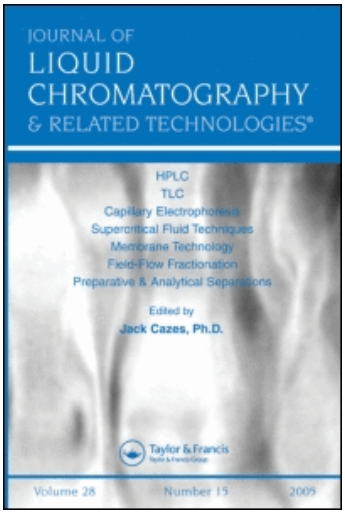

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LIQUID CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF NONYL PHENOL SURFACTANT PRESENT IN THE COMMERCIAL AND SPRAY FORMULATIONS OF AMINOCARB (MATACIL®) INSECTICIDE

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ABSTRACT

A high-performance liquid chromatographic method, using a Partisil® ODS-2 column, a mobile phase consisting of 95 % methanol in water and UV detection at 278 nm, has been developed for the determination of *p*-nonyl phenol surfactant present in the commercial formulations and spray-mixes of aminocarb insecticide. Nonyl phenol content in five commercial formulations and four spray-mixes was analysed with good reproducibility after removing the insecticide by alkaline hydrolysis and extracting the surfactant with *n*-heptane. Minimum quantification limit for the analyte was 0.03 μg in 10-μL injection volume. The method is flexible and should be applicable to analyse a variety of nonionic ethoxylated nonyl phenol surfactants present in many industrial and consumer products.

INTRODUCTION

Surface active agents, or surfactants, are amphiphilic compounds containing two structurally distinct parts, one of which is a water-soluble, polar, hydrophilic head and the other, a water-insoluble, apolar, hydrophobic hydrocarbon tail. They are commonly used in pesticide formulations as spray adjuvants [1]. Surfactants can improve the characteristics of the spray solutions in a variety of ways, *viz.*, as spray-modifiers, compatibility agents, spreaders of spray droplets on foliar surfaces and as penetrators of pesticide molecules through plant cuticles, which often act as barriers to the molecules [2-5].

Nonyl phenol and its ethoxylated products are extensively used as nonionic surfactants in various commercial products and as primary solvents in pesticide formulations. The base material, nonyl phenol [RC_6H_4OH; R, the side chain (C_9H_{19}) is primarily *para* substituted, consisting of isomeric branched nonyl radicals], is a pale yellow viscous liquid (MW, 225; MF, $C_{15}H_{24}O$; η, 563 cp at 20°C; v.p., 2 mm Hg at 130°C; d_4^{20}, 0.950; b.p., 293-297°C; n_D^{20}, 1.513; and f.p., –10°C) with mild phenolic odor, practically insoluble in water and dilute aqueous sodium hydroxide but soluble in organic solvents, and is not rapidly biodegradable. The addition of nonyl phenol to pesticide formulations not only modified their properties, but also enhanced the spreading and cuticular penetration of the active ingredient (AI) [2-5]. During broadcast application of insecticide spray-mixes over forest areas using aircraft, the presence of non-evaporators like nonyl phenol in the spray-mixes greatly improved the targetability and deposition of droplets on foliar surfaces, thus enhancing the efficiency of spraying [6].

Aminocarb (4-dimethylamino-*m*-tolyl N-methyl carbamate), marketed commercially as an oil-soluble formulation under the trade name Matacil® 1.8D by Chemagro Limited

(Toronto, Ontario), is used extensively as an insecticide in Canada since 1973 to control the spruce budworm, *Choristoneura fumiferana* (Clem.) larvae, a destructive defoliator of spruce-fir forests of eastern North America [7]. The commercial formulation, Matacil 1.8D, is an oil-soluble concentrate (OSC) consisting of 19.5 % AI (weight %), 30.0 % insecticide diluent-585 (ID-585)(Shell Canada Ltd., Toronto, Ontario), an aliphatic hydrocarbon fraction obtained during petroleum distillation, and 50.5 % nonyl phenol (Rohm and Haas Canada Ltd., West Hill, Ontario) [8,9]. The spray-mixes used in aerial application were prepared by diluting the commercial formulation with ID-585. Nonyl phenol is reported to be toxic to juvenile Atlantic salmon, *Salmo salar* L. [10].

The amount of nonyl phenol present in Matacil 1.8D and in spray-mixes has a considerable effect on the quality and stability of the formulation, and on the overall biological consequences of the insecticide. Therefore, to assure and to maintain adequate quality control, it has become necessary to analyse and quantify the nonyl phenol content in the commercial formulation, Matacil 1.8D, and in the spray-mixes after necessary treatments to remove the AI and other ingredients present in them. Analysis of nonyl phenol in forestry formulations has not been reported earlier in the literature. However, an HPLC method to quantify nonyl phenol residues in forestry matrices was published [11]. Attempts to form volatile and readily detectable fluorobutyrl [12,13] and dinitrophenyl [14] derivatives with the phenolic group and analyse them by GLC-ECD were not successful due to steric hindrance of the bulky nonyl group [11]. Similarly, GLC-FID methods using packed columns containing solid support Chromosorb W-HP coated with OV-1, OV-17, SE-30 etc., were tried. However, the FID was found to be insensitive, and when higher concentrations were injected, the peak

symmetry and consistency in retention times (RTs) were lost. These trials indicated that under the experimental conditions used, the GLC methods using either ECD or FID were not successful and they did not provide unambiguous identification and quantification of nonyl phenol present in the aminocarb formulations and spray-mixes. Therefore, the objective of the present study was to develop a simple, reliable and rapid reverse phase HPLC method to monitor nonyl phenol concentrations found in the commercial formulations of aminocarb (Matacil 1.8D) and their spray-mixes used in the forest insect control programs in Canada.

MATERIAL AND METHODS

Nonyl Phenol Standard

Nonyl phenol standard containing 92 % of the *p*-isomer was supplied courtesy of Rohm and Haas Company, Spring House, PA, USA. The listed impurities in the sample were: *o*-isomer, *ca* 3 %; 2,4-dinonyl phenol, *ca* 3 %; and other structural isomers, *ca* 2 %.

Stock and Standard Solutions

A stock solution of nonyl phenol containing 1.00 mg/mL was prepared by accurately weighing 100.0 mg of the nonyl phenol standard and dissolving it in 100 mL of HPLC-grade methanol. The standard solutions, ranging in concentration from 1.0 μg/mL to 100 μg/mL, were prepared by serial dilution of the stock solution with methanol. All solutions were stored in a refrigerator at 4°C.

Formulations and Spray-Mixes

The five commercial formulations of aminocarb (Matacil 1.8D)(labelled as OSC 1 to 5) and the four spray-mixes (labelled as SM 1 to 4) used in the study were supplied by Chemagro Ltd., Toronto, Ontario, Canada.

Solvents

All solvents and water used in the study were HPLC-grade, supplied by Caledon Laboratories (Georgetown, Ontario) and were tested for their spectral purity prior to use. They were filtered using Millipore® 0.20-μm filters and degassed prior to use in the HPLC.

HPLC Instrumentation

The liquid chromatograph used was a Hewlett-Packard (HP) model 1084 B, fitted with a UV variable wavelength (190-600 nm) detector, interfaced with a variable volume Rheodyne® injector equipped with 10 to 100 μL loops and an autosampler (HP 79842). The computing facilities in the instrument included a microprocessor and an electronic integrator linked to an LC terminal (HP 79850 B) to provide the area, area %, retention time (RT) etc., for each chromatographic peak. Full description of the instrument is given in an earlier publication [15]. The operating parameters were as follows:

Column:	Whatman Partisil® PXS 10/25 ODS-2
Column pressure:	3.5×10^3 kPa
Mobile phase:	95 % methanol in water at 1 mL/min
Oven temperature:	40°C
UV detector wavelength:	278 nm
Injection volume:	10 μL

The instrument was calibrated daily before the analysis of formulations by injecting, in triplicate, 10-μL volumes containing 0.01 to 1.0 μg of nonyl phenol standard and recording the detector response. Calibration curves were prepared daily, before and after sample analysis, by plotting the average peak area (y-axis) against the mass (μg) of nonyl phenol injected (x-axis) to confirm the stability and response of the instrument. Quantitation was done by external standardization based on peak area.

The nonyl phenol standard, under the experimental conditions used, gave a major peak (peak A, *p*-isomer) with RT = 5.5 ± 0.1 min accounting for 92 % of the peak area and two minor peaks, one with RT = 5.1 ± 0.1 min (peak B) and the other with RT = 4.2 ± 0.1 min (peak C) both in total amounting to 5 % of the peak area. Another minor, somewhat broad peak with RT = 7.8 ± 0.3 min (peak D) accounted for about 3 % of the peak area. From the compositions of the nonyl phenol standard used in this study, it is apparent that peak A corresponded to the *p*-isomer of nonyl phenol, peaks B and C could be the *o*- and other structural isomers of the analyte, and peak D with long RT could be inferred as that of 2,4-dinonyl phenol.

Separation of Nonyl Phenol from Formulations and Spray-Mixes

The commercial formulations (Matacil 1.8D) and the spray-mixes were shaken well and aliquots of each (500 μg of formulation and 1.5 mg of spray-mix) were weighed accurately into separate ground-glass stoppered Erlenmeyer flasks (150-mL). Fifty mL of aqueous methanolic (5 %) sodium hydroxide (0.10 M) containing 1 % sodium chloride was added to each flask, the flasks were then placed in a Blue M MagniWhirl® constant temperature water-bath set at 40 ± 1°C and shaken at medium speed for 4 h to hydrolyse the aminocarb

insecticide. The alkaline solution corresponding to each sample was transferred quantitatively to a 150-mL separatory funnel and partitioned thrice, using each time 50 mL of *n*-heptane. The heptane layers were pooled, passed through a column of anhydrous sodium sulfate (20 g) to remove the moisture, flash-evaporated at 35°C to near dryness and the residues were then dissolved in methanol. The methanolic solution was filtered (Millipore 0.20 μm filter) to remove particulates, transferred to a stoppered graduated centrifuge tube and the volume was adjusted by concentration under a stream of dry nitrogen (Meyer N - EVAP®) for HPLC analysis. Methanolic solution of each sample was injected (10 μL), in triplicate, into the liquid chromatograph, the average peak area was calculated and the nonyl phenol concentration was then computed from the prepared calibration curve.

RESULTS AND DISCUSSION

Linearity of UV Detector

The purity of the nonyl phenol (*p*-isomer) standard received from the manufacturer to calibrate the UV detector was not high. It contained only 92 % of the *p*-isomer admixed with positional and structural isomers as well as other impurities amounting to about 8 %. Prior to the analysis of commercial formulations and spray-mixes, the linearity of the UV detector response to *p*-nonyl phenol, was checked by injecting 10-μL aliquots of each standard solution at least thrice. Results were plotted as average peak area *versus* concentration of *p*-nonyl phenol in the standard. The curve was linear in the concentration range of 0.03 μg/10 μL to 1.0 μg/10 μL and passed through the origin ($r = 0.996$). Also, the reproducibility of peak area measurement for the concentration range was > 95 %. The standard deviation

(SD) in the peak area measurement for each individual concentration in this range was nearly equal to its mean value. However, the situations were not the same for the concentrations below 0.03 μg/10 μL (0.01 and 0.02 μg/10 μL). The points not only did not fall on the linear curve but also the SD values were high, indicating the poor detector response at low concentrations. Considering the structural characteristics of the analyte, this is understandable because, apart from the π-electrons in the aryl ring and the lone pair of *p*-electrons on the phenolic oxygen, there is no strong UV absorbing chromophoric group in the molecule. Therefore, at low analyte concentrations we could expect poor detector response, leading to errors in the measurement.

From the observed linearity over the concentration range studied (0.03 to 1.0 μg/10 μL), the limit of quantification (LOQ) for the *p*-nonyl phenol was established conservatively as 0.03 μg. On the other hand, the limit of detection (LOD) could reach as low as 0.01 μg; however, below the 0.03 μg level the detector response would be highly variable and in accordance, the associated signal-to-noise ratio would also be high.

HPLC Chromatogram of the Standard

The problems associated with analysing surfactants are that they occur as mixtures differing in molar masses and structures, and are often mixed with low levels of impurities or contaminants resulting from the manufacturing process [16]. Even the so-called "chemically pure" material usually contained detectable levels of isomeric and other contaminants as impurities; this is true in the case of nonyl phenol also. Unless proper chromatographic resolution is attained, it is very likely that we may over-estimate the concentration of the interested analyte. Despite these problems, under the present

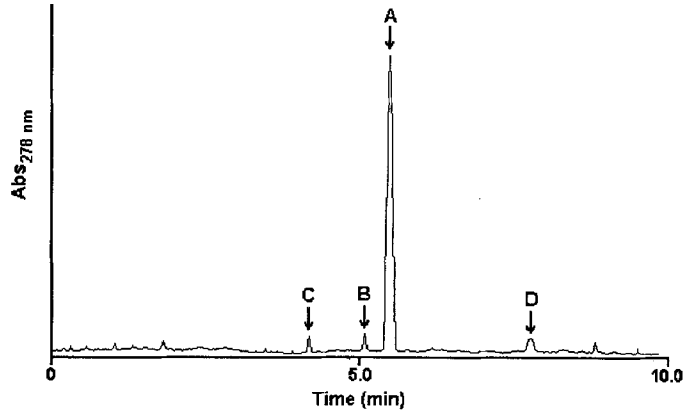

Figure 1. Chromatographic trace of nonyl phenol standard after injecting 10-μL volume containing 50 μg nonyl phenol/mL. Peak A, *p*-nonyl phenol (RT = 5.5 min); peaks B (RT = 5.1 min) and C (RT = 4.2 min), *o*- and structural isomers; and peak D, 2,4-dinonyl phenol (RT = 7.8 min).

experimental conditions used, we were successful at isolating and resolving the chromatographic peak corresponding to the *p*-nonyl phenol from other isomers and impurities in the standard.

A typical chromatogram of the nonyl phenol standard, determined by injecting 0.5 μg in 10 μL onto the HPLC column, is shown in Figure 1. The chromatographic peak A with RT = 5.5 min, corresponding to the *p*-nonyl phenol component, is well resolved and symmetrical. The two minor peaks, B (RT = 5.1 min) and C (RT = 4.2 min), are also well resolved and symmetrical and these two are assumed to correspond to the *o*-isomer (peak B) and a structural isomer (peak C) whose composition and geometry are unknown. Similarly, the broad peak (peak D) with RT = 7.8 min is presumed to belong to the impurity 2,4-dinonyl phenol [9], although the exact composition of this impurity was not revealed to the author by the manufacturer.

Nonyl Phenol in the Formulations and Spray-Mixes

The five commercial formulations (Matacil 1.8D)(OSC 1 to OSC 5) contained on average 49.5 % (range 47.1 to 51.2 %) of *p*-nonyl phenol, compared to the manufacturer's value of 50.5 %. The four spray-mixes (SM 1 to SM 4) contained on average 15.9 % (range 14.4 to 17.2 %) of the material compared to the expected value of 16.8 %. Both sets of data show good agreement between the expected and measured values, indicating the usefulness of the method reported in this paper to analyse the *p*-nonyl phenol component present in the commercial formulations and spray-mixes of aminocarb insecticide.

Typical chromatograms obtained for the commercial formulation (OSC 1) and the spray-mix (SM 1) are shown in Figures 2 and 3, respectively. In addition to the four distinct peaks (A to D) observed in the standard (Figure 1), these chromatograms contained a number of additional peaks, large and small, indicating the presence of UV absorbing impurities in the solvent, ID-585, as well as in the technical aminocarb used for preparing the commercial formulation (Matacil 1.8D) and the spray-mixes. The latter were prepared by diluting the commercial formulation with ID-585, roughly in the ratio of 1:2. However, no interference peak masked the peak A, which corresponded to the *p*-isomer of nonyl phenol. This is also true for the peaks B and C. On the other hand, examination of Figures 2 and 3 show that an interference peak appeared as a shoulder to peak D and its size increased while analysing the spray-mix, because it had higher concentration of ID-585 compared to the commercial formulation. This clearly indicated that a UV absorbing impurity was present in ID-585 which co-eluted with nearly similar RT as the 2,4-dinonyl phenol (peak D). Apart from this, the distinct separation of peak A, corresponding to the *p*-nonyl phenol, clearly indicated that the extraction and separation procedures used in the study and the

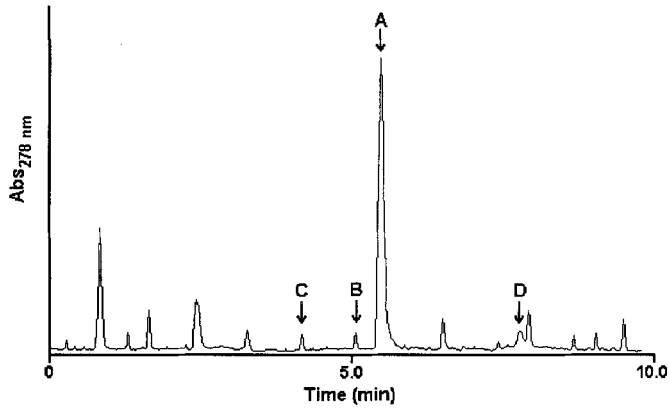

Figure 2. Chromatographic trace of 10-µL injection of Matacil® 1.8D (OSC 1) extract. For peak definitions and retention times, refer to Figure 1.

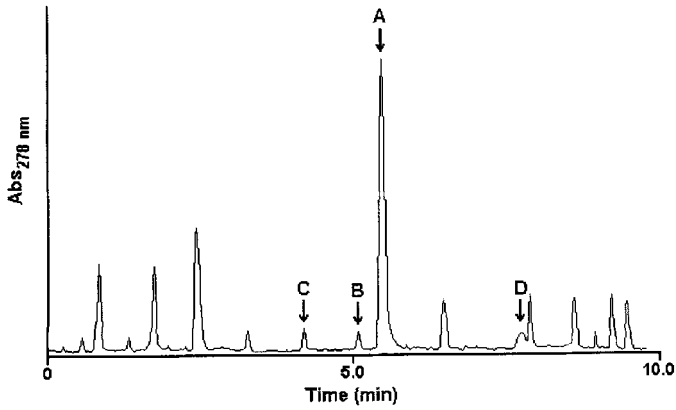

Figure 3. Chromatographic trace of 10-µL injection of Matacil® 1.8D (OSC 1) spray-mix (SM 1) extract. For peak definitions and retention times, refer to Figure 1.

instrumental parameters chosen are excellent, and are ideally suited to analyse and quantify the *p*-nonyl phenol component present in the commercial formulations (Matacil 1.8D) and their spray-mixes used in the forest insect control programs in Canada.

CONCLUSIONS

In recent years, quality assurance and quality control of pesticide formulations used in forest spray applications have become mandatory requirements. Therefore, it is necessary not only to know the exact amount of active ingredient present in the formulation but also to analyse and report the concentrations of potentially toxic adjuvants present in the formulation. This requirement came because some of the emulsifiers used previously in the spray formulations were reported to enhance viral activity in mice and caused Reye's syndrome in children [17]. Today, HPLC methods are used extensively in formulation analysis because they are fairly simple to perform without much cumbersome derivatization and provide rapid and reliable results. The method reported in this paper presents a rapid, accurate procedure for determining the *p*-nonyl phenol in aminocarb formulations and, after necessary modifications in the methodology, has potential for application to analysis of various ethoxylated alkylphenols present in many industrial and consumer products.

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