Investigation of particular parameters of a semiconductor ammonia gas analyzer

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Abstract. Selective methods and a highly sensitive automatic semiconductor gas analyzer VG-NH3 have been developed for detecting ammonia in a mixture of toxic, flammable and explosive gases. The basic metrological and operational characteristics of the developed selective automatic ammonia analyzer are estimated. These devices allow determining ammonia in a wide range of its concentrations and have the best metrological and operational characteristics that meet the requirements of the GOST (National State Standard).

1. Introduction
Ammonia is one of the most common industrial emissions. The main source of ammonia is gaseous emissions from manufacturing of nitric acid, sodium hydrogen carbonate, mineral fertilizers, etc. Semiconductor sensors and analyzers have the highest sensitivity of ammonia [1,2]. Due to the high toxicity and explosiveness of ammonia, a research aimed at developing methods and means for its detection at the level of both micro- and macro-concentrations become a matter of great importance.

Semiconductor gas analyzers have the highest sensitivity in ammonia detection. This work is dedicated to development of an automatic highly sensitive ammonia gas analyzer (VG-NH3) and the determination of the influence of external factors on its analytical signal. Highly sensitive ammonia gas analyzers VG-NH3 were developed using a selective semiconductor sensor based on titanium and iron oxides [3] to measure the ammonia concentration in a gas-air sample. Depending on the analytical task to be solved, the range of VG-NH3 measurements varies from 0–100 mg/m3 (analyzer for analytical monitoring of atmospheric air) to 0–2.5% vol (analyzer for monitoring of pre-explosive concentrations of ammonia in a gas mixture). The operational principle of the developed semiconductor gas analyzer is based on catalytic oxidation of a detected component adsorbed on the surface of the gas-sensitive material of the semiconductor sensor [4]. The analyzer ensures the detection of ammonia in a wide range of concentrations with an accuracy of 0.1 mg/m3. The signal from the primary converter of the device is transferred to a differential converter assembled on three operational amplifiers, which regulates and, if necessary, increases the signal. Then the signal is fed to an analog-to-digital converter operating on the principle of double integration. The ADC decoder generates a seven-segment code to be fed to the LED indicators, while device scale has four digits.

2. Experimental procedure
During the experiments, the ranges of the detected ammonia concentrations were determined, the basic errors and the areas of variation of the output signal were found, and additional errors were tested
when the temperature, pressure and humidity of the gas medium changed. The gas analyzers were tested at the ranges of ammonia concentrations of 0-100 mg/m$^3$ and 0-2.5 vol. %, in laboratory and operational conditions. Laboratory conditions: tested gas medium temperature is 20±5 °C; tested gas medium pressure is 760±30 mm Hg; tested gas medium relative humidity is 40-60%; analyzed mixture temperature is 20±0.0 °C; device supply voltage – alternating current 220±10 V.

Operating conditions: gas mixture temperature is from +5 to +50 °C; gas medium pressure is 600-800 mm Hg; gas medium relative humidity is 25-95%; sensor tilt angle – up to 30%. The gas analyzer was tested under normal and operational conditions. 5 gas analyzers VG-NH$_3$ with a measurement range of 0-100 mg/m$^3$ and 0-2.5% vol. were subjected to tests. In all cases, the conditions, procedure, methods and number of tests corresponded to GOST 13320-81, the composition and parameters of calibration gas mixtures (GM) corresponded to the nominal values given in table 1.

**Table 1.** The results of gas mixture composition and parameters determination for testing VG-NH$_3$ with a measurement range of 0-100 mg/m$^3$ and 0-2.5% vol.

| Item No. | Content corresponding to the points for the measuring range, % | Content of NH$_3$ in GM, mg/m$^3$ (the rest is air) | Calibration error of GM, % | Content of NH$_3$ in GM, vol. % (the rest is air) | Calibration error of GM, % |
|----------|---------------------------------------------------------------|---------------------------------------------------|--------------------------|-------------------------------------------------|--------------------------|
| 1        | 10±5                                                          | 9.8                                               | 0.3                      | 0.11                                            | 0.01                     |
| 2        | 50±5                                                          | 52.4                                              | 0.3                      | 1.25                                            | 0.01                     |
| 3        | 95±5                                                          | 97.9                                              | 0.3                      | 2.44                                            | 0.01                     |

The measurement range and the basic error were tested by supplying the gas mixture to the inlet of the gas analyzer in the following sequence: No. 1-2-3-1-3, where the number of GM corresponded to the content of the measured component (%): No. 1=10±5; No. 2=50±5; No. 3=95±5; all experiments were repeated at least 5 times. The results of the measurement range verification of the VG-NH$_3$ automatic ammonia gas analyzer with a measurement range of 0-100 mg/m$^3$ are shown in table 2.

**Table 2.** The results of the measurement range verification of the semiconductor ammonia gas analyzer (VG-NH$_3$ with a measurement range of 0-100 mg/m$^3$, n=5, P = 0.95).

| Ammonia input, mg/m$^3$ | Ammonia detected, mg/m$^3$ | (x±Δx) | S | Sr·102 |
|-------------------------|----------------------------|--------|---|--------|
| 9.8                     | 9.5±0.2                    | 0.16   | 1.7 |
| 52.4                    | 51.6±0.6                   | 0.48   | 0.9 |
| 97.9                    | 97.0±1.4                   | 1.13   | 1.2 |
| 9.8                     | 9.7±0.2                    | 0.16   | 1.7 |
| 97.9                    | 96.7±1.5                   | 1.21   | 1.2 |

As follows from the above data (table 2), the dependence of the gas analyzer signal on the concentration of ammonia in the mixture is a straight-line in the studied intervals. The basic absolute error of the analyzer at the test points was determined by the formula:

$$\Delta = A_i - A_0.$$  \hspace{1cm} (1)

where $A_i$ is the concentration of the measured component at the test point of measurements, induced on the indicator; $A_0$ is the true concentration of the measured component at the test point of measurement indicated in the passport to GM. The basic reduced error of gas analyzers with ranges of 0-100 mg/m$^3$ was determined by the difference between the readings of the gas analyzer and the true concentration values referred to the measurement range:

$$Y = A_i - A_0/C_t - C_i.$$  \hspace{1cm} (2)
where \( C_f - C_i \) are final and initial limits for measuring the concentration of the gas media components to be detected, mg/m\(^3\) (%). The results of determining the error of the automatic ammonia gas analyzer VG-NH\(_3\) with a measurement range of 0-2.5% vol. are shown in table 3.

### Table 3. The results of determining the error of the gas analyzer VG-NH\(_3\).

| Item No. | Content of NH\(_3\) in mixture, % vol. | NH\(_3\) detected, % vol. | Basic absolute error (Δ) | Basic reduced error (ϒ) |
|----------|--------------------------------------|--------------------------|--------------------------|--------------------------|
| 1        | 0.14                                 | 0.13                     | 0.01                     | 0.4                      |
| 2        | 1.28                                 | 1.26                     | 0.02                     | 0.8                      |
| 3        | 2.41                                 | 2.38                     | 0.03                     | 1.2                      |
| 4        | 0.14                                 | 0.13                     | 0.01                     | 0.4                      |
| 5        | 2.39                                 | 2.36                     | 0.03                     | 1.2                      |

The calculated maximum value of the reduced analyzer error based on the obtained experimental data was 1.2%, respectively (table 3). The determination of the variation in the readings of VG-NH\(_3\) was carried out under normal conditions by passing GS No. 1; 2 and 3 through the gas analyzer. Variations (B) in the readings of the gas analyzers were determined by the formula:

\[
B = A_{\text{max}} - A_{\text{min}}. \tag{3}
\]

where \( A_{\text{max}} \) (\( A_{\text{min}} \)) is the reading (component content determined by the output signal) when arriving the test point from the side of larger (smaller) content values. The gas analyzer is considered to have passed the test if the inequation \( B < B_g \) (\( B_g \)-allowable signal variation) holds at each of the test points. From the experimental data it was found that the variation in the readings of the gas analyzer does not exceed the permissible value according to the GOST.

The study of the selectivity of ammonia detection by the developed analyzers was carried out using certified compositions of gas mixtures in accordance with the requirements of the technical specifications for gas analytical devices for closed ecological systems and chemical industry facilities. The selectivity of the automatic ammonia analyzer was determined with the presence of carbon monoxide, methane and hydrogen. The experiments were carried out at a temperature of 20 ± 2 °C and a pressure of 750±10 mm Hg. The results obtained when testing the selectivity of VG-NH\(_3\) are presented in table 4.

### Table 4. The results of testing the selectivity of the automatic ammonia analyzer VG-NH\(_3\) (n = 5, \( P = 0.95 \)).

| Gas mixture content, % vol. | Ammonia detected, % vol. |
|-----------------------------|--------------------------|
|                             | VG-NH\(_3\)\(_1\) | VG-NH\(_3\)\(_2\) | VG-NH\(_3\)\(_3\) |
| NH\(_3\)-1.23+air (rest)    | 1.20±0.02  | 1.34   | 1.16±0.02  | 1.39   | 1.21±0.02  | 1.33   |
| NH\(_3\)-1.41+H\(_2\)-2.0+air (rest) | 1.35±0.02  | 1.19   | 1.38±0.02  | 1.17   | 1.35±0.03  | 1.79   |
| NH\(_3\)-1.09+CO-2.25+air (rest) | 1.09±0.02  | 1.48   | 1.10±0.03  | 2.19   | 1.06±0.02  | 1.52   |
| NH\(_3\)-1.51+CH\(_4\)-1.88+air (rest) | 1.48±0.03  | 1.63   | 1.48±0.03  | 1.63   | 1.49±0.03  | 1.62   |

As follows from the experimental data, the presence of carbon monoxide (up to 2.25%), hydrogen (up to 2.0%) and methane (up to 1.88%) in the analyzed mixture does not affect the output signal of the ammonia sensor. From the above data (table 5) it also follows that the developed analyzer, in the studied concentration range, allows the selective determination of ammonia in the presence of hydrogen, carbon monoxide and methane. The analyzer error due to unmeasured components does not exceed 1.0%.

The additional error of the VG-NH\(_3\) caused by the change in the environment temperature was tested in the temperature range from -10 to +60 °C with increment of 20 °C. The experiments were carried out at atmospheric pressure of 750±30 mm Hg using a gas mixture with an ammonia content of 50
mg/m$^3$. The sequence of establishing the temperature in the chamber is 20 °C (the optimum temperature established when determining the basic error) –10; 0; +10; +40; +60 °C. Testing the additional temperature error was carried out in the following sequence: the gas analyzer was placed in a thermostat in which normal test conditions were already created. The basic error was tested after the initial stabilization of the conditions (in 1 hour). The temperature in the chamber was brought to –10 °C and the gas analyzer was kept powered on at this temperature for 1 hour, the other conditions were similar. Then, a calibration gas mixture No. 3 was supplied to the inlet of the gas analyzer. In order to equalize the temperature of the mixture and the thermostat, there was used a coil made of a copper tube, which was placed in the thermostat. The gas mixture was fed into the gas analyzer at a rate of 20±0.1 l/h. Only after carrying out such preliminary operations and achieving a certain stabilization of the gas analyzer we started to analyze gas mixtures. Tests were carried out at least 5 times. The influence of the temperature of the gas medium on the additional error of the gas analyzer (in %) for each point was determined by the formula:

$$\gamma_{\text{add.}} = \gamma_{\text{bas.}} - \gamma_{\text{norm.}}$$  \hspace{1cm} (4)

where $\gamma_{\text{norm.}}$ is the basic error in the calibration characteristic; $\gamma_{\text{bas.}}$ is the basic error of the gas analyzer for each measurement. The results of determining the additional error of the gas analyzer due to a change in the environment temperature (from –10 to +60 °C) are presented in table 5. From the results it follows that, in the temperature range from 10 to +60 °C, the error does not exceed 1.5% and is much less than the basic error of the device itself.

Table 5. The results of determining the additional error of the gas analyzer ($\gamma_{\text{add.}}$) VG-NH$_3$ at different environment temperatures.

| Experiment temperature, °C | Input NH$_3$, mg/m$^3$ | Detected, NH$_3$, mg/m$^3$ | VG-NH$_3$  | Y$_{\text{add.}}$ | The error at the experiment temperature (t), $\gamma_t$ |
|----------------------------|------------------------|-----------------------------|------------|----------------|--------------------------------------------------|
| 20 norm.                   | 50.0                   | 49.3                        | 0.7        | 0.4            | 0.3                                              |
| 60                         | 50.0                   | 48.9                        | 1.1        | 0.7            | 0.7                                              |
| 40                         | 50.0                   | 49.0                        | 1.0        | 0.3            | 0.7                                              |
| 10                         | 50.0                   | 48.6                        | 1.4        | 0.7            | 0.7                                              |
| 0                          | 50.0                   | 46.3                        | 3.7        | 3.0            | 4.9                                              |
| –10                        | 50.0                   | 44.4                        | 5.6        | 4.9            | 4.9                                              |

At a temperature of 0 °C, a noticeable decrease in the readings of the device was observed, which is apparently associated with the condensation of the products of ammonia or water oxidation on the inner surface of the chamber ceramic-metal mesh. In such a case, the molecular diffusion of the controlled gas ceases and the output signal disappears.

The tests of exposure to high or low atmospheric pressure were carried out in the range of 650-850 mm Hg using an example of an analysis of a gas mixture No. 3 with an ammonia content of 75 mg/m$^3$. The experiments were carried out in the following sequence: after an external examination, the gas analyzer was included in the circuit and put to normal test conditions. After initial stabilization, the basic error was determined under normal test conditions. The pressure in the system was set using fine adjustment valves, flow control was carried out by flow meter. The experiments were carried out in the pressure range of 650-850 mm Hg. Table 6 presents the results of determining the additional error of the gas analyzer ($\gamma_{\text{add.}}$) due to pressure changes.

As follows from the above data, the additional error in the studied interval (650-850 mm Hg) due to pressure changes is 0.2-0.5% and does not exceed the value of the basic error. The maximum additional error is observed at 850 mm Hg and equal to 0.5%. The permissible additional error in accordance with GOST 13320-81 for pressure changes for this class of gas analyzers should not exceed the
basic error. The value of the analyzer error due to changes in the humidity content of the analyzed gas mixture was determined as the difference between the signals of the humidified and non-humidified mixture of the analyzed gas under normal conditions. The tests to study the effect of humidity were carried out in the following sequence: the device was placed in a humidity chamber in which normal test conditions were established. After the initial stabilization, the main error of the device was determined for GM No. 3 with an ammonia content of 50.0 mg/m³. An hour later, the error was determined by supplying GM No. 3 humidified to 95% to the inlet of the gas analyzer. The results of the VG-NH₃ humidity resistance tests revealed that the change in the signal of the gas analyzer in the studied humidity range is 0.5–0.9 mg/m³.

Table 6. The results of determining the concentration of NH₃ at various pressures (n=5, P=0.95).

| Pressure, mm Hg | NH₃ input, mg/m³ | NH₃ detected, mg/m³ | x ±Δx | S | Sr·10⁻² | Basic absolute error Δ | Yadd. |
|----------------|------------------|---------------------|-------|---|--------|-------------------------|-------|
| 760±10         | 75.0             | 74.0±0.5            | 0.4   | 0.54 | 1      | -                       |       |
| 650±10         | 75.0             | 73.7±0.4            | 0.32  | 0.43 | 1.5    | 0.3                     |       |
| 750±10         | 75.0             | 73.8±0.7            | 0.56  | 0.76 | 1.2    | 0.2                     |       |
| 850±10         | 75.0             | 73.5±0.3            | 0.24  | 0.32 | 1.5    | 0.5                     |       |

The total additional error characterizing the set of error values from the influence of various factors was determined by the formula:

\[ Y_{add} = \pm \sqrt{Y_{1add}^2 + Y_{2add}^2 + Y_{3add}^2} \] (5)

where \( Y_{1add} \), \( Y_{2add} \), \( Y_{3add} \) are the values of additional errors obtained when changing the influencing factors. According to GOST 13320-81, the maximum permissible value of the total additional error should not exceed the doubled value of the permissible basic error limit. The total additional error of the gas analyzer due to changes in temperature, humidity and pressure of the gas medium in all cases was ±1.15%.

3. Conclusion

Thus, as a result of the experiments, selective methods and a highly sensitive automatic semiconductor gas analyzer VG-NH₃ have been developed for determining ammonia from a mixture of toxic, flammable and explosive gases. The basic metrological and operational characteristics of the developed selective automatic ammonia analyzer are estimated. These devices allow determining ammonia in a wide range of its concentrations and have the best metrological and operational characteristics that meet the requirements of the GOST. HB-NH₃ is characterized by high accuracy, reproducibility, rapidity and selectivity of detection. The analyzer can operate continuously in various ammonia content monitoring systems, as well as in combination with signaling devices to indicate ammonia leakage.

The use of the semiconductor method reduces the error of analysis, increases the stability of the device's readings and its operational life, improves reproducibility and selectivity with continuous automatic determination of ammonia in gas mixtures.

References

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