ZMOD4410 – TVOC Sensing

Total volatile organic compounds (TVOC) is the sum of all volatile organic compounds (VOC) and it is referred to as a typical indicator for air contaminants. This document contains information on methods for detecting TVOC with the ZMOD4410 Metal Oxide Gas Sensor Module.

Contents

Figures

Tables

1. Introduction

This document gives additional background information on methods for detecting total volatile organic compounds (TVOC) with the ZMOD4410 Metal Oxide Gas Sensor Module and answers typical questions for individual VOC and TVOC detection. The ZMOD4410's *3 Sensor "S,"* sensitivity, selectivity, and stability are discussed.

TVOC is the sum of all volatile organic compounds (VOC), and it is referred as a typical indicator for air contaminants, especially for indoor air quality[1]. Many technologies for VOC detection have been established in the last decades with different emphasis.

Examples:

- Highest possible sensitivity for one specific VOC
- Precise selectivity to distinguish between individual gases
- Extremely accurate measurements, for example, for research
- Robust technology for harsh environments, for example, industrial applications
- Low-cost effective methods for mass market

Each user must find a compromise to meet the user's specific measurement requirements. Renesas' gas sensor modules are chemiresistors using a catalytic reaction of the gas air molecule on a metal-oxide (MOx) surface. The advantages of this technology are high sensitivity to both TVOC and individual VOCs, a robust design, a small mechanical size, and low-cost production in high volume as well as other advantages.

Usually the TVOC concentration is given as either:

- Molar ratio: ppm (parts per million) or ppb (parts per billion)
- Physical concentration: mg/m^3 (mass per volume)

It is easy to convert from ppm to mg/m^3 as seen in (Equation 1):

$$c \ [\text{ppm}] = \frac{V}{M} * c \ \left[\frac{mg}{m^3}\right] * 10^3$$

(Equation 1)

For an ideal gas at ambient temperature (25°C) and atmospheric pressure (1013 mbar), *c* is the concentration in ppm or mg/m^3, *V* is the molar volume (0.024465 m^3·mol^{-1}), and *M* is the molecular mass of the individual VOC in g·mol^{-1}. Table 1 gives some conversion examples for typical VOC gases. More trivial is the conversion from ppm to ppb since 1ppm equals 1000ppb.

Table 1. Concentration Conversion for Typical VOC Examples

VOC Name	Chemical Formula	Molar Mass [g·mol^{-1}]	Molar Ratio [ppm]	Concentration [mg/m^3]
Ethanol	C_2H_5OH	46.069	1	2.0057
			0.5311	1
Acetone	C_3H_6O	58.080	1	2.3740
			0.4212	1
Formaldehyde	CH_2O	30.026	1	1.2273
			0.8148	1
Toluene	C_7H_8	92.141	1	3.7662
			0.2655	1

The native output for the ZMOD4410 is an Ethanol (EtOH) concentration[2] in ppm, which is converted into a TVOC concentration in mg/m^3. Although the ZMOD4410 is a non-selective TVOC sensor, the conversation factors from Table 1 may also be used in case of changing from one VOC gas estimation to another one.

---

[1] For more information, see the white paper *Overview of TVOC and Indoor Air Quality* located on the [ZMOD4410](#) product page.

[2] Ethanol is the most common indoor pollutant and therefore ZMOD4410 factory calibration and algorithm is based on this gas.

2. Methods for VOC and TVOC Sensing

2.1 Volatile Organic Compounds (VOCs)

In recent years, volatile organic compound (VOC) measurements have gained increasing importance due to the widespread occurrence of VOCs and the need to monitor VOCs in comfort, environmental safety, automation, health, and medical care applications. Depending on the application, a single VOC or the sum of all organic compounds, referred to as the total VOC (TVOC), may be present.

To fit the demands of these applications, a multitude of VOC measurement techniques have been developed within the last decades. Figure 1 gives an overview of the most significant techniques and detectors: thermal-conductivity detectors (TCD), non-dispersive infrared sensors (NDIR), Fourier-transform infrared spectroscopy (FTIR), gas chromatography (GC), mass spectrometry (MS), electro-chemical electrolyte detectors (ELD), flame ionization detectors (FID), photoionization detectors (PID), pellistors, and metal oxide (MO_X) sensors. Depending on their size and complexity, the instruments, which are introduced in the following section, might also be differentiated as portable or stationary devices. Here the demand in inexpensive, miniaturized, portable, and highly sensitive sensors is driving the current industrial sensor development.
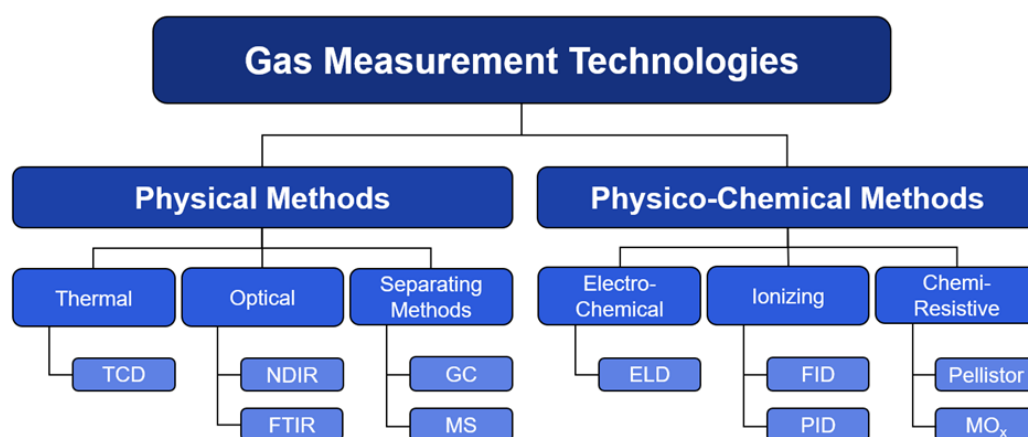

Figure 1. Overview of the Most Significant Gas Sensing Technologies

2.2 Physical Methods

These instruments rely on physical measurement principles and do not change the chemical composition of the test gas.

2.2.1. Thermal-Conductivity Detectors (TCD)

Thermal-conductivity detectors use a comparison between the thermal conductivity of the test gas and a reference gas. For this method, the cooling powers of two heater elements (having one heater in the test gas and the other in the reference gas) are compared. An increased gas concentration will give an increased thermal conductivity of the test gas, which lowers the temperature and resistance of the heating element. This resistance change is measured and compared to the reference gas.

Due to the simplicity of this technique, it can be applied to both organic and inorganic gases, where sensitivities of up to 1ppm are achievable. However, the lack of selectivity makes the sensor most suitable for well-defined process-control applications or use with other separation techniques.

2.2.2. Non-Dispersive Infrared (NDIR) Sensors

NDIR instruments use infrared (IR) absorption spectroscopy to infer the composition and concentration of individual gases within a test gas. For this, an infrared beam from an IR source is passed through the test gas and the absorption is measured for each wavelength in a spectrum analyzer. The recorded spectra are compared to reference spectra of the individual gas components. By applying the Lambert-Beer law, it is possible to infer the concentration of each component within the test gas and thus its composition.

Due to its working principle, an NDIR sensor can only detect infrared-active compounds. These are mostly heteronuclear or polar molecules such as CO, CO_2, hydrocarbons, ammonia, and many more. Homonuclear molecules, such as most pure gases, cannot be detected as their excitation frequencies lie outside of the spectral range used for NDIR. Major drawbacks of this technique are that gases with similar absorption spectra are hardly distinguishable from each other and NDIR sensors can only provide information on known gas components.

2.2.3. Separating Measurement Techniques

Separating technologies have in common that by using the principle of separation (either by chemical reaction or by mass) the instrument becomes very complex, large in size, and expensive. Due to very low detection limits and extremely high precision, these instruments are handled as a gold standard. However, there are no sensors available using this technology approach and only stationary instruments are available in highly specialized labs.

2.2.3.1. Gas Chromatography (GC)

Gas chromatography is based on the difference in diffusion velocity of gases through a separation tube (chromatography column). A sample of the test gas is injected into the chromatography column together with a continuous flow of carrier gas. Inside this column, the individual components of the test gas are differently strongly bounded to the filling material and column walls. Thus, stronger-bound molecules are slowed. This leads to a separation in time of the individual gas components at the exit of the chromatography column, where they can be measured individually. A very common method for collecting VOC gas samples in the field is the use of polymer adsorbents. This sample gas tube is then analyzed by thermodesorption to release the VOC into the GC instrument.

2.2.3.2. Mass Spectrometry (MS)

Mass spectrometry is a technique relying on the mass and charge separation of ion beams in an analyzing magnetic field. For this, an electron beam ionizes a fraction of the test gas in a high vacuum environment. The resulting cloud of ionized gas is accelerated in an electric field and passed through a strong magnetic field. Within this analyzer field, the ionized gas beam splits into its various components depending on the ratio of molecular mass and charge ($^m/_z$ ratio). Here the lightest and most heavily charged ions are deflected primarily due to the Lorenz force. The intensity of the resulting fan of sub-beams is measured in an angular array of Faraday cups. Each Faraday cup corresponds to a certain mass-to-charge ratio, and these ratios are specific to chemical compounds and molecules.

By measuring the mass spectrum, it is possible to infer the occurrence and concentration of chemical compounds within the test gas. Due to its highly sensitive and fundamental working principle, MS can be applied to almost any gas and is capable of detecting the smallest amounts of gases, even at sub-ppb levels. A disadvantage of mass spectrometry is that organic molecules in particular are partially fractionalized during the ionization and therefore different gases could result in similar fractions.

2.3 Physico-Chemical Methods

Unlike physical instruments, physico-chemical detectors are based on a combination of chemical reactions and physical measurement techniques. Due to ongoing chemical reactions, the test composition of the test gas is chemically changed during the measurement.

2.3.1. Electro-Chemical Electrolyte Detectors (ELD)

The electrolytes used in ELD sensors can be divided into solid state or liquid materials, which influence the cost, size, and design. Their working principle is based on the ionization of the test gas at one electrode and diffusion of the ionized gas through an electrolyte medium towards the counter electrode. For solid electrolytes, this comes with a high power consumption to heat the element to several hundred degrees Celsius.

The resulting current is proportional to the gas concentration and can be directly measured for the amperometric measurement mode (amperometry). Although these sensors use a well-established technique, they naturally suffer from large drift, especially the liquid electrolytes, which tend to dry out at operation temperatures above ambient conditions, causing large changes in sensor behavior.

2.3.2. Ionizing Methods

2.3.2.1. Flame Ionization Detectors (FID)

Flame ionization detectors measure an ion current between a hydrogen burner nozzle and a nearby collector electrode. The test gas is injected into a very hot (2500°C to 3500°C) hydrogen flame, where it is thermally decomposed and ionized. An applied voltage of a few hundred volts between the burner nozzle and collector electrode generates a measurable current.

Due to the measurement principle, FIDs are non-selective detectors and only measure the sum concentration of ionizable compounds. One of their major advantages is their applicability to a wide range of gases and gas concentrations. These include, first and foremost, the flammable gases and VOCs. However, FIDs are rather insensitive to inert gases and liquids such as H_2O, CO_2, N_2, or Ar.

2.3.2.2. Photoionization Detectors (PID)

In photoionization detectors, the hydrogen flame of FIDs is been replaced by ultraviolet (UV) light. This UV light could come from a passive (sun light) or active (for example, LED) source. PIDs are comparable to FIDs in applicability and resolution and are often used as analyzers in gas chromatographs. These instruments can work over a wide range of gas concentrations and have excellent sensitivity for VOC, which is why they are sometimes used for handheld devices. It must be noted that PID instruments are typically calibrated with Isobutylene only. Even when they give a VOC output this will only be correct for the calibration gas. To convert this to a different gas (for example, Ethanol) an individual conversation factor is needed. This factor is based on the molecular weight of the target gas and usually given by the PID manufacturer. In case the device reports in ppm, a conversation factor of approximately 10 must be used. The PID will report lower and its signal must be multiplied by 10 to make the PID device comparable.

2.3.3. Chemi-Resistive Methods

2.3.3.1. Catalytic Combustion Sensors (Pellistors)

Pellistors are catalytic sensors in which the exothermal reaction of flammable gases with oxygen is used to cause a temperature and resistance change in a platinum wire. The platinum wire acts as a heater and thermometer simultaneously and is covered in a catalytic substance. The catalyst enables the exothermal oxidation of flammable compounds, which heat the catalyst and platinum wire. This temperature change is measured as a resistance increase of the platinum wire and is proportional to the gas concentration.

Due to their chemical and physical robustness and capability to detect flammable gases, pellistors are often used in explosion-prone and safety-critical environments. A disadvantage of these sensors is their large power consumption and sensitivity to lead, sulfur, and halogen hydrocarbon poisoning. Furthermore, the lower limit of detection is relatively high (for example, 100's to 1000's ppm).

2.3.3.2. Metal Oxide Sensors (MO$_X$)

This well-known method for VOC detection has been used for years in a wide range of applications. Traditional metal-oxide sensors use an MO$_X$ material deposited onto a ceramic substrate, which leads to good performance and long life, while more modern MO$_X$ sensors take advantage of silicon micromachining to create a robust but thermally isolated micro-hotplate (MHP), resulting in extremely low power consumption, miniature size and low prices due to their small dimension and high volume production. Typical MO$_X$ materials are doped semiconducting materials such as SnO_2, WO_3, and TiO_2, etc. At elevated temperatures, gas molecules can adsorb onto the MO$_X$ surface and generate free charge carriers. The consequential resistance change can be measured at two electrodes. Hence, the sensor raw signal strongly depends on the ambient atmosphere, utilized materials, production technology, time, and temperature. All organic compounds will catalytically react on the MO$_X$ surface and cause a resistance decrease or increase, depending on the gas oxidizing or reducing behavior.

3. TVOC Detection with Renesas' MO$_X$ Gas Sensors

Metal oxide (MO$_X$) based gas sensors have been developed since the 1960's and have already been on the market for nearly 50 years. Key to this technology is the MO$_X$ chemistry as well as a well-designed MEMS structure, reliable technology, and firing process. This section provides a description of Renesas' superior MO$_X$ gas sensor technology using the ZMOD4410 Gas Sensor Module as an example.

Detailed information is given for particular critical sensor characteristics, including the following:

- Sensitivity (also referred as accuracy for a specific target gas)
- Selectivity and cross-sensitivities (sensitivity to other gases)
- Stability (long-term behavior)
- Poisoning (resistance against poisoning gases)

Gas sensors can be operated in different modes; for example, continuous temperature operation or duty cycling to reduce power. Due to optimization in each mode, the sensor characteristics are not influenced by any of the ZMOD4410 operation modes offered by Renesas.

Renesas is in a strong position to fulfill all requirements for indoor air quality (IAQ) monitoring and TVOC detection according to the UBA study[3]. Details can be found in the ZMOD4410 Datasheet and the white paper *Overview of TVOC and Indoor Air Quality*. The governmental sensor research institute Kurt Schwabe Institute (KSI) did extensive independent investigations for IAQ and Renesas' ZMOD4410 gas sensor and reported excellent conformance to the UBA study and to EPA standards. In addition to the VOCs mentioned in the UBA study, Renesas' gas sensors have also excellent sensitivity to other VOCs and even non-VOC components (for example, ammonia), which are part of IAQ.

The ISO 16000-29 standard specifies test methods for evaluating the performance of VOC detectors with different technologies. However, a calibration according to this old standard is not useful for indoor air quality measurements with metal-oxide sensors because it does not reflect the use case or the expected VOC gases and concentrations of interest. Hence, Renesas tested a large number of typical indoor VOC gases in a wide concentration range.

3.1 Sensitivity

The ZMOD4410 is designed to be an excellent sensor for all VOC compounds. There are different possibilities for describing the sensitivity to gas sensors and for performing a raw sensor signal calculation:

- Ratio of resistances
- Calculation of slopes

3.1.1. Ratio of Resistances

A very common definition of the sensitivity is the ratio R_{Air}/R_{Gas}, where the sensor's resistance in clean air (R_{Air}) is divided by the sensor's resistance at a specific gas concentration (R_{Gas}). During these tests, other parameters such as the environmental conditions do not have to change. Figure 2 and Figure 3 show an identical set of data: The raw sensor resistance and sensitivity (resistance change ratio) for the reaction over a large concentration range for the ZMOD4410 to ethanol as a VOC representative. This sensitivity description is commonly used to present the sensor signal for a specific concentration range.

---

[3] Umweltbundesamt, Beurteilung von Innenraumluftkontaminationen mittels Referenz- und Richtwerten, (Bundesgesundheitsblatt - Gesundheitsforschung - Gesundheitsschutz, 2007).
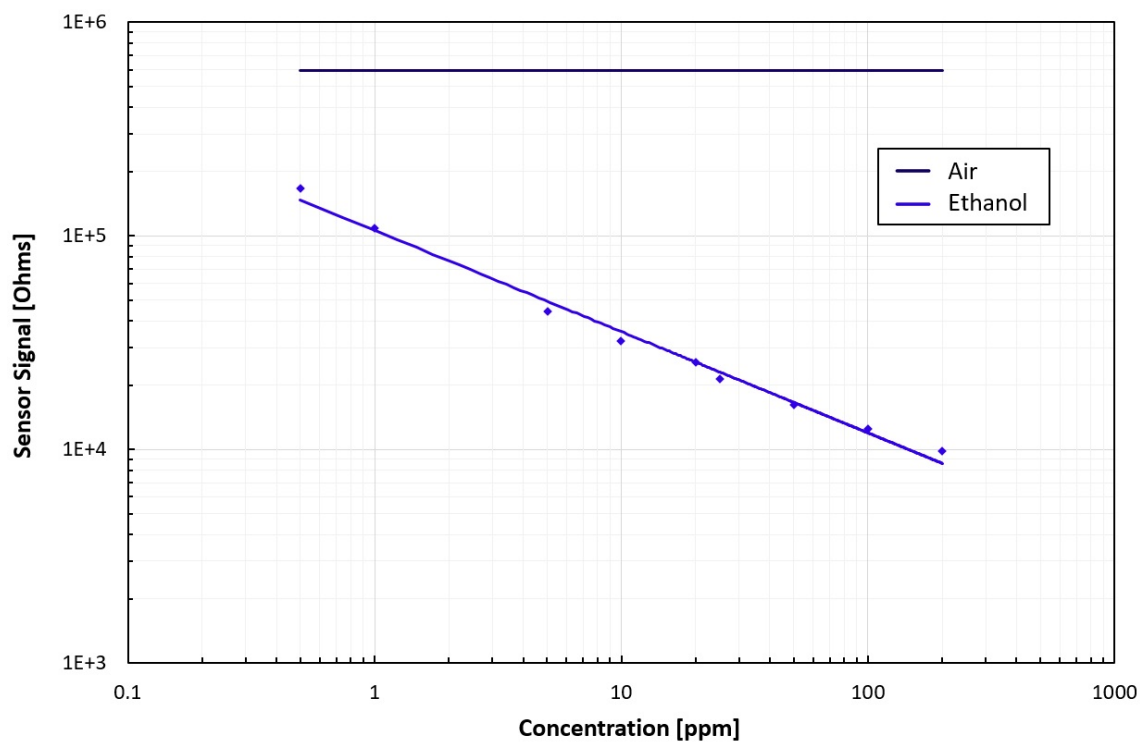
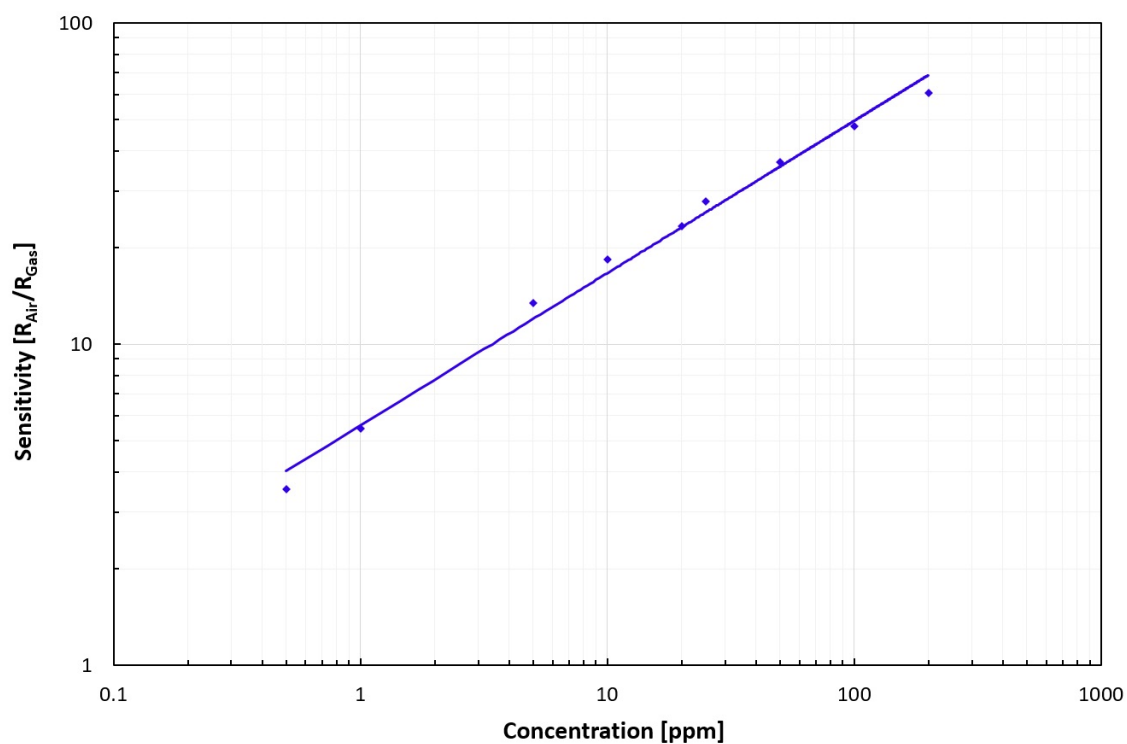**Figure 2. ZMOD4410 Resistance Response to Ethanol**

Figure 3. ZMOD4410 Sensitivity to Ethanol

3.1.2. Calculation of Slopes

The traditional mathematical function for gas sensors describe the sensor reaction with a logarithmic function. It is commonly used since the introduction of MOx gas sensors in the 1970's for a general description and mathematical modelling of the sensor behavior for concentration calculations. The sensor response to a gas is given by (Equation 2):

$$\log(R) = \log(A) - \alpha \times \log(c) \tag{Equation 2}$$

where:

R = Resistance, A = Intercept, α = Slope, c = Concentration

In this description, the slope (α) is an indication of the sensitivity. For a constant environment, α is a function of operation temperature and usually shows a maximum due to a chemical equilibrium of adsorption, reaction, and desorption.

Note that Renesas' ZMOD gas sensors use the traditional slope algorithms in their "1st Generation". The "2nd Generation" uses an AI machine learning algorithm, which is not based on slope and intercept but on intensive sensor training data using neural networks. This allows a much better accuracy and consistency for VOC concentration measurement using MO_X sensors.

3.2 Selectivity

Selectivity is a response to a target gas species while cross-sensitivities are unwanted interfering reactions. Like most other gas detection methods, MOX sensors show an interference reaction in the case where several gases are present in the ambient environment.

3.2.1. Selectivity to VOC and Non-VOC

Generally speaking, VOC is an overall name for several subclasses of different chemicals. The sensitivity towards typical air quality components[4] as well as other VOC gases and some non-organic gases is shown in Figure 4. The most common cross-sensitivities in a home environment include sulfur gases, including hydrogen sulfide (H_2S) and other volatile sulfur compounds (VSC), and humidity, although some applications will consider these gases a component of air quality. The ZMOD4410 is also able to detect safety-relevant gases for indoor air, such as carbon monoxide (CO); however, the sensor is not designed to detect these interferants reliably and therefore should not be, and is not approved for use in any safety-critical or life-protecting applications. Renesas disclaims all liability for such use.

---

[4] For more information, see the white paper *Overview of TVOC and Indoor Air Quality* located on the ZMOD4410 product page.
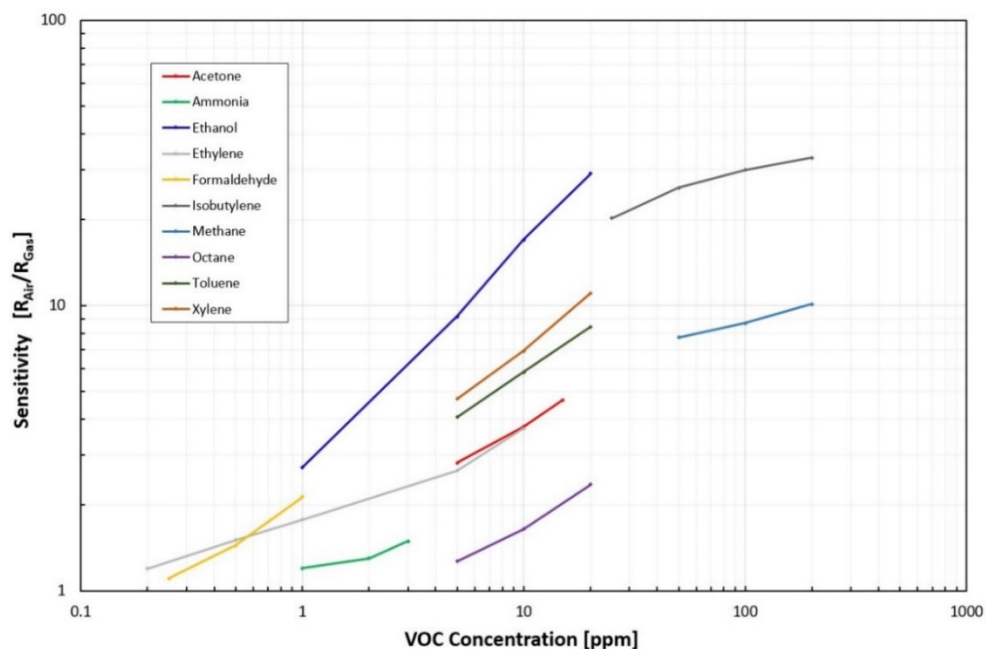
Figure 4. Sensitivity to Different VOC Gases

3.2.2. Sensitivity towards Formaldehyde

Formaldehyde (CH_2O) is also referred to as methanol and the simplest of the aldehyde molecule class. One of its main applications is use in the production of wooden products and coatings. Formaldehyde has a boiling point of -19°C and that is the reason why it usually occurs as vapor and can cause outgassing in home furniture. Due to its toxicity in the ppb range, it is one of the VOCs getting the highest concern from customers.

Although the ZMOD4410 is designed to detect all the different classes of VOC, a focus is often pointed towards formaldehyde. The ZMOD4410 can detect concentrations down to 50ppb (see Figure 5).
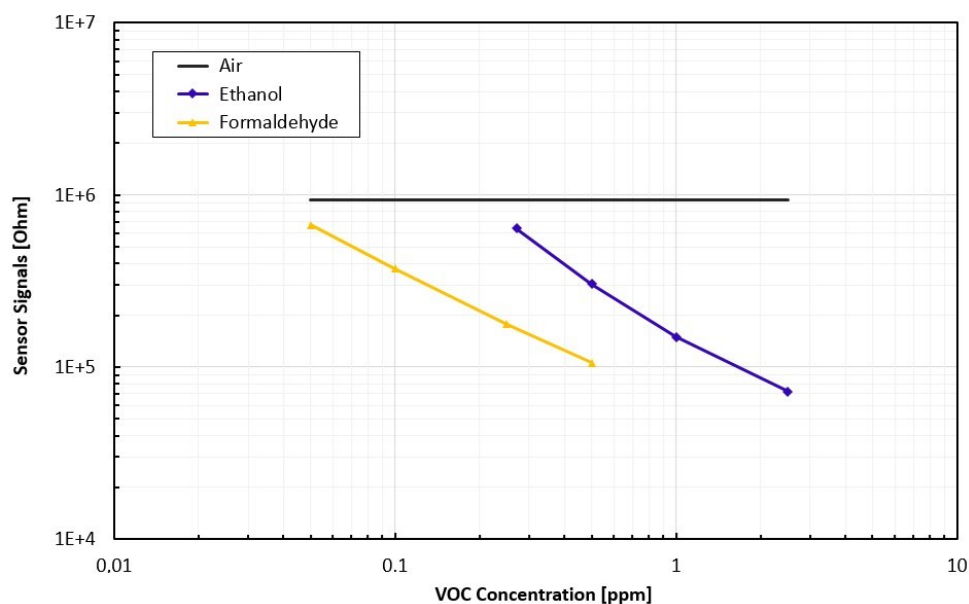

Figure 5. Sensitivity to Formaldehyde

3.3 Stability

Nearly all sensor and measurement instruments suffer from drift; in other words, shifting readings and sensitivity over time. Thus, during development, a priority must always be to minimize drift by optimizing the sensor technology itself. This includes design of materials and fabrication methods, adequate sintering technology, and optimal operation conditions. The goal must be to obtain a long lifetime while achieving high accuracy and minimizing or avoiding the need for recalibration.

Renesas has a history of developing metal-oxide materials for more than two decades. Although, the digital ZMOD gas sensor and deposition method used are more recent, it has been developed based on the experience of older analog MO_X sensors, which are still on the market and in operation for long-term testing. Figure 6 shows example resistance data for the developed MO_X material, which has been in operation for more than 16+ years for hydrogen sulfide (H_2S) detection and is still in operation. The sensor response are very similar and shows excellent sensitivity even after this long time of operation.
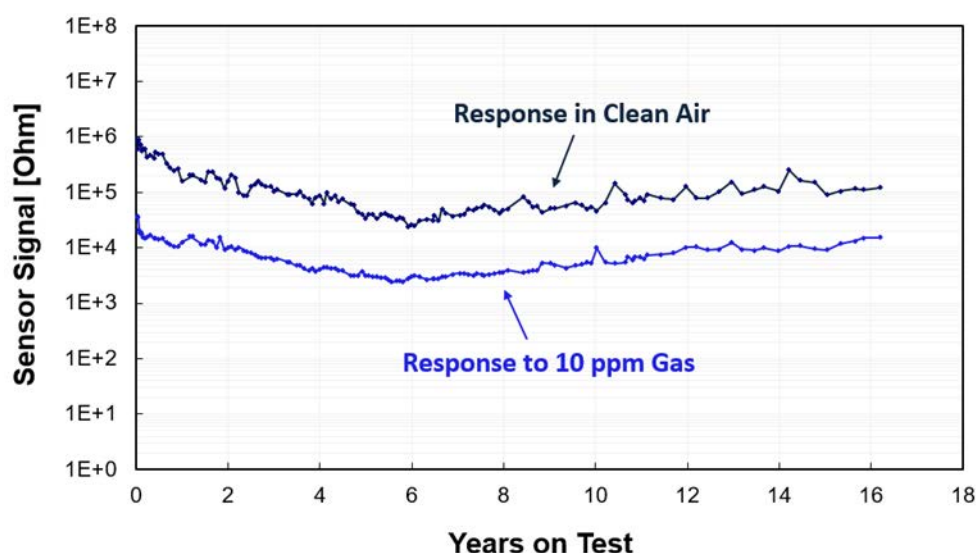

Figure 6. Example for Renesas Long-Term Stable MO_X Materials

3.4 Poison Resistance

Some gases have the ability to damage the sensor permanently. They react with the sensor surface and passivate the catalytic active centers of the metal oxides. Depending on adsorption behavior and chemical bonding, some gases desorb again at elevated temperatures. A treatment at temperatures above the operation temptation may be useful to "clean" the MO_X surface. However, thermal stress resulting from excessive cleaning may lead to long-term reduction of the sensor performance.

A common ambient gas, which passivates the MO_X surface permanently and leads to damage of the sensor, is siloxanes. These chemicals occur in several household products; for example, silicon oil, antifoaming agent, rubber materials, food preservation, personal care products, and many more. Siloxanes are VOCs that include a silicon structure; for example, octamethylcyclotetrasiloxane (D_4) has the chemical formula $C_8H_{24}O_4Si_4$. At elevated temperatures, especially above 300°C, chemical cracking takes place at the catalytic surface and silica (SiO_2) is formed[5]. Silica is a well-known sensor poison because of its glazing. Because of the wide usage of siloxanes in home environments, it is essential to prove that these VOC gases do not lead to sensor signal drift or loss in sensitivity for indoor air quality applications.

---

[5] T. Mundry, Einbrennsilikonisierung bei pharmazeutischen Glaspackmitteln - Analytische Studien eines Produktionsprozesses, PhD thesis (Berlin: Humboldt University Berlin, 1999).

Renesas' ZMOD4410 Gas Sensor Module has been exposed to different siloxanes to prove poison resistance. High concentrations of siloxanes have been applied to the metal oxide successively for several weeks to simulate the sensor module's lifetime.

Most siloxanes are noncritical and non-toxic to the environment[6] and concentrations above 0.0014ppm[7] do not represent use cases for an average indoor air contamination. See Table 2 for typical expected siloxane concentrations for indoor air[7]. Hence, applying higher concentrations yields an accelerated lifetime test and will give information on long-term behavior for MO_X sensor operation.

Table 2. Typical Expected Siloxane Concentration for Indoor Air

Chemical	Guidance Value Indoor Air [µg/m³]	Guidance Value Indoor Air [ppb]
Octamethylcyclotetrasiloxane (D_4)	7	0.57
Decamethylcyclopentasiloxane (D_5)	22	1.4

Renesas has performed several tests with multiple gas sensor modules to characterize their siloxane resistance in detail. A summary is shown in Table 3. During siloxane exposure, tests with different ethanol concentrations have been repeated to monitor the sensitivity. Figure 7 gives an example of the sensor signal change accuracy for exposures with 10ppm and 20ppm ethanol. It shows the average of 15 sensor modules working in parallel, including their standard deviation for a 25-day period of exposure to siloxanes.

Table 3. Tests Performed with Siloxanes

Chemical	Concentration [ppm]	Test Duration [days]	Total Concentration [ppm·h]	Signal Drift during Exposure [%]
Octamethylcyclotetrasiloxane (D_4)	25	25 days	15200	4.4
Decamethylcyclopentasiloxane (D_5)	25	25 days	15500	5.3

From all testing discussed above, it can be concluded that siloxanes do not harm the ZMOD4410 Gas Sensor Module over its lifetime even at concentrations much higher than expected in an indoor air environment.
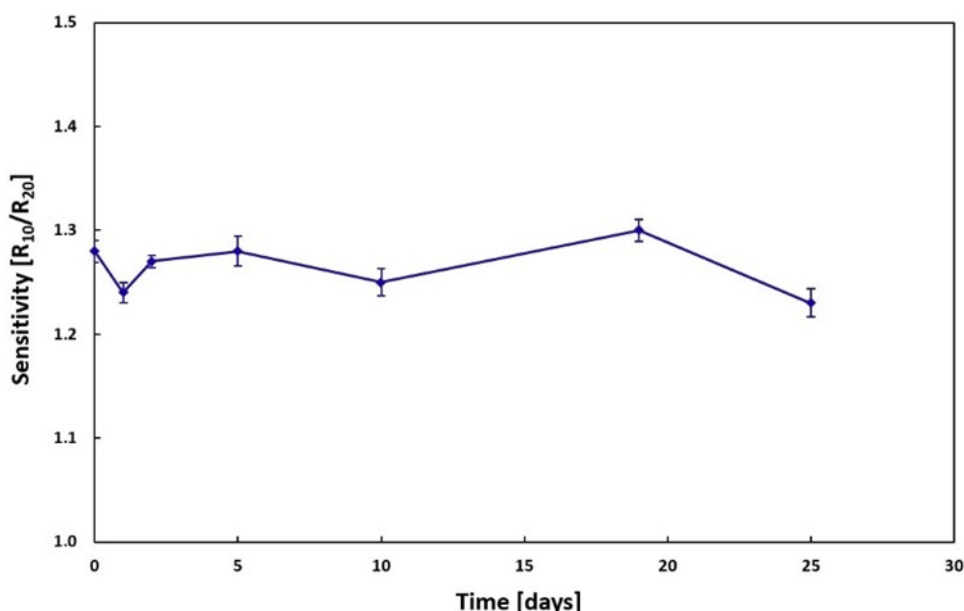

Figure 7. Sensitivity Change for the Renesas ZMOD4410 Gas Sensor Module during Siloxane Exposure

---

[6] ECCC, Report of the Board of Review for Decamethylcyclopentasiloxane (Siloxane D5) established under Section 333(1) of the Canadian Environmental Protection Act of 1999, (Ottawa, Canada: 2011).
[7] Association of Ecological Research Institutes e.V. (AGOEF), AGÖF Guidance Values for Volatile Organic Compounds in Indoor Air, (Springe-Eldagsen, Germany: 2013).

4. Revision History

Revision	Date	Description
1.02	Apr 19, 2022	▪ Updated plots with the latest measurements. ▪ Rebranded to Renesas.
1.01	Mar 4, 2019	▪ Updated with information on other Operation Modes. ▪ Added sections for formaldehyde and introduction.
1.00	Jun 1, 2018	Initial release.

IMPORTANT NOTICE AND DISCLAIMER

RENESAS ELECTRONICS CORPORATION AND ITS SUBSIDIARIES ("RENESAS") PROVIDES TECHNICAL SPECIFICATIONS AND RELIABILITY DATA (INCLUDING DATASHEETS), DESIGN RESOURCES (INCLUDING REFERENCE DESIGNS), APPLICATION OR OTHER DESIGN ADVICE, WEB TOOLS, SAFETY INFORMATION, AND OTHER RESOURCES "AS IS" AND WITH ALL FAULTS, AND DISCLAIMS ALL WARRANTIES, EXPRESS OR IMPLIED, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTIES OF MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE, OR NON-INFRINGEMENT OF THIRD PARTY INTELLECTUAL PROPERTY RIGHTS.

These resources are intended for developers skilled in the art designing with Renesas products. You are solely responsible for (1) selecting the appropriate products for your application, (2) designing, validating, and testing your application, and (3) ensuring your application meets applicable standards, and any other safety, security, or other requirements. These resources are subject to change without notice. Renesas grants you permission to use these resources only for development of an application that uses Renesas products. Other reproduction or use of these resources is strictly prohibited. No license is granted to any other Renesas intellectual property or to any third party intellectual property. Renesas disclaims responsibility for, and you will fully indemnify Renesas and its representatives against, any claims, damages, costs, losses, or liabilities arising out of your use of these resources. Renesas' products are provided only subject to Renesas' Terms and Conditions of Sale or other applicable terms agreed to in writing. No use o any Renesas resources expands or otherwise alters any applicable warranties or warranty disclaimers for these products.

(Disclaimer Rev.1.0 Mar 2020)