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Quantitative determination of benzalkonium chloride in treated wood by solid-phase extraction followed by liquid chromatography with ultraviolet detection

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Abstract

Ammoniacal copper quat (ACQ) compound wood preservative is comprised of copper and quaternary ammonium compounds with benzalkonium chloride (BAC) as the active ingredient. Solid-phase extraction (SPE) followed by liquid chromatography with ultraviolet detection (LC–UV) was developed for quantitative determination of BAC in treated wood. Five species of wood were used, Japanese cedar (*Cryptomeria japonica*), Japanese larch (*Larix leptolepis*), Yezo spruce (*Picea jezoensis*), Sakhalin fir (*Abies sachalinensis*), and western hemlock (*Tsuga heterophylla*). BAC used in the present study was composed of 66% C12, 33% C14 and less than 1% C16. BAC was added to each wood species (500 mg) then extracted with HCl–ethanol (20 ml) and quantitatively determined with LC–UV (262 nm). Wood extractives from the heartwood of each species, except western hemlock, interfered with quantitative determination of BAC, but SPE with an Oasis MCX cartridge was effective in preventing this. Using the present methods, BAC homologue peaks were clearly confirmed without interference. Recoveries from wood ranged from 92 to 101% and the limit of quantitation was approximately 240 μg/g wood for the C12 and C14 homologues.

Keywords: Solid-phase extraction; Benzalkonium chloride; Wood preservation

1. Introduction

Wood and wood products are frequently used in residential construction, decking, utility poles, and so on. However, wood is attacked by many organisms, principally fungi and termites, resulting in serious strength loss. Consequently, preservation of wood is necessary for inhibition of attack by these degrading agents, particularly when it is used in frequently wetted areas or placed in ground contact.

In recent years, environmental concerns have drastically changed the active ingredient of wood preservatives, resulting in restricted use of chromated copper arsenate (CCA) in many countries. In Japan, use of CCA in wood preservation drastically decreased in 1997 [1] and it was deleted from the revised Japan Industrial Standard on 20 May 2004 [2]. Alternative copper-based preservatives comprised of a combination of copper and organic biocides are now mainly used for wood preservation in Japan.

Ammoniacal copper quat (ACQ), one such copper-based preservative, is comprised of a combination of copper and quaternary ammonium compounds [2] with benzalkonium chloride (BAC) as the active ingredient. Active ingredients of wood preservatives are specified to guarantee protection, thus accurate quantitative determinations of BAC in wood are needed. In Japan, the amount of BAC in treated wood is regulated by the Japanese Agricultural Standard (JAS) [3] and Japan Housing and Wood Technology Center (HOWTEC) [4]. The methods of JAS [3] and HOWTEC [5] involve BAC extraction from treated wood using acidic ethanol followed

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by removal of the extracted BAC in the resulting solution as an ion-pair complex using orange dye. Ultraviolet (UV) spectrophotometry is then used for quantitative measurements of BAC. On the other hand, the method of the American Wood-Preservers' Association (AWPA) is based on two-phase titration [6].

The technical products of BAC consist of C12, C14 and C16 alkyl chain homologues, which possess different physical, chemical and microbiological properties. Consequently, determination of individual homologues is important not only for assuring preservation of wood, but also for investigations requiring quantitative determination. However, the above methods provide no information on the individual BAC homologues, and furthermore, all are thought to interfere with co-extraction of various compounds, because wood, particularly heartwood, contains a number of extractives [7].

Liquid chromatography (LC) has been used for determination of BAC in various fields [8–16]. LC can successfully separate each homologue allowing them to be determined respectively. However, when BAC is extracted from treated wood with organic solvent, co-extracted components in the sample solution might interfere with analysis using LC with ultraviolet (UV) detection (LC–UV). Furthermore, wood extractives are comprised of many components that differ with the species of wood, thus interference will also vary according to species. On the other hand, using mass spectrometry (MS) and tandem mass spectrometry (MS–MS) as detection methods can avoid such interference, since they are highly selective with regard to information on molecular weight. These methods already been applied to determination of BAC in various fields [13–16]. However, LC–MS and LC–MS–MS methods require more sophisticated laboratory equipment than LC–UV. Thus, quantitative determination of BAC in treated wood using LC–UV could be useful if the selectivity of the methods used was increased. To avoid interference and increase selectivity with LC–UV analysis, sample preparation methods such as liquid–liquid extraction are needed to remove wood extractives from the sample solution.

At present, solid-phase extraction (SPE) is the most popular sample preparation method [17–19] and accepted in routine analysis as an alternative to liquid–liquid extraction. To develop the sorbents used in SPE, cartridges with various selectivities are available. We previously reported the applicability of SPE with Oasis MCX in avoiding interference from wood extractives during determination of cyproconazole and tebuconazole [20]. Oasis MCX was able to separate these basic biocides and lipophilic co-extractives, and therefore, we speculated that Oasis MCX could separate BAC from the co-extractives interfering with LC–UV analysis.

The purpose of the present work is to confirm interference by extractives from various wood species during quantitative determinations of BAC using LC–UV, and to develop a SPE method to avoid these confirmed interferences. To our knowledge, this is the first report to document the application of SPE in quantitative determination of BAC in treated wood using LC–UV.

2. Materials and methods

2.1. Reagents

BAC was obtained from Sigma–Aldrich (Tokyo, Japan). The alkyl chain homologues of BAC composed 66% C12, 33% C14 and less than 1% C16. A commercial ACQ product was provided by Koshii Preserving Co. Ltd. (Osaka, Japan) and consisted of C12 and C14 homologues (76:24, w/w). These percentages were confirmed using LC–UV (LC conditions are described below), assuming the same UV sensitivity response with each homologue. High-performance liquid chromatography (HPLC) grade methanol and acetonitrile, ammonium formate and formic acid were purchased from Kanto Kagaku (Tokyo, Japan), and aqueous ammonium hydroxide solution (28%) was obtained from Kishida Chemical (Osaka, Japan). Ammonium chloride and hydrochloric acid (HCl) were obtained from Wako Pure Chemical (Osaka, Japan).

2.2. Sample preparation

Heartwoods of Japanese cedar (*Cryptomeria japonica*), Japanese larch (*Larix leptolepis*), Yezo spruce (*Picea jezoensis*), Sakhalin fir (*Abies sachalinensis*) and western hemlock (*Tsuga heterophylla*) were ground with a Wiley mill then BAC (10 or 1 mg/g wood) as methanol solution was added to the resulting wood powder (500 mg) before drying at room temperature. Five hundred milligrams of spiked and non-spiked wood were extracted with 20 ml HCl–ethanol (3/100, v/v) for 2 h in an ultrasonic bath. Amounts of BAC were within a range (7.4–1.8 mg/g) calculated from JAS's retention amounts for K4 (required retention amount: 5.2 kg/m^3 as ACQ) and K2 (1.3 kg/cm^3 as ACQ) [3], assuming that the specific gravity of wood is about 0.35 g/cm^3 and that ACQ contains copper (as CuO) and BAC at a weight ratio of 1:1. The solutions were filtrated under a vacuum then 5 ml of each was applied to SPE. One milliliter of each filtrate was then evaporated to dryness. The residues were dissolved in mobile phase then filtered through a 0.45 μm membrane for HPLC analysis.

2.3. Treatment of wood blocks with ACQ

Blocks of each wood species (20 mm × 20 mm × 10 mm) were dried for 48 h at 60 °C then stored at room temperature until use. Weighted wood blocks were placed in treating solution including about 0.3% (w/w) of BAC then under 90% vacuum for 20 min. They were kept in the solution at atmospheric pressure and temperature for 2 h. Solution uptake by all blocks was determined by weighting before and after treatment. Treated blocks were dried at 60 °C for