

The comparison of two types sensors for ammonia emission continual measurement

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ABSTRACT: Measurement of the ammonia emissions by two different types of sensors (PHOTO ACOUSTICS analyzer INNOVA and SOLID STATE sensor SP-53) was carried out in laboratory with one material of litter, wood-shavings (with dry or wet material). The initial ammonia concentration and humidity of material were changed. The output data of these sensors were continually saved and processed. A small difference was found out between the output data of these sensors. The difference depends not only on ammonia concentration and humidity of material but also on the duration time from the beginning of measurement. All experiments of ammonia concentration were carried out with three initial values of humidity and ammonia concentrations within used material. The decrease of ammonia concentration (its velocity) in investigated material has been measured with laboratory device and registered for twelve or more hours during each experiment.

Keywords: ammonia emissions; solid state sensor; litter; wood-shavings

Ammonia (NH_3) is an important substance playing a vicious role in the nitrogen cycle. Agricultural NH_3 emission has become one of the major worldwide air pollution problems. Nowadays it has enticed more and more attention from the legal and public. VAN DER HOEK (1998) estimated that 80–95% of the total emission in Europe issues from agricultural practices (animal manure contributes over 80% and less than 20% comes from fertilizer use). High concentrations of NH_3 inside the animal buildings also represent health hazards for humans and animals (REECE et al. 1980). The concentrations NH_3 20–40 ppm (it is approximately 14.7 to 29.4 mg/m³ of air) brings e.g. increase for example respiratory diseases as sneezing, pneumonia etc. with comparison of lower concentrations of NH_3 at level 5–15 ppm.

The understanding and control of NH_3 's origin and the ability to control NH_3 in animal facilities is done by sampling and measurement techniques, including suitable sensors for ammonia measuring, instruments and procedures (JELÍNEK, PECEN 2003). Furthermore technical difficulties in field sampling and measurement require more careful study. To obtain good information about NH_3 in animal facilities, suitable measurement techniques

must be adopted and one or more measuring variables have to be chosen depending on measurement objectives. To obtain precise information about atmospheric NH_3 concentrations inside and outside animal buildings, measurement of concentrations at required locations is indispensable while all the other variables are optional (they are relatively less important). To obtain NH_3 emission from animal building or facilities, the measurement of NH_3 concentration difference between the outgoing and incoming air is essential along with the air exchange rate.

Most NH_3 concentration measuring devices offer direct reading in volumetric concentrations. Mass concentrations, however, are required to calculate NH_3 emissions. It is known that the volume of gas depends on temperature and pressure and is not constant and it is possible to convert volumetric concentration into mass concentration.

MATERIAL AND METHOD

All experiments were carried out with one material, wood-shavings. Two values of its humidity were used (9–10% or 17–18%) and three values the initial ammonia concentration of the samples mate-

Supported by the Czech University of Agriculture in Prague, Project CIGA No. 31120/1313/313131, and by the Ministry of Agriculture of the Czech Republic, Project QF 3140.

rial. The required initial ammonia concentration in samples was prepared by adding of NH_3 ammonia water (with concentration 24%), 1.5 g; 3 g or 6 g, respectively. The initial mass each sample of wood-shavings was 600 g. The samples were placed into the container as shows Fig. 4. This container was connected to the air flow inlet (with small velocity of air jet). The air flays through the container and its output is connected with gas sensors case. The same five gas sensors SP-53 were placed in one case as in shown in Fig. 5. The air samples for gas analyzer INNOVA were taken from this case. The time of sampling was two minutes and data from all gas sensors and the gas analyzer were saved in computer's. Each experiment has been running for twelve hours at least. The longest time of one measuring was thirty six hours.

Gas analyzer and Photo Acoustic Spectroscopy (PAS)

The basic principle of this method is following. The gas to be measured is irradiated by intermittent light of pre-selected wavelengths. The gas molecules absorb some of the light energy and convert it into an acoustic signal that is detected by a microphone as shows Fig. 1. These non-dispersive infrared analyzers measure the spectral absorption of a gas at one spectral band of the IR spectrum. The sensor consists of an electro acoustic element

connected to a Kundt's tube. The PAS instrument can measure multiple gases. When the gas samples are drawn from ambient air around the analyzer, the measurement time is maximum about 30 s for one gas or water vapour. Increasing the length of the sampling tube increases the measurement time. The PAS requires relatively high investment and it is subject to interference of water at high relative humilities. It is the fact that the PAS requires less frequent calibration as compared with NO_x analyzers. There are few types of these instruments and one of them is INNOVA.

Solid state sensors

The solid state (electronic) gas sensor is a relatively new and young measurement instrument and method. It is designed as a result of the semiconductor technology boom that is used for manufacturing electronic sensors of this type. These sensors are used for detecting and concentration measure many toxic gases, not only NH_3 concentration as write PECEN (2005). The basic principle of these sensors is the change of their conductivity depending mainly on interaction of measured gas and sensitive material (the layer on the sensing element) of the sensor. Semiconductor compounds electrical properties depend on the composition of the surrounding atmosphere. Since 1962 year, this effect has been used to develop of conductometric

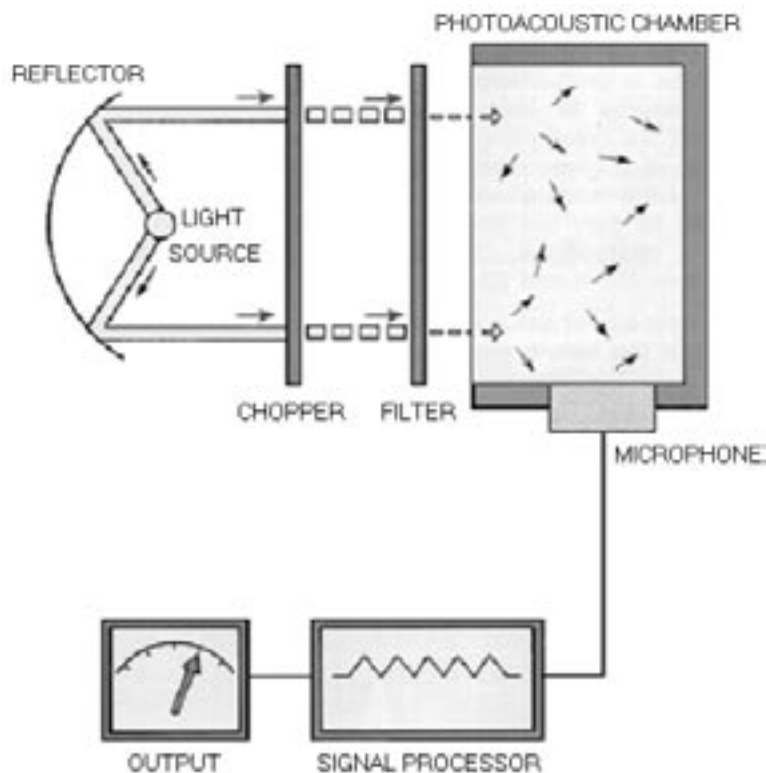


Fig. 1. Principal scheme the typical set-up of PAS method is presented. The "own" sensor represents photoacoustic chamber and microphone. Next parts of this set-up are used for example to resolve the radiation and its modulation (chopper) include the signal processing. The optical filters can be mounted on a mechanical unit to allow detection of different gases in a sample

gas sensors using thin films or porous ceramics of n -type semiconductor oxides, such as SnO_2 or ZnO . However, the gas detection mechanism is unspecific (for mentioned materials). Nowadays new materials with higher sensitivity were invented as referred by LAUQUE et al. (2004).

Commonly there are several advantages of solid state sensors as simplicity, quick response, low price, low production costs, long life and etc. Their disadvantages are insufficient accuracy, drift, big influence humidity and temperature of the gas on concentration value of measured gas.

At present, many solid state sensors are based on use micro hotplate that creates "sensing element" of sensor. This is the principle of used gas sensor SP-53 from Japan company FIS. Figs. 2 and 3 show more details about this type of gas sensor. Sensing element is kept at higher temperature (about 400°C , it depends on kind of sensitive material) and it has to be adjusted on constant value because the temperature changes bring nonlinear changes of gas concentration measured through the conductivity changes of the sensor. A serious problem of solid state gas sensors is their strong dependence on surrounding conditions, especially temperature and humidity. The resistance characteristic of gas sensor with SnO_2 represents the sensor's humidity-dependent zero point on humidity (HORN, CZAJOR 2002). Authors of this paper derived new model describing the influence of temperature and humidity on the zero point of semiconductor gas sensor and the known effect that sensitivity increases with higher humidity is implicitly considered.

There are several advantages of solid state NH_3 gas sensors as simplicity, quick response, low price, automatic measurement, long life and etc. Their disadvantages are: insufficient accuracy, drift, big influence of humidity and temperature of the gas

on concentration value of measured gas. The most important disadvantage of gas sensors with SnO_2 is impossibility of their use for different gases. It may be reduced by the use of sensor matrix which contains the array of sensors with different sensitivities to particular gases. Second problem, nonlinearity of these sensors is partly solved by another method of calibration curves (ZAKRZEWSKI, DOMANSKI 2002). The proposed method depends on the fact that not the sensitivity but the conductivity of the sensor is a measure of the gas concentration. This method was used on commercially produced solid state sensors of Figaro company.

RESULTS AND DISCUSSION

All above mentioned experiments were carried out in series and they were statistical processed (into a form tables for each initial value ammonia concentration and for two values of material humidity). The decrease of initial ammonia concentration in sample material was investigated in relation with time dependence. The humidity of wood-savings was taken as the parameter. Tables 1 and 2 show the basic relation between the quantities mentioned above and one value of initial ammonia concentration (from three in all series) in wood-savings. This value of ammonia concentration is very often presented in animal housing facilities. The other two values of initial ammonia concentration in the same material were processed by the same way onto form tables but they are not presented in this paper. The curve character shown in these tables is similar as in Tables 1 and 2. In any case this data describing the decrease of initial ammonia concentration measured by INNOVA should be taken as "the etalon" for the comparison with the data measured simultaneously by five solid

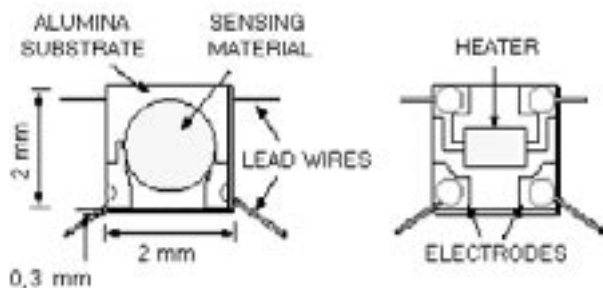


Fig. 2. Physical dimensions of the sensors. The gas sensitive material is formed on small alumina substrate. A thick film heater of ruthenium-oxide is printed on the reverse side of the substrate a placed in the housing

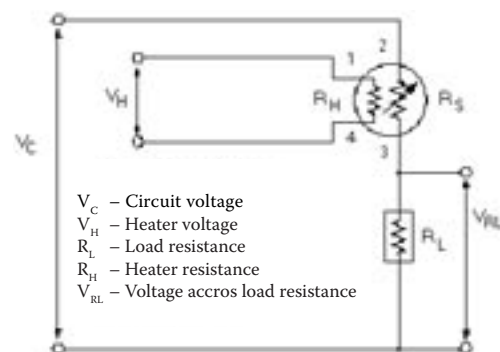


Fig. 3. Basic operating circuit for this model. The change of the sensor resistance R_S is obtained as the change of the output voltage across the resistor R_L . The SP-53 gas sensor is a tin dioxide semiconductor with good sensitivity to low concentration of ammonia

Table 1. Values of ammonia concentration in dry wood-shavings of humidity of 9–10% and its changes during experiment. Five same sort sensors SP-53 were placed in one case and the input sampling air into INNOVA was taken from this case too. The line seven means the different between the maximum and the minimum value of ammonia concentration from all five sensors. The line eight means the arithmetic average from values of all SP-53. The ninth line shows the ammonia concentration values measured by INNOVA and last row shows the rate these values for both types of sensors

	Hour												
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
Ammonia concentration measured by FIS sensors SP-53 (mg/m ³)	S _A	21.5	17.8	16.0	13.7	11.6	10.2	9.3	8.3	8.2	7.9	7.8	7.7
	S _B	19.3	14.9	12.2	10.3	9.1	8.2	8.0	7.2	7.0	6.7	6.6	6.4
	S _C	19.4	14.7	11.7	9.8	8.5	8.1	7.7	7.1	6.9	6.6	6.3	6.2
	S _D	21.0	17.6	15.2	12.5	11.2	9.9	9.3	8.4	8.1	7.9	7.9	7.6
	S _E	19.7	15.3	12.6	10.4	9.2	8.3	7.8	7.5	7.1	6.8	6.3	6.3
Min-max (mg/m ³)		19.3–21.5	14.7–17.8	11.7–16.0	9.8–13.7	8.5–11.6	8.1–10.2	7.7–9.0	7.1–8.4	6.9–8.2	6.6–7.9	6.3–7.9	6.2–7.7
Average concentration S _A –S _E (mg/m ³)		20.2	16.1	13.5	11.3	9.9	8.9	8.0	7.7	7.4	7.2	7.2	6.8
INNOVA (mg/m ³)		8.4	6.8	5.7	5.0	4.5	4.1	3.7	3.3	2.9	2.7	2.5	2.4
INNOVA/average concentration S _A –S _E (–)		0.42	0.42	0.42	0.44	0.45	0.45	0.43	0.41	0.39	0.37	0.36	0.35

Table 2. The values of ammonia concentrations in wet wood-shavings of humidity of 17–18% and their changes during the experiment (description of data in individual lines is equivalent to Table 1)

	Hour												
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
Ammonia concentration measured by FIS sensors SP-53 (mg/m ³)	S _A	14.8	12.3	9.6	9.1	8.4	7.6	7.2	7.0	6.5	6.2	5.9	5.8
	S _B	12.0	9.5	7.8	6.7	6.3	6.0	5.5	5.3	4.8	4.5	4.1	4.0
	S _C	11.6	9.0	7.8	6.7	6.4	5.8	5.6	5.3	4.6	4.3	3.9	3.6
	S _D	14.0	11.8	9.7	8.8	7.9	7.3	7.2	6.9	6.3	6.2	5.9	5.7
	S _E	12.0	9.8	7.9	6.8	6.4	6.0	5.5	5.1	4.7	4.1	4.2	4.0
Min-max (mg/m ³)		11.6–14.8	9.0–12.3	7.8–9.7	6.7–9.1	6.3–8.4	5.8–7.6	5.5–7.2	5.1–7.0	4.6–6.5	4.1–6.2	3.9–5.9	3.6–5.8
Average concentration S _A –S _E (mg/m ³)		12.9	10.5	8.6	7.6	7.1	6.5	6.2	5.9	5.4	5.1	4.8	4.6
INNOVA (mg/m ³)		5.8	4.8	4.1	3.6	3.2	3.0	2.6	2.4	2.1	2.0	1.9	1.8
INNOVA/average concentration S _A –S _E (–)		0.45	0.46	0.48	0.47	0.45	0.46	0.42	0.40	0.40	0.39	0.39	0.39



Fig. 4. View of the laboratory device. The big plastic container has inside a material of the litter, wood-shavings (see the container in the middle). Another container, on the table before a fume chamber, shows the measuring sensor. It is placed on the top of the container. The workplace involves measure four samples at this time



Fig. 5. Housing of two sensors in one case is at front. Two small white boxes on left part in the figure consist auxiliary electronic circuits of the sensors. The case is for housing one sensor and next two empty case for five sensors you can see at the back the figure. The case with five sensors was used for their calibration. Standard measurement of ammonia concentration is done with two sensors in one case

state sensors SP-53. The accuracy of the INNOVA is better than the SP-53 gas sensors and INNOVA sensitivity is approximately ten times higher than the SP-53.

Figs. 6 and 7 show the record of this conjoint measure. The curve obtained from INNOVA is the lowest thick line in above mentioned Figs. 6 and 7. Tables 1 and 2 (Figs. 6 and 7 too) show the difference between values of measured ammonia concentration. This difference has been slightly changing during measurement for all SP-53 gas sensors. From this point of view there are “two”

groups of SP-53, as shown in Figs. 6 and 7. First group consists of two sensors ($S_A + S_D$) and second group of sensors ($S_B + S_C + S_E$). It seems to exist a difference between “two” groups of SP-53 gas sensors that is caused by manufacturing tolerance of gas sensors including their calibration process. The influence of right value the resistor R_L (Fig. 3) and its setting up is very important.

The bigger difference in measured data is between the SP-53 gas sensors and the INNOVA analyzer as shows in Figs. 6 and 7. This different has been changing during measurement. The tenth

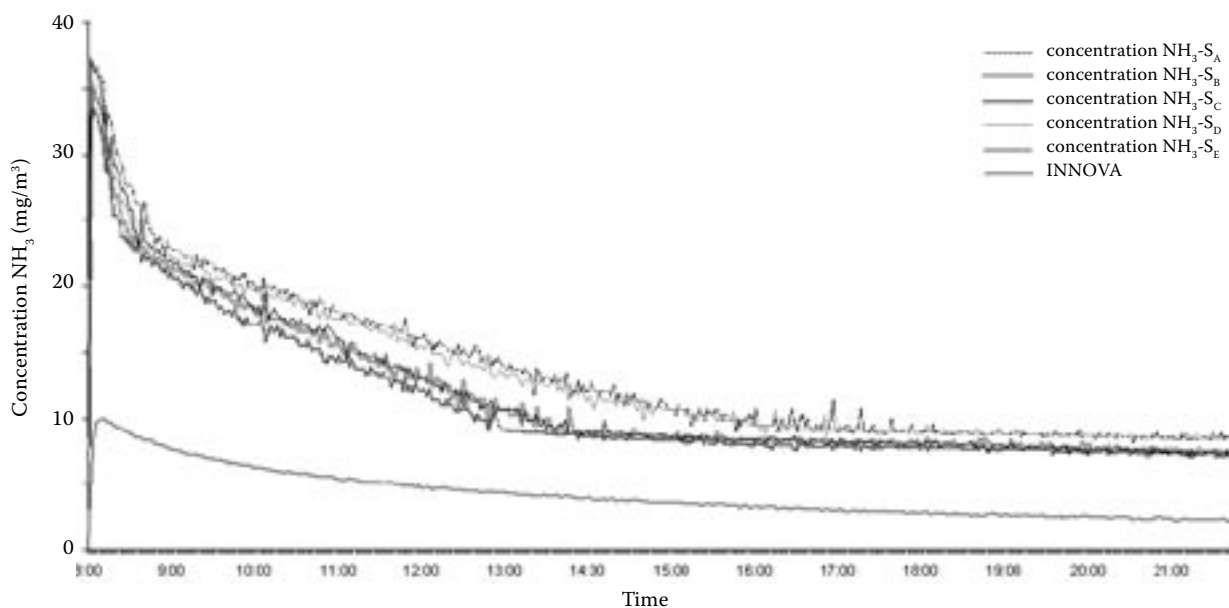


Fig. 6. The curves indicate decrease of ammonia concentration in wood-shavings measured out in the laboratory. The material with the humidity 9–10% was measured at the same time by SP-53 (five pieces of gas sensors) and INNOVA analyzer

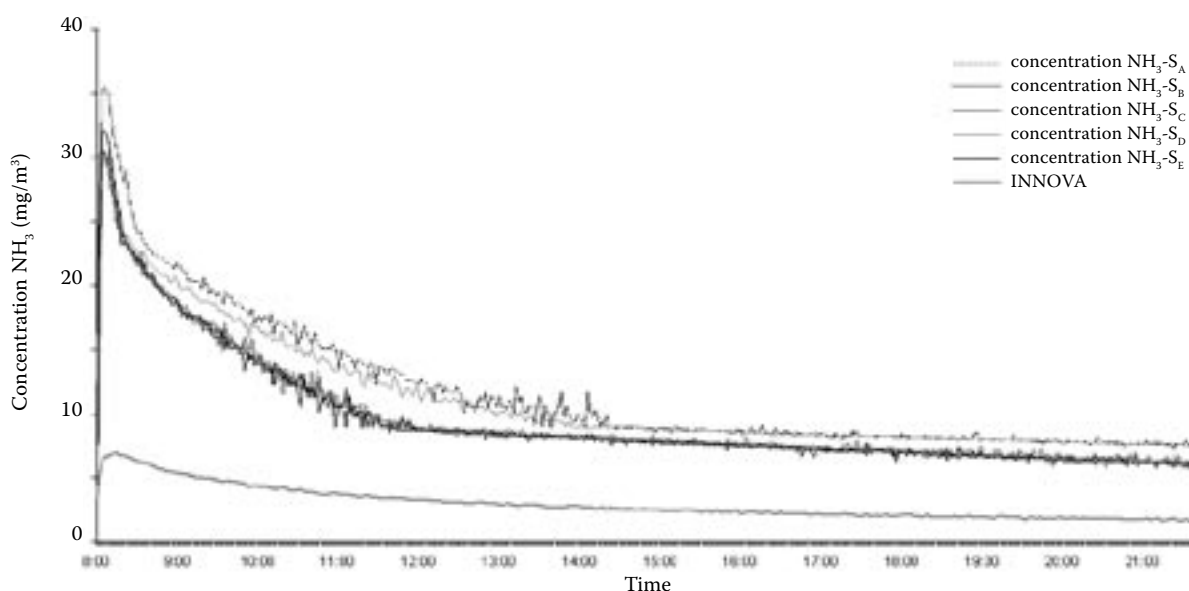


Fig. 7. The curves were measured for the same material as in Table 2, only its humidity is 17–18%

row in Tables 1 and 2 presents the rate between ammonia concentration measured by both types of gas sensors and for this purpose was calculated as the average value of ammonia concentration all the SP-53 gas sensors (the row eight in both tables). The difference in measured data of both type of gas sensors may be due to inaccuracy of calibration or its changes during long time. This different was observed in another series of measuring but its value was not the same. The difference in work principle of both types of gas sensors may be partly a reason of obtained data difference.

A simple comparison both tables and figures (i.e. Tables 1 and 2, Figs. 6 and 7) can prove that measured values of ammonia concentration of both sensors type are higher for wood-shavings with lower humidity and decrease of ammonia concentration is faster as it is shown in Table 1 with comparison on the Table 2. Wood-shavings with higher humidity better bind free molecules of NH_3 to molecules of H_2O . In this case, the sensors measure less molecules of NH_3 in gas form (compare the Figs. 6 and 7). Similar behaviour shows various materials too for comparison two different values of their humidity (for the same initial value of ammonia concentration in material). In the future better explanation this phenomena is needed.

The last rows in both tables show the rate of ammonia concentration of both gas sensors types. The maximum of the rate is in Table 1 between 5. and 6. hour and for Table 2 (wet material) after three hours. After this maximum, the value of rate is less changeable. It should be preferred to carry

out some elaborate checks of measured data before next processing of long time measurement.

CONCLUSION

This paper describes results one measuring series of ammonia concentration with one type of waste material i.e. wood-savings. Similar measure was done for saw dust and paper. In all cases the decrease of ammonia emissions (its velocity) was found out. The last series of these measurements verified some knowledge obtained in formerly done experiments. The SP-53 gas sensor's properties are rather problematic but another similar type of gas sensor that could replace them does not exist. Next statements characterize the conclusions of this paper:

The value of ammonia concentration depends on humidity of measured materials and the values of ammonia concentration are lower for wet material. This dependence has to be carefully expressed in measured data processing. The humidity of each sample must be measured carefully.

The SP-53 (solid state gas sensors) have to be calibrated or recalibrated often by simple means before and after the measuring or during the measurement it is carried out for long time.

The SP-53 gas sensors detect very low concentration of ammonia in surrounding air (few ppm). This low level of ammonia concentration can be easily distorted.

An influence grain size of sensor sensitive material on output data is one unknown question.

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Received for publication October 11, 2005

Accepted after corrections October 31, 2005

Porovnání dvou typů senzorů pro kontinuální měření emisí amoniaku

ABSTRAKT: Bylo provedeno měření emisí amoniaku pro jeden materiál podestýlky – dřevěné hobliny. Měření se realizovalo v laboratoři dvěma typy senzorů (na fotoakustickém principu a polovodičovým senzorem). Měnily se počáteční koncentrace amoniaku v materiálu a jeho vlhkost. Výstupní údaje ze senzorů se kontinuálně zaznamenávaly a zpracovávaly. Byl zjištěn rozdíl ve výstupních datech obou typů senzorů. Tento rozdíl nezávisí pouze na vstupní vlhkosti a koncentraci amoniaku v materiálu, ale také na době od začátku měření vzorku. V celé sérii měření rychlosti poklesu koncentrace amoniaku v materiálu byly použity tři vstupní koncentrace amoniaku a dvě různé vlhkosti materiálu. Každá kombinace vstupních údajů byla opakována nejméně třikrát a každé měření probíhalo nepřetržitě nejméně 12 hodin.

Klíčová slova: emise amoniaku; polovodičový senzor; podestýlka; hobliny

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