Some causes of differences in the NH_3 concentration measured with the semiconductor sensors by one manufacturer

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Abstract

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The paper deals with continuous monitoring of NH_3 desorption from material used as bedding in animal breeding establishments, using five semiconductor sensors SP-53 (FIS Inc.). In lab experiments, two groups of sensors from two categories, to which the manufacturer divided the sensors based on the value of their resistance R_S, were used. Also the influence of air humidity over the values of NH_3 concentrations measured by individual sensors was monitored. The study ascertained statistically relevant differences between NH_3 concentration values measured by both groups of sensors, in the range from 8.5% to 23.1%. The biggest differences were confirmed for relative air humidity around 85%. It was verified that setting a convenient value of the load resistance R_L with regard to the R_S of each sensor, along with the selection of limited range of measured temperatures and relative air humidity, leads to satisfactory correction of the sensor output data, regardless of the division of sensors in categories pursuant to the value of their resistance in manufacturing.

Keywords: load resistence; sensor resistence; air humidity; continuous NH_3 monitoring

Semiconductor gas sensors have some characteristic properties (Carotta et al. 2007) that, to some extent, determine the way and range of their use. The output signal of semiconductor sensors manufactured using the technology of thin layers from various active materials (for instance SnO_2) depends on the concentration of measured gas, and this dependency is non-linear (Nakata et al. 2001). However, at the same time, the output signal of the sensor is also subject to some other outside influences such as temperature and, in particular, humidity of the measured gas. The principle of a semiconductor sensor with surface adsorption activity is based on the exchange of electrons caused by gas adsorption in active layer of the oxide and is based on the stripe model of the semiconductor (Henrich, Cox 1996). If semiconductor of type n and reduction gas (i.e. also NH_3) is considered, the presence of reduction gas leads to the decrease of specific resistance of the active layer and conductivity increases. With regard to the nature of semiconductor material (a metal oxide) and work-

ing environment (air), not only the oxygen, but also air humidity plays an important role during the activities of semiconductor sensor. Oxygen vacancies operate as donors and increase the surface conductivity of the active layer (Wang et al. 2010), similarly to air humidity (Barsan, Weimar 2003). It is air humidity and its influence on the measured gas concentration that is one of the often discussed disadvantages of these gas meters, if the humidity of the measured gas changes in wide interval of values (Ionescu 2000). Moreover, with this type of sensor, it is very difficult to keep one value of its resistance during its manufacturing, which is important for sensor calibration and for respecting the measuring range of humidity and temperature of the measured gas. Since the range of resistance of the manufactured sensors usually oscillates from units to tens of units of $k\Omega$, these sensors are distributed into categories according to the type of their resistance during manufacturing. The division according to resistance is also carried out for SP-53 sensors that were used in the described and discussed experiments. The manufacturer (FIS Inc., Kitazono, Itami, Hyogo, Japan) of SP-53 sensors states that the resistance of SP-53 sensors is from 20–100 kΩ, and that is why the SP-53 sensors are divided into six categories according to their resistance value. Each category is then divided into three groups. The purpose of this division is to unify the course of characteristics of individual sensor during manufacturing so that the ratio of their resistance for two fixed NH_3 concentrations, e.g. 50 ppm and 150 ppm (with same temperature and humidity of the measured air) differed at maximum by 0.1, in each group.

The paper deals with determination of differences in NH_3 concentration measured by five semiconductor sensors SP-53 (FIS Inc., Kitazono, Itami, Hyogo, Japan) during continuous monitoring of NH_3 desorption from the sample of sorption material used as bedding in animal farming. It also deals with verification of the way of correction that would ensure concordance between the values measured by all semiconductor sensors used for measuring. The paper focuses in particular on the influence of differences in resistance values of sensors on the measured NH_3 concentration values and the possibility to limit this influence. It also discusses the influence of air humidity on the measured NH_3 concentration. The stable environment is, in general, characterized by rather aggressive environ-

ment towards most used technical preparations and equipment. Air humidity combined with the concentration of various gases is one of the aggressors. In the indoor environment of stable buildings with forced ventilation, the air temperature usually does not change significantly over 24 hours. Indoor temperature is automatically controlled according to the outdoor temperature so that the stabled animals have optimal thermal conditions according to their type and category. However, air humidity is a slightly different case. Air humidity in buildings changes depending the most on current atmospheric conditions. According to the experience of authors from the measurement of this parameter in the stable environment, air humidity can change by tens of percent and move in a rather wide interval (even 35–85%) during 24 hours. These changes can then significantly influence higher uncertainty of measurements during continuous monitoring of NH_3 concentration using semiconductor sensors. This quality is typical for gas sensors of this type. That is why careful determination of thermal and humidity range of the measured gas is critical.

MATERIAL AND METHODS

All experiments were conducted under laboratory conditions. For NH_3 concentration measurement, electronic sensors developed by Ing. Miroslav Češpiva in the Research Institute for Agricultural Engineering p.r.i. (RIAE) and equipped with SP-53 semiconductor sensors (FIS Inc., Kitazono, Itami, Hyogo, Japan) were used. During experiments, the total of 5 sensors was used simultaneously equipped with five semiconductor sensors SP-53 located in one calibration and measuring case. To calibrate and recalibrate the semiconductor sensors and during all experiments, 1412 (i.e. 1312) Photoacoustic Multi-Gas Monitor (Innova AirTech Instruments A/S, Nærum, Denmark) with the 1309 Multipoint Sampler showing one-order higher accuracy of results compared to the stated sensors, was used. Multi-gas Monitor was also used as a standard during the measurements of NH_3 concentration in all experiments.

The NH_3 concentration source were samples of material used as bedding, in particular in poultry farming (wood shavings) prepared in the laboratory. For laboratory experiments, laboratory containers that were developed and tested for meas-

uring concentrations of selected gases released not only from bedding samples but also other samples (sludge, composts, excrements, fertilizers, etc.) in advance, were used. An experimental container consists of the cylindrical container and the inner cylinder. Samples to be measured are placed in a uniform layer to the container bottom. Constant flow of air through the container is maintained by an axial fan. The air, together with desorbed molecules of NH_3, is drawn off by the inner cylinder, passing by five semiconductor sensors, gas analyser filter and external temperature-humidity probe of thermo-hygrometer (all located at the outlet of the container). Thus, the requirement of the same environment for measuring NH_3 concentrations both by all sensors and gas analyser was practically met.

As a sorption material, spruce shavings with median statistic dimension of a particle amounting to 2.7 mm and finesse interval of 1.12 mm were used. The required humidity of shavings for the subsequent preparation of samples for laboratory measuring was 40% and 60%. The required initial shavings humidity was ensured by spraying distilled water, applying thorough mechanical mixing and leaving them in a closed container until the control samples show 40 ± 3% (i.e. 60 ± 2%) humidity. The required initial NH_3 concentration was ensured by adding 24% of ammonia water in the amount of 3 g per shaving sample weighing 800 g. The amount of the used ammonia water was determined experimentally so that the initial values of NH_3 concentration measured from the shaving samples approximately corresponded to the NH_3 values represented by top values of NH_3 concentrations measured in the stable buildings for animal breeding with forced ventilation. The necessary amount of shavings was weighed in a plastic bag, then ammonia water was applied to it by spraying and the material was thoroughly shaken. The prepared material was left at laboratory temperature 21 ± 1.5°C for 48 hours. During this time, it was shaken regularly. The required initial relative humidity of the air (50 ± 2%, 85 ± 2%) at the output from the experimental container was again determined experimentally, so that in the course of both series of measurements (for both lower and higher relative air humidity), NH_3 concentration was repeatedly measured from approximately 30 to 85% concentration. Axial ventilator sucked fresh air in the experimental container through the humidified paper filtration insert. Thus, the maximum, i.e. initial relative air humidity values were achieved.

Humidity of laboratory samples was determined gravimetrically. The speed of air circulating through experimental containers was measured in compliance with CSN 12 4070:1990 using anemometer for measuring low air circulation speeds. Air humidity and temperature were measured by a digital thermometer – hygrometer with external probe.

The laboratory experiments had three phases:

Phase 1. Semiconductor sensors SP-53 were divided into two groups (Group A – 2 sensors, Group B – 3 sensors). The division was carried out based on the results from the repeated 24 measurements of NH_3 desorption from the prepared samples with initial relative air humidity of 50 ± 2%. The criterion was the level of identical course of NH_3 concentrations measured by individual sensors. Thus, two groups of sensors that differed in the values of measured NH3 concentrations in the 8.5–16.6% interval (sensors from Group A always showed higher concentration, with regard to the concentrations measured by the Group B sensors and Multi-Gas Monitor) were determined. The values measured by the Multi-Gas Monitor were considered correct.

Phase 2. Group A sensors were adjusted by changing the value of the load resistor so that, for same NH_3 concentration, they provided same voltage output as Group B sensors, for relative air humidity between 30 and 50% and temperature of 21°C. Then, next series of NH_3 measurements followed.

Phase 3. Third series of NH_3 measurements for higher initial relative air humidity of 85 ± 2% followed. The course of measuring was the same as in the preceding phase, only the sensors were not adjusted for this phase in any way (the values of load resistor of used sensors were not adjusted).

All results were statistically processed using Statistica 10 (StatSoft). For dividing the sensors into groups, analysis of variance (ANOVA) was used. The presented NH_3 concentrations represent arithmetic (i.e. geometric) averages. These values were calculated in compliance with the approved handbook of quality of the RIAE measuring group, where for each measurement of NH_3 desorption from a sample during at least 24 hours, mean values were calculated from the measured NH_3 concentrations taken after 30 minutes. The values presented in the results were then calculated from all repeated measurements in the given phase. In the presented charts, only every other calculated mean value is stated for clarity reasons. The mean values

of relative air humidity (RH) were calculated using the same procedure.

RESULTS AND DISCUSSION

Measurement took place in three phases. In all phases, the NH_3 concentration measurement in the circulating air was conducted using five semiconductor sensors (marked S_1, S_2, S_3, S_4 and S_5) and, at the same time, Multi-Gas Monitor was used as standard. The source of NH_3 concentration for each laboratory measurement was the sample of 800 g of spruce shavings with 3g of 24% ammonia water. The air temperature in the laboratory was 21 ± 1.5°C; relative air humidity was 34 ± 2.7%. The speed of air circulation around the semiconductor sensors was 0.25 ± 0.06 m/s. The results of NH_3 concentration measurement calculated in individual phases of the experiment are presented in the form of arithmetic mean (AM) and also geometric mean (GM). Despite the fact that division of the measured values of NH_3 concentration does not correspond to a completely normal division of occurrence, the difference in the AM and GM values is minimum, because the obliqueness of histogram is not so big. Narrower confidence interval (CI) for GM proves more even distribution and also its lower sensitivity to deviation compared to CI for AM. The AM values and their CI are more influenced by the limit values. The used type of distribution of occurrence would better accept the calculation of mean value pursuant to other rules, for instance λ transformation (Hawkins 2005).

In total, NH_3 concentrations were measured 69 times. In each phase, there were 23 rounds; the length of each round was at least 24 hours. In **Phase 1**, the temperature of analysed air was 21.2 ± 1.2°C, relative air humidity was between 51.3 and 30.1% and the initial humidity of shavings samples (sorption material) was within 37.4–41.2%. In phase 1, it was ascertained that sensors S_1 and S_4 did not show statistically relevant differences between each other ($P < 0.05$) in the measured NH_3 concentration values, and the same applied to sensors S_2, S_3 and S_5. The average NH_3 concentrations ascertained based on values measured by S_1 and S_4 sensors, however, showed statistically relevant difference ($P < 0.05$) from NH_3 concentration measured by other sensors. This difference was between 8.5–16.6%, higher differences were ascertained at

the end of measuring. Based on these results, the sensors were divided into Group A (S_1 and S_4) and Group B (S_2, S_3 and S_5). The results of this phase are stated in Table 1.

In **Phase 2**, the temperature of analysed air was 21.5 ± 1.1°C, relative air humidity was between 49.9 and 31.7% and initial humidity of the shavings sample (sorption material) was between 39.2 and 43.4%. In phase 2, the average NH_3 concentrations ascertained based on the values measured by individual sensors (S_1–S_5) already showed statistically irrelevant differences ($P < 0.05$) between each other. Prior to this phase, the values of load resistor R_Z were experimentally adjusted for Group A sensors, because the value of NH_3 concentrations measured by Group B sensors showed a smaller error when compared with the values measured by the Multi-Gas Monitor (standard). Group A sensor was fixed at 21.5°C and air humidity of 60% in this phase of experiment. The results of this phase are displayed in Table 2.

In **Phase 3**, the temperature of the analysed air was 20.7 ± 1.5°C, relative air humidity was between 85.1 and 60.7% and the initial humidity of shavings sample (sorption material) was between 58.6 and 62.3%. Average NH_3 concentrations ascertained based on the values measured by Group A sensors showed statistically relevant difference ($P < 0.05$) from the NH_3 concentration measured by Group B sensors. The differences oscillated between 10.7 and 23.1%, they were highest in the beginning of measuring, for approx. 6 hours and they progressively decreased. In this initial interval of measuring, it was also ascertained that the values measured by individual sensors (S_1–S_5) showed statistically relevant differences between each other ($P < 0.05$). The results of this Phase can be viewed in Table 2.

Differences in concentration values measured by Group A and Group B sensors are influenced by a number of factors with differing significance. Apart from probably most discussed influence of air humidity, also distribution of sensors into groups according to the value of their resistance during production will have a significant influence. The manufacturer catalogue of the used semiconductor sensors (FIS Inc., Itami, Japan) documents this division. The division was carried out based on the measuring resistance of a sensor under 20°C temperature and 60% air humidity, for two fixed concentrations of the measured

Table 1. Mean values of NH$_3$ concentrations measured using sensors S$_1$ and S$_4$ – Group A and Sensors S$_2$ and S$_3$ – Group B (both Phase 1)

Time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
									Sensors S$_1$ and S$_4$ – Group A (Phase 1)															
AM	21.21	17.56	15.56	13.18	11.31	10.01	9.23	8.63	8.35	8.09	7.90	7.67	7.55	7.47	7.35	7.01	6.94	6.74	6.73	6.50	6.40	6.36	6.28	6.10
SEM	0.99	0.91	0.85	0.69	0.54	1.01	0.59	0.95	0.72	0.53	0.84	0.76	0.42	0.69	0.36	0.33	0.53	0.61	0.68	0.73	0.54	0.69	0.73	0.84
±Δ	0.83	0.59	0.71	0.57	0.45	0.85	0.50	0.82	0.69	0.44	0.70	0.66	0.35	0.58	0.30	0.28	0.44	0.51	0.57	0.61	0.45	0.58	0.61	0.70
CI$_{max}$	22.04	18.46	16.27	13.76	11.76	10.86	9.73	9.45	9.04	8.53	8.60	8.34	7.90	8.05	7.65	7.28	7.27	7.25	7.30	7.11	6.85	6.94	6.89	6.80
CI$_{min}$	20.38	17.04	14.85	12.60	10.86	9.00	8.73	7.81	7.66	7.65	7.20	7.02	7.20	6.90	7.05	6.73	6.39	6.23	6.16	5.89	5.95	5.78	5.67	5.40
ΔCI$_{AM}$	1.66	1.42	1.42	1.16	0.90	1.86	1.00	1.64	1.38	0.88	1.40	1.32	0.70	1.15	0.60	0.55	0.88	1.02	1.14	1.22	0.90	1.16	1.22	1.40
GM	21.06	17.49	15.54	13.39	11.30	9.96	9.22	8.68	8.31	7.94	7.86	7.65	7.54	7.44	7.37	7.03	6.87	6.71	6.69	6.46	6.38	6.36	6.25	6.06
CI$_{max}$	21.85	17.82	16.26	14.30	11.76	10.39	9.73	9.60	9.02	8.46	8.57	8.33	7.91	8.07	7.68	7.47	7.22	7.22	7.26	7.11	6.84	6.96	6.89	6.84
CI$_{min}$	20.31	17.17	14.84	12.53	10.86	9.56	8.73	7.85	7.66	7.45	7.21	7.02	7.19	6.87	7.06	6.62	6.34	6.23	6.17	5.87	5.94	5.80	5.66	5.36
ΔCI$_{GM}$	1.54	0.65	1.42	1.77	0.90	0.83	1.00	1.75	1.36	1.01	1.36	1.31	0.72	1.20	0.62	0.85	0.99	0.99	1.09	1.24	0.90	1.16	1.23	1.48
									Sensors S$_2$, S$_3$ and S$_5$ – Group B (Phase 1)															
AM	19.25	15.48	14.05	12.06	10.05	9.15	8.1	7.49	7.4	7.1	6.91	6.65	6.55	6.51	6.39	6.12	5.95	5.85	5.72	5.42	5.40	5.35	5.32	5.15
SEM	0.80	1.02	0.73	0.78	0.64	0.58	0.59	0.66	0.54	0.33	0.45	0.58	0.46	0.49	0.34	0.53	0.50	0.41	0.50	0.56	0.77	0.48	0.68	0.59
±Δ	0.96	1.22	0.61	0.65	0.54	0.49	0.49	0.56	0.45	0.28	0.37	0.48	0.39	0.41	0.25	0.44	0.42	0.34	0.42	0.47	0.64	0.40	0.57	0.49
CI$_{max}$	20.21	16.69	12.85	12.71	10.59	9.64	8.59	7.85	7.85	7.38	7.18	7.13	6.94	6.92	6.64	6.68	6.17	6.19	6.14	5.84	6.04	5.75	5.92	5.64
CI$_{min}$	18.29	14.25	13.94	11.41	9.96	8.66	7.61	6.94	6.95	6.95	6.54	6.17	6.16	6.02	6.14	5.68	5.53	5.51	5.30	4.95	4.76	4.95	4.75	4.66
ΔCI$_{AM}$	1.92	2.44	1.12	1.30	1.08	0.98	0.98	1.11	0.91	0.56	0.72	0.97	0.77	0.90	0.56	0.88	0.84	0.68	0.84	0.98	1.28	0.80	1.14	0.98
GM	19.22	15.44	12.22	10.17	8.76	8.09	7.74	7.46	7.05	6.84	6.70	6.33	6.10	5.88	5.78	5.52	5.38	5.18	5.09	4.85	4.60	4.45	4.48	4.36
CI$_{max}$	19.91	16.31	12.85	10.83	9.32	8.56	8.25	8.01	7.76	7.13	7.07	6.79	6.49	6.30	6.07	5.99	5.76	5.33	5.52	5.33	5.12	4.87	5.06	4.83
CI$_{min}$	18.56	14.62	11.61	9.55	8.24	7.57	7.26	6.95	6.54	6.56	6.34	5.89	5.72	5.49	5.50	5.09	5.03	4.84	4.68	4.41	4.31	4.07	3.97	3.86
ΔCI$_{GM}$	1.35	1.69	1.24	1.28	1.08	0.99	0.99	1.06	1.22	0.57	0.73	0.90	0.77	0.81	0.57	0.90	0.73	0.49	0.84	0.92	0.87	0.80	1.09	0.97

time – start of recording began (hours); AM – arithmetic mean of NH$_3$ concentration (mg/m^3); SEM – standard error of the mean (mg/m^3); ±Δ – estimate permissible error (mg/m^3); CI – confidence interval (mg/m^3); ΔCI$_{AM}$ – size confidence interval of the arithmetic mean (mg/m^3); GM – geometric mean (mg/m^3); ΔCI$_{GM}$ – size confidence interval of the geometric mean (mg/m^3)

Table 2. Mean values of NH₃ concentrations measured using sensors of Group A and Group B (Phase 2) and sensors of Group A and Group B (Phase 3)

Sensors of Group A and Group B (Phase 2)

Time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Group B RH	49.5	46.7	45.5	42.3	41.5	41.0	40.4	39.6	38.2	38.0	37.5	37.1	36.2	36.0	35.4	34.5	34.2	34.1	33.8	33.1	32.6	32.2	31.6	31.1
AM	19.02	15.12	12.45	10.10	8.26	7.97	7.94	7.23	7.18	6.92	6.51	6.40	6.15	5.76	5.92	5.69	5.42	5.01	4.87	4.72	4.61	4.6	4.35	4.26
SEM	0.80	1.02	0.73	0.78	0.64	0.58	0.59	0.66	0.54	0.33	0.45	0.58	0.46	0.49	0.50	0.56	0.56	0.45	0.73	0.85	0.59	0.63	0.53	0.64
±Δ	0.96	1.22	0.61	0.65	0.54	0.49	0.49	0.56	0.45	0.28	0.37	0.48	0.39	0.41	0.25	0.34	0.47	0.38	0.61	0.71	0.59	0.63	0.44	0.54
CImax	19.98	16.34	13.06	10.75	8.80	8.46	8.43	7.79	7.63	7.20	6.88	6.88	6.54	6.17	6.42	6.11	5.89	5.39	5.48	5.43	5.10	5.13	4.79	4.80
CImin	18.06	13.90	11.84	9.45	7.72	7.48	7.45	6.67	6.73	6.64	6.14	5.92	5.76	5.35	5.67	5.27	4.95	4.63	4.26	4.01	4.12	4.07	3.91	3.72
AManalyzer	16.36	12.21	9.22	7.91	7.05	6.15	5.97	5.82	5.43	5.15	4.95	4.79	4.70	4.46	4.13	3.92	3.85	3.72	3.63	3.45	3.42	3.40	3.32	3.25
Group A AM	19.29	15.44	12.21	10.21	8.87	8.22	7.95	7.47	7.10	6.78	6.80	6.41	6.03	5.96	5.81	5.58	5.35	5.18	5.00	4.77	4.77	4.58	4.49	4.33
SEM	0.67	0.58	0.64	0.62	0.78	0.66	0.75	0.73	0.75	0.64	0.97	0.49	0.66	0.73	0.49	0.45	0.58	0.37	0.63	0.51	0.42	0.53	0.49	0.45
±Δ	0.55	0.48	0.52	0.51	0.64	0.54	0.62	0.59	0.61	0.52	0.78	0.40	0.53	0.59	0.40	0.38	0.49	0.31	0.52	0.42	0.42	0.44	0.49	0.38
CImax	19.84	15.92	12.73	10.72	9.51	8.76	8.57	8.06	7.71	7.30	7.58	6.81	6.56	6.55	6.21	5.96	5.84	5.49	5.52	5.20	5.20	5.02	4.90	4.71
CImin	18.74	14.96	11.69	9.70	8.23	7.68	7.33	6.88	6.49	6.26	6.02	6.00	5.50	5.37	5.41	5.20	4.86	4.87	4.48	4.36	4.36	4.14	4.08	3.95

Sensors of Group A and Group B (Phase 3)

Time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Group B RH	84.5	79.2	76.2	72.4	71.3	69.8	68.3	68.1	67.9	67.5	67.0	66.8	66.5	66.1	65.2	64.3	63.5	63.2	63.0	62.5	62.4	62.1	61.7	61.2
AM	36.21	28.09	23.93	22.51	20.82	18.47	18.05	16.82	16.17	15.96	15.29	14.98	14.88	14.51	14.02	13.83	13.72	13.58	13.26	13.10	13.02	12.95	12.88	12.68
SEM	0.82	0.75	0.80	0.73	0.79	0.72	0.69	0.68	0.67	0.62	0.60	0.52	0.53	0.49	0.47	0.44	0.41	0.38	0.42	0.40	0.36	0.38	0.35	0.36
±Δ	0.68	0.63	0.67	0.61	0.66	0.60	0.57	0.57	0.56	0.52	0.50	0.43	0.44	0.41	0.39	0.37	0.34	0.33	0.35	0.32	0.19	0.20	0.19	0.19
CImax	36.88	28.63	24.57	23.11	21.48	19.07	18.63	17.39	16.73	16.48	15.79	15.41	15.32	14.92	14.41	14.20	14.06	13.91	13.61	13.43	13.21	13.15	13.07	12.87
CImin	35.52	27.37	23.23	21.89	20.16	17.87	17.47	16.25	15.61	15.44	14.79	14.55	14.44	14.10	13.63	13.46	13.38	13.25	12.91	12.77	12.83	12.75	12.69	12.41
Group A AM	41.32	34.31	30.06	27.63	26.52	24.02	22.10	20.36	19.25	18.62	18.26	18.02	17.63	17.10	16.70	16.31	16.09	15.87	15.32	15.10	14.83	14.62	14.42	14.28
SEM	0.89	0.82	0.82	0.75	0.72	0.71	0.68	0.67	0.66	0.63	0.64	0.55	0.53	0.49	0.49	0.48	0.44	0.44	0.42	0.40	0.39	0.37	0.36	0.35
±Δ	0.72	0.69	0.69	0.63	0.60	0.57	0.57	0.50	0.55	0.53	0.54	0.46	0.44	0.43	0.41	0.40	.38	0.37	0.33	0.33	0.33	0.31	0.3	0.29
CImax	42.02	35.11	30.69	28.23	27.10	24.57	22.67	20.92	19.80	19.15	18.80	18.48	18.07	17.53	16.72	16.70	16.47	16.24	15.63	15.43	15.15	14.93	14.72	14.55
CImin	40.58	33.61	29.31	26.97	25.90	23.43	21.53	19.80	18.70	18.09	17.72	17.56	17.19	16.67	16.29	15.91	15.71	15.50	14.97	14.77	14.5	14.31	14.02	13.84
AManalyzer	21.11	16.99	13.26	11.27	10.21	8.96	8.21	7.87	7.20	6.86	6.39	6.18	5.80	5.71	5.62	5.26	5.13	4.85	4.53	4.33	3.98	3.84	3.72	3.58

AManalyzer – average mean of NH₃ concentrations measured using multi-gas analyser (mg/m³); RH – air humidity; for other abbreviations see Table 1

gas (i.e. NH$_3$), for instance 50 and 150 ppm. The difference in the ratios of sensor resistance (R_S) oscillates for pre-selected sensors and while two concentrations are applied, e.g. (R_{150ppm}/R_{50ppm}), within the range of one tenth. Dividing the used sensors in Groups A and B based on measurements carried out in Phase 1 corresponded to two neighbouring categories of sensor resistance values (40–53 kΩ, 53–70 kΩ). Value R_S has a significant influence on determination of the R_Z sensor load resistor resistance value, and therefore, also on the value of the sensor output signal (which consists of voltage taken from R_Z). By convenient choice of R_Z with regard to R_S, the output sensor signal can be influenced up to a point. That was applied to correct the output voltage of Group A sensors after Phase 1. Resistances R_Z of Group A sensors were adjusted to a value of 5.1 kΩ (the original value was 6.2 kΩ). So that their output course depending on the NH$_3$ concentration was almost identical (for the same temperature and humidity of the analysed air containing NH$_3$ molecules) with the Group B sensors. With adjusted Group A sensors, 23 rounds of NH$_3$ concentration measurements were carried out during at least 24 hours (Phase 2). The results stated in Table 2 clearly show that the measured concentrations were basically identical for all five semiconductor sensors. Careful experimentation with R_Z value while limiting the range of temperatures and humidity of analysed air can achieve significant limitation of the influence of temperature and humidity of the analysed air on the sensor output voltage value. Therefore, it can be observed that sensor correction with regard to temperature and humidity is more efficient when the range of temperature and humidity of the measured gas is narrowed, too. The problem of setting working conditions of semiconductor gas sensors, their calibration and or recalibration was addressed by many authors (Tomic 2004; Kamionka 2006; Massson 2015). Too big difference in R_S sensor resistance values is a limiting element when creating for example sensor field or matrix. In these applications, sensors of the same qualities must be used. If there is a wider range of resistance, it is difficult to make a correction to the same sensitivity, which is also a problem for electronic noses or tongues. Too variable resistance of sensors is most often connected with differing qualities of the sensors active layers, which is also obvious in other properties of the sensor.

To prove the aforementioned influence of air humidity on the NH$_3$ concentrations measured by the used semiconductor sensors, Phase 3 was carried out (Table 2). Here, relative air humidity during 24-hours measurements oscillated between 85.1 and 60.7% and the value of load resistance R_Z was not experimentally adjusted to these conditions for any of the five used sensors. The results clearly show higher difference in the measured NH$_3$ concentrations between sensors in Group A and B than in Phase 1 (also without R_Z adjustments). Higher air humidity in the beginning of the measurement (approximately first 6 hours) will probably have a rather significant influence not only on the differences in the NH$_3$ concentration values measured by each group of sensors, but also on the differences between individual sensors. The results displayed in Table 4 clearly show higher error in the NH$_3$ concentrations measured by the sensors compared to NH$_3$ concentrations measured by the Multi-Gas Monitor (standard), which, among other things, compensates the measured data to the current humidity of analysed air. In case of the semiconductor sensors of the used type, higher air humidity (i.e. higher number of molecules included in it) causes increased conductivity of the sensitive sensor layer and the sensor gives higher NH$_3$ concentration value (Hanh 2003; Pavelko 2012). This is not the only cause of this occurrence that is present in various levels in all sensors of this type. Also the type of material used for the sensitive (detection) sensor layer and size of its particles, which are, however, technological matters influence the output sensor value (Korotcenkov, Cho 2009).

CONCLUSION

Based on the executed experiments and study of related literature, the following can be observed:
– Setting a convenient R_Z value with regard to R_S for each semiconductor sensor SP-53 along with selection of a limited range of measured temperatures and relative humidity leads to satisfactory correction of the sensor output value and concurrence in the measured values of NH$_3$ concentration by multiple sensors can be achieved regardless of the division of sensors in categories according to the value of their resistance during manufacturing.
– With the limitation of the range of temperature and relative humidity of the analysed air, the influence of temperature and humidity over the re-

sulting value of concentration provided by SP-53 sensor, decreases, too.

– Error of the output value of NH_3 concentration measured by semiconductor gas sensor SP-53 is caused by the humidity of the analysed air.

– The influence of humidity of the analysed air on the output value of the SP-53 sensors can be corrected significantly.

Despite their simple character, this type of gas sensors is capable to rather well react to the changes in NH_3 concentration. This is documented also by the trend of change in NH_3 concentration in time measured by SP-53 sensors, which was in all measurements almost identical to the trend of decrease in NH_3 concentrations measured by Multi-Gas Monitor. This type of meter has one-order higher accuracy than the used sensors. One of the prerequisites for obtaining the values of concentration with the minimum error possible is good setting of these types of semiconductor sensors to the humidity and thermal conditions of the analysed air. Thus, the main advantage of this type of sensors can be leveraged – their convenient price, reasonable life cycle and minimum maintenance.

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