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NOTES

A Quality Control Standard for Fluridone Analysis[1]

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INTRODUCTION

Fluridone (1-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl]-4(1H)-pyridinone) was registered for the control of submersed macrophytes in freshwater ecosystems in 1986. Since that time we have been performing fluridone analyses for several long-term monitoring studies which require that maximum accuracy be maintained through the turnover of laboratory personnel and unpredictable changes in the materials used for solid phase extraction for HPLC analyses. One method for increasing the accuracy of chemical analysis is use of a quality control standard. Historically, internal standards have been shown to be beneficial in quantifying many pesticides (1, 4, 8, 9). However, our procedure differs in the fact that the compound used as a quality control standard is added at the beginning of the extraction process and therefore carried through the entire procedure rather than added just prior to quantitative analysis (i.e., internal standard). In this manner, any loss due to processing can be accounted for on a per-sample basis.

A herbicidal compound with similar structure to fluridone is norflurazon (4-chloro-5-(methylamino)-2-(3-(trifluoromethyl)-phenyl)-3(2H)-pyridazinone)and both have similar UV absorbance and chromatographic characteristics (unpublished data). Thus, norflurazon was evaluated as a quality control standard in fluridone analyses due to these qualities. Additionally, two fluridone analogs, 1-methyl-3,5-diphenyl-4(1H)-pyridinone and 1,4-dihydro-1-methyl-4-oxo-5-[3-(trifluoromethyl)phenyl]-3-pyridine carboxylic acid were also investigated. The goal of this research was to identify a quality control standard that could be used with existing extraction, purification, and analysis procedures that were developed for fluridone (12).

MATERIALS AND METHODS

Fluridone and the three quality control standard candidates (all >99% pure, DowElanco, Indianapolis, IN, and Sandoz Crop Protection, Des Plaines, IL) were extracted from previously prepared aqueous solutions by a procedure based on the method of West and Day (12) and modified by Fox et al. (3) with the exception that all injections were 100 µL and a C_{18}-DB (5 µm) analytical column was used rather than a C_8-DB column (5 µm). The compounds were extracted from water, purified, and analyzed alone and in combination with fluridone. Three isocratic mobile phases: methanol and water (70:30), tetrahydrofuran and water (35:65), and acetonitrile and water (40:60) were employed for all samples prepared.

A series of fluridone and the three proposed quality control standards were prepared using technical grade material. The concentrations were 5000, 1000, 500, 250, 100, 25, 10, 5, 1, and 0.1 µg L^{-1}. The solutions were analyzed by the method of Fox et al. (3). The limits of detection (LOD) and quantification (LOQ) for fluridone were determined using the model adopted by the International Union of Pure and Applied Chemistry in 1975 (5). This same model was reaffirmed as the standard by the ACS Subcommittee on Environmental Analytical Chemistry in 1980 (5).

The concentrations of fluridone and the three proposed quality control standards were determined by peak height comparison to standards [i.e., standard solutions of fluridone and quality control standard candidates evaporated under nitrogen and dissolved in methanol and water (70:30)] to quantify percent recovery. All analyses were conducted in triplicate.

RESULTS AND DISCUSSION

Two of the possible quality control standards investigated 1) 1-methyl-3,5-diphenyl-4(1H)-pyridinone and 2) 1,4-dihydro-1-methyl-4-oxo-5-[3-(trifluoromethyl)phenyl]-3-pyridine carboxylic acid demonstrated low recoveries (0-14%) and further investigation with these compounds was therefore discontinued.

The percent recovery for norflurazon ranged from 83-93% with an average recovery of 89% (mean from 22 replicates of 0.5 µg L^{-1} spiked samples with a standard error of 1%). From the same samples, percent recovery for fluridone ranged from 80-94% with an average recovery of 88% (standard error of 2%). Because the recovery of norflurazon was similar to fluridone, norflurazon can be used as a quality control standard (i.e., compound used for quality control and improving reported recovery by accounting for proce-

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dural losses) and an internal standard (i.e., compound used only for quantification).

Selectivity and resolution were the lowest in the methanol:water mobile phase (Figure 1). Both compounds were detectable but baseline resolution was not obtained. The acetonitrile:water mobile phase provided better resolution of the two compounds than tetrahydrofuran:water. The different proportions of the three binary mobile phases were initially established by maintaining overall solvent strength based on the methanol:water system (10). Once a theoretical composition was determined for the two other mobile phases, further modifications in the composition of acetonitrile:water and tetrahydrofuran:water were based on trial and error. The acetonitrile:water mobile phase was used for all subsequent analyses due to the high degree of separation attained.

Mobile phase	K^1 1	K^1 2	Selectivity (∝)	Resolution
A	2.9	3.1	1.07	0.40
B	6.5	7.7	1.18	1.52
C	7.8	14.6	1.87	5.71

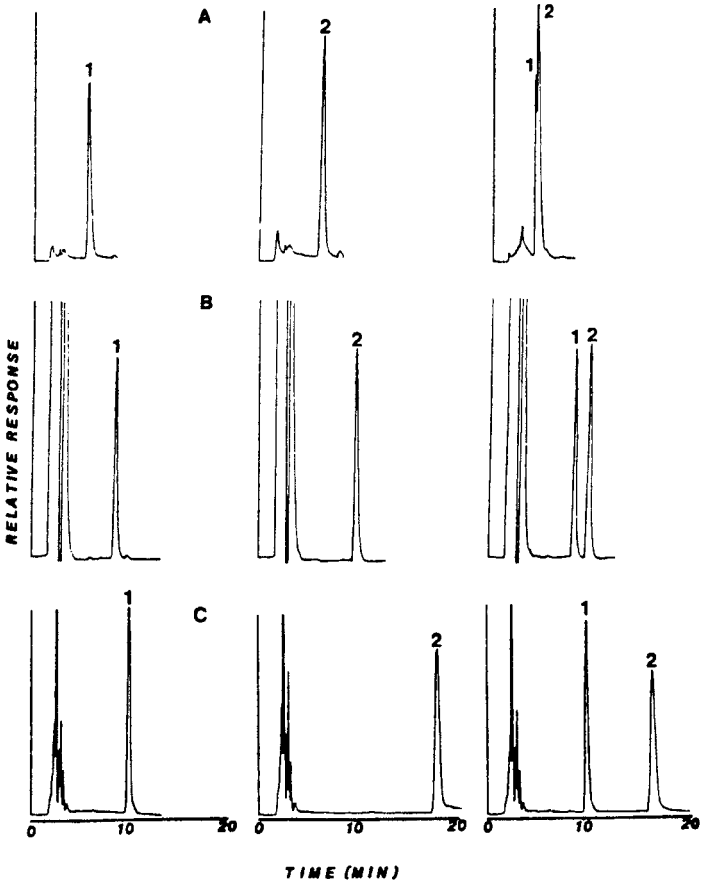

Figure 1. Chromatograms and separation characteristics obtained when analyzing norflurazon (1) and fluridone (2) in methanol:water (A), tetrahydrofuran:water (B), and acetonitrile:water (C).

Realizing the similarity between fluridone and norflurazon recoveries, our laboratory generates standard curves for both compounds. Recovery factors are generated for norflurazon, and these factors are used to correct the concentration of fluridone on a per sample basis. Periodic insertion of spiked samples insures the accuracy of this procedure.

The LOD and LOQ obtained in this study differed slightly depending upon which signal, peak area or peak height, was used for the calibration curve. When area was used, the LOD was determined to be 0.9 μg L^{-1} and the LOQ was 3 μg L^{-1}. When peak height was used, the LOD was determined to be 1.5 μg L^{-1} and the LOQ was 5 μg L^{-1}. These values are comparatively low for use of UV spectroscopy as the means of detection. Furthermore, if the sample to be analyzed is concentrated during sample preparation, then the amount of fluridone that can be detected in a sample is even lower depending upon how much of the sample is concentrated.

The greatest advantage of adding norflurazon to a fluridone-containing sample which is being prepared for extraction is that mistakes in the procedure can be detected on a per sample basis. Even if the response data from norflurazon is not used for concentration correction, the absence (or perhaps overabundance) of this compound in the final sample can reveal where problems were encountered.

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