Article

Neutralization of Formaldehyde Gas by Ammonium Bicarbonate and Ammonium Carbonate

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Abstract

Formaldehyde gas, generated by the depolymerization of paraformaldehyde and in the presence of water vapor, has been traditionally used for biological decontamination of equipment and spaces utilized for research with a susceptible biological agent. This gas has often been neutralized with ammonia gas, generated by the thermal decomposition of ammonium bicarbonate or ammonium carbonate. An elementary theoretical analysis indicates that for total neutralization the proper weight ratio of commercial ammonium bicarbonate to paraformaldehyde is 1.58, while that for ammonium carbonate to paraformaldehyde is 1.00 to 1.13. These values are supported by experimentation. The ratio for ammonium bicarbonate in particular is 44% greater than that advised in existing literature.

Introduction

There is a periodic need for biological decontamination of confined environments used by health-related industries. These environments include biological safety cabinets, isolators, incubators, and refrigerators. On a larger scale, there is an occasional need for decontamination of biological safety level 2, 3, and 4 laboratories, pharmaceutical manufacturing areas, and contaminated human or animal hospital facilities. Surface decontamination with a liquid disinfectant is often adequate. However, there may be a concern of significant contamination, ei-

ther from particularly resistant biological entities (such as bacterial endospores) or from residual organisms that are not easily accessed by a liquid application of disinfectant (such as those located in wall or device crevices or plenums, or within a laboratory ventilation system). In such cases a more rigorous treatment may be appropriate. Isolating the target area and exposing that area to a sporicidal gas is an acceptable decontamination method. Formaldehyde gas has been a common choice for this type of area decontamination.

The typical protocol for the use of formaldehyde in the United States involves the generation of formaldehyde gas by the depolymerization of paraformaldehyde (prills or flakes), with a target concentration on the order of 10,000 ppm by volume in air. A 12-hour exposure has been shown to be sufficient when used in conjunction with an established relative humidity of 60%-90% and a temperature between 60° and 90°F. These conditions will attain a log 6 kill (i.e., a survival rate of less than one bacterial spore in a million) of those bacterial spores known to be most resistant to formaldehyde gas. It is also common practice to eliminate the formaldehyde gas following the decontamination process by reaction with ammonia gas, forming the relatively safe by-product methenamine. Ammonia gas is often generated by decomposing either ammonium bicarbonate or ammonium carbonate. This paper gives an elementary review of the chemistry associated with the formaldehyde neutralization process. Published literature of this decontamination process (National

Sanitation Foundation, 2002 and Kruse et al., 1991) has erred in the determination of required relative amounts of chemicals, which this paper attempts to correct. An experimental section is included which validates the theoretical predictions, followed by a discussion concerning the use of formaldehyde as a decontaminant in context with more recently developed methodologies.

Formaldehyde has been a known bactericide for over 100 years and has been used as a fumigant for at least 40 years (Songer et al., 1971). It generally acts as an alkylating agent, combining with specific sites on proteins, RNA, or DNA. Kaitz (1961) patented the use of paraformaldehyde to generate the gas for disinfection. Alternatively, formaldehyde gas for fumigation has been generated by volatilizing formalin, an aqueous solution of formaldehyde (Cheney & Collins, 1995). This practice is more common in Europe. A typical use involves weighing out 0.3 gm of paraformaldehyde per cubic foot of the volume to be decontaminated (National Sanitation Foundation, 2002; Taylor et al., 1969). The paraformaldehyde is placed within a pan onto a hotplate and heated to 450°F. The paraformaldehyde depolymerizes to formaldehyde liquid and then rapidly boils to produces gas. Effective sporicidal action requires prior humidification to at least 60% relative humidity (Hoffman & Spiner, 1970; Spiner & Hoffman, 1971), while humidity greater than 80% may promote repolymerization. The space being decontaminated is often equipped with fans and/or blowers to aid in gas dispersal. Spores of *Bacillus atrophaeus* (previously referred to as *B. subtilis*) are commonly used as a biological indicator for formaldehyde decontaminations, as this organism has been shown to be particularly resistant to decontamination. If a contact time of at least 12 hours is maintained, greater than a log 5 kills is typical on most surfaces (Rogers et al., 2004). Removal of the formaldehyde gas is generally performed by introducing ammonia gas to the space. In a normal application, an appropriate amount of the ammonium compound capable of releasing ammonia upon decomposition is placed into pans on hotplates. Hotplates are activated following the formaldehyde gas contact period. The ammonia and formaldehyde mixture is left in contact for approximately 1 hour, during which time they react to form methenamine. Environmental monitoring of the space is performed following ventilation of the area.

Theory

Paraformaldehyde is a polymerized form of formaldehyde (CH_2O), typically represented as (Tayor et al., 1969)

$$(1) \quad HO\text{-}(CH_2O)_n\text{-}H.$$
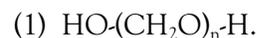
If one mathematically treats paraformaldehyde as $(CH_2O)_n$ (Merck & Co., 2001), then 0.3 gm/ft^3 corresponds to 0.010 mole formaldehyde/ft^3 (molecular weight of formaldehyde is 30 gm/mole). At standard temperature and pressure, 1 mole of air occupies 24.5 l, or 1.14 moles air/ft^3. Assuming ideal gas rules, it follows that under the above assumptions 0.3 gm/ft^3 of paraformaldehyde would generate formaldehyde to a level of 8,800 ppm by volume. Note that this is in slight contrast to a prior reference (United States Department of Health, Education and Welfare, 1975) that estimates a concentration of 10,000 ppm when using 0.3 gm/ft^3 paraformaldehyde.

The concentration calculation above can be somewhat refined. Paraformaldehyde is hydroscopic, indicating that a part of the 0.3 gm/ft^3 paraformaldehyde that is dispensed is composed of water. Furthermore, the stoichiometric form indicated in (1) suggests that the depolymerization of paraformaldehyde would generate some water byproduct. The manufacturer (Spectrum Chemical) of the paraformaldehyde used in this laboratory indicates that the paraformaldehyde consists of ca. 90% (by weight) formaldehyde, 9% water, and 1% other impurities. Using these values, 0.3 gm/ft^3 paraformaldehyde would then correspond to 0.009 mole formaldehyde/ft^3, or 7,900 ppm formaldehyde by volume.

The neutralization of formaldehyde gas by ammonia, subsequent to the decontamination period, is believed to follow the reaction

$$(2) \quad 6\,CH_2O \text{ (formaldehyde)} + 4\,NH_3 \text{ (ammonia)} \rightarrow$$
$$C_6H_{12}N_4 \text{ (methenamine)} + 6\,H_2O.$$
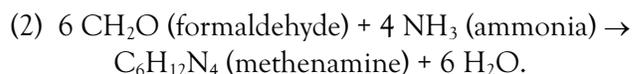
Thus, complete neutralization would require at least 2/3 mole ammonia per mole of formaldehyde. A common source of ammonia for this reaction is from the thermal decomposition of ammonium bicarbonate, $(NH_4)HCO_3$ (molecular weight = 79), by the following reaction:

$$(3) \quad (NH_4)HCO_3 + heat \rightarrow NH_3 + H_2O + CO_2.$$
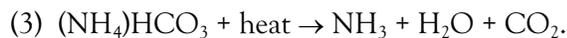
This indicates that ammonium bicarbonate releases 22% ammonia by weight. The neutralization of 0.3 gm/ft^3 of paraformaldehyde, corresponding to 0.009 $moles/ft^3$, then require 0.006 moles ammonium bicarbonate/ft^3, or 0.47 gm/ft^3. Commercially available ammonium bicarbonate (Spectrum Chemical) reportedly contains less than 1% impurities. Thus, the predicted mass ratio of commercial ammonium bicarbonate to paraformaldehyde for complete neutralization is 1.58. This value is in contrast to that of 1.1 found in previous publications (National Sanitation Foundation, 2002 and Kruse et al., 1991).

Another common source of ammonia for formaldehyde neutralization is ammonium carbonate. Rather than being a simple compound, it is a mixture composed primarily of ammonium bicarbonate and ammonium carbamate (Merck & Co., 2001) NH_2COONH_4. When thermally decomposed this mixture releases 30%-34% ammonia by weight (Merck & Co, 2001; Spectrum Chemical). Then 0.006 moles (or 0.102 gm) ammonia/ft^3, corresponds to 0.30 to 0.34 gm ammonia carbonate/ft^3 depending upon the composition of the particular batch of ammonium carbonate. This corresponds to a mass ratio of commercial ammonium carbonate to paraformaldehyde of 1.00 to 1.13.

Experiments

Neutralization experiments were performed within a Model 3110 Forma Scientific incubator, customized for this work. The chamber had an interior volume of 6.5 ft^3. The internal ceiling fan mechanism was removed to allow for better sealing. Two 5.5-in., 750W hotplates were placed in the chamber for heating the paraformaldehyde and ammonium compounds, with a 1hp fan to ensure gas mixing. The chamber had a sample port that was equipped with an external valve. A digital thermometer and humidity gauge were affixed to the chamber's transparent door so that temperature and humidity could be monitored externally. Commercially available paraformaldehyde, ammonium bicarbonate, and ammonium carbonate were used. As there was no effort being made to actually decontaminate in this experiment, no humidity was added.

In all experiments, approximately 2.0 gm paraformaldehyde (Spectrum Chemical) was placed within an aluminum pan that was in turn placed upon one of the hotplates. Varying amounts of ammonium bicarbonate or ammonium carbonate (Spectrum Chemical) were similarly placed in a second pan, which was then covered loosely with aluminum foil to minimize premature decomposition during the experiment. With both pans in place, the fan was activated and the chamber sealed. The initial chamber temperature was generally 66°F and relative humidity between 60% and 70%. The hotplate corresponding to the paraformaldehyde was energized externally for approximately 6 minutes, when all the paraformaldehyde had visibly depolymerized. The hotplate corresponding to the ammonium compound was energized 2 minutes later for 7 minutes. Although the ammonium material could not be seen during the experiment, there was no residue left in the pan following any of these trials. Residual gas in the chamber was tested after waiting between 15 and 20 minutes. A crude titration was performed by using a hand pump and tubes sensitive to 0.5 ppm formaldehyde or 1 ppm ammonia. According to the manufacturer (Dräger, 1998), the standard deviations for formaldehyde and ammonia are 20%-30% and 10%-15%, respectively. This was performed via the chamber sampling port. After opening the port, 1,000 cm^3 gas was passed through the line via the hand pump (10 squeezes) prior to measuring to ensure sampling of the mixed gas from within the chamber.

Results

As the volume for each trial was confined with no temperature regulation, both temperature and relative humidity changed during the trial. Typically, a maximum temperature between 84° and 95°F was

observed at the time that the hotplate for the ammonium compound was deactivated. Relative humidity would initially decrease with increasing temperature until the onset of the ammonium compound decomposition. This likely reflects the increase of the absolute limit of water solubility by the atmosphere in the chamber, thereby decreasing the measured relative humidity with fixed water content, countered in part by water release from the paraformaldehyde depolymerization. With the ammonium salt decomposition, the relative humidity begins to increase, likely as a result of water produced via reaction (2).

Data from the experiments for ammonium bicarbonate and ammonium carbonate neutralization are presented in Tables 1 and 2, respectively. Neutralization of the formaldehyde by ammonium bicarbonate occurred between mass ratio values of 1.55 and 1.58. Neutralization by ammonium carbonate occurred between mass ratios of 1.06 and 1.10. These results are quantitatively consistent with the predicted values above. The potential error from using Dräger tubes of up to 30% (Dräger, 1998) has no significant

Table 1
Ammonium Bicarbonate Results (n=6)

Mass Ratio [1]	Residual Concentration (ppm)	
	Formaldehyde	Ammonia
1.39	>40	ND[2]
1.55	5	2
1.58	ND	30
1.59	ND	30
1.71	ND	>300
1.82	ND	>700

[1] – Mass ratio of ammonium bicarbonate to paraformaldehyde (~2.0g)
[2] – ND = Not detected. (Sensitivity of formaldehyde ~0.1ppm and ammonia ~1ppm.)
[3] – Potential mass ratio error ~2%, concentration errors up to 30%.

Table 2
Ammonium Carbonate Results (n=2)

Mass Ratio [1]	Residual Concentration (ppm)	
	Formaldehyde	Ammonia
1.06	>5	ND[2]
1.10	ND	50

[1] – Mass ratio of ammonium carbonate to paraformaldehyde (~2.0g)
[2] – ND = Not detected. (Sensitivity of formaldehyde ~0.1ppm and ammonia ~1ppm.)

bearing on this study as they were used primarily to detect the presence or absence of formaldehyde or ammonia and not to quantitatively determine the residual concentration. The major source of error for this study was in the weighing of chemicals, in which the error was less than 1%.

Discussion

Appropriate amounts of either ammonium bicarbonate or ammonium carbonate for complete neutralization of formaldehyde gas have been demonstrated by both theoretical and experimental results. In particular, the ideal mass ratio of ammonium bicarbonate to paraformaldehyde has been shown to be substantially greater than that recommended in previous publications (National Sanitation Foundation, 2002 and Kruse et al., 1991).

Actual decontamination of enclosed equipment or spaces by formaldehyde gas is rarely ideal in terms of paraformaldehyde being quantitatively converted to formaldehyde gas and still present at the time of neutralization. Generally some gas leakage occurs during the depolymerization and contact time, particularly when decontaminating laboratory suites, manufacturing areas, or buildings. Furthermore, repolymerization of formaldehyde to paraformaldehyde may occur, particularly on colder surfaces within the exposed space and in the event of excess moisture within the space (Cheney & Collins, 1995). This potential residue, often referred to as "fall-out," is not well neutralized by gaseous ammonia. A common practice is to wipe surfaces with dilute liquid ammonia subsequent to gaseous neutralization and venting, in order to remove the solid residue, as well as to remove any methenamine residue (reaction [2]). Other mechanisms of loss may include absorption into certain materials (Braswell et al., 1970) and decomposition of formaldehyde, particularly in the presence of biological materials. Thus, it is likely that using the ideal mass ratio for ammonium bicarbonate or ammonium carbonate will result in excess ammonia gas at the cessation of neutralization. However, as the amount of formaldehyde gas loss cannot be predicted in advance, it remains most logical to use ratio values derived previously.

Although the use of formaldehyde gas for biological decontamination has been long accepted as very effective and economical, newer methodologies are replacing it for many applications. One principle issue with formaldehyde, as mentioned previously, is the likelihood of a residue remaining within the decontamination space that then requires further cleaning. Formaldehyde gas, often thought of as a potential human carcinogen, has recently been reclassified by the World Health Organization (WHO) as having definitive carcinogenic properties (International Agency for Research on Cancer, 2004). There are also other toxic effects due to exposure to formaldehyde, although safe practices in the use of paraformaldehyde minimizes risks. Any other suitable sporicidal alternatives, such as chlorine dioxide gas or hydrogen peroxide vapor, are similarly dangerous if one is exposed to concentrations typically used without appropriate personal protective equipment. OSHA has set 8-hour time-weighted average permissible exposure levels for formaldehyde chlorine dioxide and hydrogen peroxide at 0.75, 0.1, and 1.0 ppm, respectively, while typical usage levels for decontamination are at least a factor of 1,000 greater. Another advantage to chlorine dioxide gas and hydrogen peroxide vapor is that neither leaves a residue. Nevertheless, given the lower cost and general familiarity with formaldehyde gas as a decontaminant, it is likely to remain a tool within the industry for the foreseeable future.

Conclusion

This paper discussed the common practice of generating ammonia gas for the neutralization of formaldehyde gas used in space decontamination. It has been shown by simple mass balance that the appropriate mass ratio of commercial ammonium bicarbonate to paraformaldehyde is 1.58. As commercial ammonium carbonate contains a mixture of ammonia-generating compounds, one can at best predict an appropriate range of mass ratios of ammonium carbonate to paraformaldehyde for neutralization, that being 1.00 to 1.13. Experiments conducted within an enclosed volume using these chemicals have confirmed these values.

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