Verification of continual measuring methodology of ammonia emissions in animal husbandry

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ABSTRACT: Measuring of the burden gases emissions within the agricultural activity is increasingly significant with respect to the international obligations of the Czech Republic. For the principal agricultural burden gas – ammonia – there was suggested and tested a continual measuring method including concrete, precise, single measurement for verification of its accuracy. In the paper are presented first results of measuring emissions from litter in chicken broilers farming.

Keywords: ammonia; toxic gases emissions; litter; poultry; spectrometry

The permanent deterioration of environment in the world forces the responsible authorities to create conditions for optimal development of both industry and agriculture. Agriculture is a specific sector producing 95% of total ammonia quantity in the world. For its reason there was started process in the framework of the European Economy Commission of the UN focused to the problem of the "abatement technology for animal husbandry". It was necessary to suggest and to verify methods of ammonia concentration continual measuring in the housing facility and outdoor environment. In addition there was suggested and verified the control methods for measured physical variables. The verified measuring methodology was incorporated into the legislative. In 2001 there was in drawn-up a new act on atmosphere control in the Czech Republic amended by the executive regulation for agriculture regarding the methodology of ammonia concentration measuring. This methodology provides how to perform the continual measuring and the sensors allocation.

The measured air sample is taken – off at a certain instant of time for the purpose of investigated ammonia values comparison. The sample features are determined by the different authorised methods. For example, spectrometer is a suitable apparatus for this comparative measuring.

All the spectrometric measuring methods are based on the knowledge, effects and reactions resulting from the interaction between electromagnetic radiation and material. Therefore there are two reagents. One of them (radiation) is measured to find out its features. At the same time there are observed reactions to the interaction. It is important that the acquired data inform us about examined substance atoms and molecule internal structure or, if need be, its concentration in mixture with other substances.

Interpretation of radiation influence upon a substance is possible to be realised on basis of its dual hypothesis, i.e. wave – corpuscular character, when radiation has – according to this theory – wave properties (refractivity, reflectivity, flexibility) and simultaneously properties of energy elementary quantum flux – photons – moving as particles of certain wavelength in accordance with the de Broglie's relation. Each electromagnetic radiation is characterised by some basic quantities, e.g. frequency, wavelength, wave number (wave numbers per trajectory of 1 cm, unit equals cm^{-1}), radiation spreading velocity, radiation photons energy etc. Result of interaction between the electromagnetic radiation and substance depends also on their properties and particularly on the radiation energy. Observed or registered phenomena of that process can be used for:
– substance existence proof,
– substance structure research,
– substance concentration determination.

This is a relatively rough limitation. By comparison of all methods used for this purpose (spectrometric in particular) will be found out that all these interactions can be decided into two groups:
– Interactions with energy change between investigated substance and radiation;
– Interactions where the substance only effects the passing through radiation properties and an energy change is not realised.

For the gaseous substance concentration specification it is more suitable to use interactions with an energy change between the substance and radiation. These interactions are based on the fact that atoms and molecules are able to change their energetic state through the energy acceptance or radiation. Generally, the substance energy change (its particles) is considered in following form:
– absorption, i.e. substance energy increasing, when this energy is converted to the substance by the electromagnetic radiation (its absorption by the substance),

– emission, i.e. substance energy decreasing, when this energy is radiated from the substance in form of the electromagnetic radiation.

All these energetic changes can be detected by some suitable spectrometric method. Quantification of the interacting electromagnetic radiation is usually provided by evaluation of radiation absorption by the substance. Transmittance is defined by the ratio of the monochromatic radiation flux transmitted by the substance after the absorption and by radiation flux intensity entering into the substance.

In the process of emission the substance reduces its energy in general. This energy is obviously radiated in the form of electromagnetic radiation and thus the given substance structure is important from point of view of the reaction course.

The radiation applied in practice has the wavelength approximately from 0.1 nm to 1 m. The spectrometry categories are:
– roentgen (0.1–200 nm),
– ultraviolet and visible (200–800 nm),
– infrared (0.8–500 μm) (NIR, MIR, FIR),
– electron paramagnetic resonance (0.05–1 cm),
– nuclear magnetic resonance (1 cm–1 m).

For the verification of correct methodological process, specified in the Regulation, an apparatus BUCK M500 operating in the MIR range was used.

Absorption spectrometry in the MIR range

The absorption spectrometry in the range MIR is realised in the infrared spectrum of the electromagnetic radiation of wavelength ranging from 2.5 μm to 50 μm. This range corresponds with the wave numbers from 4,000 to 200 cm^{-1}. Therefore the evaluation and measuring relates only to the molecules absorption spectrum. Within the IR radiation absorption there are generally increased the molecule vibration and rotation energetic levels. This difference of energetic levels is small for molecules, and is sufficient for evocation of long – wave IR radiation absorption in contrast to the electron status detection in atoms where the more intensive, visible radiation is required. Basically, it concerns the vibration and rotation movement of the molecule atoms. The radiation absorption detection and spectrum appreciation depends considerably on the size and complexity of the molecule, because individual influences are combined and applied simultaneously. An important factor is the spectrophotometer construction, consisting in principle of three main parts: source of radiation, monochromator and detector.
– Polychromatic radiation source are usually glowing sticks emitting radiation within the wide range of the radiation wavelength.
– Monochromator consists of reflection grating providing infra-red radiation decomposition onto set of monochromatic radiation of particular wavelengths which can be recognised with high accuracy.
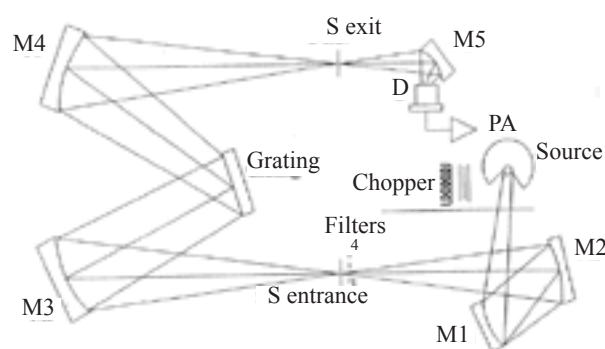

Fig. 1. The measuring space is a site where the cells with samples are placed. Its length is physically limited in the apparatus by S entrance and S exit and is max. 77 mm

Specification:

M 1, 2, 3, 4	mirrors
Grating	
Chopper	ray interrupter
Source	IR radiation source
Filters	4 changeable filters
S entrance	input slot of measuring space
S exit	output slot of measuring space
D	passed IR radiation detector
PA	detector signal amplifier

– Detector of radiation is based on thermal or electric influence of detector active substance. Currently are mainly used the pyroelectric detectors, e.g. TGS (triglycine sulphate). The detector features are very important from aspect of the total result. Response velocity, sensitivity and resolution ability in connection with the monochromator grating are the most significant properties of the detector.

Fig. 1 represents the diagram of the used apparatus of medium level quality. The working range of the wavelengths of that spectrometer is from 2.5 μm (4,000 cm) to 16.6 μm (600 cm). Initial one ray leaving the source of radiation is divided into the two rays by means of the rotation concave mirror and after the passage through the measured substance the both rays are again amalgamated to the one, which is detected. The grating has 75 scratches per 1 mm. The inlet is fitted by 4 filters for appropriate wave length. The infra-red (IR) source is a stick of surface temperature of 1,025°C. By this radiation wavelength it is possible to detect the ammonia molecules, water pollution by crude oil substances etc. The apparatus equipped by the grading monochromator has some disadvantages and limitations. It concerns mainly lower sensitivity, spectrum slow recovery, low ratio signal – noise and lower resolution within whole range of the wavelength. These problems can be removed by use of the Fourier's transformation in the infra-red spectroscopy (FT – IR or FTIR). This method of measuring provides transmission of the obtained signal from the spectrometer detector into the infra-red spectrum by the mathematical operation – Fourier's transformation.

Quantitative analysis in the IR spectrometry enables to identify substance in the sample from the obtained infra-red spectrum on the basis of the typical vibration (frequency) of corresponding substance's atoms, bond between substance's atoms and molecule spatial configuration. The vibrations of high energy are considered, situated nearby the MIR wave numbers higher values (between 4,000 and 1,600 cm^{-1}). For example, group N–H has the vibrations level about 3,500 cm^{-1}.

The other group, i.e. bond valence vibrations, has the specific location for particular elements and bond types.

Quantitative substance determination is carried out in the IR spectrometry mostly in both solid and liquid state of substance, less in gaseous state. The Lambert-Beer's law is used for this method.

$$\log \frac{I}{I_o} = -\varepsilon\, cd$$

where: I – radiation passed through the sample,
I_o – radiation impingement on the sample,
c – substance concentration,
d – sample thickness,
ε – molar linear absorption coefficient.

The departures from this law are possible (sample low homogeneity, particles size, chemical reaction in sample, apparatus failure). The L–B law validity should be verified by the calibration curve construction and the sample concentration can be found out within the range of this calibration curve.

Characteristics of the utilised IR spectrometer M500

This apparatus is determined for the IR spectrum creation within the range from 2.5–1.6 μm, mainly of liquid and solid transparent substances. Its design is limiting the gaseous substances measuring due to the small measuring space for cells with samples. For gases it is required to use longer optical trajectory in the sample, i.e. a longer cell to reach well perceptible obtained difference of the radiation energy absorption.

The apparatus is compact, its weight is 25 kg and enables the connection with computer and printer for purpose of spectrum presentation. The basic technical data:

Principle: Double-ray design, i.e. one IR ray is divided by means of single-ray optics and microcomputer correction of background.

Optics: 4 interference filters (low-pass filters) for frequencies: 4,000, 3,060, 1,980 and 980 cm. Monochromator with grating (75 scratches per 1 mm). Measuring ray is interrupted by constant frequency 23.6 Hz.

Scanning speed: 3, 6, 12 and 24 minutes from 4,000 to 600 cm^{-1}.

Output: 0–1V analog for direct record. RS-232 for PC input.

Detector: Surface 2 mm^2, DLATGS (deuteriated-L--alanin-triglycid sulphate). Sensitivity – 2 V/mW, frequency 23.6 Hz.

IR source: 4 sticks produced from Cr-Ni alloy with ceramic surface of temperature 1,025°C. Source power input 36 W.

Sample size: Cross – section max. 155 mm^2, length 77 mm.

Resolution: nominally 4 cm at 2,000 cm and 2 cm at 1,000 cm.

Memory operation: Background automated scanning in full range is conducted during every speed choice of sample scanning and the found values are stored in memory. These values are automatically compared during the sample scanning. It is possible to update the stored background anytime.

A–D converter: One multiplex, 12-bite D–A converter is used for analog signal conversion to digital form. A–D conversion is realised on principle of approximation controlled by the firmware. Individual points of spectrum are stored in memory in digital form.

Data output: Waves number, transmittance or absorption is presented on the built-up LCD display. The complex graphics and text are displayed on PC through the GRAMS software.

Spectrometer M500 – technical description and operation

4,250 points at scanning speed 3 minutes are generated within the reference mode. Data (values) of these points are stored in the RAM memory. The values are represented by figures from 0 to 4,096. The value of each the number is stored in digital form. Each of the stored number represents one point of the referential spectrum. Two adjacent numbers correspond with the scanning step, i.e. wave number change by 0.8 cm^{-1} in range from 4,000 to 600 cm^{-1}. After the reset the spectrometer is prepared for the sample scanning (for measuring). Value of each number from measured sample (point of spectrum) is divided by the value of the same number (point) stored in the memory. After this quotient multiplication ×100 the transmittance T is acquired. Other form of the measuring output is utilisation of these data in-line, i.e. in rough form (radiation absorption data for each point of spectrum). The output is realised through the RS 232 interface. The analog signal can be used directly for logger output.

The sample, chopper motor and A–D converter scanning speed are synchronised to eliminate spectrum output data distortion by inaccuracies during the scanning. The timing is derived from the quartz watch of the microprocessor. Size of each spectrum point is always obtained from one cycle of the chopper or the scanning step. For every period of the chopper the scanner motor has 4, 2, 1 or 1/2 of revolutions. It is in accordance with the scanning speed 3, 6, 12 and 24 minutes. One scanning step at speed of 3 minutes corresponds with the wave number change by 0.8 cm^{-1} (for 24 minutes of scanning time this change is by 0.1 cm^{-1}).
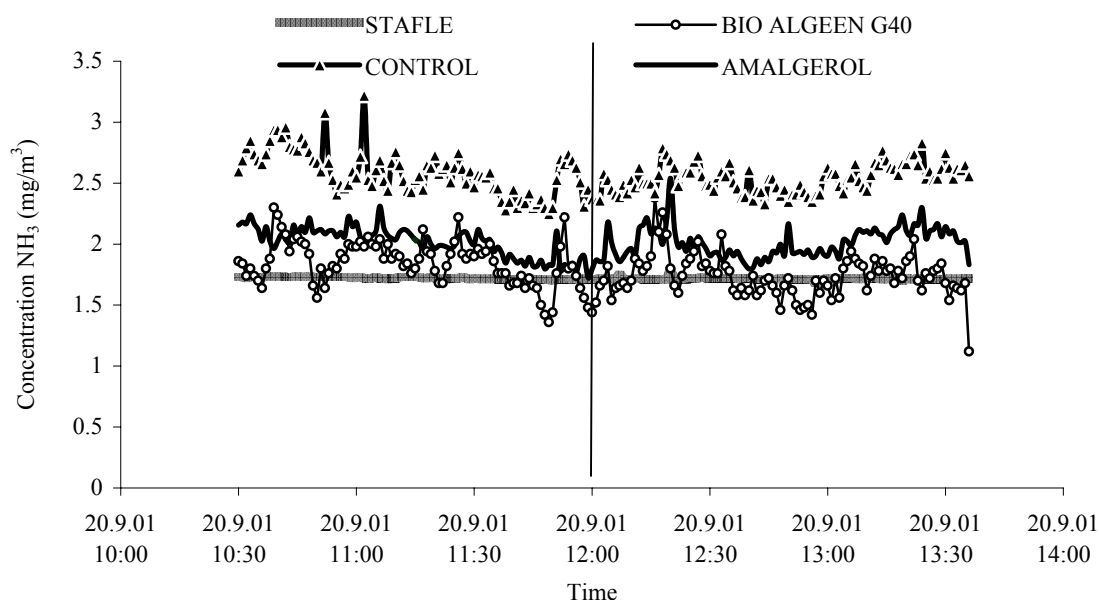
Fig. 2. Stafle ČERAZ 20.–21. 9. 2001

Measuring methodology

The scope is to verify methodology of continual measuring of ammonia concentration in animal husbandry using the precise infra spectrometer M500. In the first phase of measuring there is carried out practical examination of the spectrometer M500 adaptation for measuring of ammonia concentration by the continual measuring method and by spectrometer M500 in chicken broilers housing. The continual measuring of ammonia concentration (emissions) was carried out by the verified method of Research Institute of Agricultural Engineering (JELÍNEK 1999).

The gaseous mixture sampling for concrete measuring is performed into bags. The sample of gas is withdrawn from the bags to the cell. The concentration measuring accuracy is given by comparison of the value from the continual measuring and the gas laboratory verification.

RESULTS OF MEASURING

2 trials conducted by the Spectrometer M500 were focused to:
– determination of substance type (in mixture),
– determination of substance concentration.

The initial experiments were made to determine usual liquids – hydrocarbons mainly – in mixture with water. These substances were known in advance from the other measurement of absorption bands in the spectrogram. Thus their determination was easy. These two substances (water, hydrocarbon) were used for training of spectrometer operators. No problems with the liquid samples were recognised when the absorption bands position was known in advance. Nevertheless, determination of quite unknown liquid substance by this method is much more complicated because the "spectrum library"

is not available. The last "liquid samples" were mixtures of water and ammonia of different concentrations. The ammonia was identified well but its concentration was determined with considerable difference.

The consequent experiments with the gaseous samples were carried out in the similar way. For the first samples (mixture of air and ammonia) no absorption was measured. The reason for it was a short cell and a low mixture density. The longer cell was damaged and unusable. The next cell was made from combined material (perspex and glass). The spectrum improvement also brought increase of the gas pressure in the cell (by about 20%). The limitation is caused by the cell construction. Because the special material transmitting the IR radiation was not available, silicon glass was used. Finally, the third cell was designed, connecting the measuring advantage of higher pressure of gas mixture with the adaptation of faces made from special glass with the half-transmitting coating on the internal side of the face.

Fig. 3. Gas withdrawal for control by spectrometric method according to the valid methodology

All the mentioned measures and adaptations are focused to the IR radiation absorption increase in the sample in order to obtain the measurable difference of absorption recorded by detector. This problem would be probably solved by utilisation of the long cell (e.g. 1 m). Nevertheless, this solution is not possible without considerable mechanical adaptation of the spectrometer. This is a reason for current adaptation of the spectrometer measuring space including the cell.

Fig. 4 present the spectrogram of "normal" air of temperature 22°C and relative humidity about 63%. The water absorption bands are distinctly visible: (3,800 to 3,500 cm), i.e. 2.63–2.86 μm, (2,000–1,300 cm), i.e. 5 to 7.7 μm and absorption band of carbon dioxide (2,400 to 2,300 cm), i.e. 4.16–4.35 μm. The places of filter exchange are marked by the letter F (four places as presented in the apparatus description). The maximum value for 900 cm is 11.1 μm. It is caused by the grating anomaly. The spectrum was acquired in this type of spectrometer by means of special cell for gases measuring.

A verification of the continual measuring of ammonia emissions was implemented within the experiment carried out on ČERAZ farm in Soběslav. The hall capacity was 28,800 chickens of age 18 days. The ammonia emissions from the straw litter and treated by enzymatic agent (Amalgerol and G-40) were measured. The measuring was conducted within 48 hours (Fig. 2). In Fig. 3 is shown method of gas withdrawal for laboratory measuring by spectrometer M500. The air in the stable was used for both samples at 12.00 o'clock and the gas sample for untreated litter was taken off at the same time. In Fig. 4 is demonstration of the one spectrum record of withdrawn gaseous sample from the litter treated by agent G-40.

The ammonia presence is evident mainly in the range 3,800–3,400 cm^{-1}, i.e. 2.7–2.94 μm. The lines in the range (1,900–1,400 cm), i.e. 5.26–7.14 μm belong to water. The other distinctive lines in the record have their origin in the agent composition. By recounting of average value within the range 3,600–3,800 cm the value of 1.49 NH_3 mg/m^3 was found. Similarly were found also other two values of the spectrometric measuring. Table 1 presented a concentrations comparison for the three measured places from continual and spectrometric measuring:

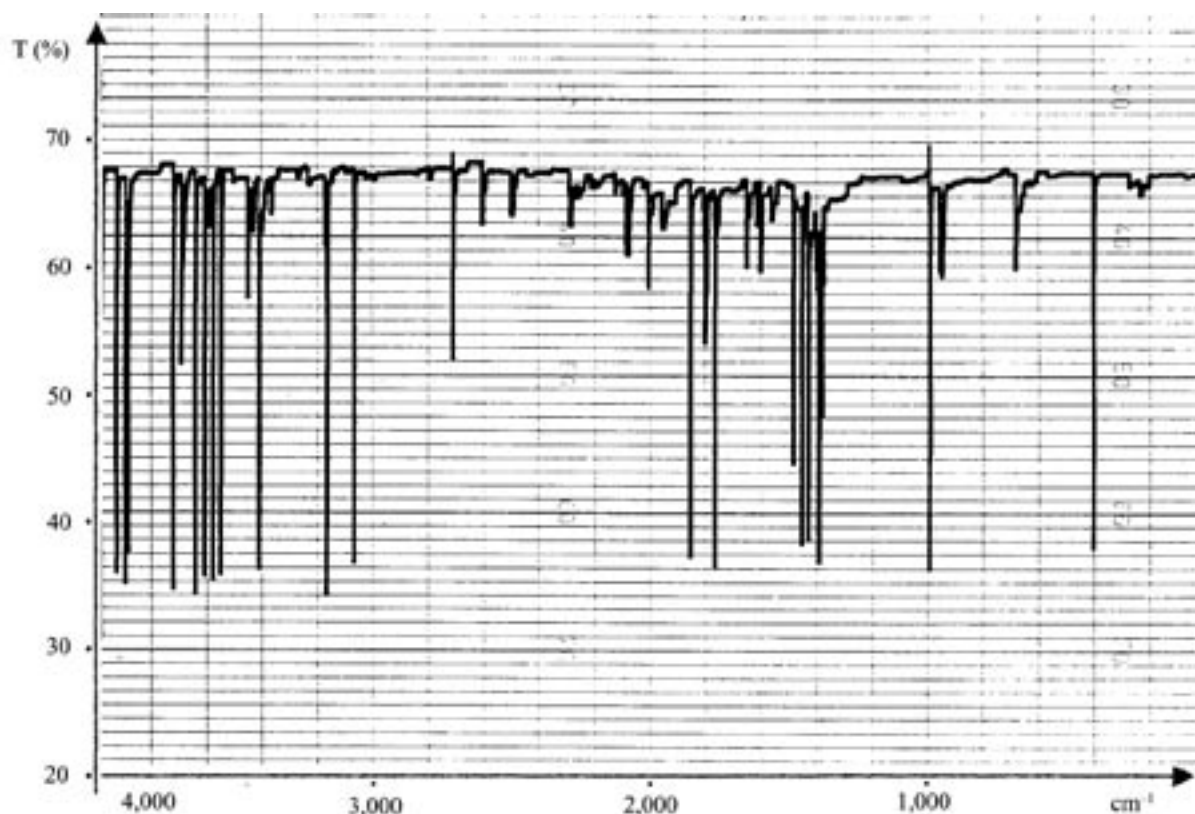| Litter treatment by agent	Continual measuring [NH_3 (mg/m^3)]	Spectrometric measuring [NH_3 (mg/m^3)]	Measuring error
Amalgerol	1.80	1.78	−1.1
Bio Algeen G-40	1.50	1.49	−0.7
Control	2.35	2.34	−0.4

Fig. 4. Demonstration of gas spectrum record withdrawn from litter treated by agent G-40

It is evident from the presented results, that measuring error did not exceed 2% in any case. This result is fully in accordance with the requirements of authorised measuring, i.e. the maximum error of 2%. The fact that the measuring errors differ can be explained as follows: the bag for measured gas retaining is filled within certain time and from the continual measuring is evident, that process of ammonia release from the litter is changing permanently.

CONCLUSION

The method of continual measuring of ammonia emissions originating in the animal husbandry together with precise measuring method of ammonia concentration is able to replace measuring methodology using expensive foreign appliances. This method enables to determine ammonia emissions changes from the suggested "reducing technologies".

References

JELÍNEK A. et al., 1999. Zjišťování emisí amoniaku ze zemědělské činnosti. Zem. Techn., *45*: 19–27.

Ověření metodiky kontinuálního měření emisí amoniaku z chovů hospodářských zvířat

ABSTRAKT: Nutnost měření emisí zátěžových plynů ze zemědělské činnosti je vzhledem k mezinárodním závazkům České republiky na jejich snížení stále aktuálnější. Pro hlavní zátěžový plyn ze zemědělské činnosti – amoniak – byla navržena a odzkoušena kontinuální měřicí metoda včetně konkrétních, přesných jednorázových měření pro ověření její přesnosti. Jsou uvedeny první výsledky v podmínkách měření pro emisi z podestýlky v chovech kuřecích brojlerů.

Klíčová slova: amoniak; emise toxických plynů; podestýlka; chov drůbeže; spektrometrie

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