

## Improvement of the Ammonia Analysis by the Phenate Method in Water and Wastewater

Ga-eun Park, Ha-na Oh, and Samyoung Ahn\*

Department of Environmental Education, Suncheon National University, #413 Jungangno, Suncheon, Jeonnam 540-742, Korea. \*E-mail: sahn@suncheon.ac.kr

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The amount of phenol and NaOH for the colorimetric determination of ammonia in Korean standard methods (KSM) is found to be highly excessive compared to the standard methods of several other countries. The absorbance of indophenol formed by the Berthelot reaction for ammonia analysis was measured under the various reaction conditions classified in experiment groups 1, 2, 3, 4 and KSM and American standards methods (ASM), and the relationships between the absorbance of indophenol and concentration of ammonia were compared. The amount of phenol can be reduced to 10 g (current 25 g in KSM) and NaOH can be reduced to 1.76 g (current 11 g in KSM) for the preparation of 200 mL phenate solution, and the absorbance sensitivity increased. The concentration of the phenol and NaOH correlatively affect the pH of the solution, which is a critical variable in achieving the maximum sensitivity and rapid and stable color development.

**Key Words:** Ammonia analysis, Phenol, pH, Indophenol, Standard methods

### Introduction

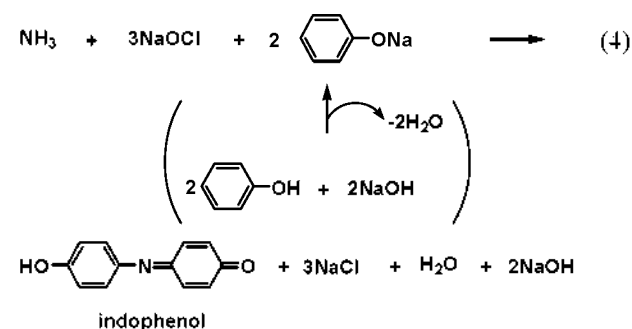
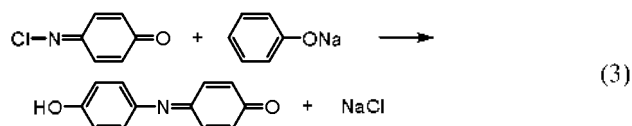
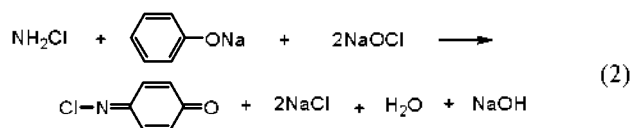
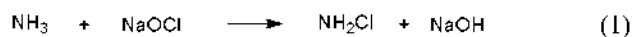
Since Korean standard methods (KSM) for water and waste water analysis were established in 1991,<sup>1</sup> they have been revised and enlarged to reflect the newly introduced environmental contaminants, more advanced analytical method and the stricter requirements for the environmental regulation by public. Through these continued efforts, standard methods are expected to provide the most reliable and up-to-date and accurate scientific and technological descriptions and knowledge for the analysis of environmental pollutants. Although standard methods is essentially analytical protocols using mechanical and physical treatment, chemical reactions and instruments which are more or less standardized globally, each country can have their own and unique standard methods adapted to its specific conditions with regards to its natural conditions, level of scientific advancement and the demands of the society. KSM has been also been established under this concept, by creating its framework, referring to other countries' standard methods, and finally resulting in its own unique methods.

In this respect, the ammonia analysis by the phenate method of KSM for water and wastewater has raised the question why and how this method including reagent dosage and procedure and instrument is established, and whether it can be further improved and optimized. Upon comparing KSM to those of other countries, such as the United States, Germany and Japan, we found that the dosage of phenol and NaOH are far more excessive in Korea. Phenol is a systemic poison and constitutes a serious health hazard. It is controlled by the governmental center for chemical safety management (CCSM), so it is desirable to minimize the usage of it if possible.

The Berthelot reaction, first reported in 1894 and named after the French chemist, is the reaction of ammonia with phenol and hypochlorite to form blue indophenol in basic solution.<sup>2</sup> Since its initial development, modifications have been made.<sup>3-6</sup> Indophenol reaction can be described by eq.(1) ~ (3).<sup>7</sup> Ammonia

(NH<sub>3</sub>) reacts with a hypochlorite (OCl<sup>-</sup>) to form a monochloramine (eq. 1), which in turn reacts with two phenates to form an indophenol dye (eq. 2 and eq. 3). Stoichiometry of the overall reaction tells us that the 1mol of NH<sub>3</sub> reacts with 2 mol of phenate and 3 mol of OCl<sup>-</sup> to form 1 mol of indophenol.

Concentration of NH<sub>3</sub> is determined by measuring the absorbance of indophenol at λ = 630 nm. In these reactions, NH<sub>2</sub>Cl, NaOH and phenol are important reagents for the indophenol formation. Although NaOH is not a component element in indophenol molecule, NaOH plays an important role by influencing in each step of the Berthelot reaction. It helps the formation of



hypochlorite ( $\text{OCl}^-$ ) and phenate. The stability of  $\text{NH}_2\text{Cl}$  is known to be affected by the  $\text{NaOH}$  concentration (eq. 1).<sup>8</sup> According to the recent work<sup>9</sup> on the mechanism of the formation of benzoquinone chlorimine (eq. 2), phenol and chloroamine forms a cation/radical-anion/radical pair as a transient species, the cation/radical undergoes attack by  $\text{NH}_2\text{Cl}$ -anion/radical leading ultimately to benzoquinone chlorimine. The negative charge on oxygen of phenate can stabilize the cation/radical species and help to form a benzoquinone structure. Phenate, rather than phenol, also effectively contributes to the single electron transfer mechanism which is suggested for the formation of indophenol at the final step (eq. 3).<sup>10,11</sup>

Considering the stoichiometric ratio of each reagent and the necessity for the excessive usage of them to ensure the complete formation of indophenol and the role of  $\text{NaOH}$  etc., question arises what could be the optimum dosage of each reagents and the reaction conditions for the best ammonia analysis by the indophenol method.

The reagents dosage (phenol,  $\text{NaOH}$ ,  $\text{NaOCl}$ , Nitroprusside) for the ammonia analysis in KSM is compared with other countries, such as United States (ASM), Germany (DIN 38406-5; VDI 2461 Blatt 1), and Japan (JIS K 0400-42-60; JIS K 0099) and summarized in Table 1.<sup>12-16</sup> Germany and Japan use the sodiumsalicylate and sodium dichloroisocyanurate (sodium

dichloro-S-triazine-2,4,6-trion;  $\text{NaDCC}$ ) for water and wastewater instead of phenol and hypochlorite, respectively. However, the basic principle is same.<sup>17,18</sup> Sodiumsalicylate is a derivative of phenol, which has  $-\text{COONa}$  functional group at ortho position of phenol and  $\text{NaDCC}$  can produce free available chlorine in the form of hypochlorous acid ( $\text{HOCl}$ ) by hydrolysis. For the ammonia analysis in air, both countries use phenol and hypochlorite, and these are also compared in Table 1.

Table 2 shows the relative molar ratio of reagents for ammonia analysis; the calculation of molar ratio of the reagents was based on the highest detection amount of ammonia in each country. In KSM the amount of phenol is 4 times excessive and  $\text{NaOH}$  is 10 times excessive and  $\text{NaOCl}$  is 1.5 times excessive than that of ASM. In the case of German and Japan, compared to ASM, a larger amount of  $\text{NaOH}$  is used for the ammonia analysis in air sample. However, this is due to the absorption of ammonia gas in the acidic (boric acid or sulfuric acid) solution during sampling procedure. The acidic absorption solution consumed some amount of  $\text{NaOH}$  to neutralize it. Nevertheless,  $\text{NaOH}$  dosage in both countries is also smaller than that of KSM. For the water sample, both countries use sodiumsalicylate and sodium dichloroisocyanurate instead of phenol and hypochlorite, respectively, and the optimum pH of solution was proposed to be pH 12 ~ 13 at which the formation

**Table 1.** Comparison of reagents amount for ammonia determination in various countries

Na-tions	Phenol (MW. 94 g)		NaOH		NaOCl		Nitroprusside		Maximum detection of ammonia	Vol (mL)
	reagent solution	amount for analysis	reagent solution	amount for analysis	reagent solution	amount for analysis	reagent solution	amount for analysis		
Korea	25 g/ 0.2 L	10 mL 1.25 g 13.3 mmol	11 g/ 0.2L	10 mL 0.55 g 13.75 mmol	21 mL/ 0.1L <sup>a</sup> (1 g/ 0.1L) <sup>b</sup>	5 mL 0.05 g 1.41 mmol	1.5 g/ 1L	1 mL 1.5 mg 0.005 mmol	0.04 mg $2.86 \times 10^{-3}$ mmol 0.8 ppm	50
USA	11.89 g/ 0.1L	1 mL 0.119 g 1.27 mmol	1 g/ 0.125L <sup>c</sup>	2.5 mL 0.02 g 0.5 mmol	1.25 g/ 0.125L <sup>d</sup> (0.59g/ 0.125L) <sup>b</sup>	2.5 mL 0.0118 g 0.333 mmol	0.5 g/ 0.1L	1 mL 5 mg 0.017 mmol	0.015 mg $1.07 \times 10^{-3}$ mmol 0.6 ppm	50
Germany (air)	62.4 g/ L	8 mL 0.499 g 5.31 mmol	50 g/ L	2 mL 0.1 g 2.5 mmol	18.6 g/L <sup>a</sup> (8.85 g/ L) <sup>b</sup>	2 mL 0.0177 g 0.499 mmol	0.894 g/ L	2 mL 1.788 mg 0.006 mmol	0.05 mg $3.57 \times 10^{-3}$ mmol 1 ppm	50
Germany (water) <sup>e</sup>	130 g/ L	4 mL 0.52 g 3.25 mmol	3.2 g/ 0.1L	4 mL 0.128 g 3.2 mmol	0.2 g/ 0.1L <sup>a</sup> (0.125 g/ 0.1L) <sup>b</sup>	4 mL 0.005 g 0.141 mmol	0.970 g/ L	4 mL 3.88 mg 0.013 mmol	0.05 mg $3.57 \times 10^{-3}$ mmol 1 ppm	50
Japan (air)	5 g/ 0.5L	5 mL 0.05 g 0.53 mmol	15 g/ L <sup>f</sup>	5 mL 0.075 g 1.875 mmol	30 g ~ 100 g/L <sup>b</sup>	5 mL 0.5 g 14.1 mmol	25 mg/ 0.5L	5 mL 0.25 mg $8.4 \times 10^{-4}$ mmol	0.01 mg <sup>g</sup> $0.71 \times 10^{-3}$ mmol 0.4 ppm	25
Japan (water) <sup>e</sup>	130 g/ L	4 mL 0.52 g 3.25 mmol	32 g/ L	4 mL 0.128 g 3.2 mmol	0.2 g/0.1L (0.125 g/ 0.1L) <sup>b</sup>	4 mL 0.005 g 0.141 mmol	0.970 g/ L	4 mL 3.88 mg 0.013 mmol	0.05 mg $3.57 \times 10^{-3}$ mmol 1 ppm	50

<sup>a</sup>10% NaOCl. <sup>b</sup>Calculated for available chlorine. <sup>c</sup>100 mL from 10 g/L NaOH solution is mixed with 25 mL NaOCl. Citrate was not compared, as it is used only in ASM. <sup>d</sup>5% NaOCl. <sup>e</sup>Sodiumsalicylate instead of phenol, NDD instead of NaOCl. <sup>f</sup>Prepared in NaOCl solution. <sup>g</sup>Referred from calibration curve.

**Table 2.** Relative molar ratio of each reagent to the highest detection amount (mmol) of ammonia

Country	Reagents	NH <sub>3</sub>	Phenol	NaOH	NaOCl	Nitroprusside
Korea		1	4,650	4,668	493	1.7
USA		1	1,187	467	314	15.9
Germany(air)		1	1,487	700	140	1.68
Germany(water)		1	910	896	39.5	3.64
Japan(air)		1	746	2,641	19,859	1.18
Japan(water)		1	910	896	39.5	3.64

of 5-aminosalicylate from salicylate and chloroamine is facilitated.<sup>17</sup> Therefore NaOH dosage of both countries for the ammonia analysis in water is higher than that of ASM, but they are still less than that of KSM. The hypochlorite concentration is not particularly critical once it is reached above a certain value (usually 10%) when using nitroprusside as the catalyst.<sup>19</sup>

The excessive amount of phenol and NaOH is necessary for the high yield of indophenol, and there are plenty of reports on the wide range of concentration of phenol in diverse reaction conditions. However, it still lacks a systematic investigation on the optimum reagents concentrations from the point of the inter-relationship among phenol and NaOH dosage and pH condition.

The much higher dosage of reagents in KSM and the absence of available scientific data to explain it prompted us to examine the appropriate amount of phenol and NaOH for the effective, reliable and environmentally more benign ammonia determination in term of the analytical sensitivity and color stability.

### Material and Methods

For the colorimetric determination of ammonia, spectrophotometer (Shimadzu 160) was used at 630 nm with a light path of 1 cm. Unless specified otherwise, analytical grade reagents were obtained from chemical suppliers and used as received. All aqueous solution were made in water purified with a Milli-Q system (18 MΩ·cm).

a. Stock ammonium chloride solution: Dissolve 0.3819 g

anhydrous NH<sub>4</sub>Cl (dried at 100 °C) in water, and dilute to 1 L (100 ppm NH<sub>3</sub>-N). A standard ammonium chloride solution (5 ppm) was prepared by diluting the stock ammonium chloride solution in 20 times.

b. Sodium phenate solution: Mix 25 g phenol with 55 mL of 20% NaOH, then 6 mL acetone and water to a final volume of 200 mL.

c. Sodium nitroprusside: Dissolve 0.15 g sodium nitroprusside in water.

d. Sodium hypochlorite: Commercial solution, about 10%. This solution slowly decomposes once the seal on the bottle cap is broken. Replace about every 2 months.

**Indophenol formation.** According to the procedure of KSM, 1, 2, 4, 8, 10, 15, 20 mL of standard ammonium solution (5 ppm) was added into each of 50 mL volumetric flask and ca. 30 mL of water was added. 10 mL of sodium phenate, 1 mL of nitroprusside and 5 mL of hypochlorite solution were added, and then water was added up to the marked line (final concentrations of each solutions are 0.1, 0.2, 0.4, 0.8, 1, 1.5, 2 ppm). Mix it gently and leave it at 20 ~ 25 °C in temperature of solution for 30 min. as it is.

4500-NH<sub>3</sub> F. phenate methods was carried out according to the procedure described in the ASM.<sup>12</sup>

**Experiment design.** Four experiment groups with diverse amounts of phenol and NaOH were designed and listed in Table 3. KSA and ASM were also performed and their results were compared with the results of four experiment groups. Each experiment was repeated several times and three experimental data with minimum standard deviation are taken for statistical calculation to obtain the relation curve between ammonia concentration and absorbance.

**Absorbance sensitivity and color stability.** Absorbance of indophenol in each experiment was measured and the calibration curve was obtained by plotting absorbance against ammonia concentration. The slope of linear correlation is defined as 'absorbance sensitivity' and the slopes of experiment groups were compared to discuss the quality of ammonia analysis. The steeper the slope is, the better is the absorbance sensitivity meaning that indophenol formation is more facilitated. In addition, the absorbance was measured in 30 min., 1 h and 2 h in order to investigate the rate and stability of color development with reaction time elapsed.

**Table 3.** Phenol and NaOH dosage in reactions of each experiment groups<sup>a</sup>

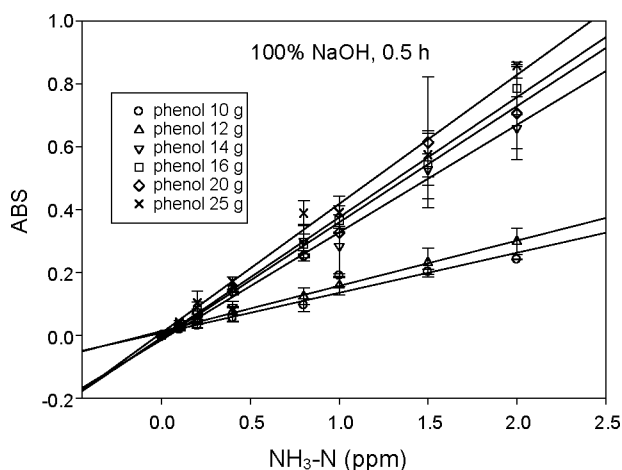
reaction	Group		experiment group 1	experiment group 2	experiment group 3	experiment group 4	American standard methods (4500-NH <sub>3</sub> F. Phenate method)
	NaOH(g)	phenol(g)					
			100%	80% <sup>b</sup>	40% <sup>b</sup>	20% <sup>b</sup>	
1	25		11 <sup>c</sup>	8.8	-	2.2	
	22		-	-	4.4	-	
2	20		9.68	7.75	3.52	1.94	phenol: 11.89 g NaOH: 1 g in 100 mL solution
3	16		7.04	5.63	2.82	1.41	
4	14		6.16	4.93	2.46	1.23	
5	12		5.28	4.22	2.11	1.06	
6	10		4.40	3.52	1.76	0.88	

<sup>a</sup>The dosage is for the preparation of phenate solution (200 mL solution) not for the mixture of the indophenol formation. <sup>b</sup>Based on the amount used in group 1. <sup>c</sup>Korea standard methods.

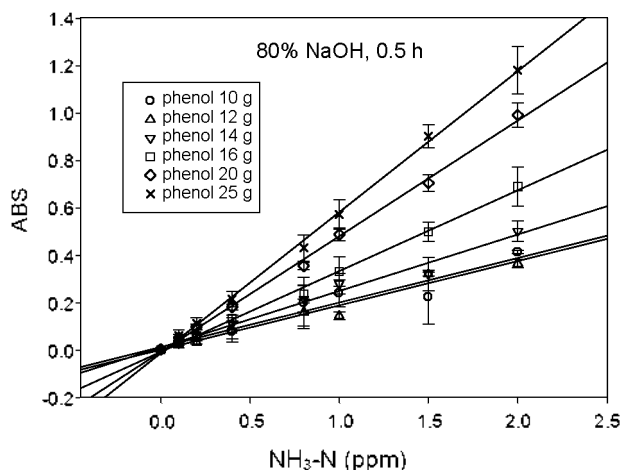
## Results and Discussion

**Influence of NaOH and phenol dosage on the absorbance sensitivity.** NaOH was used to maintain the solution under basic conditions and to form phenate. Phenol is hazardous chemical and dosage reduction, if possible, is desirable. In experiment group 1, each reaction has different dosage of phenol and NaOH; the amount of NaOH was reduced in proportion to the stepwise reduced amount of phenol. Fig. 1 shows the relationship between ammonia concentration and the absorbance of reaction 1 ~ 6 in experiment group 1 with the color development duration of 30 min. The best absorbance sensitivity among 6 reactions within group 1 was obtained in reaction 1 (phenol 25 g and NaOH 11 g), and the slope was 0.41. This condition is the same as in KSM. Upon stepwise decreasing the phenol and NaOH dosage, the absorption sensitivity (slope) decreased to 0.37, 0.38, 0.34, 0.14, 0.13 respectively.

Fig. 2 shows the result of experiment group 2, where the amount of NaOH is additionally reduced to 80% of the amount used for experiment group 1. In the case of experiment group 2, the best absorbance sensitivity among 6 reactions was



**Figure 1.** Calibration curve for the determination of ammonia in group 1.

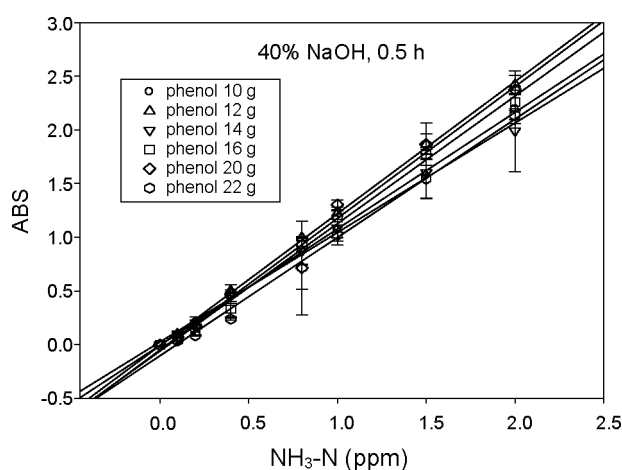


**Figure 2.** Calibration curve for the determination of ammonia in group 2.

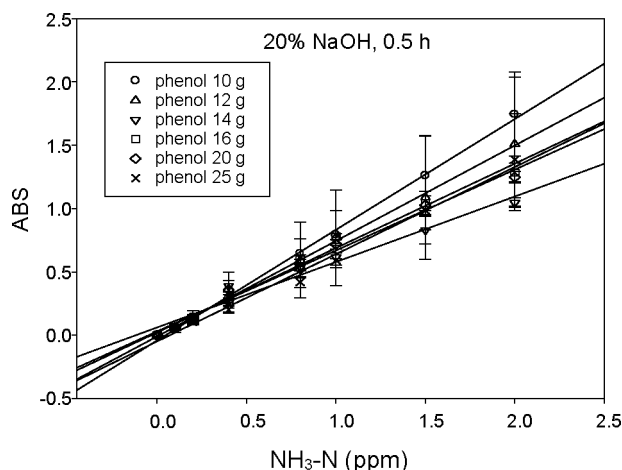
obtained in the reaction 1 with phenol 25 g and NaOH 8.8 g, and the slope was 0.59. Upon stepwise decreasing the NaOH dosage in proportion to the phenol dosage, the absorbance sensitivity (slope) decreased to 0.49, 0.34, 0.24, 0.19, 0.19 respectively. Interestingly, the best slope among the experiment group 2 is higher than that of the experiment group 1 by 0.18; the reaction with less NaOH dosage shows the better absorbance sensitivity despite the same dosage of phenol.

Fig. 3 shows the result of experiment group 3, where 40% of NaOH relative to the experiment group 1 was used. In this case, unlike the former two groups (group 1 and 2), the absorbance sensitivity of each reaction was within a narrow range between 1.02 ~ 1.23 and the values are much higher than those of the group 1 and 2. This result means that the phenol and NaOH dosage for ammonia analysis by indophenol method in KSM can be reduced without sacrificing the detection sensitivity. In fact, the sensitivity even increases.

The result of experiment group 4 was illustrated in Fig. 4, where only 20% of NaOH based on the experiment group 1 was used. The best absorbance sensitivity was obtained at 10 g phenol (reaction 6) and the sensitivity decreased with the



**Figure 3.** Calibration curve for the determination of ammonia in group 3.



**Figure 4.** Calibration curve for the determination of ammonia in group 4.

increasing phenol and NaOH dosage. However, the overall sensitivity ranged from 0.87 to 0.52, which is lower than the group 3, but still higher than those of group 1 and group 2 despite the smallest amount of NaOH. The amount of NaOH in group 4 seems to be insufficient for pH of the solution and for the formation of phenate.

For the quality control of the experiments performed in this research and also comparison with the results of the experiment groups, 4500-NH<sub>3</sub>F, phenate method for ammonia analysis of ASM was performed. The slope obtained by this study was 1.20 ( $r^2 = 0.98$ ,  $n = 5$ , data not shown), it is in a very good consistency with the precision data given in Table 4500-NH<sub>3</sub> of the ASM, where the slope of linear relationship of NH<sub>3</sub>-N concentration and optical density ranged 1.12 ~ 1.29. It means that our experiments and the results are reliable.

Among all experiment groups including ASM, the group 3 with 60% reduction of NaOH shows the best absorbance sensitivity under the conditions used for this study, and phenol can be also reduced from current amount 25 g to the maximum 10 g.

**NaOH dosage and pH of the solution.** As mentioned in section above, NaOH dosage appeared to be an important variable of the sensitivity of ammonia analysis. As the amount of NaOH influences on the pH of the solution, relationship of NaOH dosage and pH of all experiment groups were summarized in Fig. 5. Group 1 with the highest dosage of NaOH shows the highest pH, group 2 with the next higher NaOH dosage did not show a large difference from group 1 in pH of solution. Group 3 shows significantly low pH followed by group 4.

The pH deviations in groups are noteworthy. Group 3 has pH range of 10 ~ 11 and group 4 pH range of 9.5 ~ 10.8, more than one unit, while group 1 and 2 have a very narrow pH range of 12.4 ~ 12.7. For the latter, the amount of NaOH may still be far excessive so that pH of the solution may not be affected by the consumption of phenol. On the other hand, for the group 3 and 4 with much reduced amount of NaOH, the amount of phenol, which consumed NaOH to form phenate, can have a significant influence on pH of solution. For example, for ca. 4 g of NaOH dosage group 1 and 2 show pH of ca. 12.5, while group 3 shows around pH 10.2; despite of the same amount of NaOH, pH of the solutions are largely different. Phenol dosage

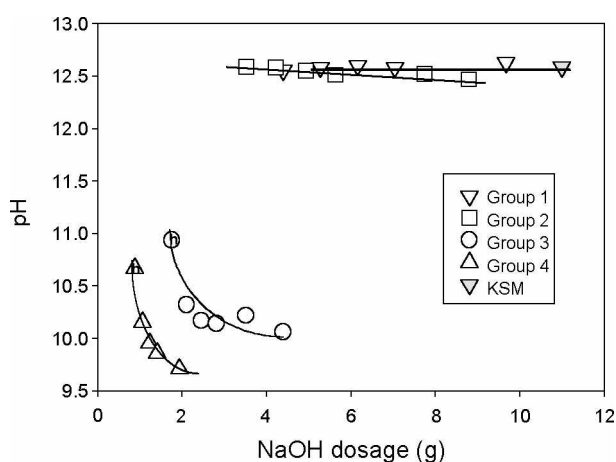


Figure 5. Dependence of pH of the solution on the NaOH dosage.

in these three cases are 10 g (group 1), 12 g (group 2) and 22 g (group 3) respectively. Therefore, it can be deduced that the consumption of NaOH by large amount of phenol in group 3 resulted in the lowering of pH of the solution.

In addition, it is eye-catching that pH of the solution increased with the decreasing dosage of NaOH (solid line), which is generally abnormal. This trend is profound in group 3 and 4, while it is weak in group 1 and group 2. The decrease of NaOH dosage is accompanied by the decrease of phenol dosage as programmed in Table 3. Therefore, the rise in pH with decreasing NaOH related closely with the decreasing phenol dosage. This phenomenon is especially obvious for the group 3 and 4: the reactions with symbol 'h' (meaning highest pH within the group) in Fig. 5 use the smallest amount of phenol in group 3 and 4, which will demand less NaOH. Therefore, pH of the solution using the smallest dosage of NaOH can be higher than other reactions using larger amounts of NaOH within the same group. This finding indicates that the phenol dosage as well as NaOH influences the pH of the solution.

**Effect of phenol dosage and pH on the color development rate and stability.** KSM recommends a color developing period of 30 min., ASM at least 1 h. This reaction time would be set under their own reaction conditions applied in each country. The changes of phenol and NaOH dosage may not only affect the absorbance sensitivity but also the color development rate and stability. Fig. 6 shows the effect of phenol dosage on the color intensity with different reaction period, 30 min., 1 h and 2 h, which is denoted by the small, medium and large symbol, respectively. For example, the circle denoted the group 3 and the small circle represents the result of 30 min. color developing time, the medium circle for 1 h color developing time, and the large circle for 2 h reaction time.

Group 3 with high absorbance sensitivity shows rapid and stable color development, especially for phenol dosage of 10 g and 12 g. It means that the reaction condition of group 3 with

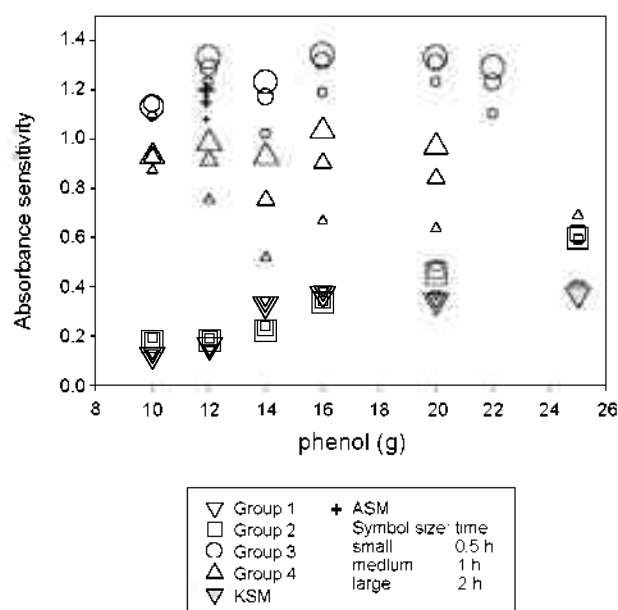


Figure 6. Color developing rate and stability vs. phenol dosage.

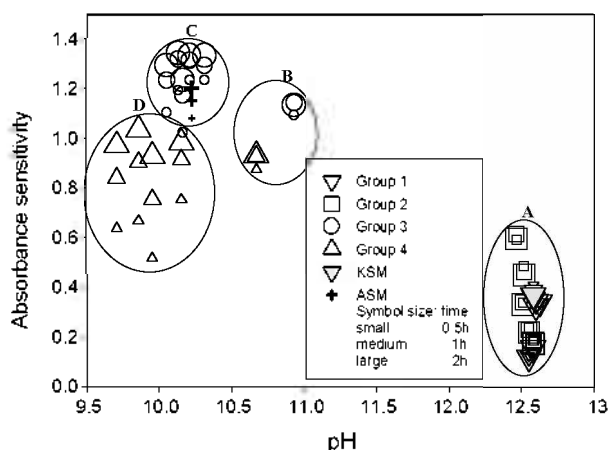


Figure 7. Color developing rate and stability vs. pH of the solution.

the reduced dosage of phenol and NaOH is also good for a rapid and stable color development as well as the excellent absorbance sensitivities. The reactions in group 4 except reaction 1 show the largest deviation of absorbance with time elapsed, indicating slower color development. Group 1 and 2 show a rapid color development and stability over all range of phenol dosage, but the absorbance sensitivities are very low ranging from 0.2 to 0.6 depending on the reaction condition.

In order to illustrate the influence of pH on the color development, the absorbance sensitivity of reactions in each group is plotted against the pH in Fig. 7. It is clearly demonstrated again that category C (reactions in group 3) has the high absorbance sensitivities and the color development is also rapid and stable in terms of the reaction time. Category D shows a relatively slow color development, so the color intensity increased *ca.* 80% after 2 h reaction time. Category A shows a rapid color development and the intensity of indophenol does not change within 2 h, but this can be attributed to the intrinsically low absorbance, as the relative change of low absorbance with time can be small. Besides, the quality of ammonia analysis in this case is poor. Two reactions in category B show the very rapid color development and relative high absorbance sensitivities. The reason for that is attributed to the pH ranged from 10.5 to 11.

Too high pH has negative effects on the absorbance sensitivity, which is verified by the category A. The lowering pH below a certain value sacrifices color stability (category D), therefore pH control is very important for the maximum absorbance and stable color development. The previous study, though different dosage, also reported that the indophenol color was stable at pH values between 11.4 and 12.4.<sup>19</sup> Fig 5 ~7 tell us that the amount of phenol and NaOH are interrelated to determine pH of the solution, which affects in turn the color development as well as the absorbance intensity.

**Consideration on the influence of pH on the reaction steps.** It is certainly not a simple process to figure out how the dosage of NaOH and phenol or pH of the solution affects the ammonia analysis. Monochloramine is the first intermediate, and the study on the kinetics of its formation and decomposition showed that there was a relatively narrow pH range (10.5 ~ 11.5) suitable for forming stable monochloramine under the

Berthelot reaction conditions:<sup>8</sup> monochloramine decomposition is extensive below pH 10.5 and the rate of monochloramine formation becomes slow after reaching the maximum at pH 9. In this stage, the catalyst, nitroprusside, is known not to affect the formation of monochloramine.<sup>20</sup>

Investigation on the Gibbs reagent, 2,6-dichloroquinone-imine, revealed that the decomposition of benzoquinone chlorimine was pH dependent; this reagent decomposed completely within 15 min at pH > 10 to form products which do not react with phenol.<sup>21</sup> Although this result was obtained in the absence of nitroprusside catalyst, it gives a hint of the possibility of this kind of side reaction. The unsubstituted chlorimine may decompose even more rapidly as it is more unstable than substituted chlorimine.<sup>22</sup>

The color of indophenol itself is yellow and the color of dissociation product, indophenol salt, is blue. The dissociation of indophenol is pH dependent and reversible. The pKa for indophenol is known to be 8.1<sup>23</sup> and Henderson-Hasselbalch equation provides the information that the blue color will intensify at the higher pH, perhaps above 10, 2 units higher than 8.1, as the ratio of indophenol salt/indophenol is almost one hundred at this pH. Therefore the lower pH seems certainly to have a negative influence on the color intensity; however it does not explain the decline of absorbance sensitivity above pH 12 as demonstrated by group 1 and 2. If the pH dependent dissociation of indophenol were a main factor for the absorbance sensitivity, a plateau of absorbance would be reached with an increasing pH.

## Conclusions

This study shows that the phenol and NaOH dosage used in current KSM is far excessive compared to those of other countries and that they can be reduced and the quality of ammonia analysis greatly improved. Under the conditions of our experiments, the amount of phenol and NaOH can be reduced maximum to 10 g and 1.76 g for the preparation of 200 mL phenate solution, respectively. These correspond to 0.5 g phenol and 0.088 g NaOH for 50 mL sample analysis containing the N-NH<sub>3</sub> concentration of 0 ~ 2 ppm. The absorbance sensitivity increased from 0.41 (current KSM) to 1.09.

The results from this study will expand the understanding on the colorimetric ammonia analysis and provide useful information to legislators and experts in this area in the process of establishing and revising the standard method for ammonia analysis in water.

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