Improvement of Determination Method of Ammonia in Indoor Air and Analysis of Monitoring Results

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Abstract. This paper mainly compares the determination of ammonia in indoor air by hypobromite oxidation method and salicylic acid spectrophotometry, and selects higher precision, higher sensitivity, larger linear range and more stable results. The reproducible salicylic acid method is improved. In this way, the salicylic acid method is more convenient, time-saving and easy to operate, and is advantageous for the application of the method in a wider range.

1. Introduction
Ammonia pollution is high in the indoor air pollution in China. [1-2] the ammonia is extremely harmful to the human body. Ammonia absorbs water in the body tissue to form ammonia water, which can dissolve tissue proteins and saponification with fat. Ammonia can destroy the activity of various enzymes in the body, which in turn affects tissue metabolism. [3-6] Ammonia has a strong stimulating effect on the central nervous system. Therefore, the determination of ammonia in indoor air is particularly important.

2. Brief description and comparison of the determination method of national standard ammonia
The current measurement methods are mainly divided into: Nessler's reagent spectrophotometry, indophenol blue method (salicylic acid spectrophotometry and phenol method), hypobromite oxidation method, QUAATRO continuous flow analyzer. [7]

The above method list is compared as shown in Table 1. The Nash method and the salicylic acid method can be used when the concentration of ammonia nitrogen is large, and the hypobromite method and the phenol method can be used when the concentration of ammonia nitrogen is small. The QUAATRO method is suitable for both low concentration and high concentration of ammonia nitrogen.

| Method            | Upper limit (mg/L) | Lower limit (mg/L) | (nm) | Reaction | pH | Applicable medium          |
|-------------------|--------------------|--------------------|------|----------|----|-----------------------------|
| Nash L20mm        | 2.0                | 0.1                | 420  | 12       | Fresh water                |
| Salicylic acid L10mm | 1.0             | 0.04               | 697  | 11.7     | Fresh water                |
| Hypobromite L50mm | 0.11               | 0.0004             | 543  | 1.6      | Fresh water, sea water     |
| Phenol L50mm      | 0.11               | 0.0007             | 640  | 12       | Fresh water, sea water     |
| QUAATRO L10mm     | 12.6               | 0.001              | 660  | 12       | Fresh water, sea water     |

Table 1. Comparison of several methods
The hypobromite oxidation method is applicable to river water and seawater media, but it is not suitable for heavy water and contains a lot of water. The method determines that the ammonia nitrogen concentration is low, generally less than 0.5 mg/L. The salicylic acid method is suitable for fresh water. Although the Nessler’s reagent method can measure a higher concentration of ammonia nitrogen, the reagent should be highly toxic and should be avoided. This method should be avoided as much as possible. It is recommended to replace it with salicylic acid. Phenol method and sufficient masking agent can be used to measure fresh water and seawater. The concentration is low and the reaction is slow. It is recommended to replace the hypobromite oxidation method with faster reaction. The QUAACTRO Continuous Flow Analyzer can continuously and quickly measure fresh water or seawater from low to high concentrations of ammonia nitrogen and can replace these methods. Moreover, it can measure multiple elements at the same time, and it is an instrument that saves time, labor, and reagents.

3. National Standard Salicylic Acid Spectrophotometry

Take 7 10 mL plug color tubes and prepare a standard series according to Table 7. Accurately transfer the corresponding volume of standard use solution (10.0g/mL) according to Table 1; dilute each tube with water to 10mL; add 1.00mL salicylic acid-sodium potassium tartrate solution and 2 drops of nitrosoferric acid to each tube Potassium solution, 2 drops of sodium hypochlorite solution, shake well, and let stand for 1 h. The absorbance was measured at a wavelength of 697 nm using a 10 mm cuvette with water as a reference. The absorbance of the reagent blank is taken as the ordinate, and the ammonia content (g) is plotted on the abscissa, and a standard curve is drawn.

| Pipe number | 0  | 1  | 2  | 3  | 4  | 5  | 6  |
|-------------|----|----|----|----|----|----|----|
| Standard use fluid /mL | 0  | 0.20 | 0.40 | 0.60 | 0.80 | 1.00 | 1.20 |
| Ammonia content /g | 0  | 2.00 | 4.00 | 6.00 | 8.00 | 10.00 | 12.00 |

4. Improved salicylic acid spectrophotometry

Take 7 25 mL plug color tubes and prepare a standard series according to Table 8. Accurately transfer the corresponding volume of standard use solution II according to Table 8; add about 20 mL of water to each tube; add 2.00 mL of color developer I to each tube and mix; add 2.00 mL of color developer II, mix Condensate to 25 mL with pure water, mix well; after heating at 40 °C in a water bath for 15 min, remove and cool for 10 min to room temperature. The absorbance was measured at a wavelength of 670 nm using a 1.3 cm cuvette with water as a reference. Taking the ammonia concentration (g/mL) as the abscissa, the absorbance of the reagent blank is subtracted from the ordinate to draw a standard curve.

| Pipe number | 0  | 1  | 2  | 3  | 4  | 5  | 6  |
|-------------|----|----|----|----|----|----|----|
| Standard use fluid /mL | 0  | 1  | 3  | 5  | 10 | 15 | 20 |
| Ammonia content /g | 0  | 1  | 3  | 5  | 10 | 15 | 20 |

The experiment was carried out according to the above procedure, and three sets of data were measured with 1 cm and 3 cm cuvettes, as recorded in Table 4:
Table 4. Salicylic acid absorbance record

| Number | 0   | 1   | 2   | 3   | 4   | 5   | 6   |
|--------|-----|-----|-----|-----|-----|-----|-----|
| Liquid volume (mL) | 0   | 1   | 3   | 5   | 10  | 15  | 20  |
| Ammonia concentration (g/mL) | 0.108 | 0.130 | 0.351 | 0.586 | 1.130 |
| Absorbance 3cm | 0.123 | 0.140 | 0.378 | 0.611 | 1.166 |
| Absorbance 1cm | 0.110 | 0.135 | 0.380 | 0.614 | 1.189 |

Remarks: Each sample is measured twice, and then the average value is obtained. The data recorded in the table is the average value; the measurement time of the six groups of data is April 9, April 10, April 11, and April 9 Day, April 10, and April 11.

Figure 1. Relationship between absorbance and ammonia concentration of each sample measured by 1.3cm cuvette

Figure 2. The relationship between the average value of absorbance measured by 1.3cm cuvette and ammonia concentration

The relationship between the absorbance of each set of samples measured by a 1.3 cm cuvette and the ammonia concentration (Fig. 1) and the average of the absorbance measured by a 1.3 cm cuvette versus ammonia concentration (Fig. 2). It can be seen from Table 4, Figure 1 and Figure 2 that the
salicylic acid spectrophotometry has good stability, high precision and good reproducibility. However, experiments to increase the concentration of the sample are needed to determine the sensitivity of the method. Therefore, an experiment was carried out by increasing the sample having an ammonia concentration of 0.012, 0.016, and 0.020 g/mL, and the experimental data was recorded.

5. Improvement of experimental methods

(a). The sulfuric acid absorption liquid was changed from 0.005mol/L to 0.010mol/L. The absorption liquid is still only suitable for the sampling stage and will not be used when the standard curve is drawn.

(b). The preparation and addition method of the chromogenic agent is different: in the original method, the salicylic acid-potassium tartrate solution is first prepared, and 10.0 g of salicylic acid [C6H4(OH)COOH] is weighed into a 150 mL beaker, and an appropriate amount of water is added, and then 5 mol is added. /L sodium hydroxide solution 15mL, stir to completely dissolve; otherwise, 10.0g sodium potassium tartrate (KNaC4H406•4H2O) dissolved in water, heated to boil to remove ammonia, cooled and combined with the above solution into a 200mL volumetric flask, with water Dilute to the mark and shake well. Potassium nitrosoferrocyanide is prepared separately and ready for use. After improvement, sodium salicylate was used instead of salicylic acid, sodium hypochlorite solution was no longer used, and sodium nitrate was used as a catalyst to prepare a color developer. There are two systems of chromogenic reagents, all of which are prepared in advance, such as chromogenic reagent I and chromogenic reagent II. This not only saves the experiment time, but also eliminates the need to use the existing ones, and facilitates the common preservation and use of the chromogenic agents.

(c). The standard use solution of ammonium chloride is changed from the original 10g/mL to 1.0g/mL, so that when the standard curve is drawn, a low concentration solution can be prepared more accurately.

(d). The color development conditions were changed from the original room temperature for 1 h to 40 C water bath for 15 min and then cooled for 10 min to room temperature.

(e). When the absorbance was measured, the wavelength was changed from 697 nm to 670 nm, and the cuvette of 1 cm path length was replaced with a cuvette of 3 cm path length.

(f). The experiment was carried out by increasing the sample having an ammonia concentration of 0.012, 0.016, and 0.020 g/mL.

Experiments were carried out according to the final improved method, and the relevant data were recorded as shown in Table 5:

| Number | 0  | 1  | 2  | 3  | 4  | 5  | 6  | 7  |
|--------|----|----|----|----|----|----|----|----|
| Liquid volume (mL) | 0  | 0.30 | 0.40 | 0.50 | 1.00 | 3.00 | 5.00 | 10.00 |
| Ammonia concentration | 0  | 0.12 | 0.16 | 0.20 | 0.040 | 0.120 | 0.200 | 0.400 |
| Absorbance | 0.082 | 0.103 | 0.139 | 0.148 | 0.182 | 0.430 | 0.629 | 1.164 |
|          | 0.088 | 0.109 | 0.115 | 0.127 | 0.207 | 0.413 | 0.651 | 1.198 |
|          | 0.083 | 0.108 | 0.112 | 0.127 | 0.199 | 0.407 | 0.630 | 1.187 |
|          | 0.085 | 0.106 | 0.116 | 0.129 | 0.203 | 0.415 | 0.654 | 1.194 |
|          | 0.089 | 0.120 | 0.125 | 0.135 | 0.210 | 0.419 | 0.648 | 1.191 |
|          | 0.079 | 0.102 | 0.111 | 0.120 | 0.198 | 0.406 | 0.643 | 1.193 |
| average value | 0.084 | 0.108 | 0.120 | 0.131 | 0.200 | 0.415 | 0.643 | 1.188 |

Observing the data in Table 5, it was found that among the six sets of data measured with samples having an ammonia concentration of 0.016 and 0.020 g/mL, the absorbance of the first group was too large. Do Dixon test on 2 data, do you need to discard this set of values.
Table 6. Hypobromite method standard deviation

| Ammonia concentration | 0.012 | 0.016 | 0.02  | 0.032 | 0.044 | 0.056 | 0.068 | 0.080 |
|-----------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Standard deviation    | 0.0904| 0.0928| 0.0683| 0.1053| 0.0802| 0.0727| 0.0855| 0.0938|

Table 7. Salicylic acid standard deviation

| Ammonia concentration | 0.012 | 0.016 | 0.020 | 0.040 | 0.120 | 0.200 | 0.400 |
|-----------------------|-------|-------|-------|-------|-------|-------|-------|
| Standard deviation    | 0.0037| 0.0030| 0.0025| 0.0016| 0.0025| 0.0074| 0.0043|

Figure 3. Comparison of standard deviation between hypobromite method and salicylic acid method

The standard deviation of the two methods was compared and analyzed in combination with Table 6, Table 7, and Figure 3. The salicylic acid method was significantly smaller than the hypobromite method, and the standard deviation at each concentration was stabilized at a very low level. In summary, the precision can be expressed by the relative deviation and the standard deviation. The salicylic acid method has a higher precision than the hypobromite method, and is more stable at different ammonia concentrations.

6. Summary
Through this study, the improved salicylic acid spectrophotometry can be used for the determination of ammonia in indoor air, and the salicylic acid method is simpler to operate than the hypobromite oxidation method, and the experimental results are more stable and reproducible. Better sex. To use green building materials, develop the habit of ventilation, and pay attention to hygiene, in order to give us a healthier and more comfortable living environment.

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