Phase 1 feasibility study report (01/05/18 – 31/08/18)

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Contents

1 Executive Summary

1. Concept and design of ammonia sensor

- Gas sensor technologies have been reviewed and are summarised in this report.
- A semiconductor type chemiresistor sensor best meets the criteria for high specificity to NH_3 gas and high sensitivity (ppb detection limits for ambient air monitoring) and low-cost fabrication. These can be based on conducting polymers (e.g. polypyrrole, polyaniline), nanomolecules (e.g. graphene derivatives) or cellulose as the sensing platform.
- The concept design (Figure 1) is a prototype chemiresistor ammonia sensor combining principles of passive diffusion sampling (e.g. CEH ALPHA sampler) to control rate of NH_3 gas diffusion into the sensor, with resistivity changes from chemisorption of NH_3 onto the sensing layer measured.
- Two types of sensing layers have been tested: 1) citric acid coated cellulose filters and 2) fluorographene (FG) thin film on Zefluor PTFE membrane (in collaboration with Tata Institute of Fundamental Research, Hyderabad, India).
- FG is recommended for further study due to tests by Tata showing:
  - i) high specificity to NH_3 (selective binding to Fluorine in FG),
  - ii) low detection limits of down to 0.44 pM ammonium in solution,
  - iii) linear response to variation in exposure time to NH_3 gas,
  - iv) higher sensitivity to NH_4^+ over graphene oxide, graphene or fluorographene oxide, and
  - v) reversibility of binding.

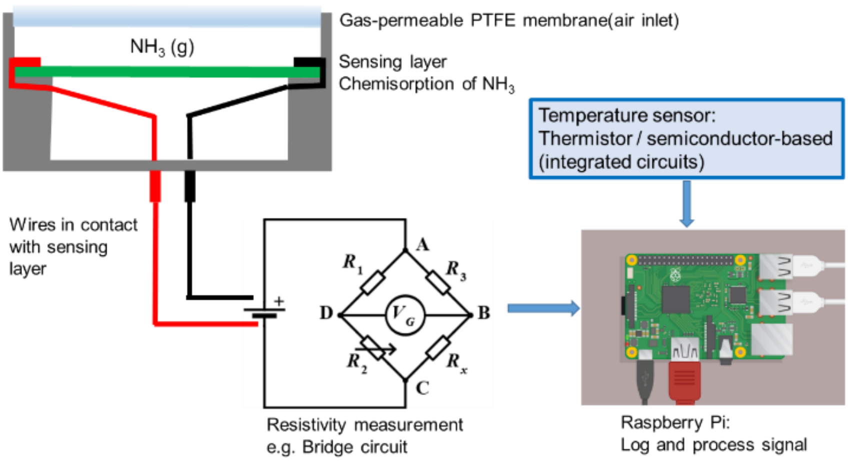


Figure 1: Concept design of prototype chemiresistor-type sensor based on the CEH ALPHA sampler. The uptake rate of NH_3 is a function of the diffusion path length (distance from PTFE membrane to sensor surface) and surface area of the sensor layer.

Gateway 1 recommendations

1. Initial test results support the premise that atmospheric ammonia gas can be detected selectively.

2. The key challenges are synthesis and coating of FG onto a suitable micro-electrode (e.g. screen printed or interdigitated). This can be done in collaboration with the Tata research group or with the University of Edinburgh (contacts in chemistry and electronics department).

3. Some parts of proposal are achievable in this financial year, see table below.

4. The authors think that the full funding should be released in order to progress. If we do not, then in the medium term, CEH will lose leadership in this core area of our science.

	Achievable?	**Notes**
Phase 2:		
Prototype specification and build (Aug-Oct)	By January 2018	
Phase 3: Prototype testing (Oct-Feb)		
• Physical characterisation tests on ALPHAs or similar device with electrodes	By March 2018	
• Deployment of 5-10 units for alongside continuous NH_3 analyser, DELTA and ALPHA to compare performance at short (10 mins to daily) to long-time scales (weekly to monthly)	IN 19/20	
Phase 4: Innovation outputs (Feb-Mar)		
• Performance report for ammonia sensor.	By March 2018	On laboratory tests
• Plan for further development and testing at existing customer sites	IN 19/20	
• Plan for expansion/outsourcing and sale, if product near market-ready.	tbd	

2 Project background

There is enormous interest and technological advances in miniaturised gas sensors for air quality monitoring. In particular, numerous sensors have come onto the market in recent years for monitoring nitrogen dioxide (NO_2) in cities. Of these, the AQMesh NO_2 gas sensor (https://www.aqmesh.com/) is widely deployed across the UK and US for monitoring NO_2 and to be deployed in a new ‘hyperlocal’ air quality network for London this year.

A market need exists for a low-cost, high sensitivity (measures down to low ppb levels) miniaturised gas sensor for ammonia (NH_3). A small number of ammonia sensors are currently available on the market, but all with low sensitivity, i.e. ppm range that are suited to industrial measurements (e.g. leak detection in refrigeration systems), but not for air quality monitoring (low ppb levels). These include the Alphasense NH3-A1 and NH3-B1, and Industrial Scientific’s personal single-gas detector GasBadge® Pro, Ventis™ Pro Series, and the MX6 iBrid, Radius™ BZ1 Area ammonia detectors.

State of the art sensitive optical instruments for automatic online monitoring of ammonia such as the Picarro Cavity Ring-Down Spectroscopy (CRDS) (https://www.picarro.com/technology/) and Quantum Cascade laser (QCL) instruments (https://www.emerson.com/en-gb/) are too large to be portable, and too expensive to be deployed at many sites.

Low-cost portable air sampling methods such as the CEH ALPHA (passive diffusion sampler) (Tang et al., 2001) and CEH DELTA samplers (active pumped sampling) (Sutton et al., 2001) developed are used widely to deliver on a large number of CEH CWI projects (~£150k per annum). They are also sold worldwide (see www.ceh.ac.uk/services/air-samplers, launched Jan 2017), but they are manual air sampling methods requiring offline analysis. These types of manual air samplers can only provide time-integrated average concentrations over a prescribed sampling period (usually weekly to monthly). They also require chemical analysis after sample collection so that the air concentrations are reported some time after the measurement.

An ammonia sensor with similar levels of sensitivity, specificity and accuracy as the CEH ALPHA and DELTA will potentially offer the following advantages:

1) potential to develop ammonia sensor networks, in the UK (complementing and enhancing existing UK networks) and worldwide (including ODA countries),

2) real-time source attribution assessments, monitoring pollutant events and plumes, e.g.

   a. compliance monitoring: Industrial Emissions Directive 2010/75/EU (IED) requires pig and poultry farms (above stated size thresholds) to reduce emissions using Best Available Techniques. The IED applies to around 70 % of the European poultry industry and around 25 % of the pigs industry (UNECE, 2010).
   b. ecosystem effects assessments: revised UNECE ‘Critical Levels’ (CLe) of NH_3 concentrations under the Gothenburg protocol to protect sensitive vegetation and ecosystems (UNECE, 2007). These set limits of NH_3 concentrations to 1 µg NH_3 m^{-3} and 3 µg NH_3 m^{-3} annual mean for the protection of lichens-bryophytes and other vegetation, respectively (Cape et al., 2009b).

3) incorporate temperature and humidity sensors to provide simultaneous climate data, important for linking climate change to air pollutant trends,

4) potential for personal monitoring / medical applications (e.g. ammonia levels in exhaled breath as diagnostic tool, and

5) potential to develop an app. for users to view and download data from the sensor. This could include for example setting thresholds (for ecosystem or human health) for sending automatic alerts to users.

This project aims to review existing and emerging sensor technologies for detection of ammonia and incorporate principles of ambient ammonia passive diffusive sampling (CEH ALPHA sampler) to develop a sensitive and specific sensor for ammonia suitable for ambient monitoring (low ppb range) and in parallel develop a phone app. to view and download data from sensor. Development of partnerships with research agencies and industry with expertise in sensor technology will be considered.

2.1 Anticipated Outcomes 2018 / 2019

Phase 1: Scoping (Apr-Jul) £11.5K

- review existing sensor technologies
- make contact with relevant research groups with expertise in sensor technology
- basic study of putting electrodes on current ALPHA samplers, perhaps could be planned to do early testing at Whim during the QA exercise (May-June)

Outcome of phase 1 (01/08/2018)

- Concept and design of ammonia sensor drawn up
- Initial trial study results: use electrodes on current ALPHA samplers as sensor for ammonia

Pending outcome from phase 1, progress to:

Phase 2: Prototype specification and build (Aug-Oct)

Phase 3: Prototype testing (Oct-Feb)

- Physical characterisation tests on ALPHAs or similar device with electrodes
- Deployment of 5-10 units for alongside continuous NH_3 analyser, DELTA and ALPHA to compare performance at short (10 mins to daily) to long-time scales (weekly to monthly)

Phase 4: Innovation outputs (Feb-Mar)

- Performance report for ammonia sensor.
- Plan for further development and testing at existing customer sites
- Plan for expansion/outsourcing and sale, if product near market-ready.

3 Review of ammonia gas sensors

What is a gas sensor? A gas sensor comprises of a transducer and an active sensing surface for converting the chemical information into another form of electronic signal like frequency change, current change or voltage change (see reviews by (Timmer et al., 2005; Yunusa et al., 2014).

Gas sensors are typically characterised by:

- Small size
- Low power consumption
- Wireless

Performance characteristics include properties such as sensitivity, selectivity, detection limit, response time and recovery time.

- Sensitivity (S) determined as: $\Delta f/\Delta c$
- S, expressed in terms of Hz/ppm or Hz/vol %
- Δc = change in analyte concentration

The main types of gas sensor technologies for ammonia and principle of operation are summarised in Table 1.

Table 1: Types of ammonia gas sensors.

Type	Sensing Platforms	Mechanism	Detection	Sensitivity	Specificity to NH_3
Catalytic	Catalytic metal oxides (MO)	Chemisorption and catalytic combustion: Reactivity of catalytic metals to NH_3. Combustion of NH_3 on catalytic surface at high temperatures (> 300^{o}C).	Resistivity: Measured by capacitor / resistor (wheatstone bridge).	ppm range	No – responds to all combustible gases
Electrochemical	Metal oxide (MO) e.g. TiO_2, SnO_2, ZnO_2, WO_3 with Au and MoO_3	Chemisorption and redox reaction: NH_3 entering the sensor undergoes an electrochemical reaction resulting in a change in electrical output.	Amperometric: change in electric current Potentiometric: change in potential across the analyte Conductometric: change in electrolytic conductivity or resistivity	ppm range	No - responds to NO
Semiconductor	Metal oxides (MO) such as SnO_2 and AlO_3	Chemisorption and oxidation: Oxidation of NH_3 on sensing element increases conductivity. Requires elevated temperature (> 200^{o}C)	Conductance change	ppm range	No – responds to other gases and vapours.
	Conducting polymers (CP)	Electrostatic interaction / adsorption and charge transfer. Polyaniline: acid-base interactions Polypyrrole: oxidation-reduction	Electronic transducers Electrochemical	ppb to ppm	Yes
	Conducting polymers (CP): Nano-molecules	Graphene Graphene oxides Fluorographene Carbon nanotubes Cellulose-based	Electronic transducers Electrochemical	ppb to ppm	Yes
Optical		Optical: lasers, spectrographs.	Optical absorbance	Low ppb to ppm range	Yes

3.1 Catalytic sensors

The theory behind catalytic sensors is that a combustible gas will burn at lower temperatures in the presence of a catalyst in a process called catalytic combustion. Most metal oxides and their compounds possess catalytic properties (Yunusa et al., 2014).

Catalytic gas sensors consist of two elements: a detector element (D) which contains catalytic material (e.g. hot wire, catalytic bead or micro-hotplate configuration) and is sensitive to combustible gases, and a compensator element (C) which is inert.

Combustible gases will burn only on the detector element. When catalytic combustion occurs, the temperature of the bead increases and changes the resistivity of the wire. Combustible gases will not burn on the compensator—its' temperature and resistance remain unchanged in the presence of combustible gases (Figure 1).

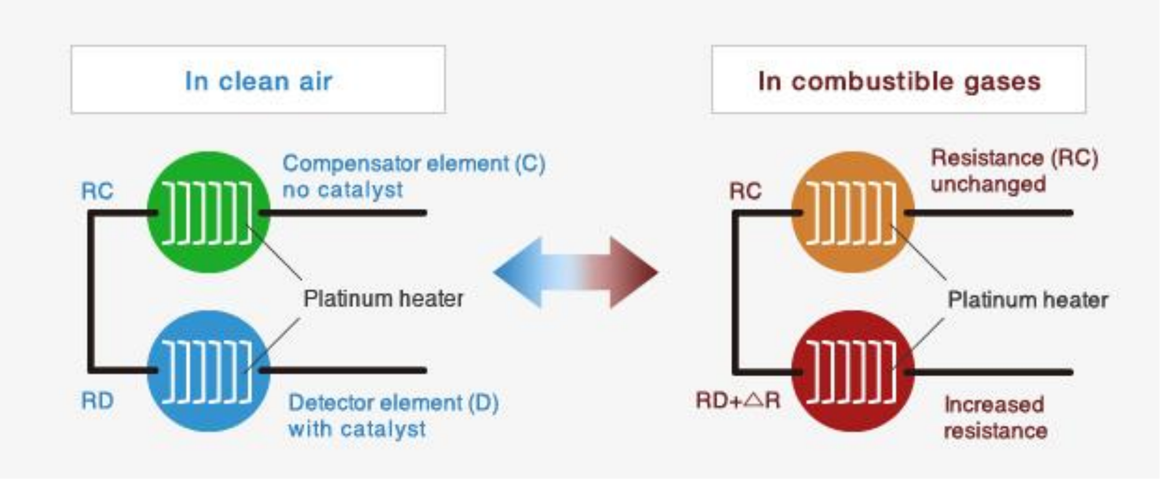


Figure 1: An example basic measuring circuit in catalytic gas sensors (reproduced from Yunusa et al., 2014).

Catalytic gas sensors are further characterised as pellistor-type and thermoelectric-type sesnors.

A Wheatstone bridge circuit is usually formed with both elements as shown in Figure 2. A variable resistor (VR) is adjusted to maintain a state of balance of the bridge circuit in clean air free of combustible gases. When combustible gases are present, only the resistance of the detector element will rise, causing an imbalance in the bridge circuit, thus producing an output voltage signal (V_{out}). The output voltage signal is proportional to the concentration of combustible gases and gas concentration can be determined by measuring the output voltage

Catalytic sensors are not specific to ammonia as it measures flammability of all combustible gases, not just ammonia. They are also very sensitive to poisoning by certain chemicals that will reduce the sensitivity and, under prolonged exposure, completely ruin the sensor. Halogen compounds (such as halogenated refrigerants and fire extinguisher compounds) will also temporarily inhibit the sensor.

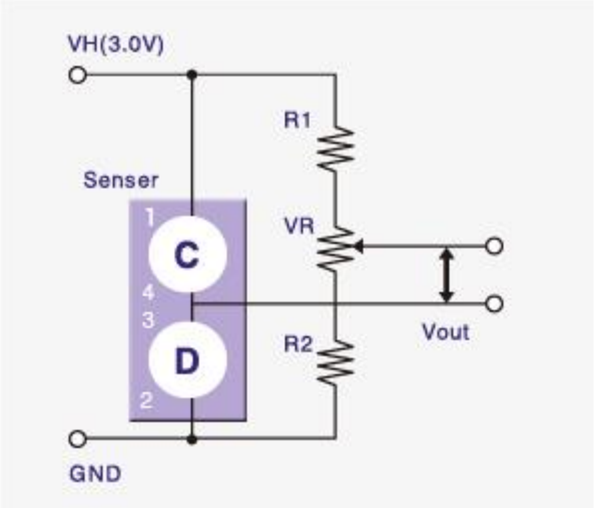


Figure 2: An example basic wheatstone bridge measuring circuit in catalytic gas sensors (reproduced from Yunusa et al., 2014).

Table 2: Catalytic ammonia sensors available on the market.

Product	**Detection range**	**Application**	**Website**
SensAlert Plus series Ammonia sensors: 823-0201-22 FM approved	50 ppm	process leak detection	http://www.schauenburg-tech.co.uk/assets/downloads/sensidyne-gas-detection-for-ammonia.pdf
SensAlert Plus series Ammonia sensors: 823-0201-21 FM approved	100 ppm		
SensAlert Plus series Ammonia sensors: 823-0201-41 FM approved	300 ppm		
SensAlert Plus series Ammonia sensors: 823-0201-42 FM approved	500 ppm		
VQ41TSB	600 ppm	process leak detection	https://www.sgxsensortech.com/products-services/industrial-safety/pellistor-sensors/

3.2 Electrochemical sensors

In electrochemical (EC) sensors, ammonia gas diffuses through a gas-permeable membrane to an electrode where it is either reduced or oxidised. The redox reaction at the electrode produces an electrical signal that is proportional to the gas concentrations.

A typical EC sensor consists of a sensing electrode or working electrode and a counter electrode, separated by a thin layer of electrolyte (Figure 3).

Electrochemical reaction with ammonia gas generates a current flow between the sensing and counter electrodes. The electrolyte facilitates the reaction between the electrode and gas and carries charge between the electrodes.

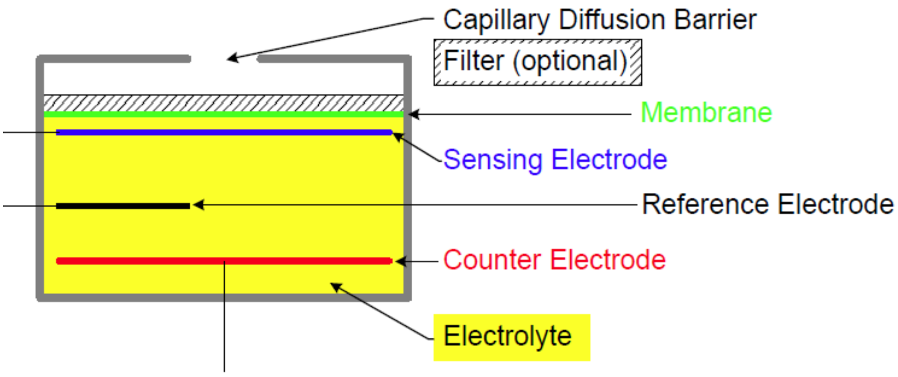


Figure 3: Schematic of electrochemical sensor (reproduced from Reindl et al. 2002).

The reference electrode maintains a constant voltage on the sensing electrode to compensate for the degradation of the electrolyte due to the reaction on the electrode surface, thereby extending the life of the sensor.

The capillary diffusion barrier, filter and hydrophobic gas-permeable membrane together control the amount of gas entering the sensor that can react with the electrolyte and prevents the electrolyte from leaking out of the sensor. The filter may be necessary to reduce cross-sensitivity in certain situations and is typically activated charcoal.

There are several variations on the specific electrochemical reaction used to detect ammonia. Some EC sensors depend on a straightforward oxidation reaction where ammonia (NH_3) is converted into nitrogen (N_2) and hydrogen “protons” (H^+) at the sensing electrode. For every two molecules of ammonia that are oxidised, six electrons (e^-) of electricity are also produced. This electrical current output is what is used by the instrument to determine the concentration of ammonia present.

At the sensing electrode:

$2\ NH_3 \rightarrow N_2 + 6\ H^+ + 6\ e^-$

The second half of the electrochemical reaction occurs at the “counter” electrode, where the hydrogen protons produced in the first half of the reaction react with oxygen to produce water.

At the counter electrode:

$O_2 + 4H^+ + 4\ e^- \rightarrow 2H_2O$

There are three main types of EC sensors:

Potentiometric, measurement of voltage. This relies on a combination of electric and ionic current to flow in a closed circuit.

Conductometric: measurement of either conductivity or resistivity. The capacitance of the sensor changes due to a selective sensing material such as polymers or other insulators. These absorbing materials serve as the dielectric layer of the capacitor and their permittivity changes with exposure to the analyte. These sensors are commonly used to detect humidity as well as carbon dioxide and volatile organic compounds. In humidity sensors, the dielectric layer comprises a water-sensitive polymer.

Amperometric: measurement of current.

In amperometric EC sensors, a constant voltage is applied and the sensor signal is a diffusion limited current. It usually consists of 3 electrodes, the working or sensing electrode, the counter electrode and also a reference electrode which are immersed in the electrolyte solution and a potentiostat for maintaining constant voltage (Baron and Saffell, 2017; Stetter and Li, 2008) (Figure 4).

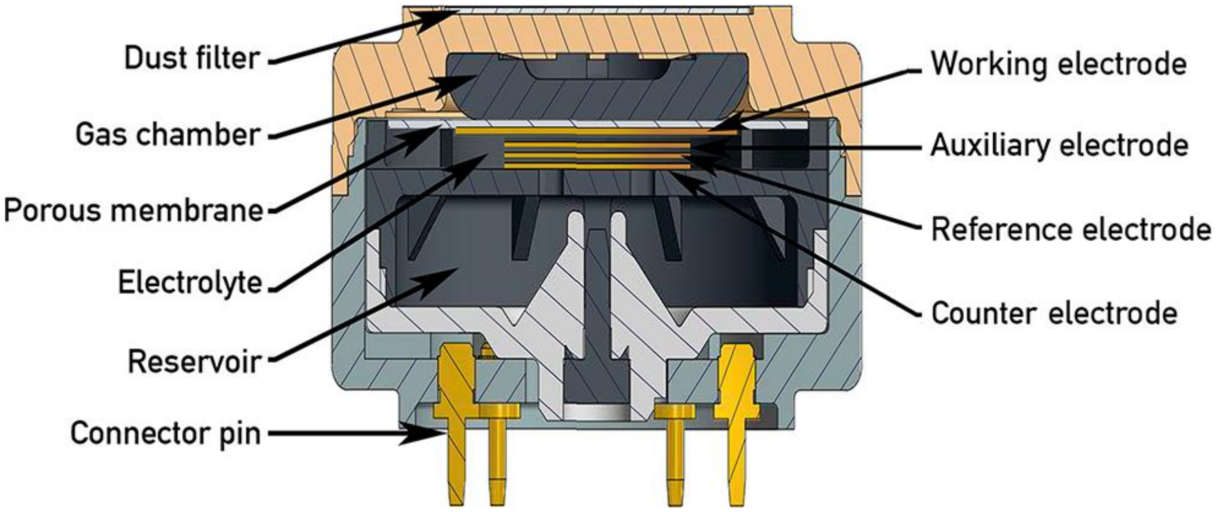


Figure 4: Design for standard amperometric gas sensors (Alphasense). Reproduced from Baron and Saffell, 2017

Table 3: Electrochemical (EC) NH_3 sensors available on the market

Product	**Detection range**	**Application**	**Website**
Alphasense Ammonia Sensor: NH3-A1 	0 – 50 ppm Sensitivity: 0.017 to 0.027 µA/ppm Resolution: < 0.3 ppm	Aquaculture gas detection, Flue gas analysis Environmental protection engineering.	http://www.as-sensor.com/products/Alphasense-Nh3-Gas-Sensor-Ammonia-Sensor-Nh3_A1-(NH3_A1-).html
Alphasense Ammonia Sensor: NH3-B1 	0-100ppm Sensitivity: 0.025 to 0.045 µA/ppm Resolution: < 0.3 ppm		http://www.as-sensor.com/products/Alphasense-Nh3-Gas-Sensor-Ammonia-Sensor-Nh3_B1-(NH3_B1-).html
Industrial Scientific's personal single-gas detector GasBadge® Pro, and ammonia (NH3) sensor 	0 – 500 ppm Sensitivity: no data Resolution: 1 ppm	Workplace monitoring	http://www.indsci.com/products/ammonia/
GS+7NH3-100 **Ammonia Gas Sensor** 	0-100 ppm Sensitivity: 0.115±0.045 µA/ppm)	Industrial application, in particular for fixed gas detectors.	https://www.sensorinstock.it/en/electrochemical/366-gs7nh3-100.html
GS+7NH3-1000 **Ammonia Gas Sensor** 	0-1000 ppm Sensitivity: 8 ± 4 µA/ppm		https://www.sensorinstock.it/en/electrochemical/367-gs7nh3-1000.html

Table 3: Electrochemical (EC) NH_3 sensors available on the market. cont.

Product	Detection range	Application	Website
ME3-NH3 Electrochemical Ammonia Sensor - Electrical current produced in electrochemical reaction of the NH_3 gas are in direct proportion with its concentration following Faraday's law 	0~100ppm NH3 (sensitivity = 0.10±0.05 µA/ppm) Resolution: 0.5ppm	industrial and environmental protectionl fields	https://www.winsen-sensor.com/products/4-series-electrochemical-toxic-gas-sensor/me3-nh3-0-50ppm.html
ME4-NH3 Ammonia Gas Sensor - Constant potential electrolysis type 	0~100ppm NH3 (sensitivity = 0.12±0.03 µA/ppm)		https://www.winsen-sensor.com/products/4-series-electrochemical-toxic-gas-sensor/me3-nh3-0-50ppm.html
ZE03 Electrochemical Gas Sensor Module 	NH3: 0~100 ppm C0: 0~1000 ppm SO2: 0~20 ppm	Portable and fixed gas detector for toxic gas	https://www.winsen-sensor.com/products/gas-sensor-module/industrial-application-gas-sensor-module/ze03.html
NH3 3E 100 SE-Gas Sensor Module - 3 electrode electrochemical sensor  Transmitter board (converts raw sensor output into industry standard 4-20 mA output). 	NH3: 0-100 ppm (sensitivity = 0.13±0.03 µA/ppm)		https://www.sensorinstock.it/en/electrochemical/643-nh3-3e-100-se.html https://www.sager.com/nh3-3e-100-se-5271106.html

The EC sensor is filled with an organic gel electrolyte mixture in which the reaction occurs. The electrolyte includes an active ingredient that is consumed in the electrochemical reaction with ammonia. Active ingredients in the electrolyte are incrementally used up as the sensor is exposed to ammonia. Thus, the lifespan of the sensor is directly related to its exposure to NH_3.

EC sensors are typically low sensitivity (ppm range, see Table 3), with some operating at temperatures as low as – 40º C up to ~ 50º C. They are very to changes in temperature and often have internal temperature compensation. Higher temperatures typically shorten the life of the sensor. Humidity is also important; a high humidity environment can pass water vapour through the membrane and dilute the electrolyte solution, a low humidity environment accelerates water loss and shortens the sensor life.

They also suffer from non-specificity.

Cross-sensitivity: H_2S, SO_2, NO, NO_2, Cl_2, HCN (hydrogen cyanide).

3.3 Optical

Optical sensors for detection of ammonia use optical absorption/emission scattering of ammonia gas at defined optical wavelengths. The instruments consists of a light emitting element, a photo-detecting element, a gas sensing element that responds to light and a filter for picking up fluorescence or phosphorescence.

Optical adsorption spectroscopy is used in the most sensitive and selective ammona detectors for ambient ammonia, with response time of 1s reported.

Sensitive optical instruments for automatic online monitoring of ammonia include:

Picarro Cavity Ring-Down Spectroscopy (CRDS):
https://www.picarro.com/technology/

Quantum Cascade laser (QCL) instruments:
(https://www.emerson.com/en-gb/).

These instruments are not suitable as portable, low-cost sensors.

3.4 Infrared gas sensor

Infrared gas sensors consists of an infrared source (incandescent light or a heated wire filament) and a detector which converts electromagnetic radiation energy into electrical signals.

The principle is that the absorption of infrared (IR) light through an ammonia/air environment is different than for air only. The chemical bonds in NH_3 absorb energy at specific wavelengths. When a chemical bond absorbs IR light, it continues to vibrate at the same frequency, but with greater amplitude after the transfer of energy.

Several companies have developed IR sensors for sensing gas-phase ammonia concentration, e.g. IR-F6-NH3-0/2%-N/4 (http://www.rmtech.net/).

Detectors can measure either the reduction of electromagnetic radiation through the sample, or the temperature rise of the sample due to the absorption of the radiation. The most common infrared detector senses the temperature rise through the environmental sample.

IR sensors are highly specific for ammonia, have long-term stability and reduced need for calibration adjustment. Limitations are the physical size of the detector assembly, the need to protect the detector against the potential effects of fluctuating temperature and humidity and substantially high costs.

Infrared detectors are generally used for monitoring high concentrations of ammonia (> 500 ppm).

3.5 Semiconductor sensors

Semiconductor sensors are also known as solid-state sensors or chemisorption (CS) sensors. The principle of operation is conductance change due to reversible gas adsorption (chemisorption) on the sensing layer.

3.5.1 *Metal Oxide (MOS) Sensors*

Metal Oxide sensors (MOS) consist of one or several metal oxides such as tin oxide (SnO_2), Molybdenum oxide (MoO_3) or aluminium oxide (Al_2O_3) and a heating element. The metal oxide sensing elements are formed either in a spherical bead or in a thin film configuration, e.g. deposited on a silica chip similar to making semiconductors called chip-type sensors (Jekel and Reindl, 2002; Yi et al., 2015).

In clean air, the electrical conductivity is low. Absorption of sample gas on the oxide surface followed by catalytic oxidation results in a change in electrical resistance of the oxide material. An electrical circuit converts the change in conductivity to an output signal that is related to the sample gas concentration being monitored.

An internal heater at the base is used to heat the sensor up to a constant temperature of about 200 – 250°C to speed up reaction rate. Figure 5 shows the schematic of a semi-conductor sensor.

In order to keep the low-power consumption of sensor while heating the sensing material to enhance its response and recovery, there has been development in micro-hotplates that can be miniaturised and integrate these types of sensors on a chip (Timmer et al., 2005; Yan et al., 2017).

Metals or additives that enhance the chemisorption of specific gases are used to make gas selective gas sensors, WO_3 based sensing material is reported to respond to NH_3 ad NO. The lowest ammonia detection limit is 1ppm, using a WO_3 ammonia sensor with Au and MoO_3 additive. The sensor is operated at an elevated temperature of > 400°C (Timmer et al., 2005).

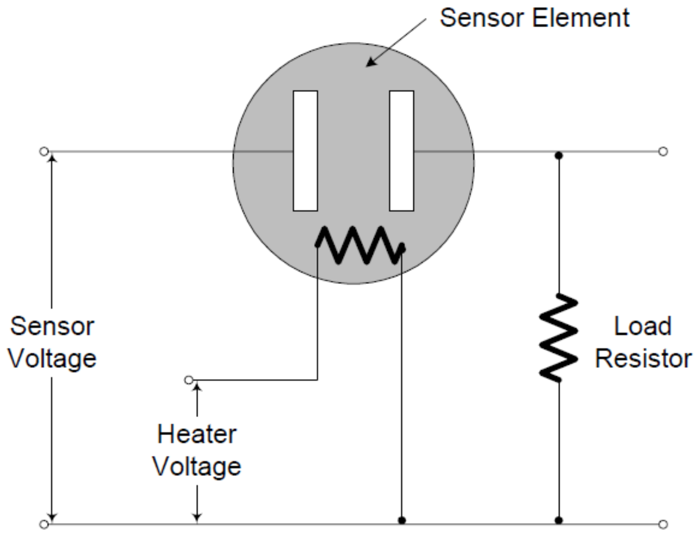


Figure 5: Schematic of a semi-conductor sensor.

The biggest advantage of the semi-conductor sensor is that it is not “consumed” during the sensing. When the gas is present, it is absorbed on the surface of the sensor. Once the ambient ammonia concentration decreases, the ammonia desorbs from the sensor’s surface. Semiconducting sensors can also be manufactured in film techniques in mass production making possible manufacture of low-cost sensors.

The main disadvantage of semiconducting sensors is cross-sensitivity to oxygen, other gases and/or water. However, the use of filters can minimize the problem. These types of sensors are generally designed to respond to the widest possible range of toxic and flammable gases and vapours and are not specific to ammonia.

Table 4: Semi-conductor MOS sensors.

Product	Detection range	Application	Website
MQ137 semiconductor sensor for ammonia (sensing material is SnO_2)	5～500ppm NH3	NH_3 gas alarm, NH_3 gas leakage alarm, Portable NH3 gas detector	https://www.winsen-sensor.com/products/semiconductor-gas-sensor/mq137.html

A Pt/NiO thin film-based resistor-type ammonia gas sensor with low detection limit of 10 ppb NH3/air, and fast speeds, at an optimal operating temperature of 300◦C was recently reported by Chen et al. 2018).

3.5.2 *Conducting Polymers (CP)*

Other types of semiconductor sensors are based on functional films of organic materials that make use of polymers (conducting polymers, CP). Different materials have been reported, such as polypyrrole (Li et al., 2016), polyaniline (Tanguy et al., 2018), graphene derivatives (Tadi et al., 2016; Travlou et al., 2015) and cellulose (e.g. cellulose/TiO2/PANI composite nanofibers; Pang et al. 2016). CP-based sensors can be highly sensitive and specific for detection of target gas under ambient conditions.

These semiconductor sensors are amenable to an array of detection mechanisms, such as electronic transducers (field effect transistor) and electrochemical (amperometric, conductometric, potentiometric and impedance).

Their ease of synthesis also allow potential development of inexpensive chemiresistors. Fabrication of the sensing layer usually involves a solution-based thin film method such as spin coating and inkjet printing.

In spin coating, thin films of polymers are deposited directly onto a substrate by in situ oxidative polymerization. The oxidant (precursor) is applied by spin coating, followed by exposure of the coated oxidant surface to monomer vapour, a process known as vapour-phase deposition polymerization (VDP) (Asatekin et al., 2010). This process has been adapated to produce high quality films of Polypyrrole (PPy) (Li et al., 2016; Patois et al., 2013) (and Polyaniline (PANI) (Tanguy et al., 2018).

Since many appropriate oxidising agents such as ammonium peroxydisulpfate are water-soluble, solution-based deposition techniques are easily adapted to coat or pattern the substrate with the precursor layer. This makes the VDP technique compatible with printing technologies.

Polymer thin-film capacitance sensor

A polymer thin-film capacitance sensor is trademarked AMMONICAP® by Vaisala. It measures the change in capacitance of an ammonia sensitive polymer film between capacitor plates.

There is however no information on the polymer film on Vaisala’s website.

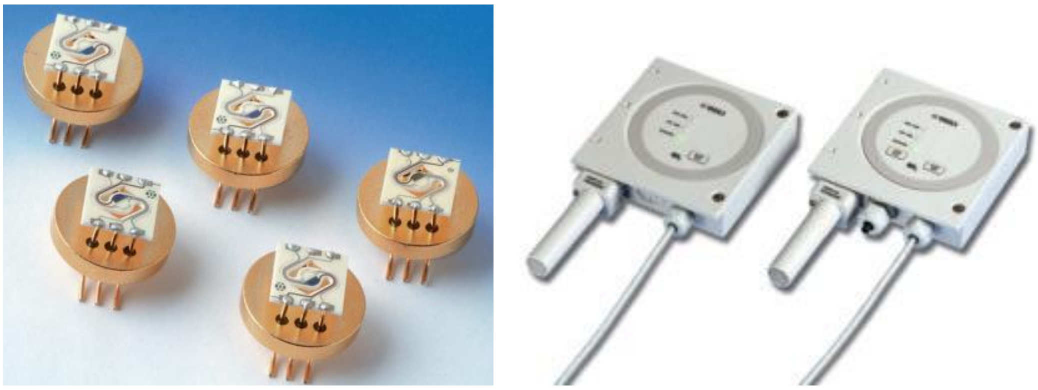


Figure 6: (Left) Vaisala’ s AMMONICAP® polymer thin film sensor, and (righ) AMT100 Series Ammonia Detectors. (*https://www.vaisala.com/sites/default/files/documents/VN157_AMMONICAP%C2%AE_for_Ammonia_Gas_Leak_Detection.pdf*).

The theory of operation is that the capacitance of a capacitor is proportional to the permittivity of the capacitor material. Absorption of ammonia changes the relative permittivity and, hence, the capacitance value. Water molecules are also absorbed in the polymer. The effect of humidity is eliminated by a novel measurement technique based on a temperature-controlled measurement cycle.

The ammonia concentration measurement is done as a cycle that includes both a heating (desorption) and cooling (absorption) period to determine and separate the effect of humidity from the response to ammonia concentration. The absorption/desorption cycle requires time (currently 18 seconds). The sensor averages multiple readings (currently 5) and gives a readout; therefore, the absorption/desorption cycle time limits the response time. The sensor continuously calculates and averages the readings.

Polypyrrole CP:

For polypyrrole (PPy) CP , the sensing mechanism is 2-fold.

1. Irreversible reaction between ammonia and the polymer
2. Ammonia can reversibly reduce the oxidized form of polypyrrole.
3. The reduction of polymer film causes a change in the conductivity of the material, making it suitable for resistometric or amperometric ammonia detection.

Sensors have also described that detect ammonia using the change in frequency of a resonator, coated with the ammonia sensitive polymer.

The irreversible reaction with NH_3 however results in an increase in mass in the polymer film, with an exposure-dependent decrease in sensitivity of the sensor with time. Although regeneration mechanisms have been proposed, this is a major drawback with the PPy CP.

Polyaniline CP:

Polyaniline (PANi) is more stable. It is deprotonated by ammonia which results in a change in conductance. A review of polyaniline ammonia sensors by Tanguy et al. (2018) describes progress in polyaniline modification techniques to achieve enhanced sensing performance.

PANi-based gas sensors are commercially available for measuring ammonia levels in alarm systems, with detection limit of 1 ppm.

High sensitivity of PANI to NH_3 gas is well characterised (e.g. Liu et al., 2009; Tanguy et al., 2018), but a major drawback is slow desorption, so that recovery after exposure to NH_3 may take significant time.

A solution to the slow desorption in PANI-base sensors and baseline drift is to maintain sensing layer at higher temperatures to enhance recovery and reversibility. The increase in temperature affects kinetics of binding between NH_3 and sensing layer and facilitates desorption of NH_3 from PANI.

A new generation of polyaniline-based chemiresistors on printed polymeric micro-hotplates is emerging (Danesh et al. 2018). Danesh et al. (2018) describes a sensor with a polyaniline sensing layer doped with poly(4-styrenesulfonic acid), a fully inkjet-printed silver micro-hotplate heater and interdigitated electrodes on a polyethylene napthalate substrate, separated by a thin dielectric film.

Graphene-based CPs

Graphene-based polymers shows tremendous potential for development of highly sensitive and selective gas sensors (e.g. (Tadi et al., 2016; Travlou et al., 2015). Charge transfer kinetics between graphene and adsorbed molecules are tuned by doping and defects to confer specificity and sensitivity towards gas molecules.

A fluorographene-based ultrasensitive ammonia sensor is reported by Tadi et al. (2016). Selective binding of ammonia/ammonium with Fluorine (F) in fluorographene (FG) via electrostatic hydrogen bonding results in a change in the impedance. Very low detection of down to 0.44 pM over a wide linear range of 1 pM to 0.1 µM was reported.

3.6 Surface Acoustic Wave (SAW) based sensor

This works on principle of transduction whereby the sensor converts an input electrical signal into a mechanical wave and reconverts back into electrical signal (Bai & Sghi 2007) (Figure 7). This is made possible by means of the interdigitated transducer known as IDTs which uses the piezoelectric effect. The IDTs are made of electrodes manufactured from aluminium, gold or platinum.

A typical SAW consists of an input and output transducer with spacings between them called a delay-line. Gas sensing in SAW is realised by the application of a sensing material like a thin polymer across the delay line which selectively absorbs the gas of interest. Detection of different gases is made possible by using different configurations of SWA's and at different frequencies, conferring high selectivity, high sensitivity and good response times.

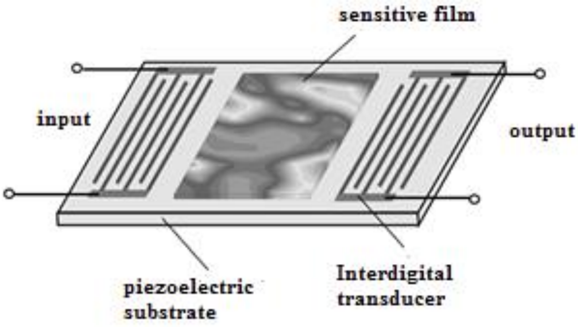


Figure 7: A SAW device to depict the principle of gas sensing

Type of Saw	Substrate Material	Frequency	Sensitivity	Ref
Two-port resonator	Lithium tantalite	100 MHz	NIL	Hao 2010
Two-port resonator	ST-Cut Quartz	98.47 MHz	5.9 Hz/ppm	Shen et al. 2010
Dual delay-line	Lithium niobate	114.7 MHz	6.91 Hz/ppm	Lin 2011

3.7 Charged Carrier Injection (CI) sensors

GfG Instrumentation has developed a sensor that operates on the principle called "charge carrier injection" and markets this technology as CI 21. The measurement technique uses a special gas sensitive material, which can selectively bind ammonia. By absorbing molecules, the ammonia carriers (Charge Carrier) are brought into the new sensor material (Injection). With special micro structured electrodes, the ammonia concentration can be determined. It is reported to have significantly reduced cross-sensitivity compared to typical solid-state sensors and, since the sensor is not consumed, significantly increased sensor life compared to electrochemical sensors.

Information are not available on the type of special gas sensitive material.

Table 5: Charged carrier injection sensor.

Product	Detection range	Website
CI 21 sensor 	20 - 200 ppm 30 - 1,000 ppm 30 - 10,000 ppm	http://goodforgas.com/wp-content/uploads/2013/12/CI-21_Data_Sheet.pdf

4 Phase 1: Scope, design and initial testing

4.1 Requirements for environmental monitoring

Objective	**Concentration range**	**Required response time**	**Temperature range**	**Application**
Monitoring ambient concentrations of NH_3	0.05 ppb to > 10 ppb (Tang et al., 2018)	Weekly to Monthly	-10 to +40ºC	Ambient air monitoring in local, regional to national-scale networks. Ecosystem effects assessments, e.g. UNECE Critical Levels of NH_3 concentrations for protection of sensitive vegetation and ecosystems (Cape et al., 2009): 1 µg m^{-3} annual mean for lichens/bryophytes. 3 µg m^{-3} annual mean for higher vegetation. Compliance monitoring: e.g. Industrial Emissions Directive 2010/75/EU (IED)
Source or hot-spot monitoring	1 ppb > 100 ppb (Loubet et al., 2008)	Daily to monthly	-10 to +40ºC	Environmental Impacts assessments, Data for validation of atmospheric transport models. Research.

4.2 Design of chemiresistor-type ammonia sensor

The concept design of a prototype chemiresistor-type ammonia sensor combines passive diffusion sampling to control rate of NH_3 gas diffusion into the sensor, with detection of resistivity changes from chemisorption of NH_3 onto the sensing surface (acidified cellulose filters or conducting polymer such as fluorographene) (Figure 8).

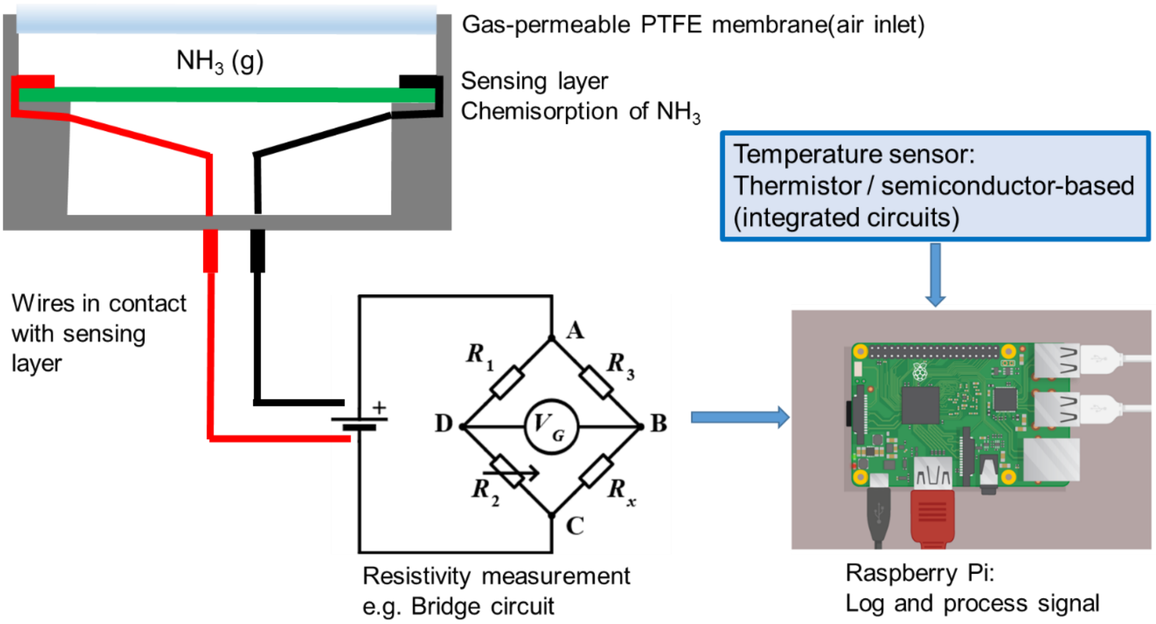


Figure 8: Concept design of prototype chemiresistor-type sensor based on the CEH ALPHA sampler.

Concept:

- Passive diffusion of atmospheric NH_3 gas through a gas-permeable hydrophobic membrane (5µm pore size PTFE membrane) to the sensing surface (an acidified filter or conducting polymer, CP).
- Chemisorption of NH_3 onto acid filters or CP results in a change in resistivity measured using, for example, a bridge circuit.
- Establish relationship between resistivity changes (Ω-m) and amount of ammonia (NH_3, µg) on the acid filters or CP.
- Algorithm to convert the relationship derived above to air concentrations (µg NH_3 m^{-3}). The volume of air sampled over a prescribed period is estimated form the uptake rate of the CEH sampler.
- Incorporate temperature and humidity sensor.
- Program a raspberry Pi to log and process signals.

4.3 Theory of passive diffusion sampling

Passive samplers operate on the principle of diffusion of gases from the atmosphere along a sampler of defined dimensions onto an absorbing medium, according to Fick's law. The theoretical uptake rate of a sampler for ammonia (U, e.g. m^3 h^{-1}) is a function of the length, L (m), the cross sectional area, A (m^2) of the stationary air layer within the sampler, and can the diffusion coefficient, D (m^2 s^{-1}) of ammonia gas (Equation 1). The diffusion path length is nominally the distance from the mouth of the sampler to the reaction surface at the other end of the tube (Tang et al., 2001).

$U = DA/L$ (1)

Where $D = 2.09 \times 10^{-5}$ m^2 s^{-1} at 10°C for NH_3

The volume of air sampled (V, m^3) for a given exposure period (t) sampling period (Equation 2):

V (m3) = U (m^3 h^{-1}) x t (h) (2)

The air concentration of NH_3 (χ, e.g. µg m^{-3}):

$\chi = (m_e - m_b) / V$ (3)

Where m_e = amount of a pollutant collected on an exposed sample (e.g. µg)
m_b = amount of a pollutant in the blank sample (e.g. µg)

The CEH ALPHA sampler (Figure 9) (Tang et al., 2001) is a high sensitivity passive sampler developed by CEH that are used in the UK National Ammonia Monitoring Networks (Tang et al., 2018) and other air monitoring projects.

Calibrated field uptake rate for ALPHA sampler @ 10ºC = 0.003241315 m^3 h^{-1}

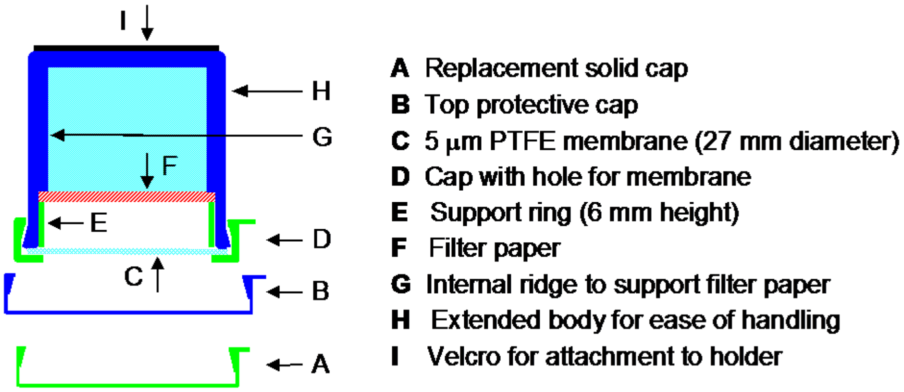


Figure 9: Outline diagram of a single ALPHA Sampler.

The ALPHA sampler provides a controlled, known uptake of NH_3 and confers the following selectivity in the sampling of NH_3:

1. Low molecular mass gas molecules such as NH_3 only can diffuse through the 5µm pore size PTFE membrane at the air inlet. Aerosols will not. Other gases that will diffuse through the membrane include: NO, NO_2, SO_2, amines.
2. Reaction and retention of NH_3 (alkaline gas) on the acid impregnated filter behind the membrane. Acid gases such as NO, NO_2 and SO_2 should not be retained. However, it is proposed to run tests to ascertain this:
    - i) extract and analyse acid impregnated paper after exposure for presence of other inorganic ions (NO_2^-, NO_3^-, SO_4^{2-}, Cl^-).
    - ii) add a second base-coated filter behind the acid filter to retain other ions that may interfere.

To increase sensitivity, the diffusion path length (i.e. the distance from the membrane to the reaction surface, 6 mm in ALPHA sampler) and the reaction surface area (3.46 x 10^{-4} m^2 in ALPHA sampler) can be modified to achieve a higher uptake rate.

4.4 Measuring resistivity

When a voltage is applied to a material or device, current will flow through it. How much current will flow is based on the resistance that the material applies to a circuit. Resistance (R) is the capacity of a circuit or material to oppose the flow of an electrical current, measured in Ohms (Ω) and is the quotient of the DC voltage U applied to a circuit, divided by the resulting current (I) though the circuit (Equation 4). Resistivity is the measurement of a device's resistance, measured in Ω-m or Ω-square .

$$R = \frac{U}{I} \qquad (4)$$

Resistance is affected by a number of factors including, surface cleanliness, humidity, temperature, applied voltage or applied current. Accuracy and sensitivity of resisitivity measurements is therefore dependent on the test conditions, sample rate, and meter resolution.

4.4.1 Surface Resistivity

This measures resistance across the surface of a material in contact with the electrodes (Figure 10).

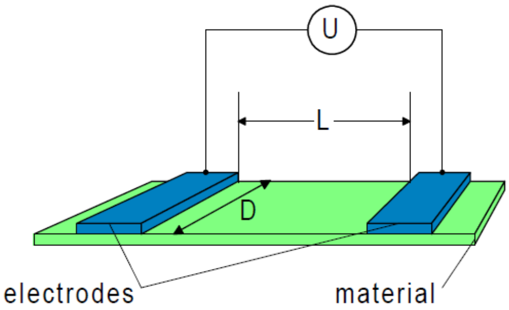


Figure 10: Basic setup for surface resistivity measurement.

Surface Resistivity (ρs) measurement units are given as Ohms per metre (Ω-m) or square Ohms per Square (Ω/square) regardless of the size of the electrode.

It is determined by the ratio pf DC voltage U drop per unit length L to the surface current I_s per unit width D (Equation 5).

$$\rho s = \frac{U/L}{Is/D} \qquad (5)$$

A surface-resistivity measurement of very conductive flat material of a uniform substance is also the resistance measurement of the volume between the electrodes, because the path of the electrode includes the depth or thickness of the test specimen.

To measure the surface resistivity of a flat material, a set of equal-sized electrodes is placed in good contact with the surface of the material, separated by a space equal to the width of the electrode. Because one divided by one equals one, the length divided by the width of the area cancels out the effect of the size of the measured area.

A typical Ohmmeter or Multimeter applies low current though a material, measures the voltage and displays the resistance in Ohms (Ω). High Resistivity measurements are typically obtained using either a megohmmeter or an IR (insulation resistance) meter.

4.4.2 *Bulk resistivity (or volume resistivity)*

This is the measurement of resistance(R) multiplied by the cross-section of a specimen (Width, W x Thickness, T) divided by the Length (L) of the material between the electrodes (Equation 6). The electrodes are in contact with both sides of the material at each end.

$$R\ (W \times T)/L = \Omega\text{-cm} \qquad (6)$$

4.5 Controlled temperature and humidity test chamber

A modification of the Portable Relative Humidity and Aerosol Generator System (PReHAGS) (Mullinger 2016) is used to generate different humidity conditions in a test chamber at ambient laboratory temperatures (

Figure 11,

Figure 12).

Humid air flow and dry air flow are separately controlled by two Mass Flow Controllers (MFCs) in the system and mixed together to create a total blended flow of air that flows through the test chamber at a specified humidity.

A custom labview program allows the users to set the flow rates of the two MFCs and to monitor the temperature and relative humidity inside the test chamber (Figure 13).

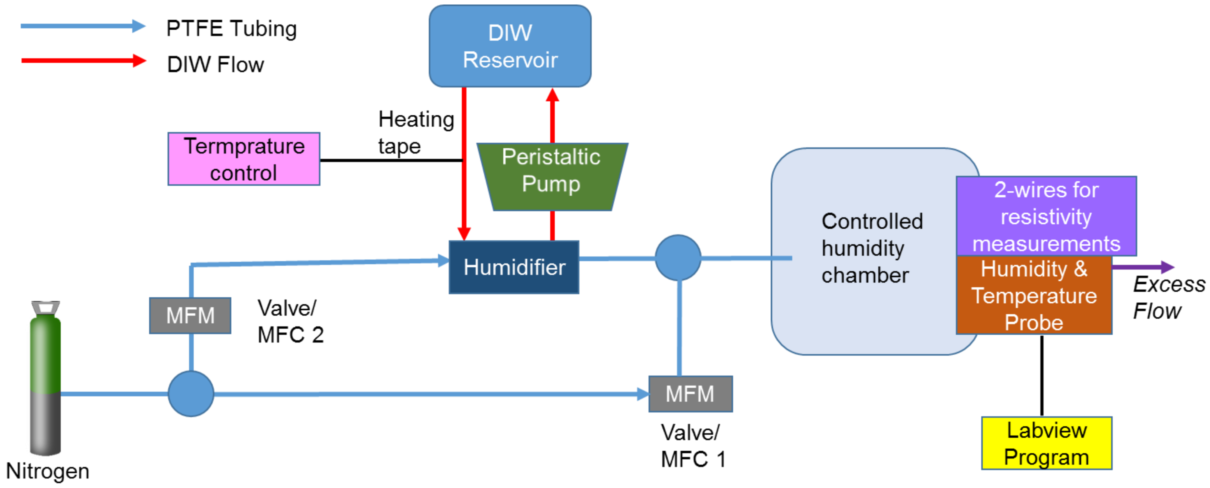


Figure 11: Schematic of equipment for generating different humidity conditions in a controlled humidity test chamber. Mass Flow Controller (MFC)/Valve 1: dry air flow, Mass Flow Controller (MFC)/Valve 2: humid air flow, MFM: Mass Flow Meter, DIW: Deionised Water. Adapted from Mullinger et al., 2016)

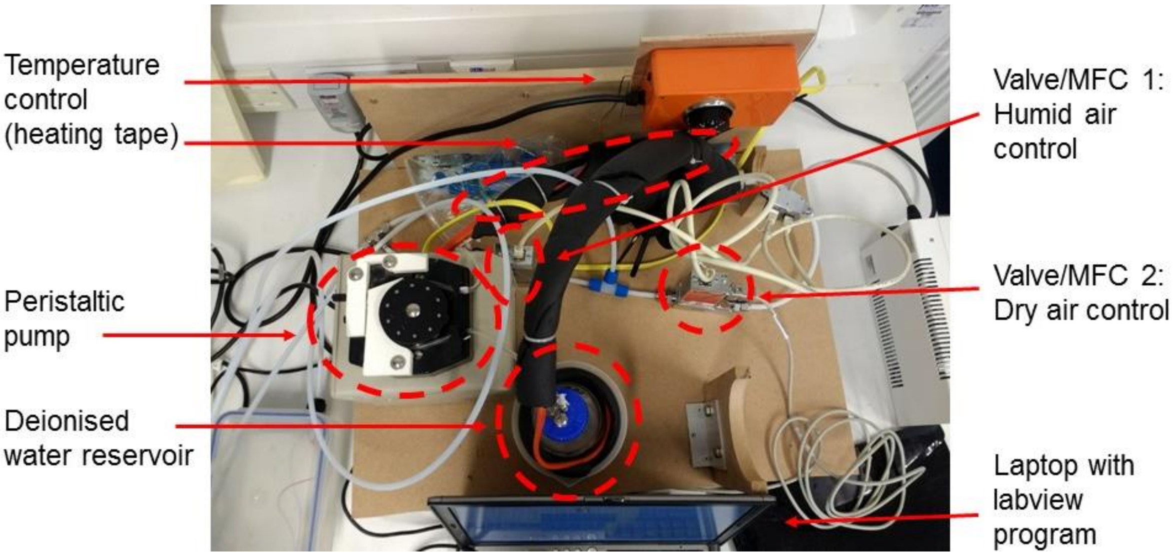
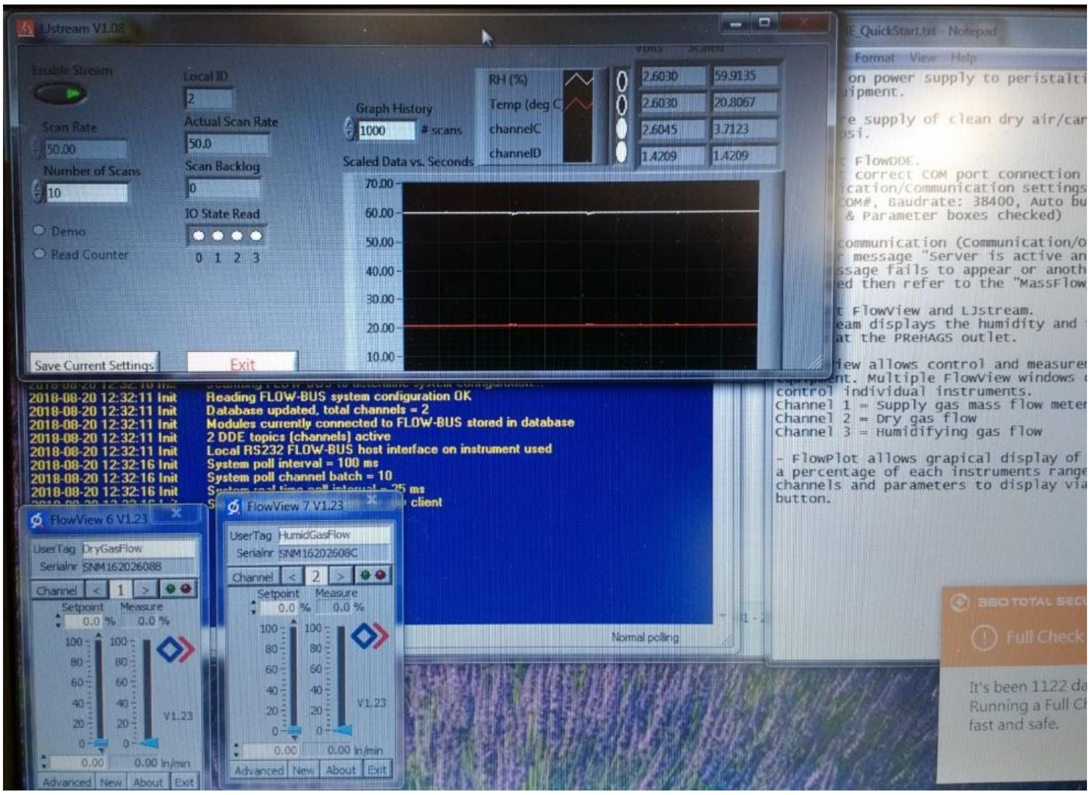


Figure 12: Picture of equipment for generating different humidity conditions in a controlled humidity chamber.



Local ID: 2
Scan Rate: 50.00
Actual Scan Rate: 50.0
Number of Scans: 10
Scan Backlog: 0
Graph History: 1000 # scans

	Volts	Scaled
RH (%)	2.6030	59.9135
Temp (deg C	2.6030	20.8067
channelC	2.6045	3.7123
channelD	1.4209	1.4209

```
2018-08-20 12:32:11 Init    Reading FLOW-BUS system configuration OK
2018-08-20 12:32:11 Init    Database updated, total channels = 2
2018-08-20 12:32:11 Init    Modules currently connected to FLOW-BUS stored in database
2018-08-20 12:32:11 Init    2 DDE topics (channels) active
2018-08-20 12:32:11 Init    Local RS232 FLOW-BUS host interface on instrument used
2018-08-20 12:32:16 Init    System poll interval = 100 ms
2018-08-20 12:32:16 Init    System poll channel batch = 10
```

UserTag: DryGasFlow
Serialnr: SNM16202608B
Channel: 1
Setpoint: 0.0 %
Measure: 0.0 %
0.00 — 0.00 ln/min

UserTag: HumidGasFlow
Serialnr: SNM16202608C
Channel: 2
Setpoint: 0.0 %
Measure: 0.0 %
0.00 — 0.00 ln/min

```
on power supply to peristalti
ipment.

e supply of clean dry air/car
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 FlowDDE.
 correct COM port connection
cation/Communication settings
OM#, Baudrate: 38400, Auto bu
 & Parameter boxes checked)

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ed then refer to the "MassFlow

t FlowView and LJstream.
eam displays the humidity and
at the PReHAGS outlet.

iew allows control and measure
nt. Multiple FlowView windows
control individual instruments.
Channel 1 = Supply gas mass flow meter
Channel 2 = Dry gas flow
Channel 3 = Humidifying gas flow

- FlowPlot allows grapical display of
a percentage of each instruments range
channels and parameters to display via
button.
```

Figure 13: Labview program: humidity is monitored and controlled by adjusting air flow through Mass Flow Controller (MFC)/Valve 1: dry air flow and Mass Flow Controller (MFC)/Valve 2: humid air flow.

4.6 Initial tests

Objectives are:

- Design a circuit to measure resistivity changes on sensing surface (acidified paper or conducting polymer).
- Establish relationship between resistivity changes (Ω-m) and amount of ammonium (NH_4^+, µg) on the acid filters or CP under different relative humidities (50 – 90 %).

4.6.1 Sensing material: Cellulose filters

a) 24 mm diameter Swiflab cellulose filter circles (type used in CEH ALPHA samplers).
b) Acid-impregnated filter: 24 mm filter impregnated with 6 µg citric acid (50 µl of 12 % citric acid solution – ALPHA protocol).
c) NH_3 doped acid-impregnated filter: Acid-impregnated filter + 0.3 µg NH_4^+ (50 µl of 6 ppm NH_4^+ solution made from $(NH_4)_2SO_4$)).

0.3 µg NH_4^+ on the acid filter is equivalent to exposure to:

- ~ 5 mg NH_3 m^{-3} / ~ 7 ppm NH_3 for 1 minute
- ~ 4 µg NH_3 m^{-3} NH_3 / ~ 5 ppb NH_3 for 1 day

The amount of NH_3 collected on an acidified filter after exposure periods of i) 1 minute (

Table 6) and ii) 1 day (Table 7) for a range of atmospheric NH_3 concentrations may be estimated according to Equation 6:

$$NH_3\ (\mu g) = \chi\ (\mu g\ NH_3\ m^{-3})\ x\ [U\ (m^3\ h^{-1})\ x\ t\ (h)] \qquad (6)$$

Where: U = 0.003241315 $m^3\ h^{-1}$ @10°C (see section 4.3)

Table 6: Estimated amount of NH_3 collected on acidified filter of ALPHA sampler for a sampling duration of 1 minute (volume of air sampled = 0.00005 m3).

Atmospheric concentrations		**Sampled by ALPHA**
[NH_3] ppb	**[NH_3] µg m^{-3}**	**[NH_3] µg on ALPHA filter**
0.1	0.07	0.000004
1	0.74	0.000040
2	1.48	0.000080
5	3.70	0.000200
10	7.40	0.000400
25	18.5	0.000999
50	37.0	0.001999
100	74.0	0.003998
250	185.0	0.009994
500	370.0	0.019988
1000	740.0	0.039976
10000	7400.0	0.399762

Table 7: Estimated amount of NH_3 collected on acidified filter of ALPHA sampler for a sampling duration of 1 day (volume of air sampled = 0.0778 m3).

Atmospheric concentrations		**Sampled by ALPHA**
[NH_3] ppb	**[NH_3] µg m-3**	**[NH_3] µg on ALPHA filter**
0.1	0.07	0.0058
1	0.74	0.0576
2	1.48	0.115
5	3.70	0.288
10	7.40	0.576
25	18.5	1.44
50	37.0	2.88
100	74.0	5.76
250	185.0	14.4
500	370.0	28.8
1000	740.0	57.6
10000	7400.0	575.7

4.6.2 *Sensing material: Fluorographene*

Contact was made with the authors of the Fluorographene research paper (Tadi et al. 2016) in India.

Web.: http://www.tifrh.res.in/~tnn/

Dr. Narayanan of the Tata Institute of Fundamental Research in Hyderabad kindly agreed to grow FG film on a range of membranes sent to their lab.

Due to stability issue at 400ºC of the membranes supplied, the research team in India had to modify their normal procedures.

- Zefluor PTFE = OK. Successful
- PTFE membrane type 1 = unsuccessful (polypropylene support of PTFE melted at 400ºC)
- PTFE membrane type 2 = unsuccessful (polypropylene support of PTFE melted at 400ºC)
- Nylon membrane = unsuccessful. Melting point of Nylon = 200ºC.
- They additionally provided samples of Fluorographene on GFC filters (47 mm circles cut into quarters).

Membranes used in resistivity tests:

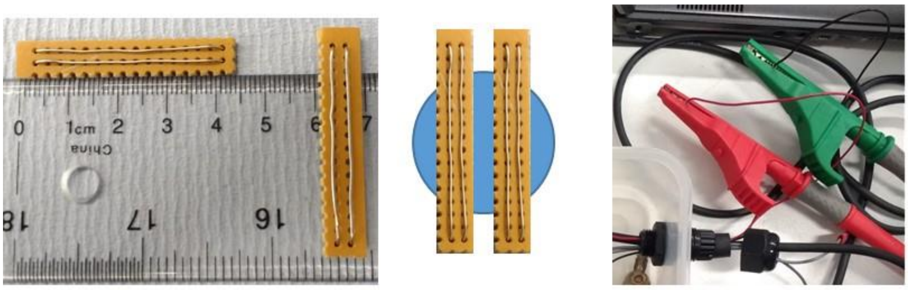
a) 25 mm Zefluor PTFE membrane
b) Fluorographene thin film (FG) on Zefluor (substrate)
c) NH_3 doped FG on Zefluor (FG surface doped with 0.3 µg NH_4^+ (50 µl of 6 ppm NH_4^+ solution made from $(NH_4)_2SO_4$)).

0.3 µg NH_4^+ on the acid filter is equivalent to exposure to:

- ~ 5 mg NH_3 m^{-3} / ~ 7 ppm NH_3 for 1 minute
- ~ 4 µg NH_3 m^{-3} NH_3 / ~ 5 ppb NH_3 for 1 day

4.6.3 Resistivity measurement - Test 1

Electrodes were made from wire soldered onto strips of PCB boards (insulator). Filters under test were sandwiched and clamped between two pairs of the electrodes (Figure 14).



24 mm filter circle sandwiched between 2 pairs of strip electrodes

Crocodile clips

Figure 14: A pair of strip electrodes makes a bulk-resistivity measurement on the filter crossing between them.

A Megger MFT1730 multimeter (Figure 15) was used to measure resistivity, with crocodile clips making contacts with wires from the electrodes. A voltage of 100 VDC was applied to the filter, with resistivity recorded in MOhms (MΩ).

Note that this was an existing instrument available at CEH Edinburgh capable of measuring the range of high resistances encountered.

Figure 15:Megger MFT1730 multimeter used to measure resistivity.

Test results

Very high (MOhm) resistance is seen in the filters (Table 8; Table 9). This was poorly controlled in the tests (e.g. inconsistent electrode spacing), but the order of magnitude was consistent.

In summary there does seem to be a difference in response between untreated papers, acid coated papers and doped acid coated papers (Table 8; Table 9).

Table 8: Bulk resistivity measurements of cellulose filters. All readings were carried out at 100 VDC.

	24mm filter	Citric acid coated filter	Citric acid coated filter + 0.3 µg NH_4^+	Temperature and Humidity
Measurement 1 (MΩ)	>999	740	960	24^{0}C, 60 % RH
Measurement 2 (MΩ)	>999	>999	>999	24^{0}C, 60 % RH
Measurement 3 (MΩ)	>999	740	935	24^{0}C, 60 % RH

Table 9: Further tests on humidity-dependent resistivity measurement. All readings were carried out at 100 VDC.

	24mm filter	Citric acid coated filter	Citric acid coated filter + 0.3 µg NH_4^+
Resistivity Measurement (MΩ)	>999 to 200 @ 24^{0}C 70 - 80 % RH	>999 to 200 @ 24^{0}C 50 - 70 % RH	>999 to 200 @ 24^{0}C 60 - 70 % RH

4.6.4 *Resistivity measurement - Test 2*

Further tests were conducted:

- More detailed and controlled conditions: slowly adjusting humidity and allowing sufficient equilibration times.
- Improved design of electrodes with fixed spacings (Figure 16).

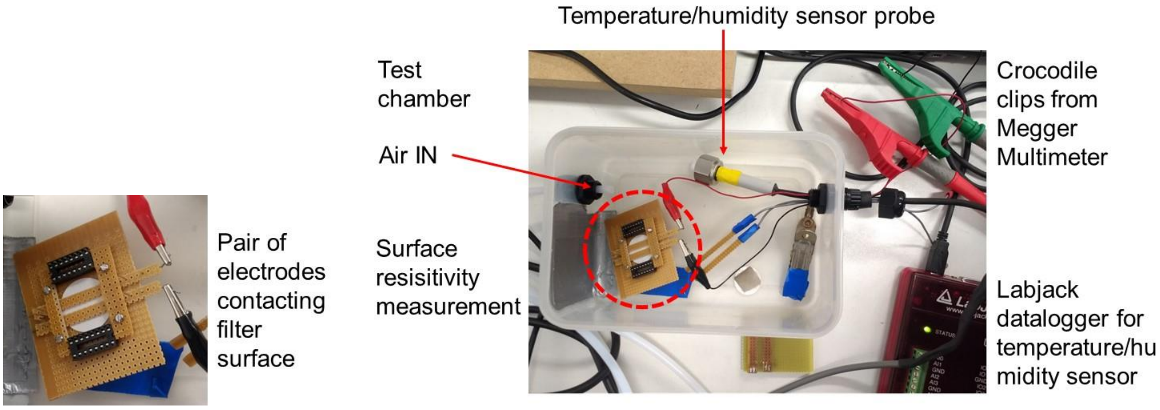


Figure 16: Experimental set-up for resistivity measurements inside test chamber. The test chamber is shown with the cover removed. The electrodes are spaced with 2 tracks width between them.

24 mm cellulose filters

A difference in resistivity response was observed between blank and doped acid filters, with lower resistance readings on the doped acid filter than the blank over the humidity range tested (Figure 17).

The results show that resistance measurements are very sensitive to changes in humidity. Further tests are warranted:

- Repeat resistance measurements comparing blank vs doped (0.3 µg NH_4^+) at different humidity conditions (20 – 90%) to confirm differences.
- Acid filters doped with different amounts of NH_4^+ (using solutions prepared from NH_4OH, not $(NH_4)_2SO_4$, to eliminate contribution to resistance from the SO_4^- ions).

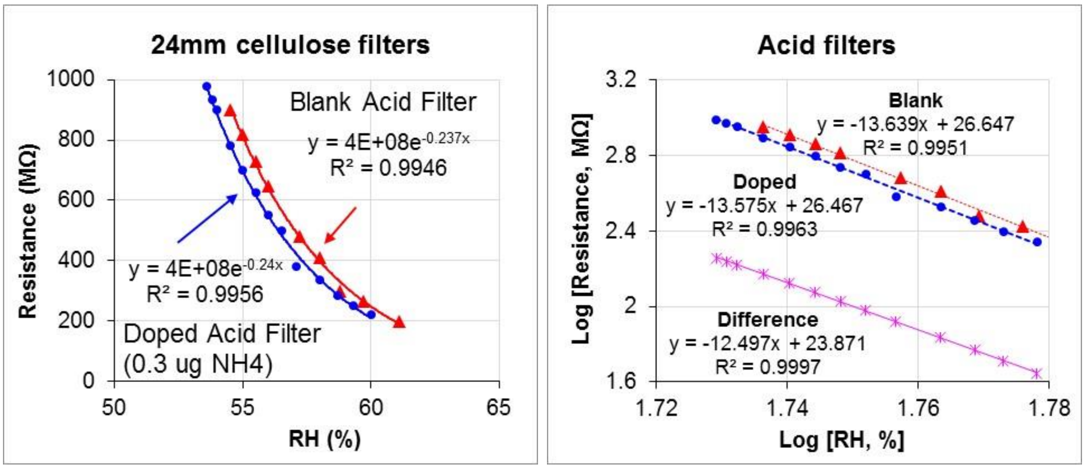


Figure 17: Surface resistivity measurements on 24 mm diameter cellulose filter circles. All readings were carried out at 100 VDC. Acid paper = filter coated with 6 µg citric acid. Doped Acid Filter = acid paper doped with 3 µg NH_4^+. Difference = [Blank – Doped] estimated from the derived exponential relationships for the blank and doped filters, respectively.

Fluorographene

Zefluor membrane: Zefluor is pure PTFE. At RH < 72%, resistance is > 999 MΩ. Resistance decreased exponentially with humidity in the range 72 – 84 % tested (Figure 18).

FG on Zefluor membrane: FG is a semi-conductor material. Initial resistivity measurements on FG shows that the FG is less sensitive to humidity than Zefluor, with resistance changing from > 999 MΩ at RH > 79% and decreasing exponentially with increasing humidity (Figure 18). Similar resistivity readings for both Zefluor and FG on Zefluor occur at around 83% RH.

The same test conducted on other FG-Zefluor membranes however showed no change in resistivity with humidity, with resistance remaining above maximum (> 999 MΩ) over the 20 – 90 % humidity range tested.

The differences in response may be attributed to variations in the quality of the FG thin film (black FG particles) coating on the Zefluor membrane. Visually, some have a more homogeneous black film than others, and some of the Zefluor PTFE membrane are distorted / misshapen (due to high temperatures of around 400°C in synthesis/coating process).

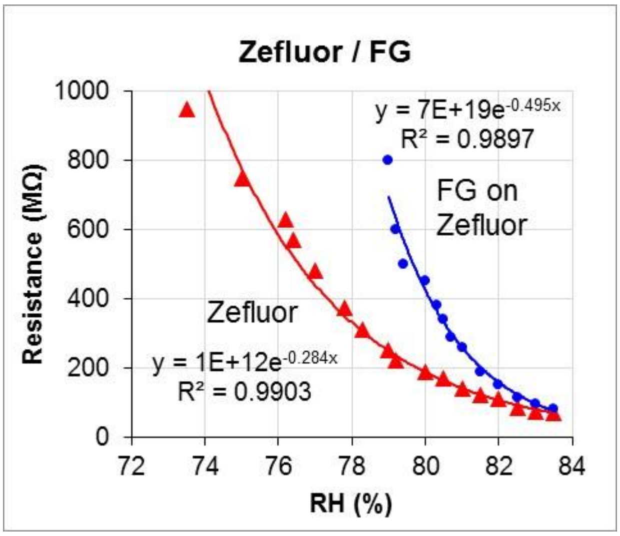


Figure 18: Surface resistivity measurements on Zefluor and Fluorographene (FG) on Zefluor. All readings were carried out at 100 VDC.

Doped FG on Zefluor membrane: initial results are inconclusive, with resistivity values remaining above maximum (> 999 MΩ) over the 20 – 90 % humidity range tested.

5 Proposed further tests

5.1 Improved resistivity measurements

Requirements:

- Resistivity measurements at low voltage (e.g. around 12 V).
- Electrodes/circuits with accurate, sensitive and reproducible measurements.
- A multimeter with low voltage settings that can measure high resistance values and with an PC option to log data continuously.

With recent development in Microelectronics Systems (MEMS), micro-electrodes with very small electrode surface area have been developed in the fabrication of electrochemical sensors.

This makes integration of micro-electrodes with Fluorographene onto a Chip in fabrication of a chemiresistor sensor possible.

The types of micro-electrodes available on the market are screen-printed electrodes (SPE) and Interdigitated Electrodes.

Screen Printed Electrodes (SPE)

Fluorographene coated/modified Screen Printed Electrodes (purchased from Taiwan) are used by TATA in India for their research work on FG.

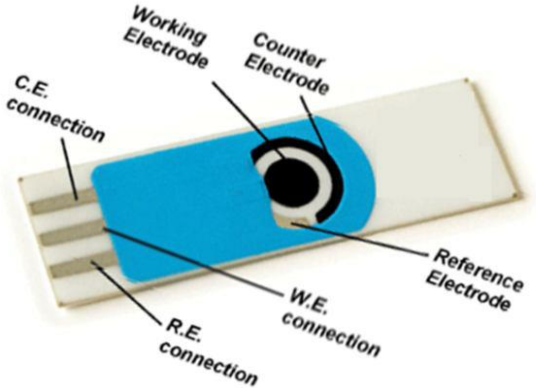


Figure 4: The structure of a commercial screen printed electrode.

Manufacturers from the internet:

- https://www.gamry.com/cells-and-accessories/electrodes/screen-printed-electrodes/
- http://www.dropsens.com/en/screen_printed_electrodes_pag.html#membrane

Interdigitated Electrodes/ Microelectrodes

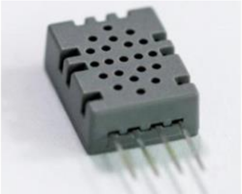
Manufacturers from the internet:

- http://www.dropsens.com/en/interdigitated_electrodes.html
- http://www.ntelectrodes.com/

5.2 Temperature and humidity compensation

Resistivity measurements is influenced by changes in temperature and humidity.

- Stability of sensor at wide temperature and humidity range desirable.
- Monitor temperature and humidity sensors by inclusion of a sensor, e.g. ZS03 Temperature and Humidity Sensor Module.



https://www.winsen-sensor.com/products/micromolecule-humidity-sensor/zs03.html

- Develop algorithm for temperature/humidity compensation, or:
- Measure ammonia on a cycle that includes both a heating (desorption) and cooling (absorption) period to determine and separate the effect of humidity from the response to ammonia concentration.

5.3 Modify sensor dimensions to increase sensitivity

To increase sensitivity, the diffusion path length (i.e. the distance from the membrane to the reaction surface, 6 mm in ALPHA sampler) and the reaction surface area (3.46 x 10^{-4} m^2 in ALPHA sampler) may be modified to achieve a higher uptake rate.

5.4 Data logging

To start with, program a raspberry Pi to log data.

- Need an electrical circuit / algorithm to convert the change in resistivity to an output signal that is related to the sample gas concentration being monitored.
- Develop algorithms to convert resistivity outputs to air concentrations (µg NH_3 m^{-3}).
- Low time-resolution measurement is adequate for environmental air monitoring (section 4.1). The sensor can be programmed to log data once every hour or once every 24 hours and average the readings to the required time resolution (daily, weekly or monthly).

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