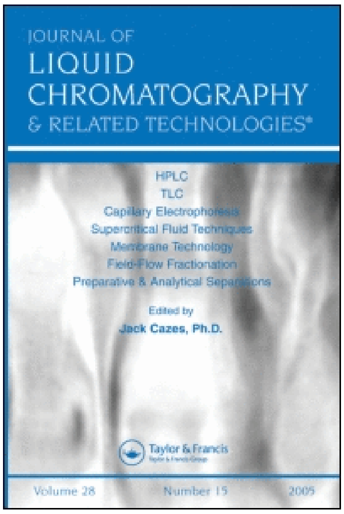

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HPLC ANALYSIS OF SODIUM 2-PYRIDINETHIOL-1-OXIDE IN AQUEOUS METALWORKING FLUIDS VIA DERIVATIZATION WITH NBD-C1

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ABSTRACT

A method is described for the analysis of the fungicide, 2-pyridinethiol-1-oxide, in aqueous metalworking fluids. Derivatization is extremely rapid with NBD-C1 using minimal sample preparation. HPLC analysis is complete within a 10 minute run and has shown to have minimal interferences at 425 nm in the absorbance mode.

INTRODUCTION

Maintenance of aqueous metalworking fluids requires routine monitoring of the biocide levels for several reasons. First, for adequate control of the microorganisms, minimum levels must be maintained in the system. Second, excessive levels of biocide potentially poses a serious health hazard to the worker contacting the fluid. Numerous biocides now exist of which sodium 2-pyridinethiol-1-oxide is a common and potent fungicide for aqueous based metalworking fluids.

Several wet chemical methods for the sodium 2-pyridinethiol-1-oxide now exist (1,2) but are rather tedious and are subject to matrix interferences. In-use metalworking coolants are typically contaminated with hydraulic oils, cleaners, and water conditioners in addition to the high level of metals normally encountered. The inherent chelation properties of the analyte (1-3) undoubtedly has prevented direct analysis of the analyte by HPLC in this and other labs even with the aid of ion pairing reagents.

Attempts to isolate the analyte and derivatize with 3,5-dinitrobenzoyl chloride by the method of Valdez and Reier (4) proved only marginally successful. Although pseudo-linear results were obtained for the derivative, the plot of absorbance vs. ppm of the derivative did not intercept zero. This was attributed to either a fixed level of the sodium 2-pyridinethiol-1-oxide binding irreversibly on the C-18 reverse phase cartridge or possible chelation of the analyte with residual metals in the metalworking fluid or the deionized water. Thus, the analysis required a standard addition type of treatment to insure accuracy and therefore was deemed unacceptable.

Reaction of the sodium 2-pyridinethiol-1-oxide with 7-chloro-4-nitro-2,1,3-benzoxadiazole (NBD-Cl) (Figure 1) is found to be

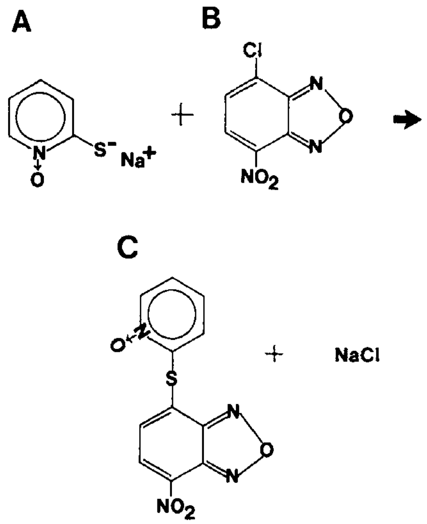

FIGURE 1. Reaction of (A) sodium 2-pyridinethiol-1-oxide and (B) 7-chloro-4-nitro-2,1,3-benzoxadiazole yielding the corresponding (C) derivative and sodium chloride.

extremely rapid yielding quantitative results by HPLC. Matrix interferences are either absent or minimal in the cases studied.

MATERIALS AND METHODS

Chromatography System

Separations were performed on a Perkin-Elmer 3B high pressure liquid chromatograph with an LC-100 oven set at 60°C. A model LC-75 UV detector was used with absorbance set at 425 nm. The UV curve was obtained by the LC-75 autocontrol in the scan mode. The column was a prepacked 4.6 mm x 25 cm LC-8 from Altex (Berkeley, Ca) protected with a guard column (Upchurch Scientific). An isocratic flow system was used, 40/60 acetonitrile/water, operating at 1 ml/min.

Materials

Sodium 2-pyridinethiol-1-oxide was obtained from Olin Chemical (Stamford, Conn) in three forms; crystalline, 40% aqueous based, and 6.4% aqueous based with additional components. The 7-chloro-4-nitro-2,1,3-benzoxadiazole (NBD-Cl) was purchased from Regis Chemical (Morton Grove, Il). Gelman 0.45 micron disposable Acrodisc^{tm} filters were obtained from VWR Scientific.

Methods

Samples of sodium 2-pyridinethiol-1-oxide were made up from 10 to 400 ppm in aqueous solution. A solution of the NBD-Cl was made up at 10,000 ppm in acetonitrile.

For the standard solutions, 250 ul of the sample was placed in a 2 ml vial. A cap with a teflon lined septum was then secured to the vial. Next, 250 ul of the 10,000 ppm NBD-Cl/Acn solution was added by syringe injection into the vial. The solution was allowed to set at room temperature for 5 minutes at which time 10 ul was injected into the liquid chromatograph. The metalworking fluid samples were diluted by a 5-fold factor with deionized water and then filtered through a 0.45 Gelman filter. Otherwise the samples were treated in an identical manner.

RESULTS AND DISCUSSION

Analyses of thiols in aqueous solutions have been performed both by precolumn (5,6) and postcolumn (7) derivatization techniques. Nishikawa and Kuwata (5) utilized NBD-Cl for the derivatization of low molecular weight alkyl thiols. Comparisons were made between thiol derivatization in a basic aqueous media and on Florisil Sep Paks^{tm}. Our experiments indicated that NBD-Cl could also be used for the derivatization of sodium 2-pyridinethiol-1-oxide even in complex matrices such as metalworking fluids. The reaction was complete with 5 minute reaction times at room temperature whereas the earlier work (5) required 60 minutes. In addition, no catalysts or pH adjustments were necessary.

Initial measurements for both standard samples and metalworking fluid submissions were made using 1 hour reaction times and 2.0 micromole/ml of potassium hydroxide. (The potassium hydroxide was reportedly (5) necessary for quantitative results.) Reduction of the reaction times to 5 minutes showed no quantitative difference in the sodium 2-pyridinethiol-1-oxide-NBD-Cl derivative. Removal of the potassium hydroxide also showed no differences. The greater reactivity of the thiol studied is thought to be a result of the aromatic stabilization of the ion and reaction intermediates. The short reaction times gave the side benefit that peaks from unknown side reactions were minimized, although they did not substantially interfere with the analyte peak (Figure 2).

Standards were made up using analyte crystals, 40% solution, and 6.4% solution. A plot of absorbance vs. the ppm of analyte-NBD-Cl derivative gave linear results (Figure 3). Of particular concern was whether in complex matrices such as metalworking fluids, complexation of the sodium 2-pyridinethiol-

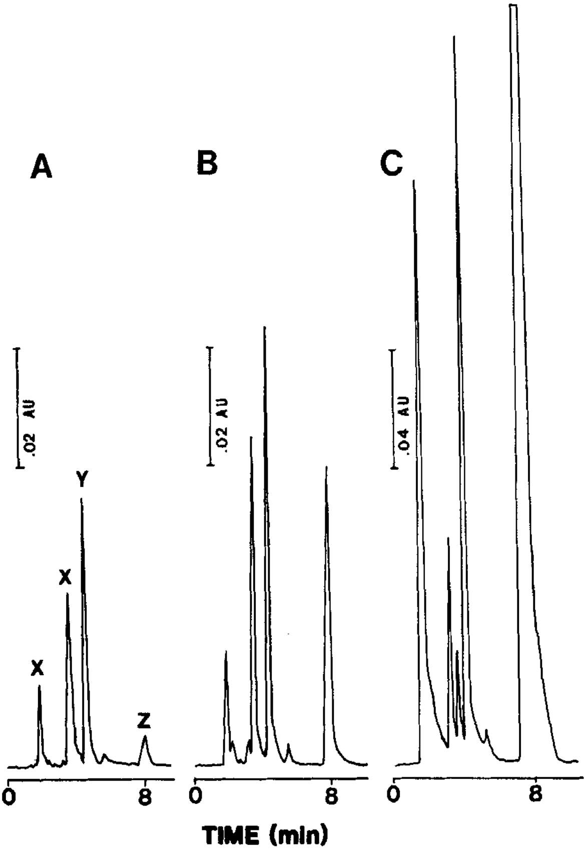

FIGURE 2. Chromatograms of 64 ppm sodium 2-pyridinethiol-1-oxide-NBD-Cl derivative at (A) 425 nm, (B) 400 nm, and (C) 235 nm. The peaks are described as (X) unknown side reactions, (Y) 2-pyridinethiol-1-oxide-NBD-Cl, and (Z) unreacted NBD-Cl.

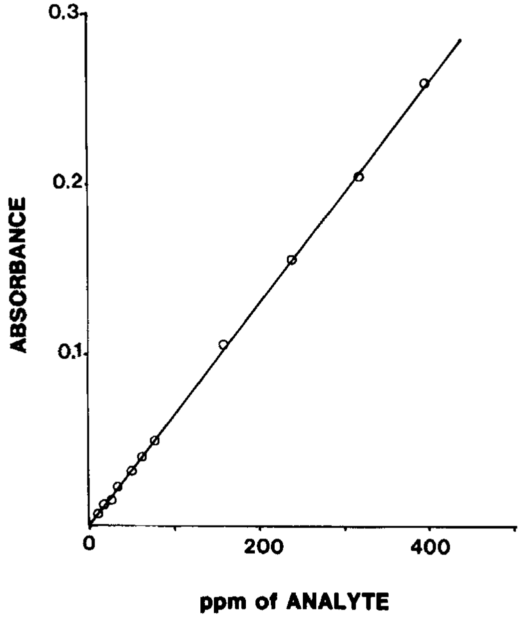

FIGURE 3. Calibration curve for the NBD-Cl derivative of sodium 2-pyridinethiol-1-oxide. The plot measures absorbance vs. ppm of the derivative.

1-oxide with the metals present (Fe, Al, Mg, Ca, Sn, Co, B etc.) might hinder the reaction or cause chromatographic problems. To test this 3 in-use samples from 3 different aluminum can manufacturers known to use the analyte were taken. Each sample was analyzed (3 repetitions) by direct comparison to the calibration curve (Figure 3) with the determined values given in Table 1. Then, to a single sample from each facility, 2 standard additions were made. The resulting standard addition plots showed excellent linearity with correlation coefficients given in Table 1. Comparison of the values obtained by extrapolation of the standard

TABLE 1

Methods Comparison - Calibration Curve vs. Standard Addition

Aluminum Plant	Calibration Curve			Standard Addition	
	n	Mean	RSD	Extrap. Value	Corr. Coeff.
Plant #1	3	203 ppm	1.6%	206 ppm	0.9999
Plant #2	3	108	1.1	110	0.9999
Plant #3	3	83	3.1	78	0.9979

addition plots to the direct values obtained using the calibration curve yielded indistinguishable results (Table 1). This result indicated that reaction of the analyte with the derivatization reagent was not subject to the potential chemical interferences encountered in these samples.

In addition, 3 in-use samples from 3 separate facilities thought to be free of the analyte were analyzed. (The samples were also chosen such that 3 different types of metalworking fluids were examined.) Found to be free of the sodium 2-pyridinethiol-1-oxide, each sample was then spiked with 32 ppm of the analyte. Derivatization and analysis of these samples matched standards at 32 ppm in deionized water indicative of 100% recoveries. Therefore, the analysis appears to be free from chemical matrix effects.

To further test the robustness of the procedure, the pH dependence of the derivatization reaction was tested. A typical metalworking fluid sample was derivatized and quantitated chromatographically. Separate samples were modified to pH 5.5 with

TABLE 2

Effect of pH on 2-Pyridinethiol-1-Oxide derivatization with NBD-Cl

Sample	Modifier	pH	Absorbance
Sample obtained from aluminum can manufacturer in Southeast	-	8.5	0.103
	-	8.5	0.105
	1N HCl	5.5	0.100
	0.1N NaOH	9.5	0.105

1N HCl and to pH 9.5 with 0.1 N NaOH and then again derivatized and quantitated. In each case virtually identical results were obtained with an example given in Table 2.

All measurements were made in the absorbance mode despite the fact that the NBD-Cl is generally regarded as a derivative for fluorescence measurements. The reason for the use of the absorbance mode was that a fluorimeter was not available for this study. Nevertheless, the derivative showed excellent selectivity and moderate sensitivity. Although detection limits were not determined, our experience indicates that levels down to 1 ppm are easily attainable. For further reduction of the detection limits, measurements may be taken at the wavelength maximums of 235 nm, 265 nm, and 400 nm (Figure 4). At the shorter wavelengths there is greater probability of interferences from the the metalworking fluid matrix and the unreacted NBD-Cl, but in the samples studied they did not appear overwhelming (Figure 2). This discussion does not preclude the fact that spectrofluorimetric detection would be most applicable for low level ppb detection, but when unavailable

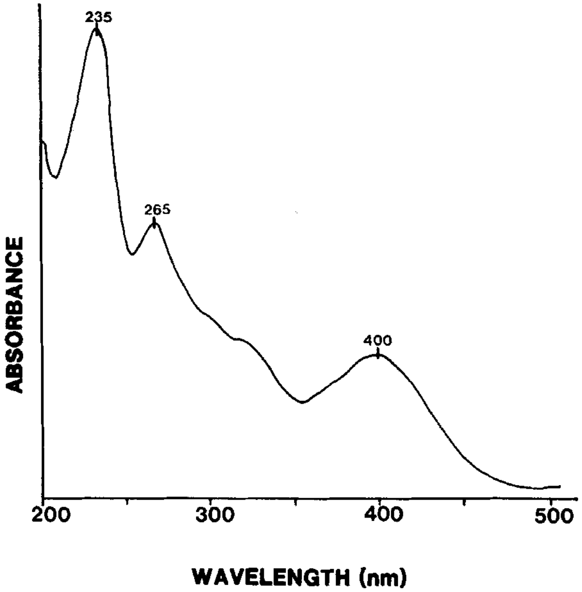

Figure 4. Absorption spectrum of the NBD-Cl derivative of sodium 2-pyridinethiol-1-oxide. For the absorption spectra of NBD-Cl, see reference 5.

UV detection is perfectly amenable at moderate detection requirements.

Finally, dilution of the metalworking sample can be eliminated in cases when further increases in sensitivity are necessary. The dilution and filtration steps were incorporated to remove particulates in the samples and inhibit precipitate formation in the reaction vessel. But even when present, sporatic results were not encountered. Nevertheless, for injection of relatively clean samples, the sample preparation steps are recommended.

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