

## Practical Paper

# Methods for controlling stored urine odor in resource-oriented sanitation

Shervin Hashemi and Mooyoung Han

### ABSTRACT

Urine odor is a major challenge in the development of resource-oriented sanitation (ROS). One common solution to overcome odor issues is to use energy-consuming ventilation practices. However, historically ancient Koreans practiced separation of urine and feces, followed by the collection and utilization of gathered sanitary matters. Furthermore, ancient Persians developed solutions to urine odor issues. This study investigates the role of  $\text{NH}_3$  concentration on odor production in stored urine using the standard threshold odor number (TON) measurement. Trends in pH and  $\text{NH}_3$  production, as well as their interactions with TON, were investigated by simulating ancient Korean practices that stored urine under anaerobic conditions at different temperatures. The results show a direct relationship between the concentrations of  $\text{NH}_3$  and TON. Storing urine under anaerobic conditions leads to the production of  $\text{NH}_3$ , which intensifies as temperature increases. The effect of pH and  $\text{NH}_3$  concentrations on the TON of stored urine explains the ancient Persian approach, given that additives, such as acetic acid and sodium bicarbonate, are effective for removing urine odor. Such approaches can be successfully applied to ROS systems.

**Key words** | ancient practices, resource-oriented sanitation, sustainable sanitation, threshold odor number (TON), urine odor

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### INTRODUCTION

Resource-oriented sanitation (ROS) has been increasingly considered as a substitute for current wastewater treatment systems in developing countries because it helps fulfill the sixth Sustainable Development Goal (SDG-6) (Han *et al.* 2016; Han & Hashemi 2017). Source-separated urine that can be used as fertilizer forms the basis of these systems (Hashemi & Han 2017a). However, the production of urine odor at the collection and storage stages tends to make these systems unpopular and hinders their widespread acceptance (SANitar-Recycling ESCHborn 2012; Hashemi & Han 2017b).

The separation of urine at its source has a long history, especially in Asia. Korea practiced urine separation and utilization as fertilizer from the Silla dynasty to the Joseon dynasty (57 BC–1897 AD), using special closed urine jars called

yogang and ojum-janggun. Although there is no evidence of any particular practice for odor prevention, these jars could act as sealed anaerobic storages, used for storing source-separated urine (Han & Kim 2014; Han & Hashemi 2017). Ancient Persians used vinegar and baking soda as a means to remove odors from materials contaminated with urine (Menocal *et al.* 2000). A Persian chemist named *Zaryab* transferred this knowledge to the Europeans during his stay in Andalusia in the ninth century (Holod 1992). A scientific investigation of the application of the mentioned ancient practices may be helpful for improving the acceptability of ROS systems.

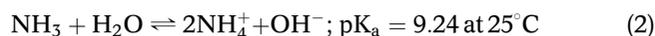
Foods and drugs have a substantial impact on the smell of fresh urine (Hashemi & Han 2017b). In stale urine, odor can be caused by a number of odorous compounds, such

as ammonia, trimethylamine, and various types of volatile fatty acids (Zhang *et al.* 2013; Hashemi *et al.* 2016). To control odor, managing ammonia is important because of its notably higher concentration compared to other odorous compounds (Wolrath *et al.* 2005).

Following excretion, urea ( $\text{CH}_4\text{N}_2\text{O}$ ) is the predominant component of fresh urine after water (Udert *et al.* 2006). As soon as urine is excreted from the human body, urea is converted to ammonia ( $\text{NH}_3$ ) by the enzyme urease via the reaction presented in Equation (1). This process usually lasts 15–20 days until the urine stabilizes, meaning that no more  $\text{NH}_3$  is produced (Hashemi *et al.* 2016):



Then,  $\text{NH}_3$  reacts with water and increases the pH of the urine, as demonstrated in Equation (2) (Bates & Pinching 1949):

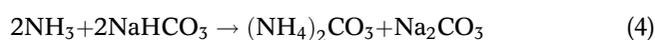


In Equation (2), at a constant temperature of  $25^\circ\text{C}$  and  $\text{pH} > 9.24$ ,  $\text{NH}_3$ , the major compound in the system, dissolves in water by forming hydrogen bonds with water molecules. Because of evaporation and the higher electronegativity of oxygen compared to nitrogen, hydrogen bonds between  $\text{NH}_3$  and water molecules break easily, and  $\text{NH}_3$  is released as a gas (Hashemi *et al.* 2016).

As in ancient Persian practices and as demonstrated by Equation (3), adding acetic acid ( $\text{CH}_3\text{COOH}$ ) reduces the pH and converts  $\text{NH}_3$  into ammonium ions ( $\text{NH}_4^+$ ) (Equation (3)) (Hashemi 2015):



Adding sodium bicarbonate ( $\text{NaHCO}_3$ ) induces a chemical reaction with  $\text{NH}_3$  and produces ammonium carbonate salt ( $(\text{NH}_4)_2\text{CO}_3$ ) (Equation (4)). This reaction increases the pH of the solution and creates favorable conditions for the precipitation of ammonium carbonate salt as a solid fertilizer (Hashemi 2015):



Both of these practices that target  $\text{NH}_3$  were used for deodorizing urine in ancient Persia. The former practice changes  $\text{NH}_3$  into an ionic form and the latter precipitates it as sediment.

Several medical and urological studies have focused on urine odor (Pelchat *et al.* 2011); however, there is not enough research on the causes of urine odor and how to overcome it in the context of ROS practices. Although the storage of source-separated urine does not necessarily require forced ventilation and energy, most current studies still suggest ventilation or remote storage as solutions to remove urine odor. These methods are energy- and resource-intensive, and they make urine storage less desirable (Zhang *et al.* 2013). Accordingly, developing *in situ* methods to overcome urine odor and increase public acceptance of ROS systems is essential.

The objectives of this study are as follows:

1. Investigating the ability of  $\text{NH}_3$  to produce urine odor using the standard method of threshold odor number (TON).
2. Examining the trends in  $\text{NH}_3$  (and smell) production during storage under anaerobic conditions, simulating ancient Korean practices.
3. Introducing solutions to control urine odor by simulating ancient Persian approaches.

## MATERIALS AND METHODS

### Urine sample preparation

Fresh urine samples were collected from public waterless urinals installed in Building 35 at the Seoul National University using three 10-L plastic containers (total volume of 30 L). The urine came from men between the ages of 25 and 35. The pH and total ammonia concentration of these samples were measured immediately after sampling. Total  $\text{NH}_3$  was measured according to the USEPA standards (USEPA 1983) using a UV/Visible spectrometer (model HS-3300, Humas Co., Daejeon, Republic of Korea). The initial pH was measured using an Aquaprobe (model AP-2000, Aquaread, Broadstairs, UK). The urine sample in one of the plastic containers (10 L) was labeled 'Fresh Urine' and immediately used in the 'Urine under Anaerobic Conditions Experiment.'

The two remaining urine containers (20 L) with sealed lids were stored in a digital incubator (model GY-03616-45, Cole-Parmer, Vernon Hills, IL, USA). The temperature was set to 15 °C, following World Health Organization (WHO) guidelines (Schönning 2001; WHO 2016). The pH and total NH<sub>3</sub> concentrations of this sample were measured for 20 days. No significant changes in measured characteristics were detected after the 17th day, indicating that the sample had stabilized. These samples were labeled 'Stale Urine' and used in the 'TON comparison among urine and ammonia solution' and 'effect of pH and ammonia concentration on TON of urine' experiments. Table 1 presents the characteristics of the fresh and stale urine samples.

### TON comparison among urine and ammonia solutions; experimental setup

Seven 500-mL beakers were filled with standard NH<sub>3</sub> solutions with concentrations of 5, 100, 500, 1,000, 2,000, 3,000, and 5,000 mg/L provided by Daejung Chemical & Metals Co. (Siheung-Si, Gyeonggi-Do, Republic of Korea). The pH of each sample was measured to be 12. Similarly, seven 500-mL beakers were filled with stale urine collected using the method described in the previous subsection. NH<sub>3</sub> concentrations in the seven samples of stale urine were set to 5, 100, 500, 1,000, 2,000, 3,000, and 5,000 mg/L using deionized water (14 samples in total) to compare the TON of NH<sub>3</sub> solutions and stale urine samples.

Furthermore, the pH and temperature of both sets of sample were set to constant values. The pH of all stale urine samples was adjusted to 12, using 1 mol/L solution sodium hydroxide (NaOH) provided by Daejung Chemical & Metals Co. (Siheung-Si, Gyeonggi-Do, Republic of Korea). The temperature was set to 15 °C using the Standard Benchtop Chilling/Heating Block equipment from Cole-Parmer (Vernon Hills, IL, USA).

**Table 1** | Initial characteristics of urine samples

Samples	pH	Ammonia concentration (mg/L)
Fresh urine	6.4 ± 0.2	Not detected (<0.001 mg/L)
Stale urine (after 20 days)	9.8 ± 0.2	6,152

The TON was measured according to the USEPA-approved Standard Method 2150 B (APHA/AWWA/WEF 2012). Twenty people participated in the experiments as smell testers to execute the TON measurement for samples. The testers included an equal number (four) of individuals from Africa, the Americas, Asia, Europe, and Oceania. Each set of testers included two males and two females, aged 25–32, who were healthy and had no nasal problems or difficulties with respect to their sense of smell. All study participants provided informed consent, and an appropriate ethics review board approved the study design.

### Urine under anaerobic conditions; experimental setup

This experiment was conducted to simulate the ancient Korean practice of urine collection and storage. Three sets of six samples of 300 mL fresh urine (18 samples in total) were prepared using 500-mL glass bottles. The lids of the bottles were sealed. The temperatures of the six samples were set to 5, 10, 15, 20, 25, and 30 °C using the Standard Benchtop Chilling/Heating Block equipment. This apparatus was placed inside an Anaerobic System Machine model VS-5600A by Vision Scientific Co. (Bucheon-Si, Gyeonggi-Do, Republic of Korea).

Samples were analyzed for pH and total NH<sub>3</sub> concentrations for 30 days following USEPA standards (USEPA 1985). The measurements were conducted every 2 hours until the pH stabilized. After stabilization, measurements were conducted every 3 days. Three sets of samples were prepared to obtain triplicate measurements. The arithmetic means of the measured values were used as the final dataset.

### Effect of pH and NH<sub>3</sub> concentrations on the TON of urine; experimental setup

This experiment was conducted to simulate the ancient Persian practice of removing urine odor and to investigate the effect of pH and NH<sub>3</sub> concentrations on the TON of urine. For this experiment, two sets of samples (20 samples in total) were prepared using 500 mL beakers filled with stale urine. Set 1 (six samples) had different pH values while Set 2 (14 samples) had varied NH<sub>3</sub> concentrations. NH<sub>3</sub> and pH were not controlled in the samples of Set 1 and Set 2, respectively. Sample temperatures were

maintained at 15 °C using the Standard Benchtop Chilling/Heating Block equipment in accordance with the WHO guidelines.

Set 1 contained six samples, and the pH was set to 3, 5, 7, 9, 11, and 13 using citric acid and sodium hydroxide solutions, both provided by Daejung Chemical & Metals Co. (Siheung-Si, Gyeonggi-Do, Republic of Korea). Set 2 was prepared using 14 samples with NH<sub>3</sub> concentrations ranging from 500 to 5,500 mg/L, increasing at 500-mg/L intervals. The NH<sub>3</sub> concentration adjustments were carried out using deionized water. First, NH<sub>3</sub> and pH were measured for each sample in Sets 1 and 2, respectively. Then, all of the samples in both sets were analyzed for TON.

## RESULTS AND DISCUSSION

### Quantifying and comparing odor of NH<sub>3</sub> solutions and stale urine using TON

Figure 1 presents the changes in TON for different NH<sub>3</sub> concentrations of standard NH<sub>3</sub> solutions and stale urine at the

same temperature and pH conditions. The experiment was conducted five times with the same setup but under different temperature and pH conditions, and the same trend was observed in each repetition.

For all NH<sub>3</sub> concentrations, the TON values for standard NH<sub>3</sub> solutions and stale urine were very close. This implies the significant ability of NH<sub>3</sub> to cause the odor in stale urine. Since our ultimate goal is to reduce urine odor during the storage stage of ROS practices, we should control NH<sub>3</sub> concentrations in the system.

### Urine stored under anaerobic conditions

Figure 2 presents a contour diagram for changes in the pH of urine samples kept under anaerobic conditions at different times and temperatures.

In general, the results showed rapid pH increases in less than 12 h. At low temperatures, pH rose at a slower rate, while at higher temperatures, it increased at a much faster rate. The pK<sub>a</sub> in Equation (2) is strongly related to temperature. For instance, at 5 and 30 °C, pK<sub>a</sub> was 9.90 and 9.09, respectively (Bates & Pinching 1949). Since lowering the

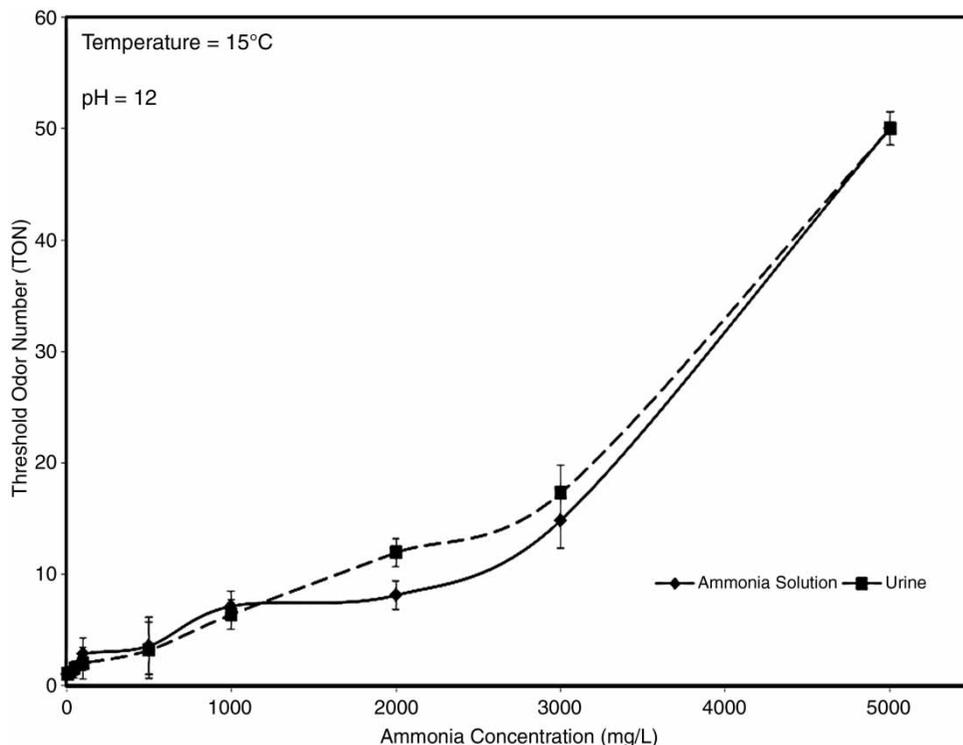
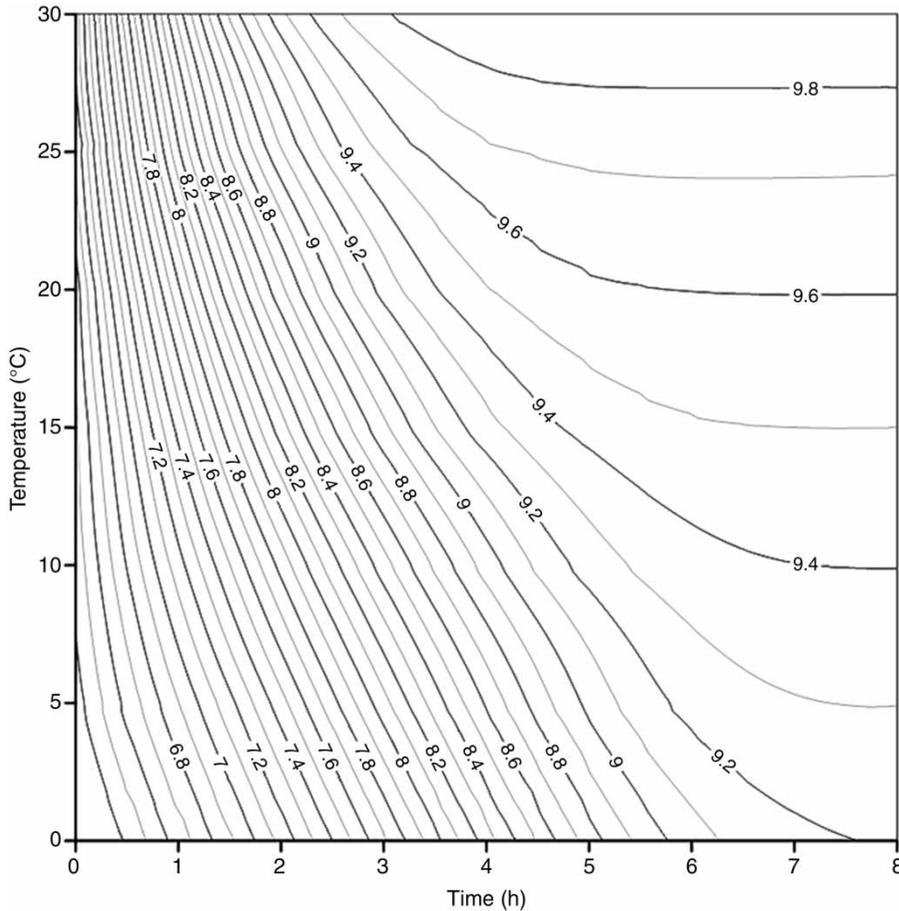


Figure 1 | Changes in threshold odor number (TON) and ammonia concentration for stale urine vs. pure ammonia solution.



**Figure 2** | Contour diagram of changes in pH with time and temperature in urine samples kept in anaerobic conditions.

temperature can increase the pKa value, there is a higher potential for  $\text{NH}_3$  to be converted to the gas-phase at a higher temperature, which is not favorable for odor reduction.

These trends are somewhat similar to the results of Cook *et al.* (2007). However, the sampling method and the temperature values used in that study are not realistic for application in ROS practices. Furthermore, Cook *et al.* (2007) did not specifically discuss the relationship between pH and  $\text{NH}_3$  (odor) production because the objectives of the study were medical in nature.

Figure 3 presents a contour diagram for the production of  $\text{NH}_3$  with time in urine samples kept under anaerobic conditions at different temperatures.

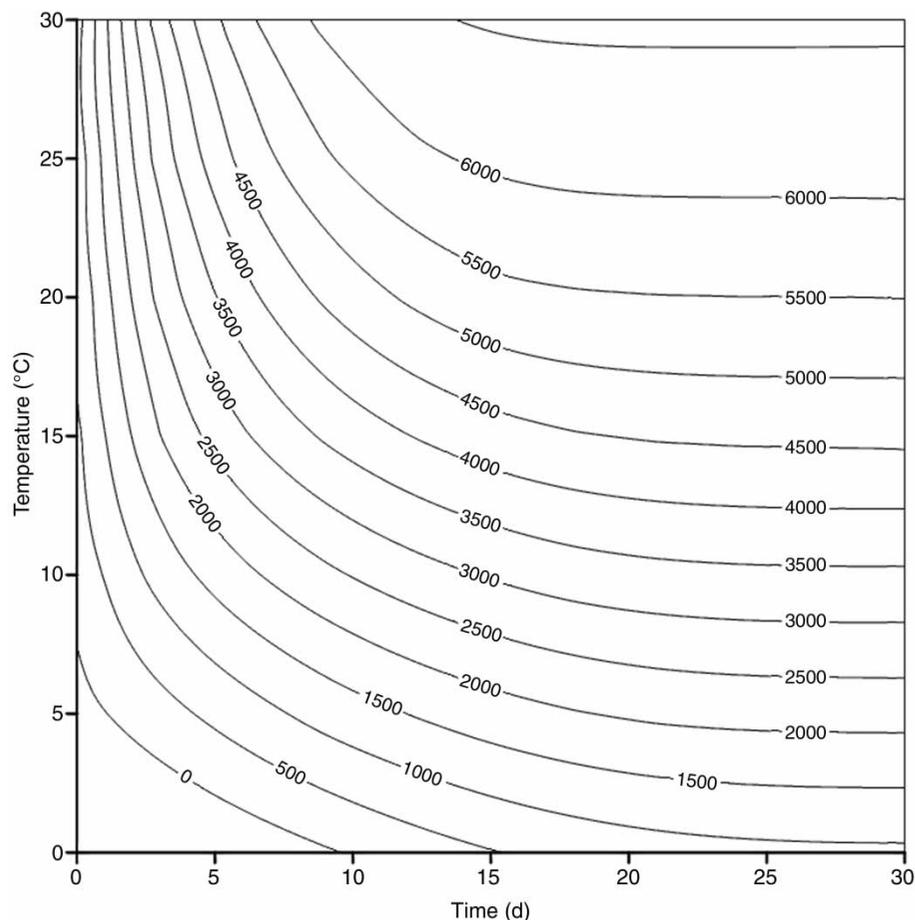
In order to reduce odor production, the concentration of molecular  $\text{NH}_3$  must be reduced. The general trend of the results shows that the  $\text{NH}_3$  concentration first increases and then becomes constant. However, at lower

temperatures ( $5^\circ\text{C}$ ) there is less stabilized  $\text{NH}_3$  (about 2,100 mg/L) with a longer stabilizing time (about 21 days). Meanwhile, at higher temperatures ( $20^\circ\text{C}$ ), the stabilizing time reduces (about 15 days), but more  $\text{NH}_3$  is produced (about 5,500 mg/L).

These results demonstrate that the enzyme urease process, as explained in Equation (1), is faster and more efficient at higher temperatures. According to the results presented in Figure 2, urine pH is also higher under anaerobic conditions, which means that  $\text{NH}_3$  is more likely to be in the molecular form; therefore, higher odor production is observed.

#### Effect of pH and $\text{NH}_3$ concentrations on urine TON

Figure 4 presents the urine TON as a contour diagram, which describes the correlation between pH and  $\text{NH}_3$



**Figure 3** | Contour diagram of the changes in  $\text{NH}_3$  with time and temperature in urine samples kept under anaerobic conditions.

concentrations. As presented in this diagram, TON is higher at higher pH and  $\text{NH}_3$  concentrations.

The results show that the stale urine is in a large TON zone. In order to lower the odor production, there are two possible solutions:

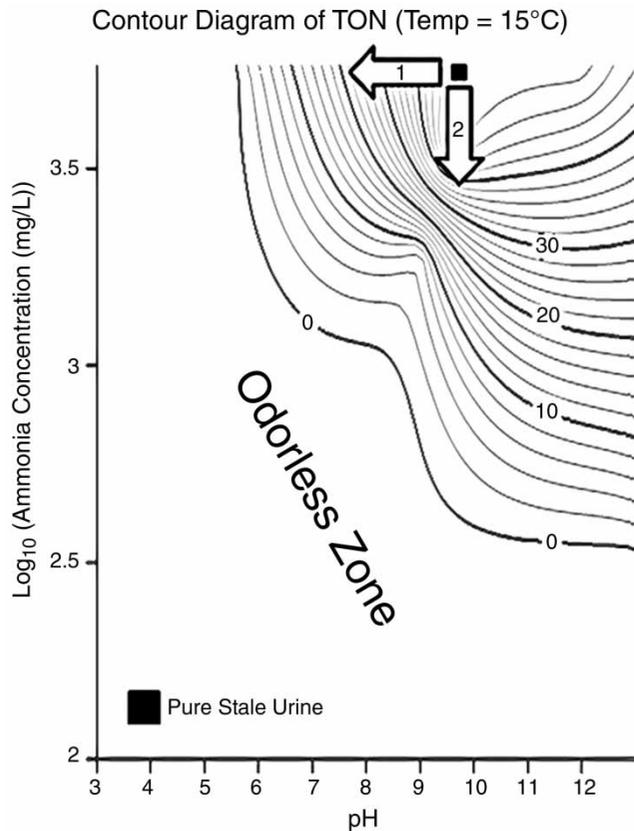
1. *Reducing pH (Arrow 1)*: At a lower pH,  $\text{NH}_3$  transforms into its ionic form,  $\text{NH}_4^+$ , resulting in less odor production, which explains how using acetic acid, as in the ancient Persian practice, can be effective in removing urine odor.
2. *Reducing  $\text{NH}_3$  concentration (Arrow 2)*: Another way to limit the evaporation of  $\text{NH}_3$  is to reduce its concentration by making it settle out as sediment. As in the ancient Persian practice, sodium bicarbonate can precipitate molecular  $\text{NH}_3$  by producing

ammonium carbonate, which reduces odor production as well.

### Practical applications

$\text{NH}_3$  is the main reason for urine odor during storage, and it limits the social acceptability of ROS systems. The odor can be managed by considering the conditions, objectives, and requirements of the system via *in situ* methods.

The control of the concentration of molecular  $\text{NH}_3$  can be achieved by actions such as reducing the storage temperature to  $15^\circ\text{C}$  or lower (as recommended by WHO), adjusting the pH to be less than the  $\text{pK}_a$  of the storage temperature, and using additives. In practice, the amount of additives is strongly related to the pH and  $\text{NH}_3$  concentration of



**Figure 4** | Correlation of pH and ammonia concentrations with urine TON. Deodorization strategies could be based on reduction of pH (Arrow 1) and ammonia concentration (Arrow 2).

stored urine. Accordingly, smart systems using Information Technology (IT) could be utilized to measure the pH and  $\text{NH}_3$  concentration and subsequently estimate the sufficient amount of effective and harmless additives with respect to the related chemical stoichiometry.

This study reports laboratory-based results supporting ancient practices as efficient methods of controlling the odor of stored urine. Further field studies and economic analyses are required for the selection of additives, which should be decided on a case-by-case basis accounting for economic aspects such as costs and benefits.

## CONCLUSIONS

In this study, we found a direct relationship between the odor in stale urine and  $\text{NH}_3$  concentrations using the

standard TON measurement. The results showed that higher molecular  $\text{NH}_3$  concentrations resulted in more  $\text{NH}_3$  evaporation, causing stronger odors.

This study tested an approach derived from an ancient Korean practice of storing urine under anaerobic conditions. The results show that increasing the pH and  $\text{NH}_3$  production is heavily related to the storage temperature. Given that higher temperatures result in higher pH and  $\text{NH}_3$  production, more efficient odor management is required, especially in warmer climates and areas where the limited access to energy makes the installation of ventilation systems impossible.

The effect of pH and  $\text{NH}_3$  concentrations of stale urine on TON at a constant temperature showed that using suitable additives to reduce pH and  $\text{NH}_3$  concentrations could result in the efficient management of stale urine odor. This explains the efficiency of the widespread use of ancient Persian practices. Similar methods can be applied to ROS systems to prevent odor production without using energy-consuming ventilation systems.

## ACKNOWLEDGEMENTS

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