Short term mobility

Report on Gas sensing Monitoring

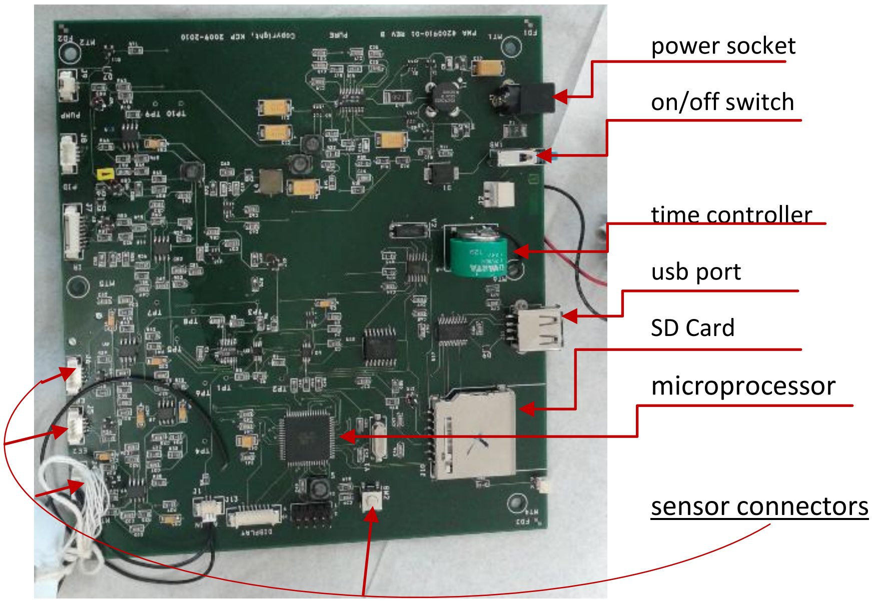
During the period of short term mobility (STM), spent in Manchester at School of Chemical Engineering and Analytical Science, I had the opportunity to explore topics concerning devices for gas sensing useful for environmental monitoring.

Some knowledge has been acquired on the devices using polymeric sensors to detect ammonia. A device, based on electrochemical sensors and PID (photodeionization detection) sensor, has been also investigated to monitor the presence of NO2, SO2 CO and VOCs, respectively. Moreover, a device using Arduino system has been realised. For this aim it was necessary to acquire specific knowledge.

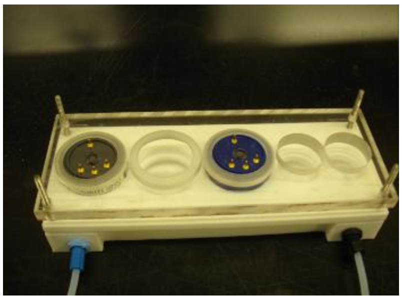
Gas sensing Monitoring Device

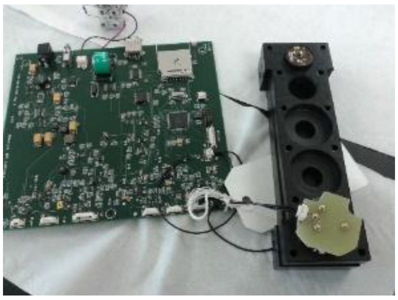
In general, the main components of a device for gas sensing monitoring have been examined in depth and they are reported in the following figures.

A fundamental station consists in an elettronic board containing a microprocessor, an on/off switch, a micropump to draw air across sensors, specific sensor connections, a time controller, a power socket, an usb port and a SD card to record data.



The sensors are collocated into a PTFE support, called sensor head, inside of which passes the environmental air sucked by a micropump.,

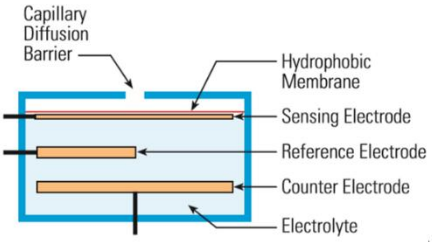




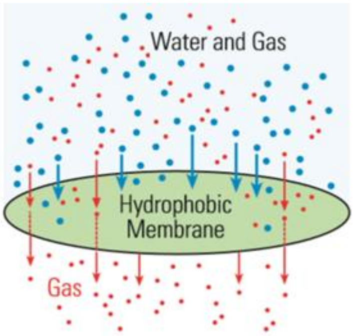
During the STM period, the attention has been focused on the realization of a gas sensing device. In detail, electrochemical sensors have been explored and the sensor calibration step has been studied in depth.

Electrochemical sensors

Electrochemical sensors operate by reacting with the gas of interest and producing an electrical signal proportional to the gas concentration. A typical electrochemical sensor consists of a sensing electrode (or working electrode), and a counter electrode separated by a thin layer of electrolyte.



Gas that comes in contact with the sensor first passes through a small capillary-type opening and then diffuses through a hydrophobic barrier, and eventually reaches the electrode surface. This approach is adopted to allow the proper amount of gas to react at the sensing electrode to produce a sufficient electrical signal while preventing the electrolyte from leaking out of the sensor.



The gas that diffuses through the barrier reacts at the surface of the sensing electrode involving either an oxidation or reduction mechanism. These reactions are catalysed by the electrode materials, specifically developed for the gas of interest. With a resistor connected across the electrodes, a current proportional to the gas concentration flows between the anode and the cathode. The current can be measured to determine the gas concentration. Because a current is generated in the process, the electrochemical sensor is often described as an amperometric gas sensor.

Electrochemical sensors require very little power to operate. In fact, their power consumption is the lowest among all sensor types available for gas monitoring. For this reason, the sensors are widely used in portable instruments that contain multiple sensors. They are the most popular sensors in confined space applications. A sensor's life expectancy is predicted by its manufacturer under conditions that are considered normal. However, the life expectancy of the sensor is highly dependent on the environmental contaminants, temperature, and humidity to which it is exposed.

Calibration of sensor

Regarding the calibration, it is an important step when a new gas sensing device is realized and have to be used in right way.

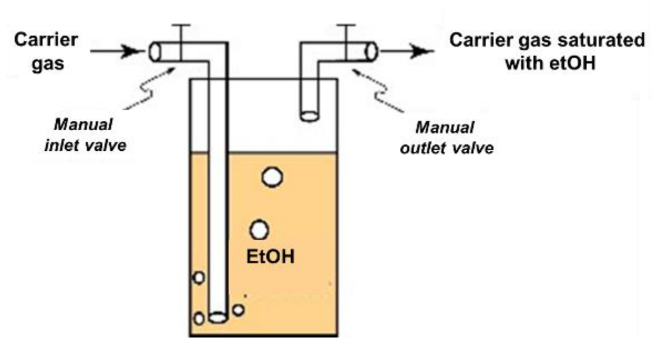
The calibration is carried out in several successive steps where electrical signals are acquired. In general, electrical signals are acquired in the absence of the specific gas sample (Setting and the "Zero" Reading or the zero point), in the presence of the specific gas at the maximum concentration (saturation concentration at controlled temperature and pressure), and then in presence of known concentrations of gas obtained after appropriate dilutions.

Many analytical procedures use pure nitrogen or pure synthetic air to establish the zero point.

Compressed air has the advantage that it is easy to regulate and can be carried around in a bottle. Moreover it is very accessible and convenient. However, compressed air contains small concentrations of hydrocarbons, carbon monoxide, carbon dioxide, and possibly other interference gases. An important aspect not to be underestimated is the signal due to environmental moisture that could interfere in the final signal. Some sensors may need moisture to get a proper reading. The air is typically very low in humidity. A solution to this is that the air can be filtered through activated charcoal to remove most of the unwanted gases and water vapour can be added into the air in a controlled way using a humidifier in the sampling system. After this conditioning, the air can be used to calibrate most types of sensors. (However, it is important to note that carbon monoxide is not removed by charcoal filters. Furthermore, a soda ash filter should be used to remove carbon dioxide.) The calibration steps can be quite easy or it can be very complicated and expensive, depending on the gas type and concentration range. As regards the concentration range, it is possible to reach the wanted concentrations by using a bubbler or a permeation tube. The latter allows to reach lower concentrations, therefore it is possible to carry out the calibration in a lower range.

Bubbler

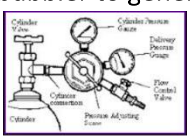
The first, shown in picture and reported shematically in figure, consists in a container, filled with analyte in liquid form, and two tube.

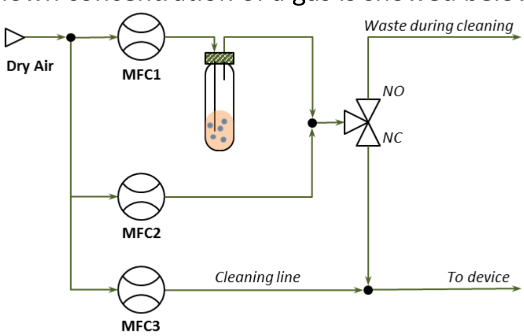


These are incorporated in bubbler, and one is longer than the other. The longer one allows the carrier gas to flow into bubbler favouring the dissolution of analyte and the its passage in the gaseous phase to form a saturated gas solution in the head space. Then, the forming gas bubbles can be moved away by the carrier gas through the shorter tube. The whole process is regulated by inlet and outlet valves and the sequence of opening/closing of which is very important.

The vapour pressure of analyte depends on the temperature. In order to keep a constant vapour pressure inside the bubbler, the bubbler is placed in a thermal bath whose temperature is precisely controlled by a thermostat.

The scheme of a system using the bubbler to generate a known concentration of a gas is showed below





The gas arrives through a pressure regulator that makes the pressure step-down from the cylinder pressure. Then the carrier gas, generally, N2, or dry air, arrives to a three mass flow controllers (MFC), showed in picture and hereinafter described, which adjusts the gas flow in such a way as to obtain a specified flow. A mass flow controller (MFC1) is used to deliver carrier gas to a bubbler from which the highest analyte concentration is generated. A second mass flow controller (MFC2), positioned into a second line but joined to the first, is used to controls the flow of air used to create appropriate dilution of a single analyte. In fact, different analyte concentrations are obtained changing the setting of these two MFCs. A third mass flow controller (MFC3), regulating an independent carrier gas line, was used as a reference stream (instrumental zero or zero point) and to clean also the sensors after the measurement.
Obviously, before to arrive on the sensors, the analyte is properly mixed and the whole system can be controlled by valves. They ensured that, during the cleaning phase of the sensors, no analyte is delivered to the array and the flow is constant and direct towards an exhaust line. During the measurement phase, the valves allow the analyte stream to reach the sensors, after the dilution step.
During the measurement, MFC3 is turned off, the valve is in its normally closed state (NC), and the diluted analyte concentration flows to the device. To clean the sensors, the valve is switched to the normally open (NO) conditionand MFC3 is switched on, with a flow equilibrating the sum of MFC1 and MFC2. It is worth noting that in this case the analyte stream continues to flow during the cleaning phase (through a waste line), avoiding any fluctuation in the analyte concentration.
In order to calculate the concentration of an analyte, we need to know the vapour pressure value. The Antoine equation allows to calculate this parameter, it describes the relation between vapour pressure and temperature for pure components:

$$\log_{10} p = A - \frac{B}{C + T}.$$

where p is the vapour pressure, T is temperature and A, B and C are component-specific constants that can be found in literature.
Considering that when the environmental pressure is equal to 1 atm (mmHg), the concentration of a saturated gas, expressed in ppm, is calculated by the following formula

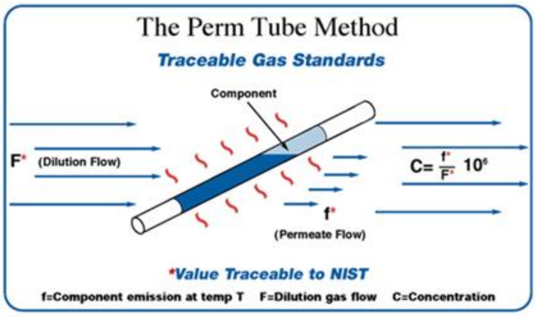
ppm = VP(mmHg)/760(mmHg)*10^6

where VP is the vapour pressure calculated by Antoine equation.

Permeation tube

The cited previously permeation tube is the second system used to obtain different known concentrations of a gas. The analyte is in the form biphasic liq/gas and the gaseous part can permeate through a membrane to the maximum concentration. Subsequently, it is diluted by an inert gas such as the air flow.

The two systems , the bubbler and the permeation tube, work in an almost similar. In the first distinguish a bottle containing an analyte in a liquid form, in which it is bubbled clean, dry air. This blowing of air favours the passage of the analyte in the form of steam that comes into equilibrium with the liquid phase up to the attainment of a saturated environment in the head space. Instead, the permeation tubes use a permeable membrane to dispense a small flow of chemical vapour. The most common type is a small tubular device that has liquid analyte sealed inside the tube. A very small but stable flow (nanograms-per-minute) of analyte vapour is emitted through the tube wall at constant temperature. The emission rate of the tube is determined by measuring the rate of weight loss. These tubes are used in KIN-TEK Gas Standards Generators to create dynamic gas standards with concentrations traceable to NIST database through physical standards. Immersing the tube in a carefully controlled flow of inert dilution gas forms a trace concentration mixture of the analyte.



The emission rate of a permeation tube is dependent on the following factors: physical characteristics of its permeable membrane, permeability of its chemical analyte through the membrane, temperature of the permeation tube and partial pressure across its permeable membrane.

Each certified permeation tube is serial-numbered and the certification data is kept on file for 5 years.

KIN-TEK makes several types of Trace Source™ disposable and refillable permeation tubes for different compounds.

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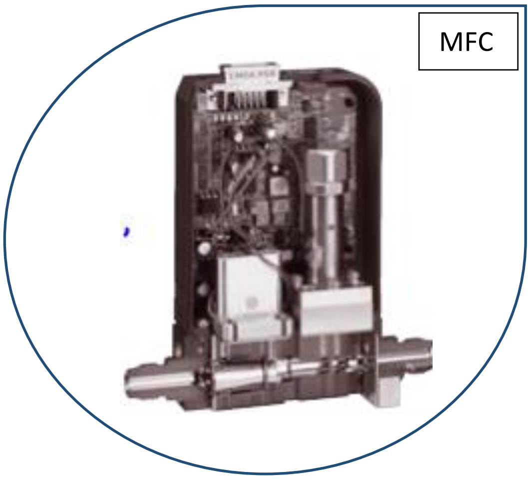
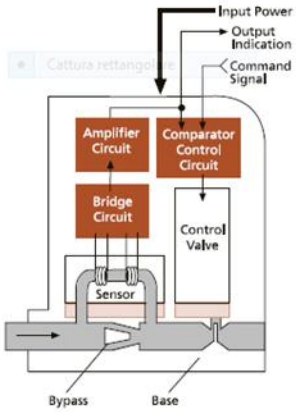
MASS FLOW CONTROLLER

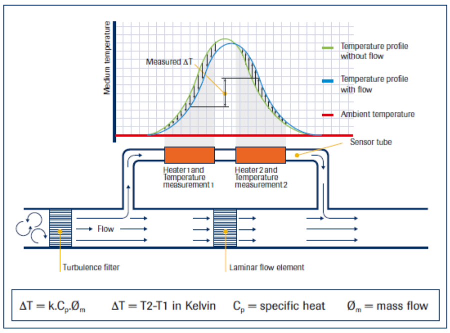




The main components of a mass flow controller are an inlet port, an outlet port, a mass flow sensor and a proportional control valve. In more detail, to help understand how an MFC works, we can also say that a mass flow controller can be separated into four main components: a bypass, a sensor, an electronics board and a regulating valve. The bypass, also known as the flow splitter, maintains a constant ratio of gas flow through the sensor and main flow path. As a result, the total flow can be determined by measuring just the portion of gas that passes through the sensor.

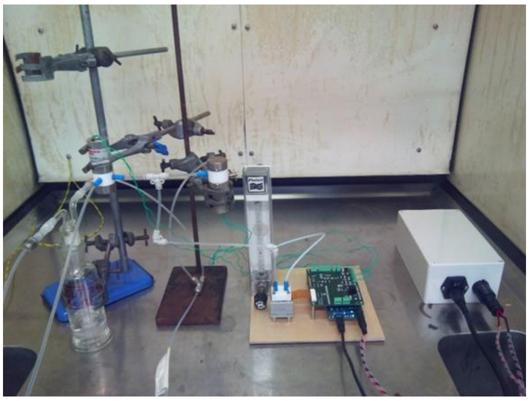
The control valve establishes the flow of gas by responding to a signal that compares the actual flow to the set point. Actuators driving the control valve in MFCs are either piezoelectric, solenoid, or thermal actuators, depending on the model. However, the heart of a mass flow controller is a thermal sensor. It consists of a small bore tube with two resistance-thermometer elements wound around the outside of the tube. The sensor tube is heated by applying an electric current to the elements. A constant proportion of gas flows through the sensor tube, and the cooling effect creates a temperature differential between the two elements. The change in the resistance due to the temperature differential is measured as an electrical signal. The temperature differential created between the elements is dependent on the mass flow of the gas and is a function of its density, specific heat, and flow rate. Mass flow is normally displayed in terms of

volume of the gas either in standard cubic centimeters per minute (sccm). The bypass forces a constant proportion of the incoming gas to be fed into the sensor. The gas flow through the sensor tube causes heat to be transferred from the upstream resistance-thermometer element to the downstream resistance-thermometer element. This temperature differential is linearized and amplified into a 0 to 5 V flow output signal by means of a bridge circuit. The output signal is compared with the external set point signal to the mass flow controller. The error signal that results from comparing the output signal with the set point signal directs the control valve to open or close to maintain a constant flow at the set point level.
The following diagram describes the principle of operation of a mass flow controller. The flow is divided between a heated sensing tube (the sensor), where the mass flow is actually measured, and a flow restrictor or bypass, where the majority of flow passes.



The bypass is designed in a way that flow thru the sensor and the bypass is always proportional to the flow range for which the mass-flow controller is built.

During the STM period spent in Manchester a device based on Arduino system, reported in picture has been realized. The sensor calibration has been carried out taking advance of the acquired information above described.



The continuation of this activity is strongly desired and now it is possible thanks to the acquired knowledge and ongoing initiatives.

Tito scalo 11-11-2014

Firma
Nunzia Cicco