Vapor-Phase Acetylation of Reed (*Arundo donax*) at 20 °C and 60 °C: A Method for Reducing Cheilitis Risk

Yoshikazu Arai [1], Eiichi Obataya [1], and Naoko Okiyama [2]

[1] Institute of Life and Environmental Sciences, University of Tsukuba, Ibaraki 305-8572, Japan

[2] Department of Dermatology, Graduate School of Medical and Dental Sciences, Institute of Science Tokyo (IST), Tokyo 113-8519, Japan

1. INTRODUCTION

Reeds (*Arundo donax*) are used as the vibrating plates of woodwind instruments, including oboes, clarinets, and saxophones. As a natural material that has been in use for centuries, many musicians believe that reeds are harmless. However, reeds can cause serious cheilitis and perioral contact dermatitis, as shown in Figure 1. This oboist repeatedly contracted cheilitis and perioral dermatitis after brief contact with the reed. Similar cases have been reported,[1-8] and various types of contact dermatitis related to musical instruments have already been summarized.[9-12] Musicians who develop this allergy must use synthetic reeds, which do not always perform satisfactorily, or face the prospect of quitting.

Figure 1 Allergic contact dermatitis of an oboist induced by a reed (*Arundo donax*) in an Oboist

We recently found that the allergic reactions of woodwind musicians disappear after acetylation of their reeds at 120 °C for 8 h.[13] Although the mechanism underlying the anti-allergic effect of acetylation remains unknown, this process has been demonstrated to be effective in preventing reed allergies. However, no reed makers currently produce acetylated reeds at present, likely because the demand is limited. The conventional method of acetylation requires special equipment and technical skills that are not easily accessible to musicians themselves. Thus, it is difficult for the musicians to get acetylated reeds.

To enable musicians to acetylate their own reeds at home, we have established a simpler and safer method: vapor-phase acetylation at low temperatures. The vapor-phase system is not suitable for the industrial acetylation of large lignocellulosic materials such as structural lumber, because the permeation of acetic anhydride vapor is slower than the acetylation of wood at high temperatures. One study showed that only the surface of lumber was non-uniformly modified by vapor-phase acetylation at 120 °C.[14] However, the vapor-phase system is advantageous for small-scale acetylation of reeds because it minimizes reagent consumption and does not require the removal, recovery, and purification of the reagent after treatment. Because the vibrating reeds of woodwind instruments are thin (< 1 mm) and short (< 50 mm), they can be uniformly modified in vapor-phase systems, particularly at low temperatures. Although a lower temperature requires a longer treatment time, this is outweighed by the ease, simplicity, and safety of the system for musicians and their attending doctors aiming to prevent the allergies.

Here, we propose a method for the vapor-phase acetylation of reeds at 60 °C using a glass bottle and inexpensive home appliances. In addition, we also propose a method for vapor-phase acetylation at room temperature (20 °C) using sodium acetate as a catalyst.

2. MATERIALS AND METHODS

2.1 Oboe reed specimen

Reed internodes were cut and split into short rods, and their cortex and inner parts were removed using a plane specially designed for making oboe reeds. The shapes and dimensions of the reed specimens are shown in Figure 2. To precisely evaluate the catalyst loading (CL) and weight percentage gain (WPG) due to acetylation, the specimens were leached in water for more than one week to remove the water-soluble extractables. After removal of the extracts, the specimens were first air-dried and then oven-dried at 105 °C overnight to determine their oven-dry mass (M_U). The density of the specimens ranged from 510 to 690 kg/m^3, with an average of 638 kg/m^3. Commercially available clarinet reeds (Vandoren, model V12) were also used as a reference.

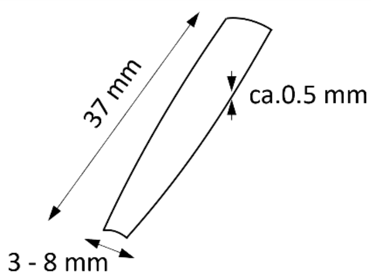

Figure 2 An example of oboe reed specimen

2.2 Catalyst impregnation

Figure 3 shows the acetylation flow at 20 °C. Prior to acetylation, some of the specimens were impregnated with sodium acetate (SA) or potassium acetate (PA). The reed specimens were soaked in

2.5, 5, 10, 20, or 30% w/w aqueous solutions of SA or in 10% w/w aqueous solutions of PA at 20–25 °C for 1 week. The catalyst-impregnated specimens were air-dried for 8 h and then oven-dried at 105 °C overnight to measure the dry mass (M_{CL}). The catalyst loading (CL) was evaluated using the following equation:

$$CL\ (\%) = 100 \times (M_{CL} - M_U)/M_U. \quad (1)$$

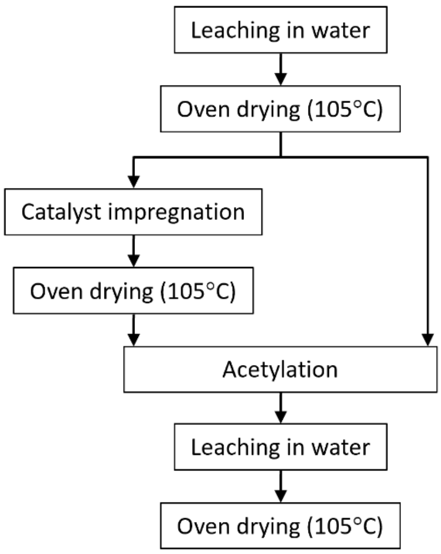

Figure 3 Treatment flow diagram at 20 °C

2.3 Vapor-phase acetylation

The setup for vapor-phase acetylation is shown in Figure 4. Four oboe reed specimens (0.3–0.4 g) were placed in a glass bottle (200 mL) with 5 g of acetic anhydride. Contact between the specimens and the liquid acetic anhydride was prevented by glass beads at the bottom of the bottle. The bottle was tightly closed and heated at 60 °C for 4 weeks in a commercially available beverage warmer (HR-EB06; Twin Bird Co., Ltd., Tsubame City, Japan), or placed in a climate-controlled room at 20 °C for 32 weeks. The temperature in the beverage warmer varied to some extent (60–61 °C) depending on the products. However, the fluctuation of the temperature was negligible (within ±1 °C). After acetylation, the specimens were leached in running water for more than 3 d to remove the remaining acetic acid and catalyst. The acetylated specimens were first air-dried and then oven-dried at 105 °C overnight to determine their oven-dry mass (M_A). The degree of acetylation was evaluated using WPG, which is defined as:

$$WPG\ (\%) = 100 \times (M_A - M_U)/M_U, \quad (2)$$

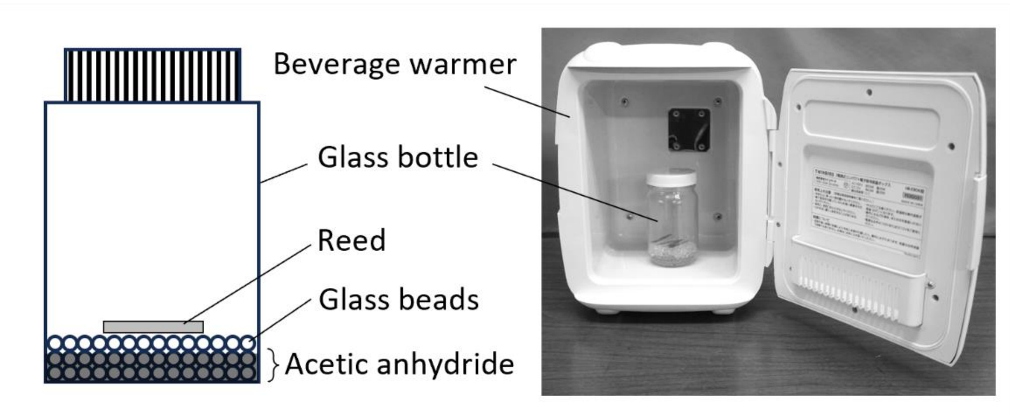

Figure 4 Apparatus for vapor-phase acetylation

3. RESULTS AND DISCUSSION

3.1 Vapor-phase acetylation at 60 °C using a beverage warmer

The allergic reaction of woodwind musicians disappeared significantly after acetylating the reeds at 120 °C for 8 h, corresponding to 16% WPG for oboe reeds and 19% for clarinet reeds.[13] Based on these results, 16% was chosen as the target WPG for the oboe reed specimens to prevent reed allergies. Figure 5 shows the WPG of the reed after acetylation at 60 °C plotted against the treatment time. The WPG value increased with time up to 14 d and then remained unchanged. The slightly higher WPG values of clarinet reeds resulted from the higher reactivity of the inner part of the reed, as suggested in a previous study.[13] For the oboe reed, the target WPG was achieved within 2 weeks. While a duration of 2 weeks might be excessive for an industrial process, it is acceptable for a home process for musicians seeking to prevent reed allergies. Additionally, the use of a common beverage warmer and a relatively low heating temperature facilitates the safe acetylation of reeds at home.

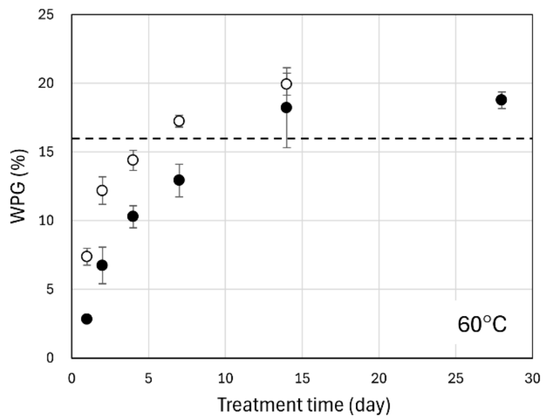

Figure 5 Weight gain percentage (WPG) from acetylation at 60 °C as a function of treatment time. *Solid circles* - oboe reeds; *open circles* - commercially available clarinet reeds; *Error bars* - standard deviations; *dashed line* - target WPG for oboe reeds.[13]

Since July 2023, ten musicians, including six patients with reed allergies, have been acetylating their reeds using this method under the technical instruction of the authors. No problems have been reported to date: the musicians were able to successfully acetylate their reeds, and none developed cheilitis during use. In fact, one of these musicians, an oboist, has won several domestic competitions in Japan since starting to use acetylated reeds, demonstrating the success of this approach.

3.2 Vapor-phase acetylation at 20 °C

In the case of wood acetylation, achieving sufficient WPG at room temperature is difficult unless the wood is previously impregnated with a catalyst. For example, the WPG value of spruce wood is limited to 10% in uncatalyzed systems at 25 °C, whereas it exceeds 20% within 1 week in PA-catalyzed systems.[15] Therefore, we attempted to acetylate reeds at 20 °C using two acetic salts as catalysts. Figure 6 shows the CL values of the SA-impregnated oboe reed specimens plotted against the concentration of the SA solution used for impregnation. The CL value was approximately proportional to the SA concentration.

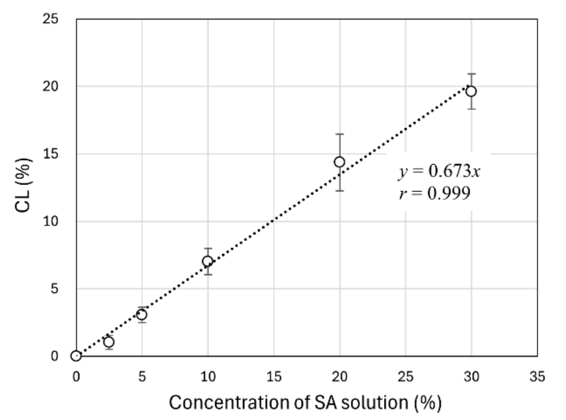

Figure 6 Catalyst loading (CL) plotted against the concentration of sodium acetate (SA) solution used for the impregnation. *Error bars* - standard deviation.

Figure 7 shows the effects of CL on the WPG of oboe-reed specimens after SA-catalyzed acetylation at 20 °C for 4 weeks. The WPG value increased from 4% to 10% with an increase in CL up to 7%, above which it leveled off. It was speculated that only the SA in the cell wall catalyzed the acceleration of the reed, whereas the excess SA remaining in the cell lumen (cavity) did not act as a catalyst. In the case of wood acetylation, excess catalyst deposited in the cell lumen hinders acetylation of the wood cell wall.[15] Based on these results, 10% w/w aqueous solutions of salts, resulting in 7% CL, were selected for use in further experiments.

Figure 8 shows the WPG of oboe reed specimens resulting from uncatalyzed, SA-catalyzed, and PA-catalyzed acetylation at 20 °C. In the uncatalyzed system, WPG reached 15% within 32 weeks (8 months). The extrapolation of the slope between 24 and 32 weeks predicted that at least 60 weeks

(15 months) was required to achieve the target WPG (16%) in the uncatalyzed system. In contrast, the target WPG was achieved within 8 weeks (two months) using the PA-catalyzed system and within 16 weeks (four months) using the SA-catalyzed system.

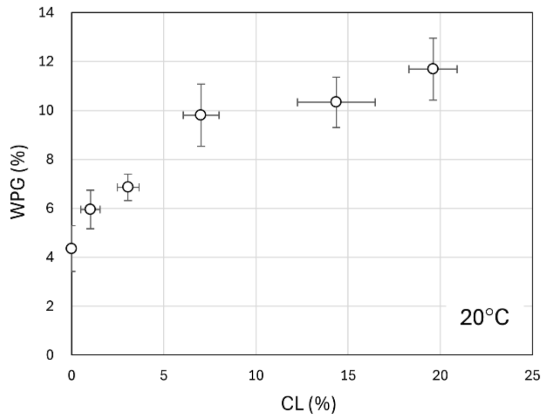

Figure 7 Effects of catalyst loading (CL) on weight percentage gain (WPG) from sodium-acetate-catalyzed acetylation at 20 °C for 4 weeks. *Error bars* - standard deviations.

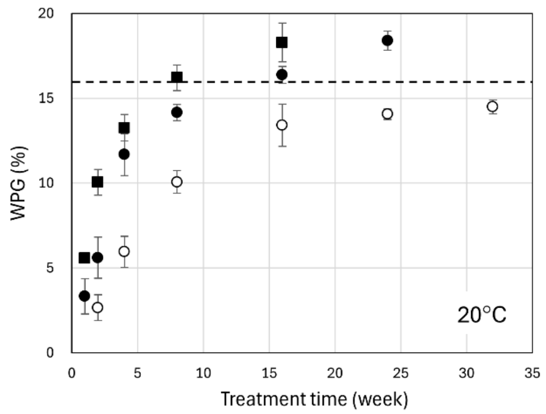

Figure 8 Weight percentage gain (WPG) of reeds plotted against the reaction time for uncatalyzed and catalyzed vapor-phase acetylation at 20 °C.
Open circles - uncatalyzed; *solid circles* - sodium acetate-catalyzed; *solid squares* - potassium acetate-catalyzed; *error bars* - standard deviations; *dashed line* - target WPG for oboe reeds (16%).[13]

Although the catalytic effect of PA was greater than that of SA, we recommend SA for musicians because it is widely used as a food preservative and is therefore safe and readily available. SA-catalyzed acetylation is beneficial for musicians, reed makers, and clinicians because it requires only a glass bottle, eliminating the need for any equipment for heating or recovering chemicals. While several months of treatment is too long for industrial acetylation, it is likely to be an acceptable timeframe for musicians using an at-home process. In this context, the only obstacle lies in the availability of acetic anhydride. In Japan, acetic anhydride is categorized as a "deleterious material" and "narcotic or psychotropic raw material" and legal procedures are required to purchase it.

4. CONCLUSION

A simple and safe method for the acetylation of woodwind instrument reeds was developed using a vapor-phase system at 60 °C with a glass bottle and a beverage warmer. The target WPG (16%) selected to prevent reed allergies was achieved within 2 weeks, enabling musicians to acetylate their own reeds using readily available home appliances. The reeds were also acetylated at 20 °C by using acetic salts as catalysts. Weight percentage gain was limited to 15% in the uncatalyzed system but reached 16% within 16 weeks when the reed was previously impregnated with sodium acetate, a readily available salt that is widely used as a food preservative. Sodium acetate allows for the easier and safer acetylation of reeds at room temperature using only a glass bottle.

REFERENCES

1. Cassandro ML, Sacchitelli F. Dermatitis due to *Arundo donax* as an occupational disease. *Folia Med (Napoli).* 1953;36:305–308.
2. Hindson TC. Clarinettist's cheilitis. *Br Med J.* 1978;2:1295. https://doi.org/10.1136/bmj.2.6147.1295-a
3. Friedman SJ, Connolly SM. Clarinettist's cheilitis. *Cutis.* 1986;38:183–184.
4. van der Wegen-Keijser MH, Bruynzeel DP. Allergy to cane reed in a saxophonist. *Contact Dermatitis*. 1991;25:268–269. https://doi.org/10.1111/j.1600-0536.1991.tb01868.x
5. McFadden JP, Ingram MJ, Rycroft RJ. Contact allergy to cane reed in a clarinettist. *Contact Dermatitis.* 1992;27:117. https://doi.org/10.1111/j.1600-0536.1992.tb05226.x
6. Inoue A, Shoji A, Yashiro K. Saxophonist's cane reed cheilitis. *Contact Dermatitis.* 1998;39:37. https://doi.org/10.1111/j.1600-0536.1998.tb05816.x
7. Ruiz-Hornillos FJ, Alonso E, Zapatero L, Pérez C, Martínez-Molero I. Clarinettist's cheilitis caused by immediate-type allergy to cane reed. *Contact Dermatitis.* 2007;56:243–245. https://doi.org/10.1111/j.1600-0536.2007.00976.x
8. Mariano M, Patruno C, Lembo S, Balato N. Contact cheilitis in a saxophonist. *Dermatitis.* 2010;21:119–120. https://doi.org/10.2310/6620.2009.09055
9. Gambichler T, Boms S, Freitag M. Contact dermatitis and other skin conditions in instrumental musicians. *BMC Dermatol.* 2004;4:3–15. https://doi.org/10.1186/1471-5945-4-3
10. Gambichler T, Uzun A, Boms S, Altmeyer P, Altenmüller E. Skin conditions in instrumental musicians: a self-reported survey. *Contact Dermatitis.* 2008;58(4):217–222. https://doi.org/10.1111/j.1600-0536.2007.01310.x
11. Crépy MN. Skin diseases in musicians. *Eur J Dermatol.* 2015;25(5):375–83. https://www.jle.com/10.1684/ejd.2015.2559
12. Patruno C, Napolitano M, La Bella S, Ayala F, Balato N, Cantelli M, Balato A. Instrument-related Skin Disorders in Musicians. *Dermatitis.* 2016;27(1):26–9. https://doi.org/10.1097/der.0000000000000153
13. Arai Y, Obataya E, Nakagawa-Izumi A, Okiyama N. Acetylation of reed (*Arundo donax*) to prevent the contact dermatitis of woodwind musicians. *Wood Sci Technol.* 2024 (accepted for publication on October 16, 2024)
14. Futemma Y, Obataya E. Non-uniform reaction of solid wood in vapor-phase acetylation. *J Wood Sci.* 2012;58: 336–341. https://doi.org/10.1007/s10086-012-1255-9
15. Obataya E, Minato K. Potassium acetate–catalyzed acetylation of wood at low temperatures II: vapor phase acetylation at room temperature. *J Wood Sci.* 2009;55(1): 23–26. https://doi.org/10.1007/s10086-008-0996-y