Postprint of: Smulko J., Trawka M., Gas selectivity enhancement by sampling-and-hold method in resistive gas sensors, SENSORS AND ACTUATORS B-CHEMICAL, Vol. 219 (2015), pp. 17-21, DOI: 10.1016/j.snb.2015.04.120

Gas selectivity enhancement by *sampling-and-hold* method in resistive gas sensors

Janusz Smulko[*], **Maciej Trawka**

Faculty of Electronics, Telecommunications and Informatics, Gdańsk University of Technology
Narutowicza 11/12, 80-233 Gdańsk, Poland

E-mails: jsmulko@eti.pg.gda.pl
*Author to whom correspondence should be addressed; Tel.: +48-58-348-6095;
Fax: +48-58-348-6373 jsmulko@eti.pg.gda.pl

Abstract: Commercial resistive gas sensors exhibit various sensitivity to numerous gases when working at different elevated temperatures. That effect is due to a change in velocity of adsorption and desorption processes which can be modulated by temperature. Thus, to reach better selectivity of gas detection, we propose to apply a known method (called the *sampling-and-hold* method) of cooling down the gas sensor in the presence of the investigated gas, and the fluctuation enhanced sensing. The adsorbed gas molecules were captured in the porous gas sensing layer and then slowly released by heating up. We observed a significant (greater than one order) change of the normalized low-frequency resistance noise during the process of slow heating up. That change was characteristic for different investigated gases. Moreover, the resistance noise reached its minimum at the temperature characteristic for the adsorbed gas. This effect can be explained by differences in the activation energy of the adsorbed gas molecules. The observed results are very promising for improving gas detection by determining the position of minimal noise intensity and can be utilized in practice.

Highlights:

- Additional information can be gathered by a single resistive gas sensor using the fluctuation enhanced sensing and a change of gas sensor working temperature
- Selectivity of gas sensor can be increased by measuring changes of resistance fluctuations when its working temperature increases after exposition to the investigated gas

Keywords: gas sensing; noise; gas sensors; fluctuation enhanced sensing.

1. Introduction

Resistive gas sensors are popular commercial sensors applied in numerous gas detection systems [1-4]. They are reliable and can work even a few years without almost any maintenance. The main driving force of improving their use is their low selectivity and sensitivity, often limiting their application to signaling a threshold crossing of the selected gas concentration. The simplest method of improving their selectivity is a temperature modulation of the gas sensing layer [5]. An improvement in gas detection can be also reached by adding some impurities activating adsorption-desorption processes [6]. These methods were investigated in various gas sensing layers [3, 7].

Another proposed method utilizes low frequency resistance fluctuations (1/f-like noise) across the gas sensing layer and is called the fluctuation enhanced sensing (FES) [8-10]. That method assures much better gas sensor sensitivity due to generation of a low frequency noise by random processes, responsible for fluctuations of the potential barrier between grains and related to adsorption-desorption processes, as observed in other grainy materials [11]. We estimated the power spectral density of generated resistance fluctuations by observing voltage fluctuations across the gas sensor biased by the DC voltage [12]. The intensity and slope of estimated power spectral density can be utilized to improve gas sensor sensitivity. Such a method was applied in practice to determine intensity of essential oil scents in aromatherapy [13].

The FES increases selectivity of gas detection as well (e.g. detection of gas mixture components by a single gas sensor [10]), but further progress is still required. That method was modified by utilizing the low frequency noise measurement after cooling down the sensor at the atmosphere of detected gas [14]. The method is called the *sampling-and-hold* FES method. The output pattern of that method is the spectrum measured at a low temperature when molecules of the detected gas are kept inside the porous gas sensing layer (adsorbed to its grains) and influence the 1/f-like noise intensity by changing the potential barrier between the grains and its fluctuations [15]. The method was applied in numerous experimental studies and the published results confirmed its usefulness in the gas sensing area [16, 17].

Consequently, we propose a modification of the *sampling-and-hold* FES method to shed light on differences in adsorption-desorption processes of various gases by applying an altered measurement procedure. The proposed modification combines the known *sampling-and-hold* FES method with activation of adsorption-desorption processes by a change of the sensor temperature. The gas molecules adsorbed to grains of the gas sensing layer require an energy sufficient to induce desorption. The presence of adsorbed gas molecules changes the potential barrier between grains and modifies the 1/f-like noise intensity. We can suppose that increasing temperature should change the low frequency noise by intensification of desorption processes and continuous release of the captured gas molecules to the moment when the gas molecules evaporate completely into the ambient atmosphere. When that process occurs, the gas sensing layer temperature should be characteristic for the adsorbed gas because it depends on its activation energy. Such an effect should certainly improve gas detection by adding this information as the input data for various detection algorithms [18, 19].

2. Measurement procedure

In this experimental study we have applied the FES method at various temperatures for the commercial TGS 816 gas sensor specimens, comprising the SnO_2 gas sensing layer. We used the procedure presented in Fig. 1. The investigated sensor was cleansed by applying overheating pulses in the atmosphere of synthetic air only. Next, after one hour of keeping the sensor in the synthetic air only and at its working temperature of 250°C, equivalent to the heating voltage of 5 V [20], the investigated gas (ammonia or ethanol) was introduced. After one additional hour the sensor was cooled down to the room temperature by decreasing its heating voltage in the ambient atmosphere of the selected gas. That stage assured adsorption of the gas molecules to the grain surface. Then, the sensor was again placed in the ambient atmosphere of synthetic air only, and was slowly heated up to its working temperature. That last phase increased the energy of the adsorbed gas molecules which were in the meantime being slowly released, and – finally – the sensor exhibited the same properties (i.e., the DC resistance, low frequency noise) as at the beginning of experiment. The sensor temperature was being raised slowly to assure stable measurement conditions of 1/f-like noise and to avoid any drifts.

3. Experimental results

Two TGS 816 type sensor specimens were used in the experiment. They exhibited different DC resistances in the same conditions due to some unavoidable technological differences in thickness of the applied gas sensing SnO_2 layer [20]. When the sensors were subjected to the presented *sampling-and-hold* procedure (Fig. 1) we observed that the sensor DC resistance preserves information about the exposed atmosphere. That result was observed for the investigated gases: ammonia (NH_3) (Fig. 2) and ethanol (C_2H_5OH) (Fig. 3). When the voltage U_H dropped below the nominal value of 5 V, and – proportionally to its value – so did the gas sensing layer temperature, the adsorbed gas molecules stayed within the gas sensing layer and changed the sensor DC resistance. That change depended on the applied ambient gas. The most intense changes of DC resistances – as a result of the applied *sampling-and-hold* procedure – were observed at $U_H \approx 3$ V (corresponding to the temperature of 160°C for the gas sensing layer) and for ammonia. It means that the temperature of 160°C is still sufficiently low to keep the adsorbed molecules at the SnO_2 grain surface. Further increasing the heating voltage results in reaching by the molecules the energy sufficient to escape the gas sensing layer and losing by the sensor its memory about being exposed to the former gas atmosphere.

The experiments were rerun a few times to check repeatability of the data. Differences between the consecutive runs have not exceeded 8%. Additionally, we have tried to determine how long the adsorbed gas molecules can be preserved within the gas sensor structure after cooling it down to the room temperature. Almost the same results of DC resistance and noise power spectral density were observed until the next day. Further prolonging that time resulted in a release of the absorbed gas molecules and slow returning to the sensor DC resistance value observed in the synthetic air, at the beginning of the experiment.

A 1 liter gas chamber was used during the experiment. The gas flow has not exceeded 0.3 l/min to avoid turbulences around the gas sensor. The measurement setup was placed in a laboratory at the atmospheric pressure and temperature of 21°C.

We have measured voltage fluctuations across the biased gas sensor simultaneously heating up the sensor to induce a release of the adsorbed gas molecules. The details of the applied noise measurement system can be found elsewhere [12]. The estimated voltage power spectral density measured at the given sensor bias DC voltage U was normalized to U^2 value, then transformed into the power spectrum of resistance fluctuations $S_R(f)$, and eventually normalized to the square R^2 of the sensor DC resistance by applying the method described in detail in literature [16]. That procedure assures that the normalized spectrum $S_R(f)/R^2$ is independent from the driving resistance connected in series with the sensor to the bias battery. The applied low noise measurement system was able to identify the 1/f-like noise generated in the gas sensor when the sensor bias DC voltage U exceeded a fraction of Volt only. For the heating voltage range $2.5\ \mathrm{V} \leq U_H \leq 5\ \mathrm{V}$ we assured that the applied sensor bias voltage was limited to the range $0.25\ \mathrm{V} \leq U \leq 5\ \mathrm{V}$. It means that the observed low frequency noise was generated within the sensor structure and the applied bias voltage was sufficiently low not to influence its temperature. The 1/f-like noise product was exposed by multiplying the quotient $S_R(f)/R^2$ by the frequency f and assuring presentation of the 1/f-like noise as a horizontal line (Fig. 4). We have observed that the 1/f-like noise dominated at the low frequency range, even up to a few kHz when the sensor was at its working (and suggested by the producer) temperature of 250°C, at $U_H = 5$ V [4, 12, 21]. At lower U_H the 1/f-like noise is buried by the thermal noise – except of the range of very low frequencies only (e.g. at $U_H = 3.5$ V the 1/f-like noise dominates only up to tens of Hz, see Fig. 4, Fig. 5) – and depends on the adsorbed molecules of the ambient gas.

The experimental data led to the conclusion that the 1/f-like noise changed its intensity due to the sensor temperature increase and this process depended on the applied gas. Such behavior should be potentially very useful for improving gas detection efficacy because it should be different for various gases. That issue can be observed more vividly by analyzing the product $S_R(f)/R^2$ measured at various heating voltages U_H and normalized to its value observed at $U_H = 5$ V. We have selected two frequencies: f = 2 Hz (Fig. 6) and f = 0.78 Hz (Fig. 7) to present the product $S_R(f)/R^2$, when the 1/f-like noise dominates at all investigated temperatures. The curves show significantly different behavior for the investigated gases: ammonia (Fig. 6) and ethanol (Fig. 7). The presented data were obtained by averaging the product $f \cdot S_R(f)/R^2$ over five frequency bins around the mentioned frequencies $f = 2$ Hz and $f = 0.78$ Hz respectively to limit the random error of the estimated power spectrum of resistance fluctuations.

Very similar shapes of the curves describing changes of the normalized product $S_R(f)/R^2$ were obtained for both investigated gases. The normalized noise intensity decreased with the temperature of the gas sensing layer reaching its minimum around $U_H \approx 4.7$ V for ammonia (Fig. 6) and $U_H \approx 4.2$ V for ethanol (Fig. 7). The rate of decreasing the noise intensity with the temperature rise was significantly different for both gases. The same experiments were repeated after a few days and we got very similar results. We have to emphasize that the observed 1/f-like noise intensity was different for both specimens of the investigated gas sensor type. It means that any practical application of the proposed method would require a preliminary calibration, as in other cases using DC resistance measurements in gas detection systems.

4. Discussion

The presented experimental results of applying the *sampling-and-hold* FES method provide an opportunity to increase selectivity of gas sensing by a single gas sensor at the cost of prolonged measurements and additional computations. We have observed a presence of minimum in the resistance 1/f-like noise intensity at the selected temperature, proportional to the applied heating voltage U_H (Fig. 6, Fig. 7). That effect can be explained by increasing intensity of desorption processes leading to a slow release of gas molecules adsorbed in the sampling phase (Fig. 1). This process reduces the 1/f-like noise till the moment when the captured gas molecules evaporate completely from the gas sensing layer. It happens at different temperatures, characteristic for the investigated gases, and can be used to improve gas detection. A further temperature raise caused an increase of low frequency noise. This effect can be explained by scaling the 1/f noise intensity linearly with the temperature when the gas sensing layer does not change its ambient atmosphere because of earlier evaporation of the captured gas molecules.

The process of releasing gas molecules starts for both gases at the heating voltage $U_H \approx 3$ V (Fig. 6, Fig. 7). We can suppose that below the temperature of 160°C, corresponding to that heating voltage, a probability of releasing the captured gas molecules is very small. The assumption of a slow release of the captured gas molecules at sufficiently low temperatures was confirmed by the fact that the same experimental results were observed even after one day of keeping the gas sensor with the “frozen” molecules at the room temperature.

The presented idea of getting information characteristic for various gases could be applied in practical gas detection systems, giving a response even within minutes. As we have seen (e.g. in Fig. 6), a change of noise intensity was observed at the heating voltage around 3 V. It means that the process of cooling down the sensor and further heating it up does not require so wide temperature range as we have applied in our experimental study. The process of relatively fast cooling and heating could be accelerated using an electronic controller (e.g. the Peltier module for cooling), using another commercial sensor having a smaller gas sensing layer volume, and limiting changes of the heating voltage to the range of 3.5÷4.5 V only. Additionally, a small gas chamber with an electric air pump would assure conditions necessary for noise measurements at the ambient atmosphere of synthetic air during heating up.

It has to be underlined that the temperature modulation of gas sensing layer was efficiently used to improve gas detection, as reported many times [3, 22-24]. Typically, we apply a stepwise change of the heating voltage to modulate the gas sensor temperature and get a sensor response in a reasonable time. We suppose that a similar procedure could be applied for the proposed *sampling-and-hold* FES procedure after necessary investigation. Thus, we could improve gas detection at a reasonable measurement time and energy consumption by utilizing a single gas sensor as reported in other gas sensing applications [25, 26]. More advanced systems would apply complex mathematical algorithms to improve detection accuracy as proposed in various gas sensing systems and to be more competitive with other methods, requiring more expensive and bulky sensors [27, 28].

5. Conclusions

In this exploratory study the DC resistance and its fluctuations were observed in TGS 816 gas sensors when the heating voltage was decreased down to zero to reach the room temperature at the presence of investigated gases, and then heated up in the ambient atmosphere of synthetic air to observe changes of resistance noise due to evaporation of the adsorbed gas molecules. The observed results confirm that the proposed modification of the well-known *sampling-and-hold* FES method reveals new information, useful for gas detection. We have observed that the product $S_R(f)/R^2$ reaches its minimum at the temperature (heating voltage U_H) which depends on the detected gas. Moreover, we can suppose that the slope determining how fast the product $S_R(f)/R^2$ changes with the temperature is characteristic for the gas preserved in the gas sensing layer. Both facts could be utilized to improve selectivity of gas detection by a single resistive gas sensor.

Acknowledgements

This work was supported by the National Science Center, Poland, number of the decision: DEC-2012/06/M/ST7/00444 "Detection of gases by means of nanotechnological resistance sensors".

References

1. N. Taguchi, Gas-detecting device, USA Patent No.: 513148631436.
2. K. Ihokura, J. Watson, The stannic oxide gas sensors. Principles and applications, CRC Press, Florida, USA, 1994.
3. G. Korotcenkov, G., B.K. Cho, Engineering approaches for the improvement of conductometric gas sensor parameters: Part 1. Improvement of sensor sensitivity and selectivity (short survey), Sens. Actuators B 188 (2013) 709–728.
4. J. Ederth, J. Smulko, L.B. Kish, P. Heszler, C.G. Granqvist, Comparison of classical and fluctuation-enhanced gas sensing with Pd_xWO_3 nanoparticle films, Sens. Actuators B 113 (2006) 310–315.
5. B. Weisz, Effect of electronic charge transfer between adsorbate and solid on chemisorption and catalysis, J. Chem. Phys. 21 (1953) 1531–1539.
6. G.J. Li, X.-H. Zhang, S. Kawi, Relationships between sensitivity, catalytic activity, and surface areas of SnO_2 gas sensors, Sens. Actuators B 60 (1999) 64–70.
7. A.P. Lee, B.J. Reedy, Temperature modulation in semiconductor gas sensing, Sens. Actuators B. 60 (1999) 55–59.
8. L.B. Kiss, C.G. Granqvist, J. Söderlund, Detection of chemicals based on resistance fluctuation spectroscopy, Swedish patent, Ser. No.: 9803019-0; Publ. No.: 513148.
9. L.B. Kish, R. Vajtai, C.G. Granqvist, Extracting information from noise spectra of chemical sensors: single sensor electronic noses and tongues, Sens. Actuators B 71 (2000) 55–59.
10. M. Kotarski, J. Smulko, Hazardous gases detection by fluctuation-enhanced gas sensing. Fluctuation and Noise Letters 9 (2010) 359–371.
11. C.G. Granqvist, S. Green, E.K. Jonson, R. Marsal, G.A. Niklasson, A. Roos & L.B. Kish, Electrochromic foil-based devices: Optical transmittance and modulation range, effect of ultraviolet irradiation, and quality assessment by 1/f current noise, Thin Solid Films, 516 (2008) 5921–5926.
12. M. Kotarski, J. Smulko, Noise measurement setups for fluctuations enhanced gas sensing, Metrology and Measurement Systems 16 (2009) 457–464.
13. M. Kotarski, J. Smulko, A. Czyzewski, S. Melkonyan, Fluctuation-enhanced scent sensing using a single gas sensor, Sens. Actuators B 57 (2011) 85–91.
14. L.B. Kish, C.G. Granqvist, R. Vajtai, Sampling-and-Hold Chemical Sensing by Noise Measurements for Electronic Nose Applications, Swedish patent, Ser. No.: 990409-5.
15. J.L. Solis, L.B. Kish, R. Vajtai, C.G. Granqvist, J. Olsson, J. Schnurer, V. Lantto, Identifying natural and artificial odors through noise analysis with a sampling-and-hold electronic nose, Sensors and Actuators B 77 (2001) 312–315.
16. H.C. Chang, L.B. Kish, M.D. King, C. Kwan, Fluctuation-Enhanced Sensing of Bacterium Odors, Sensors and Actuators B 142 (2009) 429–434.
17. H.C. Chang, L.B. Kish, M.D. King, C. Kwan, Binary Fingerprints at Fluctuation-Enhanced Sensing, Sensors 10 (2010) 361–373.

18. R.F. Machado, D. Laskowski, O. Deffenderfer, T. Burch, S. Zheng, P.J. Mazzone, & S.C. Erzurum, Detection of lung cancer by sensor array analyses of exhaled breath, American journal of respiratory and critical care medicine 171 (2005) 1286–1291.

19. P. Kalinowski, Ł. Woźniak, A. Strzelczyk, P. Jasinski, & G. Jasinski, Efficiency of linear and non-linear classifiers for gas identification from electrocatalytic gas sensor, Metrology and Measurement Systems 20 (2013) 501–512.

20. TGS 816 – product information http://www.figarosensor.com/products/816pdf.pdf.

21. L.B. Kish, Y. Li, J.L. Solis, W.H. Marlow, R. Vajtai, C.G. Granqvist, V. Lantto, J. Smulko, G. Schmera, Detecting Harmful Gases Using Fluctuation-Enhanced Sensing with Taguchi Sensors, IEEE Sensors Journal 5 (2005) 671–676.

22. M. Kotarski, J. Smulko, Fluctuation Enhanced Gas Sensing at Modulated Temperature of Gas Sensor, International Journal of Measurement Technologies and Instrumentation Engineering 2 (2012) 41–52.

23. K.A. Ngo, P. Lauque, K. Aguir, High performance of a gas identification system using sensor array and temperature modulation, Sensors and Actuators B 124 (2007) 209–216.

24. R. Ionescu, A. Hoel, C.G. Granqvist, E. Llobet, & P. Heszler, Low-level detection of ethanol and H_2S with temperature-modulated WO_3 nanoparticle gas sensors, Sens. Actuators B 104 (2005) 132–139.

25. M. Kotarski, J. Smulko, Hazardous gases detection by fluctuation-enhanced gas sensing, Fluctuation and Noise Letters 9 (2010) 359–371.

26. P. Kuberský, P. Sedlák, A. Hamáček, S. Nešpůrek, T. Kuparowitz, J. Šikula, J., & T. Syrový, Quantitative fluctuation-enhanced sensing in amperometric NO_2 sensors, Chemical Physic, (2014) doi:10.1016/j.chemphys.2014.10.021.

27. J. Wojtas, B. Rutecka, S. Popiel, J. Nawała, M. Wesołowski, J. Mikołajczyk, Z. Bielecki, Explosives Vapors–Concentrating and Optoelectronic Detection, Metrology and Measurement Systems 21 (2014) 177–190.

28. K. Dunst, G. Jasinski, P. Jasinski, Potentiometric Oxygen Sensor with Solid State Reference Electrode, Metrology and Measurement Systems 21 (2014) 205–216.

Captions to the figures

Fig. 1. Illustration of the *sampling-and-hold* FES method

Fig. 2. Changes of TGS 816 (specimen No 1) commercial gas sensor DC resistance R during heating up in the ambient atmosphere of synthetic air by increasing heating voltage U_H when the sensor was previously cooled down to room temperature in the atmosphere of synthetic air (continuous line) or ammonia 100 ppm (dashed line)

Fig. 3. Changes of TGS 816 (specimen No 2) commercial gas sensor DC resistance R during heating up in the ambient atmosphere of synthetic air by increasing heating voltage U_H when the sensor was previously cooled down to room temperature in the atmosphere of synthetic air (continuous line) or ethanol 100 ppm (dashed line)

Fig. 4. The product of power spectral density $S_R(f)$ of resistance fluctuations observed in the gas sensor TGS 816 (specimen No 1) and normalized to its squared DC resistance R^2 and multiplied by frequency f in the ambient atmosphere of synthetic air (continuous line) or ammonia 100 ppm (dotted line); the heating voltage $U_H = 3.5$ V (184°C)

Fig. 5. The product of power spectral density $S_R(f)$ of resistance fluctuations observed in the gas sensor TGS 816 (specimen No 2) and normalized to its squared DC resistance R^2 and multiplied by frequency f in the ambient atmosphere of synthetic air (continuous line) or ethanol 100 ppm (dotted line); the heating voltage $U_H = 3.5$ V (184°C)

Fig. 6. The product of power spectral density $S_R(f)$ of resistance fluctuations observed in the gas sensor TGS 816 (specimen No 1) divided by the squared sensor DC resistance R^2 at the selected frequency f = 2 Hz versus heating voltage U_H after cooling down in the ambient atmosphere of ammonia 100 ppm; the product $S_R(f)/R^2$ was normalized to its value observed at the heating voltage $U_H = 5$ V

Fig. 7. The product of power spectral density $S_R(f)$ of resistance fluctuations observed in the gas sensor TGS 816 (specimen No 2) divided by the squared sensor DC resistance R^2 at the selected frequency f = 0.78 Hz versus heating voltage U_H after cooling down in the ambient atmosphere of ethanol 100 ppm; the product $S_R(f)/R^2$ was normalized to its value observed at the heating voltage $U_H = 5$ V

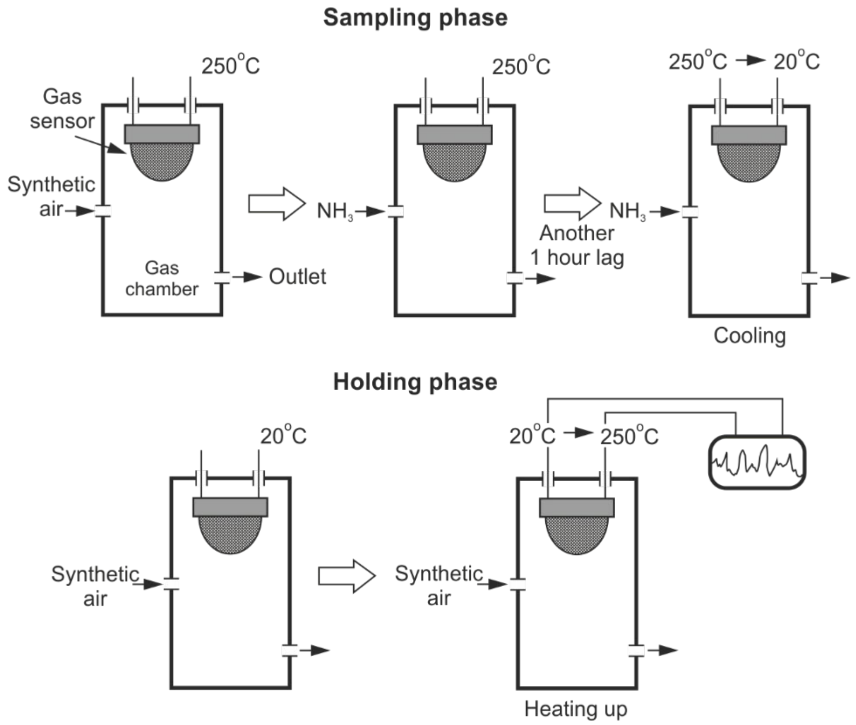
Sampling phase
250°C
Gas sensor
Synthetic air
Gas chamber
Outlet
250°C
NH3
Another 1 hour lag
250°C → 20°C
NH3
Cooling
Holding phase
20°C
Synthetic air
20°C → 250°C
Synthetic air
Heating up

Figure 1.

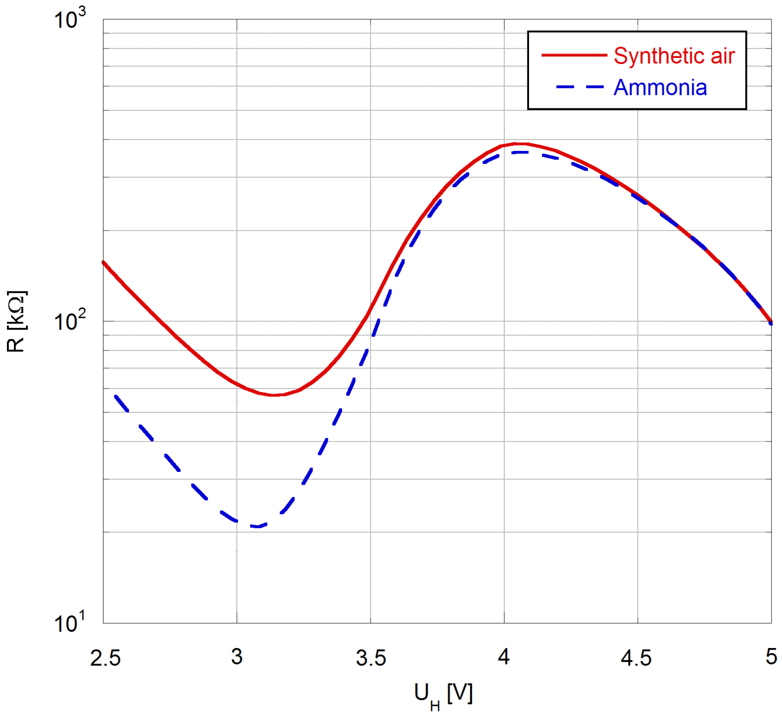

Figure 2.

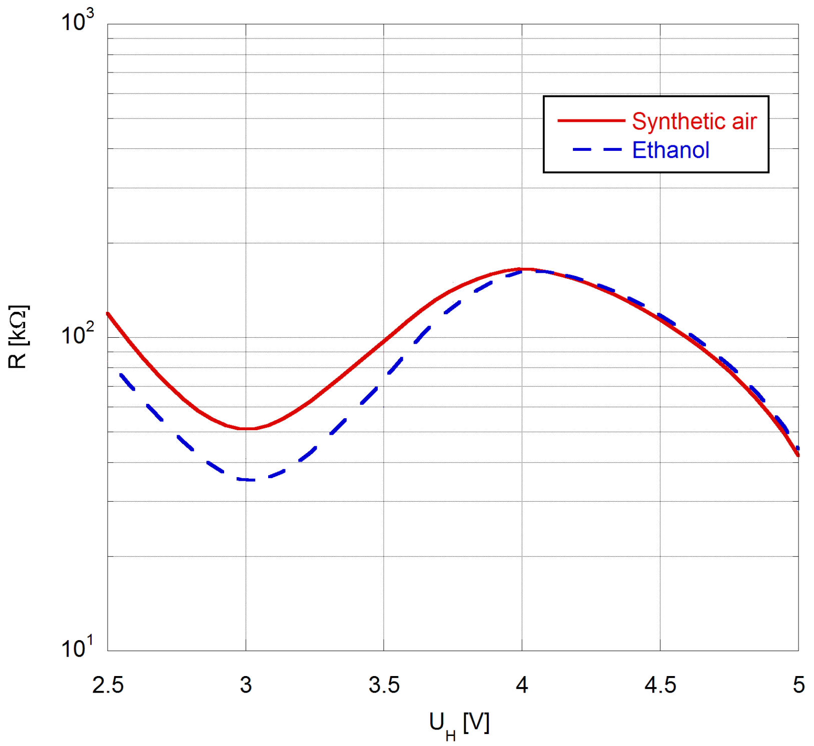

Figure 3.

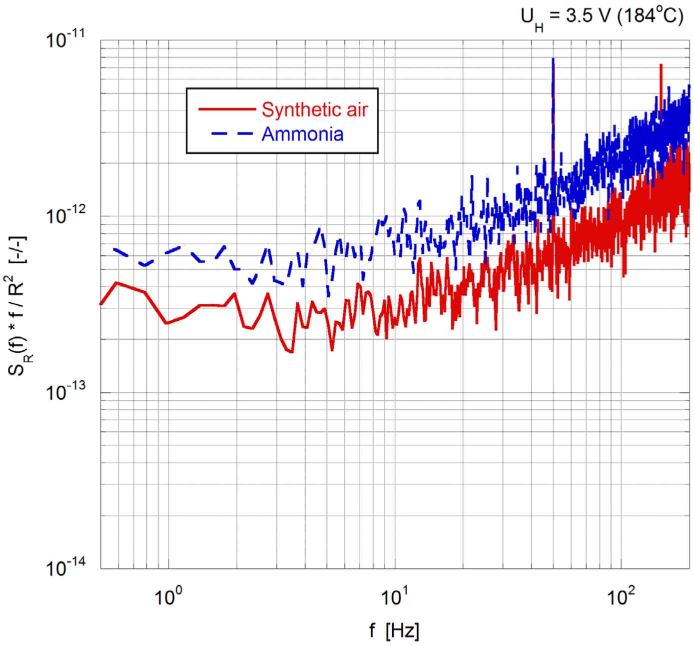
U_H = 3.5 V (184°C)
10^-11
10^-12
10^-13
10^-14
S_R(f) * f / R^2 [-/-]
Synthetic air
Ammonia
10^0
10^1
10^2
f [Hz]

Figure 4.

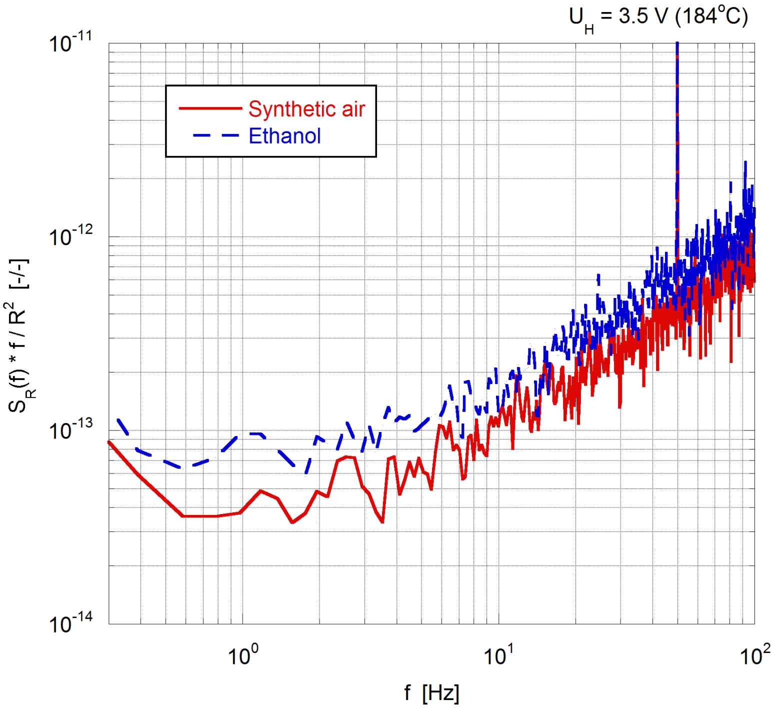
U_H = 3.5 V (184°C)
10^{-11}
10^{-12}
10^{-13}
10^{-14}
$S_R(f) * f / R^2$ [-/-]
Synthetic air
Ethanol
10^0
10^1
10^2
f [Hz]

Figure 5.

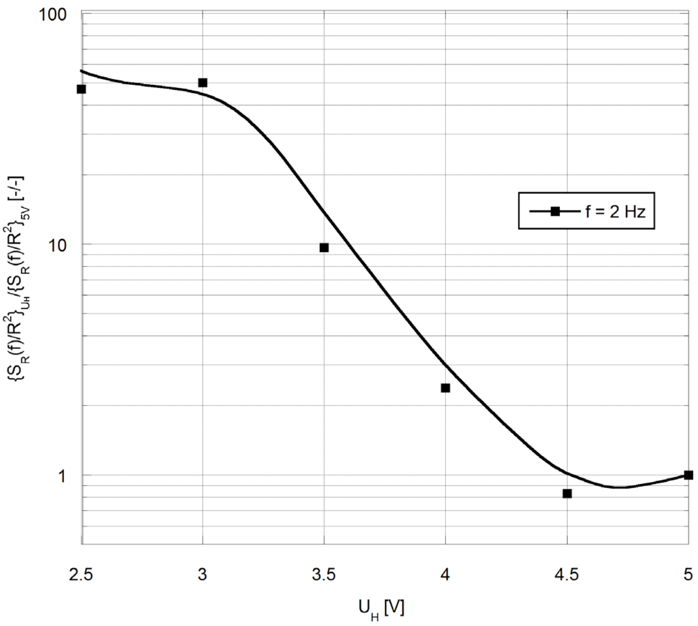

Figure 6.

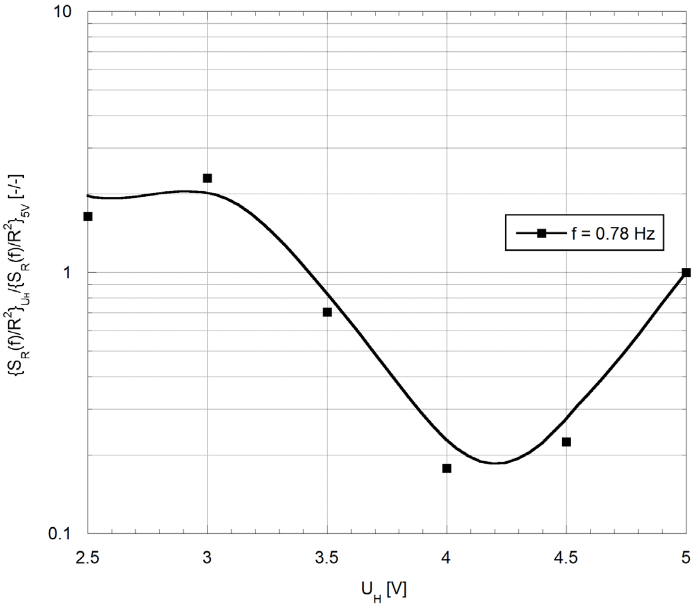

Figure 7.