

NOTE

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Spectrophotometric assay of a wood preservative, *N,N*-didecyl-*N*-methyl-poly(oxyethyl) ammonium propionate (DMPAP), in aqueous solution

Received: July 29, 2010 / Accepted: September 10, 2010 / Published online: February 26, 2011

Abstract A spectrophotometric assay based on the color reaction between *N,N*-didecyl-*N*-methyl-poly(oxyethyl) ammonium propionate (DMPAP) and 4-[4-(dipropylamino)phenylazo]-benzenesulfonic acid (propyl orange) was used to determine DMPAP concentrations as a wood preservative. The assay was carried out using a propyl orange solution at pH 2.9. The visible absorption spectrum of propyl orange showed an absorption maximum at 510 nm, which decreased linearly with increasing DMPAP concentration from 0 to 10 ppm. To apply this assay method to determine DMPAP retention in treated wood, the influence of wood extractives on the assay was investigated. Extractives from Japanese cedar, hinoki cypress, and Japanese larch were found to increase apparent DMPAP concentration. However, it was also found that measuring visible absorption at 477 nm prevented overestimation and gave precise values. This assay can be a viable alternative to the current methods for the determination of DMPAP concentrations.

Key words *N,N*-didecyl-*N*-methyl-poly(oxyethyl) ammonium propionate (DMPAP) · Quaternary ammonium chloride · Propyl orange · Treated wood · Wood preservative

Introduction

To mitigate global warming by using wooden products, preservative treatments are expected to extend the service life of wooden materials and thus delay the emission of carbon dioxide gas.^{1–4} Among several types of preservative treatments, the proportion of wood undergoing pressure treatment using quaternary ammonium compounds (QACs) has gradually increased in the past few decades in Japan⁵

because of its colorless appearance, high penetrability, low odor, and zero metal content. Although didecylmethylammonium chloride (DDAC) was the most common QAC in the past decade, *N,N*-didecyl-*N*-methyl-poly(oxyethyl) ammonium propionate (DMPAP) has been recently developed as a new type of chlorine-free QAC. This preservative is now on the list of accepted preservatives in both the Japanese Agricultural Standard (JAS) for sawn timber⁶ and the Japanese Industrial Standard for Wood Preservatives.⁷

The performance of treated wood is known to be affected by preservative retention.^{8,9} Therefore, the JAS for sawn timber sets five retention levels and evaluation methods for determining preservative retention.⁶ In the case of DMPAP, the principle of the evaluation method is similar to the DDAC evaluation method described in the American Wood Protection Association Standard (AWPAS).^{6,10} In a previous article, we discussed the demerits of the conventional DDAC assay method described in AWPAS and proposed a simple, eco-friendly, and cost-effective approach for determining DDAC retention based on a color reaction between DDAC and 4-[4-(dipropylamino)phenylazo]-benzenesulfonic acid (propyl orange).^{11,12}

It is assumed that this method will also be useful for determining DMPAP retention in treated wood. We applied the color reaction between propyl orange and DMPAP and found that propyl orange can successfully determine DMPAP concentration. The influence of wood extractives on DMPAP assay using propyl orange was also examined.

Materials and methods

Materials

A DMPAP standard containing 71.6% DMPAP (supplier: Lonza Japan) was kindly provided by Mr. Akira Makita, Dainihon Wood-Preserving Co., Ltd. Propyl orange was synthesized from sodium sulfanilate as described in previous articles.^{12,13} Wood powder was also prepared from the sapwood and heartwood of commercial timber from Japanese cedar (*Cryptomeria japonica*), hinoki cypress

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(*Chamaecyparis obtusa*), Japanese larch (*Larix kaempferi*), and Western hemlock (*Tsuga heterophylla*) according to a previous article.¹² Extraction solvent was prepared by adding formic acid to methanol until a pH meter (TOA; HM-30S) showed pH 5.0.¹⁰

Determination of DMPAP concentration using propyl orange

The assay solution was prepared by mixing about 7.2 mg propyl orange with 1120 mM sodium monochloroacetate buffer adjusted to pH 2.9 and containing 0.02% Triton X-100.¹² The DMPAP standard was diluted with the extraction solvent to make a standard solution containing 0–1000 ppm DMPAP. Then, 20 μ l standard solution was added to 1980 μ l assay solution. The visible absorption spectrum of the mixed solution was recorded on a Shimadzu UV-2400 spectrometer.

Determination of DMPAP concentration in the presence of wood extractives

Wood extractives were prepared by mixing 1 g of wood powder with 20 ml methanol extraction solvent according to the procedure given in a previous article.¹² After the extraction procedure, part of the supernatant solution was filtered with a membrane filter (DISMIC-25HP, Advantec) for use in further studies.

A sample solution was prepared by mixing filtered supernatant containing wood extractives with the same volume of DMPAP standard solution. A control solution was prepared by mixing the extraction solvent with the DMPAP standard solution. Then, 20 μ l sample solution or control solution was mixed with 1980 μ l assay solution, and its visible absorption was measured using the Shimadzu UV-2400 spectrometer.

Results and discussion

Determination of DMPAP concentration with propyl orange

Assay methods using propyl orange were developed to determine the concentration of QACs such as the distearyldimethylammonium ion¹⁴ and the nCx -trimethylammonium ion ($x = 10$ –18).¹³ The compound was also revealed to be useful for determining DDAC concentrations when used as a wood preservative.¹²

However, it is not clear whether the assay method using propyl orange can be applied to DMPAP determination. Therefore, the first step was to investigate the color reaction between propyl orange and DMPAP. The change of the DMPAP–propyl orange complex spectra in the assay solution is shown in Fig. 1. Propyl orange has a visible absorption maximum at 510 nm, and this maximum decreased with increasing DMPAP concentration. In contrast, a new peak appeared at 422 nm. An isosbestic point was observed at

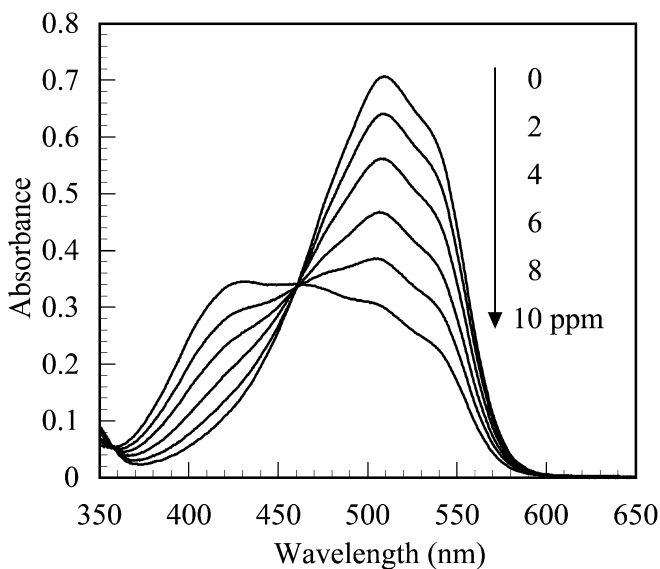


Fig. 1. Visible absorption spectra of *N,N*-didecyl-*N*-methylpropyl(oxyethyl) ammonium propionate (DMPAP)–propyl orange complex in an acidic buffer. DMPAP concentration in the assay solution varied from 0 to 10 ppm

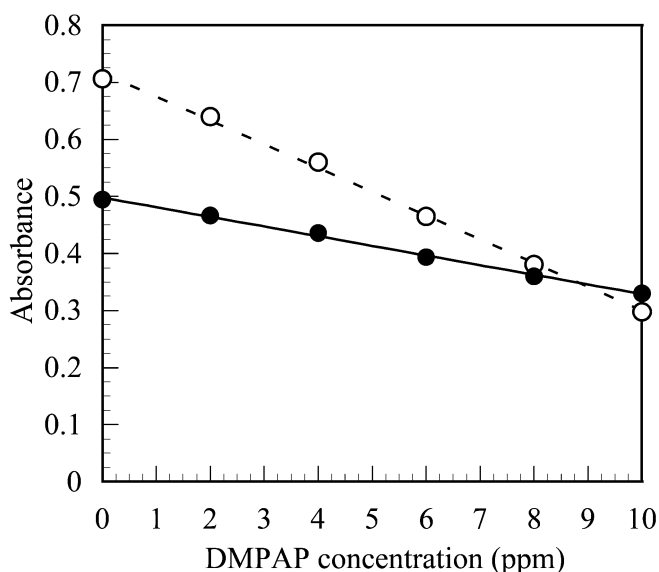


Fig. 2. The relationship between DMPAP concentration and absorbance at 510 nm (open circles) and 477 nm (solid circles). The unbroken line and broken line indicate the linear least-squares fit of absorbance at 510 nm and 477 nm against DMPAP concentration in the assay solution from 0 to 10 ppm, respectively. The lines were drawn using the following equations: Absorbance at 510 nm = $-0.042 \times \text{DMPAP conc.} + 0.72$; Absorbance at 477 nm = $-0.017 \times \text{DMPAP conc.} + 0.50$

about 460 nm. This result accorded with our previous findings using DDAC and propyl orange,¹² and with those of Momohara et al. and Motomizu et al.^{13,14}

Absorbance at 510 nm was then plotted against DMPAP concentration (Fig. 2): the absorbance linearly decreased with increasing DMPAP concentration from 0 to 10 ppm in the assay solution ($R^2 = 0.998$).

Table 1. Effect of wood extractives on relative absorbance in DMPAP assay at wavelengths of 510 nm and 477 nm (absorbance of control sample at each DMPAP concentration = 100)

Measured wavelength	DMPAP conc. ^a	Control	Japanese cedar		Hinoki cypress		Japanese larch		Western hemlock	
			Sapwood	Heartwood	Sapwood	Heartwood	Sapwood	Heartwood	Sapwood	Heartwood
510 nm	0 ppm	100 (0.1)	96.0 (0.4)	95.9 (0.2)	98.9 (0.3)	96.1 (0.1)	98.8 (0.2)	98.6 (0.2)	99.5 (0.2)	99.3 (0.4)
	10 ppm	100 (0.7)	100 (0.7)	85.0 (0.6)	93.7 (0.3)	89.6 (0.8)	95.1 (0.5)	97.3 (2.3)	99.0 (0.4)	100 (0.7)
477 nm	0 ppm	100 (0.1)	99.2 (0.1)	99.4 (0.2)	100 (0.1)	99.4 (0.3)	100 (0.1)	100 (0.2)	100 (0.1)	100 (0.1)
	10 ppm	100 (0.2)	98.3 (0.6)	99.0 (0.5)	98.6 (0.6)	103 (0.5)	98.9 (0.7)	99.4 (0.8)	99.1 (0.2)	98.5 (0.5)

Coefficient of variations are shown in parentheses ($n = 3$)

DMPAP, *N,N*-didecyl-*N*-methyl-poly(oxyethyl) ammonium propionate

^aDMPAP concentration in assay solution

The reproducibility of this assay was also investigated. A standard solution containing 0 or 1000 ppm DMPAP was prepared, and the DMPAP concentration was measured using the assay in triplicate. The results showed that the coefficients of variation were 1.2% for the assay solution containing 0 ppm DMPAP, and 2.0% for that containing 10 ppm DMPAP (data not shown). The low value of the variation coefficient indicates that this assay procedure is reproducible enough for DMPAP determination.

Application of propyl orange to determine DMPAP retention in treated wood

The previous study revealed that wood extractives interfered with the DDAC assay using propyl orange when the assay was carried out using absorbance at 510 nm. It also revealed that the influence of the wood extractives can be excluded by determining the DDAC concentration at 477 nm.¹² In this way, the influences of wood extractives and measurement wavelength on DMPAP determination using propyl orange were investigated.

To estimate the effect of wood extractives, a DMPAP standard solution was mixed with extraction solvents containing wood extractives from the sapwood or heartwood of four wood species, and the mixture was subjected to DMPAP assay. Extraction solvents in this study were prepared according to AWPAS to determine DDAC retention in treated wood.¹⁰ The AWPAS defines 0.5 g as the amount of wood powder placed in 20 ml extraction solvent. Double this amount of wood powder was used in this experiment and mixed with the same volume of DMPAP standard solution. DMPAP concentration after mixing both solutions was set to 0 or 1000 ppm, which was slightly higher than that expected for treated Japanese cedar timber at the K4 level.⁶

As shown in Table 1, wood extractives from Japanese cedar heartwood and hinoki cypress heartwood significantly decreased absorbance at 510 nm. In addition, wood extractives from hinoki sapwood, Japanese larch heartwood, and Japanese larch sapwood also influenced absorbance. In other words, DMPAP retention in these wood species is overestimated by the above assay method.

There was a similar problem in the previous study on DDAC assays using propyl orange. This was solved by changing the wavelength from 510 nm to 477 nm because

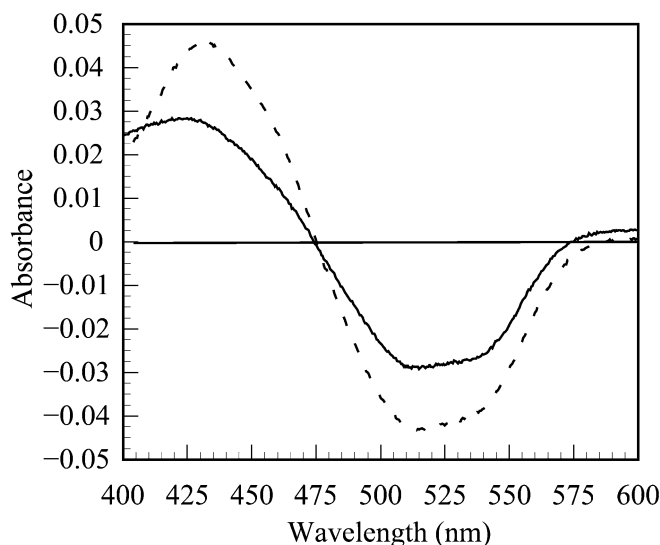


Fig. 3. Differential spectra of DMPAP-propyl orange complex in the presence and the absence of wood extractives. The difference in the visible absorption of the DMPAP-propyl orange complex in the presence and absence of wood extractives of Japanese cedar heartwood were plotted: *Unbroken line*, with DMPAP 10 ppm; *broken line*, with DMPAP 0 ppm in the assay solution

the DDAC-propyl orange complex has an isosbestic point at around 477 nm, which is not affected by the presence of wood extractives.¹² Therefore, differential spectra of the DMPAP-propyl orange complex were also recorded in the presence and in the absence of wood extractives. Figure 3 shows an example of differential spectra observed in the presence and in the absence of wood extractives from Japanese cedar heartwood, indicating the presence of an isosbestic point at 477 nm similar to the DDAC-propyl orange complex. Since there is an isosbestic point at 477 nm where absorbance is unaffected by the presence or absence of wood extractives from these wood species, visible absorbance was measured at this wavelength. Table 1 shows the visible absorbance of the DMPAP-propyl orange complex at 477 nm. The results clearly indicate that DMPAP concentration can be determined precisely at this wavelength even in the presence of wood extractives from these species. It is also shown that there is a good correlation between

absorbance at 477 nm and DMPAP concentration ($R^2 = 0.997$) (Fig. 2).

The assay method using propyl orange is a viable alternative to the conventional DMPAP assay method described in the JAS for sawn timber.⁶ It is also noteworthy that the assay method using propyl orange can be applied to DDAC and alkyldimethylbenzylammonium chloride determination.^{12,15} Therefore, determination of all QACs listed as active ingredients in the JAS for sawn timber can be determined by the assay method using propyl orange, with the advantage of delivering simplicity and cost-effectiveness in harmony with humans and the environment.

Acknowledgments We would like to thank Mr. Akira Makita for providing the DMPAP standard. This study was partly supported by the program “Research and Development Projects for Application in Promoting New Policy of Agriculture, Forestry and Fisheries” by the Ministry of Agriculture, Forestry, and Fisheries of Japan.

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