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Report on the measurements of the INP within the installation of a plasma-based reactor for odour removal at water treatment plant

OP 5-3.2 Test, investigation and feasibility report on installations on test sites | Analysis by FTIR, electrochemical sensors and chemical analytics by Helge Grosch and Ronny Brandenburg

The following report discusses the results of the measurements taken at the waste water treatment plant (WWTP) of Aquanet in Poznan (ul. Serbska 3). The scope of these measurements was to get to identify the main chemical agents in the off gas of the WWTP before and after plasma-catalytic treatment. The report will be structured as follows: First an introduction into the different measurement, their advantages and disadvantages will be given, afterwards the results will be listed and a short conclusion will be given.

1. Introduction in the methods of measurement

Three different types of diagnostic methods were used for the detection of the appearing species. For a general approach, the detection of the main species, the method of FTIR spectroscopy was used. For the detection of trace gases the gas chromatography, coupled with mass spectroscopy (GC/MS), was used. Therefore, adsorption tubes were rinsed with the exhaust gas before and after plasma section and analysed by GC/MS afterwards. The third method was the electrochemical sensing of H_2S by a handheld device.

FTIR spectroscopy:

The Fourier transformed infra red (FTIR) spectroscopy is a low invasive procedure for the detection of species in mixtures. The basic of this technology is the absorption of light by the sample. A light source emits a certain spectrum of light, which is directed through a chamber including the sample. In this chamber, the light is partly absorbed. A detector then records the transmitted light. By comparing the transmitted light at the different wavelength of the sample and the background spectrum, a transmission spectrum can be given. Since every chemical agent has a different absorption behaviour, the single agents can be identified.

Since the FTIR spectrometry deals with infra red light, all detectable species must be infrared active. This is not the case with biatomic homonuclear molecules (e.g. N_2 and O_2) and atomic radicals (O and N). Other drawbacks are the difference in detection limit of odours by FTIR and human noses at reasonable efforts (the detection limit of the FTIR can be too high to detect these) and the similarity in the spectrum of different agents (similar chemicals sometimes can't be detected) as well as the vanishing of low spectra in always appearing spectra such as CO_2 and water.





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In the used configuration, the FTIR was applied to the mixture of off gases from the WWTP. The measurements were conducted before and after the treatment of the off gas by the plasma-catalyst reactor chamber. The used FTIR spectroscope was the device "alpha" by Bruker equipped with a 4.8 m heatable long path gas cell.

GC/MS:

In gas chromatography (GC) the compounds are separated based primarily on their volatilities. Therefore, a carrier gas with the compounds (which are desorbed of the adsorption material by thermodesorption in the test tubes) moves through a GC column. The compounds partition between a stationary phase (column inner wall) and a mobile phase (gas). The differential partitioning into the stationary phase allows the compounds to be separated in time and space, while the retention time of the compound is known. After separation the compounds are detected by a mass spectrometer (MS). As adsorption medium Tenax tubes were used. The GC was the "GC 2010 with TD-20 and QP 2010" of Shimadzu and the column "Phenomenex ZB-5" was used. Their specifications can be found in the appendix.

The task of the GC/MS was to detect chemical agents present in the off gas, but below the detection limit of the FTIR as well as an identification of produced and reduced agents at the inlet and outlet of the plasma reactor. The main scope hereby was the detection of compounds including sulphur (e.g. mercaptanes, sulphides etc.) due to the fact, that these compounds are known to be strong and unpleasant odours. GC/MS analysis was performed by the laboratory "IUL Vorpommern" in Greifswald as subcontractor of INP.

Handheld device for H₂S measurements:

With courtesies of "IUL Vorpommern", the H₂S measurements were conducted with the electrochemical handheld device "GasAlertMicro 5 IR" with an integrated IR sensor for the CO₂ monitoring. This device has an electrochemical sensor, which was produced for measurements in plants such as the WWTP. The use of this device was necessary, since H₂S cannot be detected by the previous discussed methods and it is known to be a chemical agent with a strong, unpleasant scent.





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2. Results of the measurements:

FTIR spectroscopy:

The measurements with the FTIR have been carried out at the same time as the samples for the olfactometry were taken. Due to the fact, that the spectra of the different measurements don't show new species and quantification can also not be given due to the lack of calibration, only three exemplary spectra are presented.

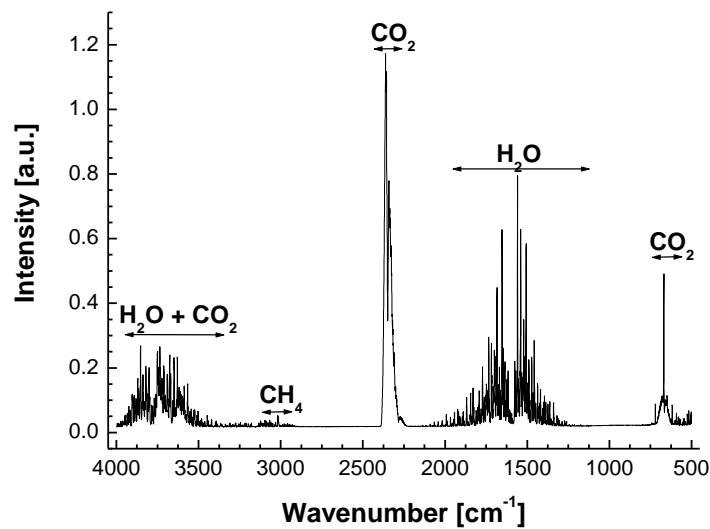


Fig. 1: Spectrum at the inlet (32 scans, 1 cm⁻¹ resolution) for configuration 2 (27.7 °C and 32.4 % relative humidity)

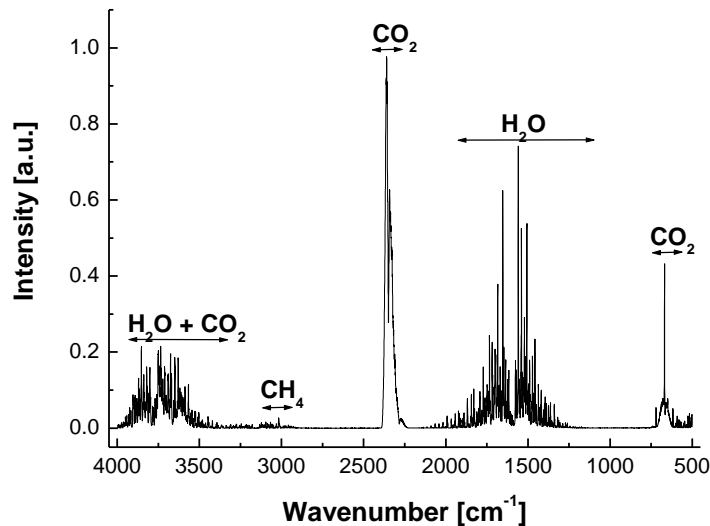


Fig. 2: Spectrum at the outlet (32 scans, 1 cm⁻¹ resolution) for configuration 2 (11.8 °C and 75.2 % relative humidity)



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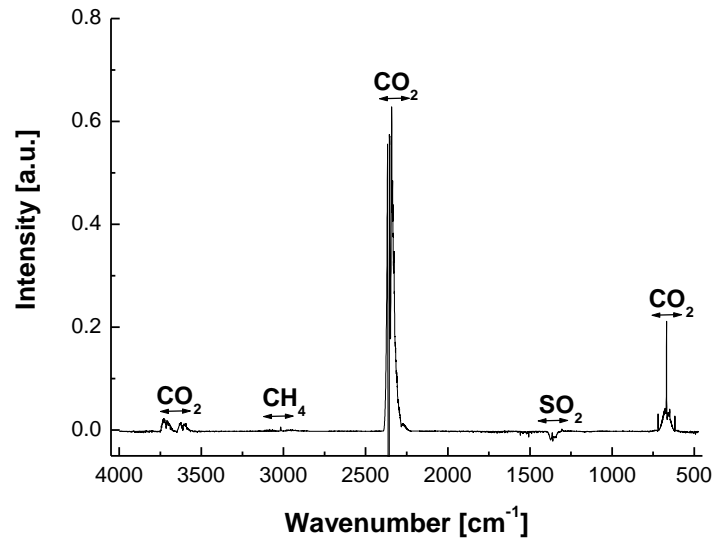


Fig. 3: outlet spectrum subtracted of the inlet spectrum (32 scans, 1 cm^{-1} resolution) for configuration 4. Negative peaks show the production of species in the reactor (lower concentration at the inlet), positive peaks show species with larger concentration at the inlet.

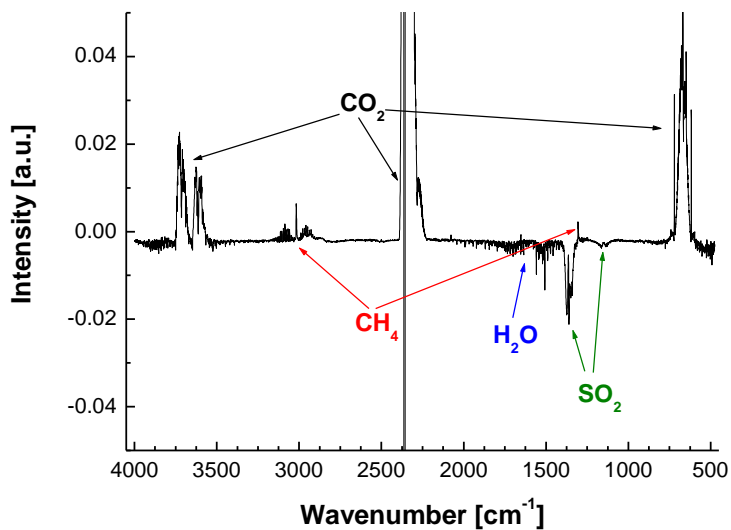


Fig. 4: Detailed view on the spectra in Fig. 3.

From these data, two main results can be concluded. The main species in the off gas are, next to not detectable N_2 and O_2 , CO_2 and H_2O (see Fig 1. and 2). Their actual values were determined by the handheld device for H_2S measurements and by the humidity probe applied at the inlet and outlet (see below). These species overrule the measurements by their intensity and therefore make a detection of other species difficult. As a second





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result, two previously unexpected species could be identified in CH_4 (visible in all spectra Fig. 1- Fig. 4) and SO_2 (see Fig. 4). Since in Fig. 4 the difference between the in- and outlet of the plasma reactor and catalyst arrangement are shown, one can determine which chemical agents increase and which decrease easily. Next to CO_2 also CH_4 have a higher inlet concentration. H_2O and SO_2 nevertheless have a higher output concentration. Still one has to keep in mind, that a certain degree of fresh air (10% according to Rafflenbeul Ingenieure) is added during the cleansing process.

GC/MS:

During each campaign two samples at the inlet and two samples at the outlet were taken. This was due to the fact that the measurements were time and cost intensive. It was meant mainly to identify the basic chemical agents and see an increase or decrease in their concentration. Here only the main agents should be named and discussed. A detailed view over all found compounds can be seen in the appendix. The main trace gas components can be seen in Table 1:

Table 1: Main trace gas components in the different configurations

	Inlet 10. Feb. 11 Config. 2 [$\mu\text{g}/\text{m}^3$]	Outlet 10. Feb. 11 Config. 2 [$\mu\text{g}/\text{m}^3$]	Inlet 11. Feb. 11 Config. 3 [$\mu\text{g}/\text{m}^3$]	Outlet 11. Feb.11 Config. 3 [$\mu\text{g}/\text{m}^3$]	Inlet 16. & 17. Feb. 11 Config. 4 [$\mu\text{g}/\text{m}^3$]	Outlet 16. & 17. Feb. 11 Config. 4 [$\mu\text{g}/\text{m}^3$]
Dimethyl sulphide	104.6	93.0	52.8	70.1	117.5 139.2	85.9 79.8
Carbon disulfide	6.4	9.4	0	2.8	42.3 34.2	86.7 106.5
Dimethyl disulfide	667.1	440.5	544.4	307.5	1346.5 1385.2	554.4 454.6
Toluene	65.1	89.1	45.7	78.2	689.3 378.0	288.1 272.1
Dimethyl trisulphide	56.1	338.4	128.2	157.4	354.0 251.2	105.5 80.0

These results show that the main components, next to the agents identified by the FTIR, are sulphur containing agents and toluene. In all sample taken at the inlet dimethyl disulfide had the highest value. It was also the component with the best reduction rate. The configuration 2 showed a slight decrease in concentration for dimethyl sulphide, while all other components increased in configuration 2 and 3. The measurements at configuration 4 showed that all main components, except of Carbon disulfide decreased. The reduction rate ranged between 26.8 % (dimethyl sulphide) and 70.2 % (dimethyl trisulphide). Nevertheless, next to the composition of SO_2 as stated above, also Carbon disulfide (CS_2) was produced during the process. CS_2 is not known for an unpleasant scent.

Table 2 shows the chemical agents, which were produced or reduced in significant height in single experiments.





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Table 2: Gases that appeared in some test with significant value

	Inlet 10. Feb. 11 Config. 2 [$\mu\text{g}/\text{m}^3$]	Outlet 10. Feb. 11 Config. 2 [$\mu\text{g}/\text{m}^3$]	Inlet 11. Feb. 11 Config. 3 [$\mu\text{g}/\text{m}^3$]	Outlet 11. Feb. 11 Config. 3 [$\mu\text{g}/\text{m}^3$]	Inlet 16. & 17. Feb. 11 Config. 4 [$\mu\text{g}/\text{m}^3$]	Outlet 16. & 17. Feb. 11 Config. 4 [$\mu\text{g}/\text{m}^3$]
Ethanol	4.5	4.3	<1	111.1	3.0 8.1	2.0 <1
Ethyl- acetate	-	-	<1	146.9	- -	- -
Isopropyl- acetone	<1	34.2	0.9	63.2	- -	- -
Limonene	143.8	136.2	44.7	51.8	46.0 73.8	11.4 6.3
Acetic acid	-	-	-	-	26.8 21.8	84.2 26.3

These components are just mentioned for the sake of completeness. In the configuration 4 it can be seen that also as pleasant scented known agents, such as limonene, are significantly reduced.

In table 3 the low concentrated sulphur containing gases are shown.

Table 3: Other detectable sulphur containing gases with unpleasant scent:

	Inlet 10. Feb. 11 Config. 2 [$\mu\text{g}/\text{m}^3$]	Outlet 10. Feb. 11 Config. 2 [$\mu\text{g}/\text{m}^3$]	Inlet 11. Feb. 11 Config. 3 [$\mu\text{g}/\text{m}^3$]	Outlet 11. Feb. 11 Config. 3 [$\mu\text{g}/\text{m}^3$]	Inlet 16. & 17. Feb. 11 Config. 4 [$\mu\text{g}/\text{m}^3$]	Outlet 16. & 17. Feb. 11 Config. 4 [$\mu\text{g}/\text{m}^3$]
Disulfide, methyl 2- propenyl	3.1	1.6	1.3	0.5	15.1 21.7	4.8 5.1
Dimethyl tetra- sulphide	2.0	19.6	5.1	19.1	11.5 8.1	3.6 2.3

The treatment of these components shows a similar effect as the treatment of sulfur containing agents with higher concentration. In the configuration 2 and 3, a non uniform behavior can be seen. For configuration 4 a significant decrease can be reported.

Other than expected, only the methanethiol, a mercaptane (which are known for their unpleasant scent), could be detected. With $8.7 \mu\text{g}/\text{m}^3$ at the inlet, its value was relative low. At the outlet none of this compound could be detected. The detection limit was below $10 \mu\text{g}/\text{m}^3$ (2-methyl-2-propanthiol) respectively $1 \mu\text{g}/\text{m}^3$ (Ethanthiol, 2-Propanthiol, 1-Propanthiol, Tetrahydrothiophen). These limits are in the range of the odour thresholds of these chemical agents. Mercaptanes are volatile compounds. Due to the relative long time between taking the sample and analysis (due to the transport from Poznan to Greifswald), it is possible, that the measurement was influenced and originally the gas contained more mercaptanes.





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Handheld device for H₂S measurements:

The measurements for the H₂S detection were carried out at the same time as the olfactometric samples were taken. Therefore, they can be compared directly.

Table 4: H₂S and CO₂ concentration at the in and outlet measured at the time of olfactometric sample taking for 4 different configurations (10.).

	Date	Time	H ₂ S (inlet) [ppm]	H ₂ S (outlet) [ppm]	H ₂ S reduction [%]	CO ₂ (inlet) [%]	CO ₂ (outlet) [%]
Config.1	10. Feb. 11	10:30	6 ppm	0 ppm	100	0.06 %	0.06 %
Config. 2	10. Feb. 11	13:15	4 ppm	0 ppm	100	0.06 %	0.06 %
Config. 3	11. Feb. 11	8:45	18 ppm	9 ppm	50	0.11 %	0.10 %
Config. 4	-	-	-	-	-	-	-

The data show, that there is a constant reduction of H₂S by the reactor arrangement. It should be mentioned, that the inlet concentration of H₂S varied significantly. At the time of main emission (measured at 17:00) of H₂S values of 21 ppm before (CO₂ at 0.13 %) and 4 ppm after the treatment (CO₂ at 0.12%) could be detected. It is also significant, that the rate of CO₂ inlet also increases at the same time as the H₂S value. It has to be mentioned, that the reduction rates of 100% are not too trustworthy, since the detection limit was reached.

A measurement at the configuration 4 has not been conducted. Since the fourth configuration was the most promising in the odour reduction, it has also been used in the measurements taken a week later (see Table 2)

Table 5: H₂S and CO₂ concentration at the in- and outlet measured at the time of olfactometric sample taking for the final arrangement.

	Date	Time	H ₂ S (inlet) [ppm]	H ₂ S (outlet) [ppm]	H ₂ S reduction [%]	CO ₂ (inlet) [%]	CO ₂ (outlet) [%]
Meas. 1	16. Feb. 11	16:45	10	0	100	0.05	0.07
Meas. 2	16. Feb. 11	19:00	34	7	79.4	0.12	0.13
Meas. 3	17. Feb. 11	15:30	43	13	68.8	0.16	0.12
Meas. 4	17. Feb. 11	17:00	46	12	73.9	0.20	0.15
Meas. 5	17. Feb. 11	19:00	24	6	75.0	0.12	0.12
Meas. 6	17. Feb. 11	20:00	30	4	86.7	0.15	0.11
Meas. 7	18. Feb. 11	11:45	41	6	85.4	0.20	0.15
Meas. 8	18. Feb. 11	13:15	29	5	82.8	0.15	0.17
Meas. 9	18. Feb. 11	14:30	12	4	66.7	0.20	0.11

In general, the inlet value of H₂S was significantly higher than at the testing of the different configurations a week earlier. It ranged from 10 ppm up to 46 ppm. Therefore, the results of the reduction are more comparable. The reduction of H₂S ranges between 100 % and 66.7 % with a mean value of 79.9 %.

Conclusion of the results:

Plasma-catalytic process removes 66 to 100 % of H₂S, which is probably the main odour. CH₄ emission is reduced as well but not completely. By-product of H₂S removal is SO₂ in small concentrations (cannot be quantified since a calibration of the FTIR is missing). This has to be attended since in combination with water H₂SO₄ can be formed, which can affect the plasma-catalyst section. Beside H₂S a number of other compounds were detected by GC analytics. Only for configuration an overall statement on the effect of the after treatment





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can be given: All sulphur containing compounds with the exception of CS_2 , decrease in concentration. In the other configurations, some compounds increase in concentration, some decrease.

However since there are no data measured after the plasma section (i.e. before the catalyst) the role of the plasma process cannot be evaluated. But from the viewpoint of these results it can be concluded that the plasma-based treatment and/or the catalyst in use are a promising method for the odour reduction at the water plant in Poznan.

