ± 1.2	80.1/24.7	5.9 ± 1.0	365.2 ± 2.4	11.2 ± 0.1	1101.6 ± 17.7
WWTP A	63.5 ± 0.4	36.5 ± 0.6	n.d	n.d	51.4/18.9	3.6 ± 1.0	42.0 ± 1.8	0.9 ± 0.1	56.3 ± 4.9
WWTP B	59.6 ± 0.2	40.3 ± 1.3	0.1 ± 0.1	3.0 ± 0.1	85.4/18.0	2.0 ± 1.0	49.8 ±0.9	1.0 ± 0.1	98.5 ± 1.3
WWTP C	59.9 ± 0.2	40.1 ± 0.3	n.d	n.d	69.5/17.0	3.1 ± 1.0	40.0 ± 1.1	0.9 ± 0.1	87.0 ± 6.0
WWTP D	63.4 ± 1.1	36.6 ± 1.0	n.d	n.d	84.5/17.2	n.a	n.a	0.9 ± 0.1	18.3 ± 4.1
Bioreactor	54.4 ± 0.9	45.5 ± 0.8	0.1 ± 0.1	n.d	87.3/37.9	3.6 ± 1.0	16.0 ± 0.7	0.8 ± 0.1	7.5 ± 1.1

n.a – Not analysed.
n.d – Not detected.
[a] The average from three measurements ± SD.
[b] Relative humidity.

concerning silica-contaminants concentration and theirs T_{eq} from nine measurement sites are arranged separately. The following section places a special emphasis on results concerning biogas components concentrations, the data interpretation, comparison and discussion.

3.1. Major components CH_4, CO_2, O_2 and N_2

The content of methane, carbon dioxide, oxygen and nitrogen in three types of analysed biogases were determined dependently from location. The highest methane content (63.5%) was detected in biogas from WWTP A and the lowest (54.4%) in the biogas from agricultural bioreactor. The obtained results clearly showed, that WWTP A from Niedersachsen region has the highest potential of biogas utilisation (Table 2). The potential profits (taking into account type of engine, engine efficiency, calorific value of biogas utilised, and costs of 1 kW h electricity production during the biogas utilisation) of biogas utilisation in WWTP A can be even 96 Euros per day. The carbon dioxide concentration was obtained in the range from 31.8% to 45.5% for ABR and Landfill C, respectively. In all locations the content of oxygen and nitrogen was not higher than 1.2% and 7.0%, respectively. The excessive concentration of O_2 and N_2 is probably caused by sampling procedure. It is connected with some air inlet into Tedlar Bag during sampling. As the literature clearly points out, the typical concentration of methane, carbon dioxide and nitrogen is closely related to biogas place of origin and is related to the nature of biogas production process [22,23]. Biogas from sewage usually contains methane in range from 57.8% to 65%, carbon dioxide from 33.9% to 38% and less than 10% of nitrogen. Biogas from farm biogas plant contained 55–58%, 37–38% and less than 2% in relation to methane, carbon dioxide and nitrogen, respectively. In case of landfill gas, 47–57%, 37–41% and 1–17% for methane, carbon dioxide and nitrogen were found, respectively [22].

3.2. VMSs and TMSOH

As a general statement, there are significant differences between VMSs and TMSOH concentration in biogas samples originating from various sources [24]. The agricultural biogases do not contain VMSs, as well as, the typical VMSs concentration in biogases coming from landfills is in the range from 9 to 75 mg/N m^3, since the results were obtained from 340 measurements of VMSs concentration on hundred European landfills [25]. Therefore, in our study this range has been accepted as a typical European value. In case of US, the average VMSs concentration was in the range 38 mg/N m^3, whereas measurements were carried out at 50 different landfills in US, as Tower reported [26]. The values obtained for VMSs and TMSOH concentrations in biogases for the needs of analysed landfills with exception of Landfill A are indicated in the values reported for Europe [25]. The content of investigated biogas samples containing VMSs and TMSOH quantification is presented in Table 3. Moreover, the overstated value of TMOSH concentration in case of Landfill D may result from the low efficiency of humidity removal by the means of active carbon filter.

It is obvious that all forms of VMSs are not contained in biogas. Cyclic form of VMSs (D3–D6) were predominant in landfill gas, whereas the L3 was not detected in all measured samples. As the results clearly indicate D4 and D5 represent more than 70% of total amounts of VMSs in analysed landfill gases. The fact, that the main component of silica-contaminants in landfill biogas is represented via TMSOH should be clearly pointed out. Simultaneously, this confirms our previous research that the amounts of TMSOH ranged up to 40% of all landfill gas silica-contaminants [21]. Total siloxanes concentration (including TMSOH) in biogases coming out from Landfills A–D was ranging from 20.5 mg/N m^3 to 84.3 mg/N m^3. Total VMSs and TMSOH concentration is essential for recalculation of siloxanes concentration per 10 kV h of produced electricity, and this value is expressed by C_{VMSs}/10 kV h unit, (included Wobbe Index of analysed biogas), and this is commonly used by engines manufacturers [27].

Unlike to biogas coming out from landfill, the biogas from WWTP is characterised by the lack of TMSOH. It could be explained by its excellent water solubility (35,000 mg/L at 25 °C) [28] and hindered volatility from water into biogas, directly. Results arranged in Table 3 confirm above property, and clearly show that the TMSOH concentration in biogas from WWTP is under detection limit. Furthermore, basing on the literature and obtained results, it could be inferred that VMSs concentration in biogas from WWTPs can reach up to 200 mg/N m^3, whereas measured concentration range usually lies below 60 mg/N m^3 [15,22]. The amounts of VMSs were reported by Dewil et al. in different European countries: Belgium (20 mg/N m^3), Switzerland (25.1 mg/N m^3) and Germany (59.1 mg/N m^3) [15] and the concentrations of VMSs did not exceed 60 mg/N m^3. Moreover, other measurements were discussed by authors Lunghi et al., Beese, as well as Arnold and Kajolinna, and obtained VMSs concentrations were in the range 5–60 mg/N m^3, 15 mg/N m^3 and 29 mg/N m^3, respectively [20,29,30]. In our experiments, biogases from WWTPs were characterised by concentration of VMSs in the range from 7.5 to 361.8 mg/N m^3 and obtained values are typical to biogases coming out from sludge decomposition process in context of amounts and silica-contaminants composition. The highest VMSs concentration of all tested biogases was detected at WWTP B, and the lowest at WWTP A. As the literature reported, the highest concentration of VMSs was found in biogas coming from Trecatti (UK), and amounted up to

Table 3
Concentration of VMSs and TMSOH and their toluene equivalent in raw biogas samples at nine locations.

	Bioreactor	Landfill A	Landfill B	Landfill C	Landfill D	WWTP A	WWTP B	WWTP C	WWTP D
VMSs and TMSOH concentrations (mg/m^3) ± SD[a]/T_{eq}									
L2	n.d	3.4 ± 0.05/1.93	0.1 ± 0.09/0.06	0.1 ± 0.06/0.06	1.5 ± 0.09/ 0.86	n.d	3.4 ± 0.07/ 1.93	n.d	n.d
L3	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
L4	n.d	n.d	n.d	n.d	n.d	n.d	0.7 ± 0.07/0.2	n.d	n.d
D3	n.d	2.8 ± 0.07/1.16	0.1 ± 0.02/ 0.04	0.5 ± 0.06/ 0.21	0.4 ± 0.06/0.17	1.6 ± 0.09/0.66	n.d	2.8 ± 0.09/1.16	0.1 ± 0.06/0.04
D4	n.d	29.1 ± 0.06/9.03	3.6 ± 0.09/1.12	11.8 ± 0.09/3.66	5.0 ± 0.09/1.55	0.5 ± 0.06/0.16	8.1 ± 0.09/2.51	0.9 ± 0.07/0.28	1.0 ± 0.06/0.31
D5	n.d	11.8 ± 0.03/2.93	6.4 ±0.07 /1.59	6.0 ± 0.09/1.49	0.9 ± 0.08/0.22	5.3 ± 0.08/1.32	340.7 ± 0.09/84.61	11.9 ± 0.09/2.96	48.4 ± 0.09/12.02
D6	n.d	1.5 ± 0.07/ 0.31	0.4 ± 0.09/ 0.08	0.5 ± 0.09/0.1	n.d	0.1 ± 0.06/0.02	8.7 ± 0.09/1.8	0.2 ± 0.06/0.04	2.5 ± 0.07/0.52
TMSOH	n.d	35.7 ± 0.09/36.46	10.1 ± 0.03/10.32	6.7 ± 0.06/6.84	12.7 ± 0.09/12.97	n.d	n.d	n.d	n.d
Sum	n.d	84.3	20.7	25.6	20.5	7.5	361.7	15.8	51.9

n.d – Not detected.
[a] The average from three measurements ± SD.

400 mg/N m^3 [31]. Within above scenario, it leads to a complete engine seizure before 200 h of its operation. Furthermore, as an UKEA [32] reported, if landfill gas (LFG) will be used as a car fuel, the VMSs and TMOH should be removed completely. On the other hand, when a biogas is utilised only for energy purposes, the manufacturers of engines [27], microturbines [1] and CHP units recommend VMSs limits to be usually in the range below 20 mg/N m^3 [33]. Therefore the equipment operators should proceed with caution. It appears, that manufacturers are setting and tightening the VMSs standards. Whilst the VMSs removal process carried to obtain described limit may reduce the cost of maintenance of the equipment, a total cost of plant operation may increase. Thus, the decisions whether or not to proceed with projects should take into account total costs of a plant operation. In context to obtained results and manufacturers limits [27], only WWTP A, WWTP C and ABR operating at German territory have VMSs concentration meeting the strict criteria (less than 20 mg/N m^3), thus they can operate without concerns about losses of the manufacturers guarantee. In case of Polish plants, both landfills and WWTP, particularly Landfill A, have a serious problem with biogas quality, moreover most of manufacturer limits are exceeded i.e. VMSs, OM (limit set at 1500 mg/N m^3) and humidity (limit set at 80% rH). It may result in the loss of free guarantee. Most of the studied plants should invest in modern technology and systems aiming for biogas purification and enrichment, as it ensures higher profits from biogas utilisation.

The T_{eq} is an important aspect of this study. There are some works, where the T_{eq} is used for enunciation of siloxanes concentration in analysed biogas samples [3,34]. Our calculations confirmed, that expression of VMSs results in T_{eq} leads to misinterpretation of siloxanes concentration in analysed samples. The main reason, that T_{eq} is not an appropriate factor for expression of siloxanes concentration is the fact, that VMSs concentration expressed as T_{eq} showed very close values to each other. Thus, it precludes an estimation of VMSs concentration in relation to manufacturers limits. Moreover, the enunciation of VMSs concentration as T_{eq} excludes the expression of individual siloxane compounds, so it is possible to express them only as a sum of VMSs in an analysed sample. On the other hand, applied T_{eq} can be extremely acceptable for expression of TMSOH value. This mathematical procedure relates to similar molecular weight of toluene (92.14 g/mol) and TMSOH (90.20 g/mol). It finally gives very similar values. Nonetheless, the results are overstated by 2% in favour of T_{eq}. Table 3 gives VMSs concentrations and theirs T_{eq}.

The GC–MS chromatograms of used standards, landfill biogas, biogas from WWTP and blank with marked VMSs and TMSOH are shown on Fig. 3. The chromatograms of biogases coming from Landfill A (Poland) and WWTP D (Poland) were not chosen randomly, in the mentioned locations the concentration and proportions of target compounds were significantly visible. The biogas composition is much more complex in landfill biogas than in biogas originating from WWTP. The reason for this is the identification of more than 30 volatile organic compounds in landfill gas, such as terpens (pinene, camphene, limonene), aromatic compounds (benzene; toluene; -m,-o,-p xylene), and alcohols. Moreover, the analysed biogas has not been purified.

3.3. VOCs, oil mist, sulphur, ammonia and halogenated compounds

The results from the experiments using Tube Detectors and TESTO Device System showed that landfill biogas from Poland (Landfill A) is characterised by significantly high hydrogen sulphide concentration, even up to 600 mg/N m^3. Moreover, the hydrogen sulphide is the main source of sulphur in biogas. Other reduced sulphur components, such as methanethiol, dimethylsulphide or mercaptanes were analysed by TuberDetectors applied, and they represented less than 2% of total sulphur concentration (data not presented). The process of hydrogen sulphide formation on the landfills can be concisely explained. Methanethiol and dimethyl sulphide are formed during the sulphur-containing amino acids degradation process [35]. Dimethyl sulphide is reduced to methane and methanethiol during methanogenic conversion, whereas the final products of methanethiol decomposition are methane, carbon dioxide and hydrogen sulphide. In contrast to high hydrogen sulphide concentration in landfill gas, the H_2S concentration in the biogases coming from WWTP A, B and C was found below 42.0; 49.8 and 40.0 mg/N m^3, respectively. The biogas from WWTP contained about ten times lower H_2S concentration than biogas from studied landfills. Described disproportion may be explained by sulphur-conversion under microbiological processes. Therefore, unlike in landfill gas, the sulphur contained in waste water is converted into sulphate ion primarily and it remains in water as stable ion. On the other hand, the low H_2S concentration is typical to systems where the iron salt is used for chemical precipitation in water treatment. The concentration of H_2S in biogas from ABR (16 mg/N m^3) was observed as the lowest among all measurement sites.

The concentration of VOCs and OM in all measured samples was determined. The concentration of VOCs in the range from 267.4 to 488.7 mg/N m^3, from 69.1 to 141.5 mg/N m^3 and from 7.0 to 17.1 mg/N m^3 for landfill gas, biogas from WWTP and agricultural biogas was found, respectively. The qualification and quantification analyses of VOCs were reported in the past [36,37]. However, as newer literature indicates, the VOCs were found in the range from 46 to 173 mg/N m^3, and from 13 to 268 mg/N m^3 for biogases originating from landfill and sewage digester, respectively [22]. Significantly higher amounts of VOCs were obtained for landfill gases. It can be related to the age of deposited waste [36]. On the other hand, predominant compounds of VOCs exist in the form of aliphatic and aromatic compounds and are derivatives of hazard-

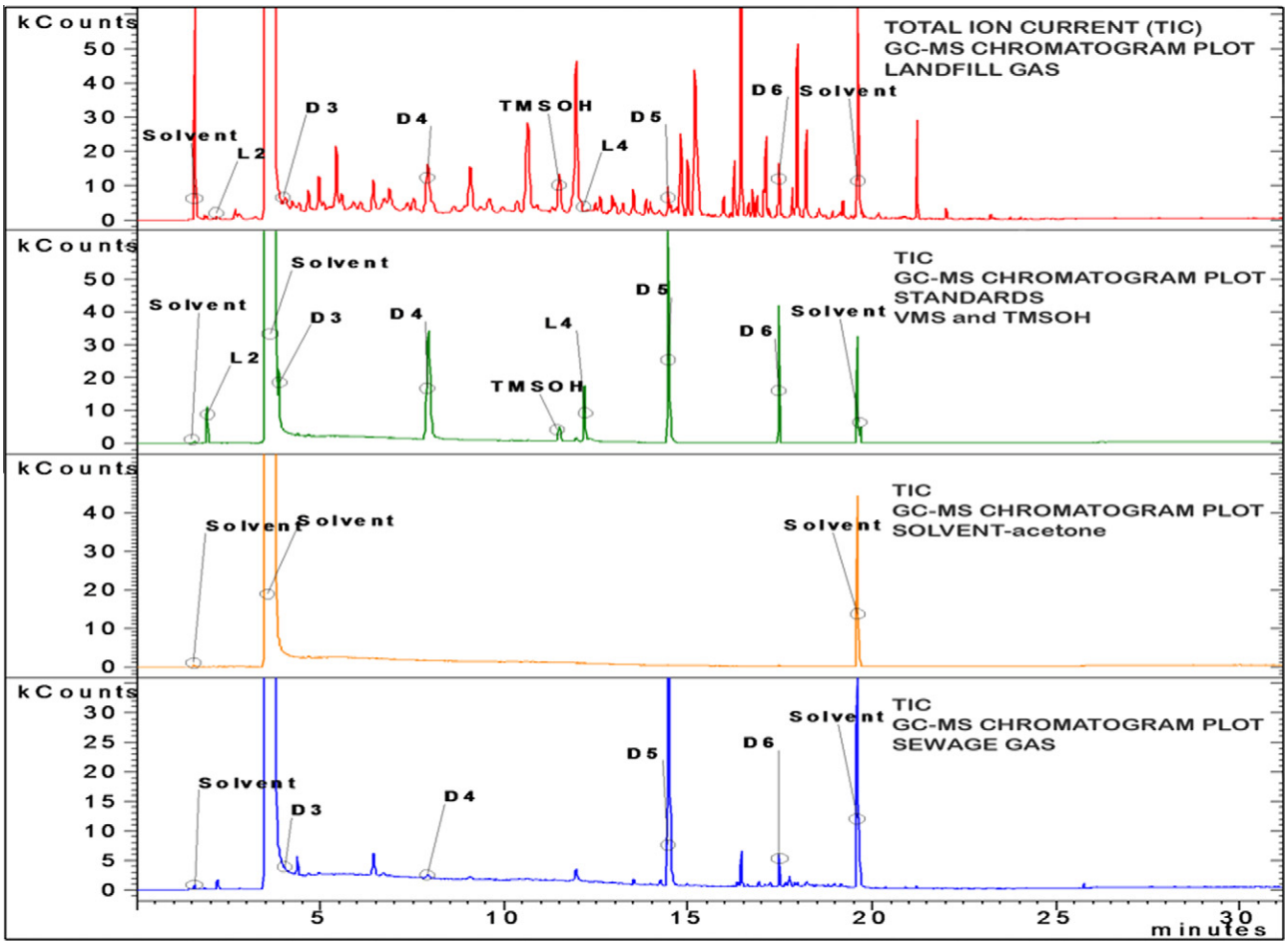

Fig. 3. Total ion current (TIC) GC–MS chromatograms of standards, blank sample (acetone), landfill gas and biogas from WWTP.

ous domestic waste, and anaerobic processes of lignins decomposition, as well [38]. Chemical compounds having the RT shorter than *n*-decane have been acceptable as a standards for VOCs determination in this study. To the best of our knowledge, contaminants in the shape of oil mist have been not reported, so far. Therefore, the concentration of OM in biogas is an important information for engine operators, as large amounts of OM in biogas lead to significant loss of lubricating proprieties of motor oil. The biogas from agricultural plant contained the lowest OM concentration (7.5 mg/N m^3) from all analysed samples. In biogas from WWTPs the amounts of OM were found between 18.3 and 98.5 mg/N m^3. The highest concentration of OM was found for biogas originating from landfills. The range of OM concentration from 1101.6 mg/N m^3 to 3600 mg/N m^3 were obtained for Landfill D and A, respectively.

The halogenated compounds were detected in the range from 11.2 mg/N m^3 to 79.5 mg/N m^3. The concentration of halogenated components in biogas from WWTP (A–D) and ABR was below 1 mg/N m^3. On the other hand, the highest concentration of NH_3 was found at Landfill A. In biogases from left eight measured sites the concentration of NH_3 was found in the range from 3.6 mg/N m^3 to 15.8 mg/N m^3. The obtained NH_3 concentrations are not beyond the range of engine manufacturers limits (limit, less than 30 mg/N m^3) [27]. Mercaptans and triethylamine-5 were quantified in the range 1–17 ppm and 1–7 ppm in all analysed samples, respectively. Finally, The obtained results clearly indicate that concentrations of mercaptans, triethylamine-5, and ammonia in case of all investigated locations are not beyond the range of biogas contaminants limits [27]. Simultaneously, described biogas contaminants do not have direct and harmful effect on the CPH operating units and microturbines, as contrasted with siloxanes and oil mist mentioned previously.

4. Conclusions

The following conclusions were drawn from the presented study on the biogas analyses, that coupled chromatography, various detection techniques and other technical methods. The tests have been carried out on the real, raw biogas coming form different utilisation plants. Moreover, the applied methods present a proof for the new concept. This is the first attempt to collect hazardous biogas components by direct sampling and determine the engine detrimental chemicals in samples having complex matrix. The testing results indicate that there are same differences between biogas composition (minor and major components) dependant on biogas place of origin. Much work towards this study has been carried out at the Nicolaus Copernicus University (Toruń, Poland) in these years, but more studies are needed to be done to improve the validation and calibration of OM measurement method. For example, a more selective and precise tests allowing measures of chemicals with lower vapour pressure, chemicals such as semi-volatile organic compounds in biogas e.g. phthalic acid diesters. Thus, the researches on biogas analysis in this study have been extended to other areas like impact of VMSs and TMOSH on the biogas production efficiency, determination of halogenated components, T_{eq} prominence and interpretation, oil mist concentration testing, and so on. However, tests on environmental samples collected from biogas streams, controlling of the relative humidity (cor-

rected via temperature), determination of hazardous components, and assessment of risk and its influence on CHP units were proven to be difficult. Finally, presented overview of biogas analysis methods with further improvements could provide an alternative way in development of bio-fuel analysis.

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References

[1] Wheless E, Pierce J. Siloxanes in landfill and digester gas update. In: SWANA 27 LFG conference; 2004.
[2] Rasi S, Lantela J, Rientala J. Trace compounds affecting biogas energy utilization – a review. Energy Convers Manage 2011;52:3369–75.
[3] Arnold M. Reduction and monitoring of biogas trace components, vol. 209. Julkaisija-Utgivare-Publisher, VTT; 2009. p. 7–65.
[4] Iglinski B, Buczkowski R, Kujawski W, Cichosz M, Piechota G. Geoenergy in Poland. Renew Sust Energy Rev 2012;16:2545–57.
[5] Iglinski B, Buczkowski R, Piechota G. Algae A source of energy and chemicals. Przem Chem 2011;90:1186–90.
[6] Iglinski B, Buczkowski R, Iglinska A, Cichosz M, Piechota G, Kujawski W. Agricultural biogas plants in Poland: investment process, economical and environment aspects, biogas potential. Renew Sust Energy Rev 2012;16:4890–900.
[7] IEA. Bioenergy programme and IEA CADDET renewable energy technologies programme. In: International perspective on energy recovery from landfill gas. IEA CADDET centre for renewable energy. UK: Oxfordshire; 2000.
[8] Piechota G, Buczkowski R. Development of measurement techniques for determination of main and hazardous components in biogas utilized for energy puropses. Global Biofuels & Bioproducts Summit. Pet Environ Biotechnol 2012;3:7.
[9] De Paepe PM, D'Herdt P, Mertens D. Micro-CHP systems for residential applications. Energy Convers Manage 2006;47:3435–46.
[10] Dong L, Liu H, Riffat S. Development of small-scale and micro-scale biomass-fuelled CHP systems – a literature review. Appl Therm Eng 2009;29:2119–26.
[11] Holm-Nielsen JB, Al Seadi T, Oleskowicz-Popiel P. The future of anaerobic digestion and biogas utilization. Bioresour Technol 2009;100:5478–84.
[12] Appels L, Baeyens J, Dewil R. Siloxanes removal from biosolids by peroxidation. Energy Convers Manage 2008;49:2859–64.
[13] Narros A, del Peso MI, Mele G, Vinot M, Fernandez E, Rodriguez ME. Determination of siloxanes in landfill gas by adsorption on Tenax Tubed and TD–GC–MS. In: Margharita di Paula S, editor. Proceedings sardinia 2009, 12th international waste and management and landfill symposium. Cagliari, Italy; 2009.
[14] EPRI. Electric Power Research Institute. Assessment for gas fuel cleanup system for waste gas fuel power generation. Electric Power Research Institute 1012763 Technical Update; December 2006. p. 117.
[15] Dewil R, Appels L, Baeyens J. Energy use of biogas hampered by the presence of siloxanes. Energy Convers Manage 2006;47:1711–22.
[16] Ajhar M, Travesset M, Yüce S, Melin T. Siloxane removal from landfill and digester gas – a technology overview. Bioresour Technol 2010;101:2913–23.
[17] Hagmann M, Heimbrand E, Hentschel P. Determination of siloxanes in biogas from landfills and sewage treatment plants. In: Proceedings Sardinia 99, 7th international waste management and landfill symposium. Cagliari, Italy; 1999.
[18] Tower P. The cost impact of biogas siloxane contamination. In: Presentation at intermountain CHP centre workshop, Salt Lake City; 2005.
[19] Moniot D. Venture engineering company, siloxane-removal-system; 2012. <http://www.ventureengr.com/blog/2009/02/siloxane-removal-system> (12.11.12).
[20] Arnold M, Kajolinna T. Development of on-line measurement techniques for siloxanes and other trace compounds in biogas. Waste Manage 2010;30:1011–7.
[21] Piechota G, Hagmann M, Buczkowski R. Removal and determination of trimethylsilanol from landfill gas". Bioresour Technol 2012;103:16–20.
[22] Rasi S, Veijanen A, Rintala J. Trace compounds of biogas from different biogas production plants. Energy 2007;32:1375–80.
[23] Collet P, Halias A, Lardon L, Ras M, Goy R-A, Steyer J-P. Life-cycle assessment of microalgae culture coupled to biogas production. Bioresour Technol 2011;102:207–14.
[24] Grümping R, Mikolajczak D, Hirner A. Determination of trimethylsilanol in the environment by LT-GC/ICP-OES and GC–MS. Fersenius J Anal Chem 1998;363:347–52.
[25] Häusler T, Schreier W. Analyse siliziumorganischer Verbindungen im Deponiegas sowie CO-Messungen zur Brandfrüherkennung. Verlag Abfall aktuell – Band 16 – Stillegung und Nachsorge von Deponien; 2005. p. 241–9.
[26] Tower P. New technology for removal of siloxanes in digester gas results in lower maintenance costs and air quality benefits in power generation equipment. In: Presentation at WEFTEC 03 78th annual technical exhibition and conference; 2003.
[27] MWM. Technical circular. Combustion gas for MWM gas engines, 0199-99-3017/4 EN, Circular supersedes: 0199-99-3017/3, MWM GmbH 12/2008; 2008.
[28] Shweigkofler M, Niessner R. Removal of siloxanes in biogas. J Hazard Mater 2001;83:183–96.
[29] Lunghi P, Bove R, Desideri U. Life-cycle-assessment of fuel cells based landfill-gas energy conversation technologies. J Power Sour 2004;131:120–6.
[30] Beese J. Betriebsoptimierung der motorischen Gasverwertung durch den Einsatz von Gasreinigungsanlagen; Siloxa Engineering AG. Presentation at Deponiegas 2007 FH Trier Saksa; 2007.
[31] Griffin P. Severn Trent Water wastewater treatment plant at Minworth. In: ST-seminar; 2004.
[32] UKEA, United Kingdom Environment Agency. Guidance for monitoring trace components in landfill gas. London: The Agency; 2004.
[33] Jeffrey L, Pierce PE. Siloxane quantification removal and impact on landfill gas utilization facilities. In: 8th annual LMOP conference and project EXPO. Maryland: Baltimore; January 2005.
[34] Rasi S. Biogas composition and upgranding to biomethane. Doctoral thesis. Jyvaskyla tudies in biological and environmental science, vol. 202. Finland; University of Jyvaskyla; 2009.
[35] Lomans BP, Pol A, Op den Camp HJM. Microbial cycling of volatile organic sulphur compounds in anoxic environments. Water Sci Technol 2002;30:1021–9.
[36] Allen MR, Braithwaite A, Hills CC. Trace organic compounds in landfill gas at seven UK waste disposal sites. Environ Sci Technol 1997;31:1054–61.
[37] Eklund B, Anderson EP, Walker BL, Burrows DB. Characterization of landfill gas composition at the fresh kills municipal solid-waste landfill. Environ Sci Technol 1998;32:2233–7.
[38] Wilber C, Murray C. Odor source evaluation. Biocycle 1990;31:68–72.