

Additional material 1 - Analytical methods – detailed information

Nitrogen, oxygen and argon were analysed by gas chromatography (Agilent with pulsed discharge helium ionization detector (PDHID, VICI) using helium as a carrier gas. The GC/PDHID sampling loop was 1 ml. The sample was transferred onto capillary column molsieve 5A plot (30 m x 0.53 mm x 50 µm) and a second capillary column molsieve 5A plot (50 m x 0.53 mm x 50 µm). The GC oven was set at 30 degrees Celsius.

Water was measured using quartz crystal microbalance, QMA401 (Michell, US). Gases are sampled directly from the gas cylinder to the analyser, a valve was used to restrict the flow to 0.333 L/min for the QMA.

Formaldehyde was measured using GC (Peak Laboratories, US) coupled with a methaniser FID. The method used a Haysep D column (186" x 1.5") with nitrogen carrier with the column held at a temperature of 170 degrees Celsius. The loop size used for sample injection was 10 ml.

Formic acid and ammonia were measured using FTIR. The instrument was a Nicolet 6700 (Thermo Fisher Scientific, UK) equipped with nitrogen purged multi-range optics, a KBr beam splitter and a liquid nitrogen cooled MCT-A detector. The spectrometer was fitted with a heated "White" type gas cell (Cyclone C5, Specac, UK), nominal path length: 8 m and volume = 2 L, equipped with a borosilicate glass body and KBr windows. The gas cell conditions were typically T = 30 °C and P = 1055 mbar with a sample flow rate of 0.7 - 1 standard litre per minute (SLM). Single beam spectra were collected between 4000 - 0 cm⁻¹ with a resolution set to 1 cm⁻¹ and each recorded spectrum consisted of an average of 180 individual spectra. The spectral range used to quantify the amount fraction of formic acid was between 1166 – 1062 cm⁻¹. The spectral range used to quantify the amount fraction of ammonia was between 975 – 956 cm⁻¹.

Helium was measured using GC-TCD (Agilent Technologies, UK). The method used one Haysep Q 80/100 mesh 2 m x 1/8" outer diameter x 2.0 mm inner diameter column and one Molesieve 5A 80/100 mesh 9 ft x 1/8" outer diameter x 2 mm inner diameter column with hydrogen carrier. The loop size used for sample injection was 2 ml.

Methane, carbon monoxide, carbon dioxide and non-methane hydrocarbons were measured GC (Peak Laboratories, US) coupled with a methaniser FID. The method used a Haysep D column (186" x 1.5") with nitrogen carrier with the column held at a temperature of 65 degrees Celsius. The loop size used for sample injection was 5 ml.

Total sulphur compounds were measured by gas chromatography with sulphur chemiluminescence detector (GC-SCD). The analysis of the sample is performed on an Agilent 7890A gas chromatograph (Agilent, USA) equipped with two detectors, a flame ionization detector and sulfur chemiluminescence detector (SCD 355, Agilent Technologies, USA). The GC-SCD sampling loop volume was 1 ml. The sample was then transferred onto capillary column used which is a HP-5, 30 m x 0.320 mm ID x 0.251 µm film thickness (Agilent, USA). The column program temperature is isothermal at 110 °C. Helium is used as a carrier gas at a flow rate of 20 ml/min.

Organo-halogenated compounds were analysed using a TD-GC (Markes International, UK) coupled with mass spectroscopy (MS) with a split FID (Agilent Technologies, UK). The compounds were adsorbed onto chromosorb tube. This system desorbs the analytes from the sorbent and releases the analytes onto a U-T6SUL cold trap. A DB-VRX column 60m x 0.25mm with a helium carrier was used for separation.

All analyses were calibrated using NPL gravimetric gas standards in hydrogen matrix gas. Gravimetric standards and/or dynamic standards (prepared by dilution using mass flow controller system (Bronkhorst, NL)) were used to generate calibration curve ranging covering the ISO 14687 threshold and the measured values (as long as it is above the limit of detection). The data was scrutinised however no result was discarded without a technical reason. The calibration curve, results of analysis and uncertainties associated were determined using NPL software XLGENline (Smith & Onakunle, 2007). An expanded uncertainty using a *k* value of 2 was used. In some cases, a more conservative uncertainty was derived from scientific experience.

Trace elements and ions analysis were performed on water sample and after gas passed through an impinger system. Then the impinger water was analysed by ICP-MS (Agilent 8800, UK) and ion chromatography (Dionex ICS-1500 Ion Chromatography System, UK). The impinger system was composed of two glass impinger with 30 ml of deionised water. An impinger system empty to eliminate water droplet, a drying system with silicogel and a flow meter. The first hydrogen fuel sample was flow through the impinger system after passing through a pressure regulator (20-30 psig) and a needle valve to reduce the flow to 0.5 L/min. Hydrogen volume of the second sample is 43.2 L. The water volume in impinger 1: 30.0205g and impinger 2: 30.2570g. A duplicate hydrogen fuel sample was performed in similar condition. Hydrogen volume of the second sample is 36.5 L. The water volume in impinger 1: 30.0349g and impinger 2: 29.9261g. The analyses were performed by ion chromatography and ICP-MS according to NPL validated method by trained staff.

Probability of occurrence - Contaminants known to impact PEMFC performance (ISO 14687) with final probability of very unlikely (0)

Argon: Three sources of argon were investigated: (i) air dissolved in seawater, (ii) air intake and (iii) pure air used as purging/inerting/actuating gas. Presence of dissolved air into the seawater or air intake in the water pre-treated in plastic tank (air exchange) are considered as sources of argon in water. The concentration of dissolved argon in water at ambient temperature and is around 20–30 mg/L using Henry's Law. The presence of argon in hydrogen above the ISO 14687 threshold is then unlikely. The ISO 14687 threshold (300 $\mu\text{mol/mol}$) is higher than the amount fraction in the water used to feed the electrolyser. Then PEM membrane (low cross-over through the membrane) was considered as a last existing barrier leading the probability of occurrence of argon to zero. As explained in the nitrogen section, the actuation of the pneumatic valves done using compressed air could potentially be a source of argon (due to leakage) in the hydrogen gas. However, it was considered very unlikely as it will be an issue for the process and detected on the pneumatic valves monitoring. Therefore, the probability of occurrence of argon was set to 0 (very unlikely) as argon contamination will be small compare to the nitrogen contamination during the same event.

Formaldehyde: The sole source of formaldehyde in the production process is its presence in seawater. The average formaldehyde amount fraction in seawater is evaluated between 4.5 to 40 $\mu\text{g/L}$ [i] corresponding to low nmol/mol level. For this reason, the probability of occurrence of formaldehyde was set to very unlikely (0). However, formalin is one of the most common disinfectants in European aquaculture [ii-iii]. The location of the seawater sampling especially in an aquaculture area would impact the probability level.

Formic acid: The sole source of formaldehyde in the production process is its presence in seawater. Even if formic acid is degradable in seawater, its presence can be influenced by human activities (manufacture, aquaculture, agriculture and service industry) in coastal are leading to seawater acidification. However, a study nearshore bay in China showed that the level of formic acid measured was on average 13.9 $\mu\text{mol/L}$ [iv] which is lower than the threshold level in ISO 14687. Moreover, the water purification system will avoid any excessive level of formic acid to reach the electrolyser. For this reason, the probability of occurrence of formaldehyde was set to very unlikely (0).

Ammonia: The main source of ammonia in the production process is its presence in seawater. Ammonia is a well-known contaminant in seawater [v]. In European Commission designated waters, the quality standards for protection of freshwater fish are 0.021 and 0.78 mg/L for unionised ammonia and total ammonia, respectively [v]. If seawater follows this guidance, undissociated ammonia will be only present at low amount fractions. The purification system involving reverse osmosis and ion exchange resin will reduce the level of ammonia and act as barrier to maintain ammonia below the ISO 14687:2019 threshold. For this reason, the probability of occurrence of ammonia was set to very unlikely (0). However, ammonia can be transported into the seawater via agriculture (animal waste) and human activities (decaying organic matter). The level of ammonia may increase to higher amount fraction due to local pollution (1-23 mg/L [vi]) especially around estuaries. A recommendation would be made to avoid operating the water pumping and purification in area known for human contamination.

Total hydrocarbons: The main source of hydrocarbons would be seawater pollution due to an oil spill or hydrocarbons release. Oil contaminant is frequent in seawater as 10–15 % of oil in the ocean is coming from oil tanker accident [vii]. The number of maritime incidents decrease however there are still major spills happening at irregular intervals. The complexity of oil contamination is the variety in oil composition from heavy hydrocarbons to smaller alkane chain (i.e. hexane, heptane) [vii]. The reverse osmosis is considered enough to remove all molecules above 200 Dalton. Smaller molecules will have different level of filtration. Implementing a protocol for seawater raw material pumping into the purification system would be the most efficient way to eliminate the risk. Most oil spill event tend to be reported or visible. It is therefore advisable that seawater pumping into the system is not operating if an oil pollution is observed or in harbour. For this reason, the probability of occurrence of total hydrocarbons was set to very unlikely (0).

[i] Largiuni, O.; Becagli, S.; Innocenti, M.; Stortini, A.M.; Traversi, R.; Udisti, R. Formaldehyde determination in seawater. Preliminary application to coastal samples at Terra Nova Bay (Antarctica). *J Environ Monit.* **2005**, 7(12), 1299-1304. <https://doi.org/10.1039/B507334K>

[ii] Tornero, V.; Hanke G. Chemical contaminants entering the marine environment from sea-based sources: A review with a focus on European seas, *Mar. Pollut. Bull.* **2016**, 112(1–2), 17-38. <https://doi.org/10.1016/j.marpolbul.2016.06.091>

[iii] Burrige, L.; Weis, J.S.; Cabello, F.; Pizarro, J.; Bostick, K. Chemical use in salmon aquaculture: A review of current practices and possible environmental effects, *Aquac. Res.* **2010**, 306(1–4), 7-23. <https://doi.org/10.1016/j.aquaculture.2010.05.020>

-
- [iv] Liang, H.; Lyu, L-N.; Sun, C.; Ding, H.; Wurgaft, E.; Yang, G-P. Low-molecular-weight organic acids as important factors impacting seawater acidification: A case study in the Jiaozhou Bay, China, *Sci. Total Environ.* **2020**, 727, 138458. <https://doi.org/10.1016/j.scitotenv.2020.138458>
- [v] Johnson, I.; Sorokin, N.; Atkinson, C.; Rule, K.; Hope, S-J. Proposed EQS for Water Framework Directive Annex VIII Substances Ammonia (Un-ionised). Science Report, 2007. Environment Agency: Bristol, England (Report: SC040038/SR2)
- [vi] Eddy, Forrest. Ammonia in estuaries and effect on fish. *J. Fish Biol.* **2005** 67, 1495 - 1513. <https://doi.org/10.1111/j.1095-8649.2005.00930.x>
- [vii] Tornero, V.; Hanke, G. Chemical contaminants entering the marine environment from sea-based sources: A review with a focus on European seas. *Mar. Pollut. Bull.* **2016**, 112, 17-38. <https://doi.org/10.1016/j.marpolbul.2016.06.091>